The Effects of Microstructure and Surface Chemistry on the Response of Gas-Sensitive Resistors

by

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Abstract

This work describes the gas-sensing properties of niobate oxide semiconductors. Three groups of compounds were investigated; (a) tetragonal tungsten bronze-type series \( \text{Ba}_x\text{Fe}_2\text{Nb}_{10-x}\text{O}_{30} \) (this was found to be basically \( \text{Ba}_x\text{FeNb}_5\text{O}_{30} \) with an impurity phase and (speculatively) intergrowths of a spinel phase), (b) rutile type solid solution series \( \text{Cr}_x\text{Fe}_{1-x}\text{Nb}_{0.4} \) and (c) mixed phase \( \text{Fe}_x\text{Nb}_{2-x}\text{O}_{4} \) (found to be a mixture of different phases of \( \text{FeNbO}_4 \) and the unreacted oxides). These materials function as gas-sensitive resistors in that they exhibit considerable changes in their electrical resistance upon exposure to reducing gases present in low concentrations in air.

Variation of stoichiometry and systematic substitution to form solid solutions were investigated with respect to their influence on the gas response to propane and carbon monoxide. These materials were synthesised using standard solid state ceramic methods and used in pellet form. They were characterized by X-ray powder diffraction (XRD), scanning-electron microscopy (SEM), Mössbauer spectroscopy, energy dispersive analysis of X-rays (EDAX) and electron probe microanalysis (EPMA) techniques.

Two major factors influencing the gas response were identified. Firstly, the response was strongly dependent on the microstructure of the material as a result of the effects of reaction and gas diffusion within the porous body. The consequence of such a reaction was a concentration gradient within the pellet and hence a variation in electrical conductivity. These effects were particularly pronounced for \( \text{Ba}_x\text{Fe}_2\text{Nb}_{10-x}\text{O}_{30} \). Secondly, in the series \( \text{Cr}_x\text{Fe}_{1-x}\text{NbO}_4 \), the responses were strongly inhibited by a surface species which could be desorbed at higher temperature. This species was found to be hydroxyl groups bound to the oxide surface. In addition, it was found that both the chromium iron niobates and the iron niobates were poisoned by prolonged continuous exposure to carbon monoxide at high temperature. It was proposed that this was due to reaction of carbon monoxide with lattice oxygen to form subsurface oxygen vacancies.
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Chapter 1: Introduction
Chapter 1: General introduction

1.1 Background

In today's industrialized society, the field of gas detection is of growing importance, with an ever-increasing requirement for sensors to detect a variety of gases in the contexts of combustion control, humidity measurement for industrial drying processes and inflammable/toxic gas detection.

Over the past decade or so, many materials have been used in a variety of gas-detection devices. These include systems based on SAW devices\(^1\), metal phthalocyanines\(^2\) (often incorporated in SAW devices), liquid electrolyte fuel cells\(^3\), solid electrolytes\(^4\) and semiconducting oxides (as gas-sensitive resistors\(^5\), p/n junction devices\(^6\) and using the Seebeck effect\(^7\)).

It was demonstrated in the 1950’s\(^8,\)\(^9\), that the adsorption of a gas on the surface of a semiconductor can cause a significant change in the electrical resistance of the material. This was first utilized commercially for the purpose of gas detection in Japan in the 1960’s and 70’s\(^10,\)\(^11\). However, one of the major problems facing the development of gas-sensor materials has been their lack of selectivity\(^12,\)\(^13\). There have been few reports of truly selective gas sensors\(^14,15,16,17\) and of these, none has come to any firm conclusion and adequately substantiated their claims as to what is responsible for the selectivity.

Many oxides show resistance changes in the presence of oxidising/reducing gases. The most popular oxide material for resistive gas-sensor application has been SnO\(_2\)\(^18\), which is an n-type semiconductor due to non-stoichiometry (oxygen vacancies)\(^19\). Other binary oxides used have been ZnO\(^20\), TiO\(_2\)\(^21\) and CeO\(_2\)\(^22\). Ternary oxides used include perovskites such as La-doped BaTiO\(_3\)\(^23\). It has also been reported \(^24\) that pyrochlores such as Bi\(_2\)Sn\(_2\)O\(_7\) and tungsten bronze-type niobates such as Bi\(_5\)Ti\(_2\)Nb\(_2\)O\(_{30}\) and Ba\(_6\)FeNb\(_9\)O\(_{30}\) show gas-sensing properties. A selection illustrating the range of materials and gases covered in the literature on gas-sensitive oxide resistors
is given in Table 1.1:

Table 1.1: A selection of materials from previous literature on gas-sensitive oxide resistors.

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<thead>
<tr>
<th>gas</th>
<th>material</th>
<th>reference</th>
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<td>CH₄</td>
<td>SnO₂ + CeO₂ + Pt</td>
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<td>SnO₂ + TiO₂</td>
<td>Chung et al.&quot;²⁵</td>
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<td>CH₄</td>
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<td>Lee et al.&quot;²⁶</td>
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<td>Ga₂O₃</td>
<td>Fleischer and Meixner&quot;³⁷</td>
</tr>
<tr>
<td>H₂</td>
<td>SnO₂ + In/Bi</td>
<td>Sberveglieri&quot;³⁸</td>
</tr>
<tr>
<td>H₂</td>
<td>TiO₂/Rh</td>
<td>Munuera et al.&quot;³¹</td>
</tr>
<tr>
<td>H₂</td>
<td>ZnO</td>
<td>Yamazaki et al.&quot;³⁹</td>
</tr>
<tr>
<td>H₂</td>
<td>In₂O₃</td>
<td>Y. Yasukawa et al.&quot;⁴⁰</td>
</tr>
<tr>
<td>H₂O vapour</td>
<td>α - Fe₂O₃</td>
<td>Pelino et al.&quot;⁴¹</td>
</tr>
<tr>
<td>H₂O vapour</td>
<td>Ba₀.₅Fe₀.₅TiO₃</td>
<td>Slunecko et al.&quot;³²</td>
</tr>
<tr>
<td>Compound</td>
<td>Reaction</td>
<td>Reference</td>
</tr>
<tr>
<td>----------</td>
<td>----------</td>
<td>-----------</td>
</tr>
<tr>
<td>H₂S</td>
<td>WO₃ + Au</td>
<td>Smith et al.⁴³</td>
</tr>
<tr>
<td>H₂S</td>
<td>SnO₂ + CuO</td>
<td>Tamaki et al.⁴⁴</td>
</tr>
<tr>
<td>H₂S</td>
<td>SnO₂</td>
<td>Ando et al.⁴⁵</td>
</tr>
<tr>
<td>H₂S</td>
<td>SnO₂</td>
<td>Lantto et al.⁴⁶</td>
</tr>
<tr>
<td>NO₂</td>
<td>In₂O₃ + SnO₂</td>
<td>Sberveglieri et al.⁴⁷</td>
</tr>
<tr>
<td>NO₂</td>
<td>LaFeO₃</td>
<td>Matuura et al.⁴⁸</td>
</tr>
<tr>
<td>NO₂</td>
<td>ZnO + Ga</td>
<td>Matsushima et al.⁴⁹</td>
</tr>
<tr>
<td>NO₂</td>
<td>SnO₂ + In + V</td>
<td>Löw et al.⁵⁰</td>
</tr>
<tr>
<td>NOₓ</td>
<td>SnO₂ doped with Cd</td>
<td>Sberveglieri et al.⁵¹</td>
</tr>
<tr>
<td>NH₃</td>
<td>Zn₄GeO₇N₂</td>
<td>Rosse et al.⁵²</td>
</tr>
<tr>
<td>NH₃</td>
<td>ZnO + Al</td>
<td>Nanto et al.⁵³</td>
</tr>
<tr>
<td>NH₃</td>
<td>WO₃ + Au</td>
<td>Maekawa et al.⁵⁴</td>
</tr>
<tr>
<td>NH₃</td>
<td>Cr₁ₓTi₀ₓO₃</td>
<td>Moseley and Williams⁵⁵</td>
</tr>
<tr>
<td>O₂</td>
<td>SnO₂ + Li</td>
<td>Sberveglieri et al.⁵⁶</td>
</tr>
<tr>
<td>O₂</td>
<td>SrTiO₃ + Mg</td>
<td>Yu et al.⁵⁷</td>
</tr>
<tr>
<td>O₂</td>
<td>CeO₂</td>
<td>Beie et al.⁵⁸</td>
</tr>
<tr>
<td>PH₃</td>
<td>SnO₂ + Cu</td>
<td>Ratcheva et al.⁵⁹</td>
</tr>
<tr>
<td>TMA¹</td>
<td>TiO₂ + either Ru or In</td>
<td>Takao et al.⁶⁰</td>
</tr>
<tr>
<td>TMA/DMA²</td>
<td>ZnO + Al</td>
<td>Nanto et al.⁶¹</td>
</tr>
</tbody>
</table>

¹ Trimethylamine
² Dimethylamine
1.2 Mechanism of gas sensitivity

Semiconducting oxides such as those in table 1.1 have generally been classed into two categories. In the first, ionic defect states\(^{61}\) are caused as a consequence of intrinsic disorder or by a change in the stoichiometry of the material (either by equilibration of the solid with the gas phase or by doping with aliovalent impurities). These defect states\(^{62,63}\) take the form of one or more of the following:

a) Schottky defect: These are pairs of atoms (anion and cation) that leave their normal lattice sites to migrate to the surface, causing the formation of a pair of lattice vacancies

```
M X M X M X M X
X M  M X  X M
M X M X M X M X
X M X M X M X M
```

b) Frenkel defect: this only involves one type of ion (usually the smaller) and occurs when it is displaced from its normal lattice position to an interstitial site

```
M X M X M X M X
X M X  X'M X M
M X M X M X M X
X M X M X M X M
```

c) anti-site defects

```
M X M X M X M X
M X M X X M X M
M X M X X M X M
```

For example\(^{61}\), in titania, Frenkel defects induced by reduction processes are oxygen vacancies and interstitial titanium. Their relative numbers are governed chiefly by the temperature; oxygen vacancies dominate below ca. 1000 °C.

1) \[2\text{Ti}^{+}_{\text{I}} + \text{O}^{+}_{\text{I}} \rightarrow 2\text{Ti}^{+}_{\text{I}}' + \text{V}^{+}_{\text{O}} + 1/2 \text{O}_2\]

2) \[2[\text{Ti}]^{+}_{\text{I}}' \rightarrow \text{Ti}^{+}_{\text{I}} + n'\]

3) \[\text{O}^{+}_{\text{I}} \rightarrow \text{V}^{+}_{\text{O}} + 2n' + 1/2 \text{O}_2\]
In this notation, superscripts denote charge with respect to the lattice and subscripts the atom normally occupying the lattice site. Thus,

' denotes a negative charge w.r.t. the lattice

. denotes a positive charge w.r.t the lattice

X denotes a neutral charge w.r.t the lattice

Here, equation 1) represents the creation of a donor state, a reduced titanium atom and equation 2) represents the activation of an electron (n') from the donor state to the conduction band

In general, the relationship between oxygen partial pressure and the electrical conductivity of a semiconducting oxide gas sensor may be represented by

\[ \sigma = A \exp(-E_A/kT)p(O_2)^{1/n} \]

where \( \sigma \) denotes the electrical conductivity, \( A \) is a constant, \( E_A \) is the activation energy for conduction, \( p(O_2) \) is the oxygen partial pressure and \( n \) is a constant determined by the type of defect involved in the equilibrium between oxygen and the sensor.

At high enough temperatures (generally at 700 °C and above), all oxides conduct in this way. Another example of such a material is ceria. For many materials, the conduction mechanism has both ionic and electronic components. Examples of mixed ionic-electronic conduction occur in oxygen ion conductors such as U:CeO₂, Ce:ThO₂ and gadolinium zirconium titanates (GZT)*. Tuller* illustrated that CeO₂ solid solutions show a variety of different conduction mechanisms according to the oxygen partial pressure. Figure 1.1 shows four regimes where different dominant defects are possible. As \( p(O_2) \) was varied, the stoichiometry adjusted accordingly, varying the concentration of the different species:

1) electrons \( n' \)

2) doubly positively charged oxygen vacancies \( V_{o}^{++} \)

3) singly positively charged oxygen vacancies \( V_{o}^{+} \)

4) doubly negatively charged interstitial oxygen \( O_{i}'' \)
Figure 1.1  Defect diagram for U:CeO$_2$, showing the concentration dependences of various defects on p(O)$_2$, for four regimes from Tuller.

In the second group of materials, there is no mobility of ionic species in the bulk. Instead, electronic defect states, which result in conductivity, are thought to be formed in the vicinity of the surface. Thus, only electron transport within the bulk is required and conduction of this nature generally takes places in the temperature range 400-600°C. In this temperature range, bulk equilibration is generally very slow and yet rapid responses to changes in oxygen partial pressure are still observed. The interpretation is, that in this temperature range, adsorbed oxygen species act as electron acceptor states at the surface. It is possible that, in a suitable temperature range, the conductivity might have both bulk (ionic and electronic) and surface (electronic) contributions.
For cases where the conduction is determined by the activation of electrons from such surface states (to be later discussed), the carrier concentrations are determined by

a) thermal excitation of carriers from the valence band
\[ X \Leftrightarrow p + n' \]
b) the ionization of donors
\[ D \Leftrightarrow D^+ + n' \]
c) ionization of acceptors
\[ A^- \Leftrightarrow A + n' \]
d) charge balance
\[ p + f_D N_D = f_A N_A + n' \]
e) conductivity
\[ \sigma = \mu_e en' + \mu_p ep \]

Where
- \( \sigma \) = conductivity
- \( e \) = electronic charge
- \( \mu_e \) = electronic mobility
- \( f_D \) = fraction of ionized donors
- \( f_A \) = fraction of ionized acceptors
- \( N_D \) = number of donors per unit volume
- \( N_A \) = number of acceptors per unit volume
- \( p \) and \( n \) are concentrations of holes and electrons respectively
- \( K_1 \) and \( K_2 \) are constants dependent upon the thermal excitation of carriers to the valence band and the ionization of acceptors

Using this scheme, Williams and Moseley* showed that conductivity can be expressed in terms of the concentrations of surface donor and acceptor states.

\[ \sigma/e = \mu_e K_3 N_D/N_A + \mu_p K_4 N_A/K_3 N_D \]

Thus, the conductance type (n or p) and the magnitude of the response will be determined by the relative concentration of donor and acceptor states.

It is a characteristic of the lower temperature regime that the conductance of an oxide may become very sensitive to the presence of reactive gases at low concentration in a background of air. It is currently postulated* that oxygen forms charged states (fig. 1.2) at the solid/gas interface by abstracting electrons from the conduction band of the oxide, to form species such as \( \text{O}^- \), \( \text{O}^{2-} \) and \( \text{O}_2^- \). Of these, \( \text{O}^- \) and \( \text{O}_2^- \) have been detected by e.s.r.*. As a consequence, charge carriers are depleted within a characteristic depth of the surface, the depletion length. These adsorbed oxygen ions
react with reducing gases (R), such as CO, to form RO, which is desorbed. The reaction to form RO results in the release of electrons to the solid to give a change in electrical conductivity

\[ \text{CO} + O^{-} \rightarrow \text{CO}_2 + n' \]

For an n-type semiconductor, this is measured as a decrease in resistance. When the reducing gas is removed from the atmosphere, the original surface state density is restored by reactions such as

\[ \text{O}_2 + n' \rightarrow \text{O}_2^- \]

Thus, surface-active materials only function in the presence of oxygen. This has been illustrated by Jones et al., who showed that the response of a single crystal of ZnO to CO is large in air, but negligible in nitrogen.

During gas sensing, anionic chemisorption (described in the following section) takes place. Here, the anionic species formed are those of oxygen, which act as acceptor states. Thus the analyte gas (for example, CO) has no direct role in the sensing mechanism; it only controls the number of surface states by reaction with oxygen. It is later shown in chapter 4, that for CO, there is indeed no direct adsorption onto the surface of the oxide.

In the case of p-type oxides, the adsorbed oxygen also acts as a surface acceptor state, but abstracts electrons from the valence band, and hence gives rise to an increase in the charge carrier (hole) concentration at the interface.
Figure 1.2 Diagram representing the principal energy states in a thin film gas sensor (the direction of current flow is parallel to the solid/gas interface), from McAleer et al.\textsuperscript{18}
Metal oxide gas sensors show sublinear responses to reducing gases. The resistance $R$, of a gas sensor, is related to the partial pressure, $p$, of a combustible gas:

$$R = R_0 p^n$$

where typically $0 \leq n \leq 1$.

Windischmann and Mark\textsuperscript{71} showed that for CO, the response was proportional to the square root of the gas concentration (detail given in appendix 1.1). In the current work, the response of a gas sensor is defined as $(R_{\text{air}} - R_{\text{gas}}) / R_{\text{gas}}$ (or $\Delta \sigma / \sigma_0$ where $\sigma$ denotes the conductivity). For an n-type material, this gives a positive number. For a p-type material, the response is defined as $\Delta \rho / \rho_0$ or $(R_0 - R_g) / R_0$, where $\rho$ denotes the resistivity. The reason for choosing this definition is illustrated in appendix 1.2. Various different definitions have been used by other authors. Thus a graph of the response vs $[\text{gas}]^{1/2}$ for CO should be linear and using this graph, it is possible to define the gradient as the sensitivity.

The model described above for response to reactive gases was proposed\textsuperscript{69,72,73} for conduction in thin films. This model is also applicable to porous bodies such as pellets. In such porous bodies, the mechanism by which the conduction takes place will depend on the nature of the intergranular contacts. Three cases of intergranular contact have been postulated\textsuperscript{61}:

1) well-sintered (large) open necks: Such necks are wider than the depletion layer thickness. Thus there exists a path of low resistance through the middle of the neck. In this case, conductance will be determined by activation of charge carriers from the bulk, which in turn will depend on the effective channel width due to gas adsorption.
Figure 1.3 (a) 'open neck' model, from Williams

2) medium sintering, narrow, closed necks: here, the neck will be fully depleted. In contrast to the open neck model, the resistance will be high throughout the neck and thus conduction will be determined by activation of electrons from surface states, being directly controlled by gas adsorption.

Figure 1.3 (b) 'closed neck' model, from Williams

3) This is applicable to a porous mass but not a thin film and applies to grains that are in contact but which have not sintered. Such very small junctions are heavily overdepleted and the contact resistance between the grains is the dominant factor controlling the conduction. The electrons must therefore overcome a surface barrier (Schottky barrier) in order to transfer from one grain to the next. Conduction would thus be determined by the charge and fractional coverage of surface species.
In reality, conduction is likely to be controlled by more than one of these mechanisms. From these models, it is clear that the nature of the sintering and the subsequent grain structure will have a major influence on the electrical response of these materials.

In both bulk and surface-sensitive materials, an increase in oxygen partial pressure leads to a conductance decrease for n-type semiconductors and a conductance increase for p-type semiconductors. Thus, by examining the effect of variation in oxygen partial pressure, it is possible to define the conductivity type of a chosen material.

1.3 Band theory related to gas sensing

The oxides in the present work are believed to act principally as extrinsic semiconductors in that over the temperature currently studied, thermal promotion of electrons from the valence band (V.B.) to the conduction band is of relatively minor importance. Instead, it is envisaged that conduction is due to a donor level beneath the conduction band.

Transition metal oxides contain a broad bonding band of oxygen 2p character separated by an energy gap from a broad antibonding band of metal s and p character. However, the d band is often narrow and the d electrons may be localized. According to Goodenough and Hamnett, the character of the d electrons with respect to
delocalization is determined by 1) the bandwidth 2) the correlation energy and 3) the stabilization of electronic energies.

In an n-type semiconductor (figure 1.4 (a)), the adsorbed oxygen acts as an acceptor state which is between the valence band and the donor level in energy. As it abstracts electrons from the donor states, it raises the Fermi level (shown earlier in figure 1.2). In this case, the conduction band becomes depleted of carriers, so that the energy is highest at the solid/gas interface. As a result of the depletive chemisorption, band bending occurs. However, in a p-type material (figure 1.4 (b)), the valence band is filled and the surface states form an acceptor level above it. In this case, transfer of electrons from the filled V.B. to the acceptor states causes no change in energy of the conduction band and (in this depletive chemisorption) no band bending occurs.

Figure 1.4 (a) Anionic depletive chemisorption on an n-type semiconductor. Extracted from Chemical Kinetics, K.J.Laidler, McGraw-Hill, New York, 1965

Figure 1.4 (b) Anionic cumulative chemisorption on a p-type semiconductor. Reference as above.
If a new transition metal ion is introduced, the carrier density will change. For example, if Cr\(^{3+}\) (d\(^5\)) is introduced to replace Fe\(^{3+}\) (d\(^5\)), the substitution of Cr\(^{3+}\) for Fe\(^{3+}\) would be expected to lead to the formation of holes and increase the p-type character. The charge density may be changed by substitutions which force a valency change in order to maintain electroneutrality. Williams\(^{61}\) reported that it was possible to lower the conductivity of barium ferrate, by substituting elements of valency 4 or 5 (Ti or Ta, for example) for iron. He found that in the series BaFe\(_{1-x}\)Ta\(_x\)O\(_{3-x}\) (0 ≤ x ≤ 0.5), BaFe(III)\(_{0.5}\)Ta\(_{0.5}\)O\(_3\) was an n-type semiconductor, but that BaFe(III,IV)O\(_{3-x}\) was p-type. It was interpreted as follows: in the n-type reduced material, Fe\(^{3+}\) is reduced to Fe\(^{2+}\), thereby creating electron-donor states and (more) oxygen vacancies were formed. However, in the p-type oxidized material, Fe\(^{3+}\) oxidizes to Fe\(^{4+}\), creating holes and also interstitial oxygen is formed.

Similarly, if Sb\(^{3+}\) is substituted into Sn\(_2\)O\(_2\), some of the Sn\(^{4+}\) will be reduced to Sn\(^{2+}\) in order to achieve the charge balance. For every y Sb introduced into Sn\(_2\)O\(_2\), for each Sn site there must be two oxygen sites. However, the Sn site may be occupied by Sn or Sb. Each Sb on an Sn site introduces one positive charge, so one Sn\(^{4+}\) is reduced to Sn\(^{2+}\) for every two Sb, leading to

\[
(S\text{Sn}^x(y-3/2y))(S\text{Sn}^{2+})y/2(S\text{Sb}^{2+})y/2O_2
\]

In general terms:

\[
(1-y)SnO_2 + y/2 Sb_2O_5 = (Sn_{1-y}Sb_y)O_2 + y/4 O_2
\]

Thus, the Sn(II) species (Sn\(^{2+/+}\)) acts as an electron-donor state, causing the conductivity to rise.

Control of the carrier density has been illustrated by Clark and Donaldson\(^{76}\), who showed that for MoO\(_3\) and WO\(_3\), it was possible to use lead and tin chlorides and bromides as electron donors, donating their non-bonding electrons to the oxide. They
formed a sol of oxide particles dispersed within a matrix of the chloride. On adding the oxide to the chloride, the conductivity rose and then decreased. Mössbauer spectra, in the cases of SnBr$_2$-WO$_3$, SnBr$_2$-MoO$_3$ and SnCl$_2$-WO$_3$ showed loss of electron density around the tin on increasing the oxide content. The authors postulated that at the halide-oxide interface, acceptor states are generated, which create holes in the s-band (Sn$^{II} = 5s^2$, Pb$^{II} = 6s^2$, Sn$^{IV} = 5s^0$ Pb$^{IV} = 6s^0$). Thus a p-type conductor was formed, so that increasing the relative oxide concentration increased the conductivity until the acceptor band became full and, due to reduced carrier mobility, the conductivity decreased. In the case of the SnBr$_2$-WO$_3$ system, the conductivity rose, decreased and then rose again. In the case of SnBr$_2$-WO$_3$, it was suggested that the second rise in conductivity was due to the involvement of a second impurity level.

It should also be possible to introduce extra electrons or holes by changing the stoichiometry. In the present work, it is initially proposed that for barium iron niobates (chapter 3) and iron niobates (chapter 5), that an increase in iron concentration would lead to the oxidation Fe$^{3+}$→Fe$^{4+}$ and hence an increase in p-type behaviour, and that an increase in niobium concentration would lead to either the reduction Nb$^{5+}$→Nb$^{4+}$ or Fe$^{3+}$→Fe$^{2+}$, and hence an increase in n-type characteristics. This is discussed more fully in chapter 3.

1.4 Selectivity

Various authors have suggested that selectivity is due to one or both of two related factors. 1) geometry and microstructure, which have subsequent effects on the rates of diffusion of the gases and 2) relative temperatures of maximum responses for different gases. It is postulated in this work that the relative rates of diffusion of the gases are strongly influenced by their rates of combustion and that selectivity is a result of concentration gradients formed within the porous body. This is in agreement with McAleer et al. With respect to these factors, it is also postulated that the microstructure of the material is of paramount importance in determining the gas response.
Morrison\textsuperscript{78} has attempted to create specificity in sensors by using surface-state additives. This was applied to two systems. In the first, it was proposed that as $V_2O_5$ is an n-type semiconductor with a very low conduction band energy, applied as a surface additive, it would be expected to act as an acceptor. In addition, it was also stated that $V_2O_5$ is an active catalyst for the oxidation of xylene (dimethylbenzene). This was added to the surface of TiO$_2$ and it was found that this combination was sensitive to xylene and that the sensitivity to xylene was much greater than to CO. However, the comparison with pure TiO$_2$ was not provided and it was also unclear whether the $V_2O_5$ was functioning merely as a catalyst or creating surface states. In the second example, it was postulated that sulphanilic acid (4-aminobenzenesulphonic acid) $NH_2-C_6H_4-SO_3H$, as an amine, would be expected to possess donor properties and that the addition of this to nickel oxide, a p-type semiconductor, would enhance the oxide’s response to oxidising gases. This caused a large response to NO$_2$. However, this response was irreversible. Again, the results for the pure material without sulphanilic acid were not shown.

To date, apart from works relating to chapter 3 of this thesis\textsuperscript{79,80}, there have been no detailed studies of the effects of firing temperature and resulting microstructure in relation to selectivity in gas sensing. Work has, however, been published on the effects of sintering temperature on the gas sensitivity. Takahashi et al.\textsuperscript{81} showed that for SnO$_2$ prepared via a sol from SnCl$_4$, HCl and urea, the sensitivity to oxygen (measured with respect to a nitrogen atmosphere) was highest for gels fired at lower temperatures (400 °C as opposed to 1100 °C). In contradiction, Ando et al.\textsuperscript{82} reported that the H$_2$S sensitivity of SnO$_2$ thin films, hydrothermally synthesised via the gel from aqueous NH$_4$HCO$_3$ and SnCl$_4$, was greatest for samples fired at higher firing temperature (700 °C as opposed to 400, 500 and 600 °C).

Although not a sintering study, a link between microstructure and gas-sensing characteristics with respect to the phase transition of TiO$_2$ from rutile to anatase in SnO$_2$-TiO$_2$ (Sb, Pt) hydrocarbon gas sensors has been briefly mentioned by Chung et al.\textsuperscript{83} but no detail has been given.
Many authors have shown that responses for different gases peak at different temperatures, thus implying some temperature dependence of the selectivity. However, only in one work\(^*\) has this been explicitly related to the relative rates of combustion and reaction of the gases. Komori et al\(^*\) showed that in a SnO\(_2\) thin layer, it was possible to obtain selectivity to methane over butane, ethanol, hydrogen and carbon monoxide at 520 °C. They postulated that this selectivity was due to the different relative combustion and reaction rates so that the other gases burn on the outside of the SnO\(_2\) film. However, the authors did not provide details of how the gas components were analyzed or present the supporting data.

Yamazoe et al\(^*\)\(^*\), in work relating to the catalytic properties of metals on SnO\(_2\), showed that it was possible to obtain selectivity to propane over hydrogen, carbon monoxide and methane, using SnO\(_2\) doped with Ag, operated at ca. 370 °C. Here it was shown that the gas responses covered different temperature ranges (fig. 1.5), CO responding at low, and propane at high temperature. However, discussion of the selectivity was not given. In this work, it was shown that the temperature required and the rate of catalytic oxidation for both C\(_3\)H\(_8\) and H\(_2\) over SnO\(_2\) were dependent on the metal additive.

![Figure 1.5](image.png)

**Figure 1.5 Responses for SnO\(_2\) sensor doped with Ag, from Yamazoe et al.\(^*\)\(^*\)**

Malchenko et al.\(^*\)\(^*\) found that with Bi\(_2\)O\(_3\) doped In\(_2\)O\(_3\), it was possible to obtain selective detection of CO in the presence of CH\(_4\) in air because of a difference in detection temperature of these two gases. Although not mentioned by the authors, a possible explanation for the difference in detection temperatures could have been the relative temperatures at which these gases combust.
In addition, Lalauze et al.\textsuperscript{34} showed that in SnO\textsubscript{2} sensors pretreated with SO\textsubscript{3}, it was possible to obtain selectivity to H\textsubscript{2}S over NH\textsubscript{3}, CO\textsubscript{2}, NO\textsubscript{x}, H\textsubscript{2}, CO and SO\textsubscript{2} at 100 °C. However, no results for the untreated SnO\textsubscript{2} sensors were presented. Like Komori et al., they showed that the relative responses to different gases were temperature dependent.

Torvela et al.\textsuperscript{14} stated that by raising the operating temperature, it was possible to practically eliminate NO and SO\textsubscript{2} interference in CO detection using SnO\textsubscript{2} films activated with a Pd catalyst, thus suggesting some degree of temperature dependence of the selectivity. Smith et al.\textsuperscript{16} stated that the selectivity in Au-loaded WO\textsubscript{3} films was temperature dependent; at 200 °C, there was a peak in the H\textsubscript{2}S response, whilst the H\textsubscript{2} sensitivity peaked between 225 and 250 °C, giving selective H\textsubscript{2}S detection.

Concentration gradients within the sensor material have been discussed in works by Williams\textsuperscript{61}, McAleer et al.\textsuperscript{77} and Shimizu et al.\textsuperscript{88}. The effects of combustion on sensor response have been outlined by McAleer et al.\textsuperscript{77}, who suggested that the observed response is dependent upon the rate of combustion and reaction of the gas on the outside of the pellet. The authors showed a porous body (fig. 1.6) as being surrounded by a combustion zone which becomes narrower as the temperature increases. Thus it was proposed that combustion of the gas results in a concentration gradient within the sensor and that if the combustion rate is high enough, all the gas is burnt in a thin outer shell of the device.

Figure 1.6  Diagram showing the gas composition profile in a porous pellet, from McAleer et al.\textsuperscript{77}
The idea of the importance of concentration gradients for sensor response in a porous body has been developed by Williams. It was shown that in a porous sensor layer, a diffusion profile with a characteristic reaction depth should be established. This diffusion profile is controlled by the pore structure of the material. The less reactive gas would reach the centre of the pellet and cause conductivity changes, whereas the reactive one would have little effect, burning on the outside. It was proposed that it is possible to promote selectivity in the response for a less reactive gas over one that is more reactive.

Shimizu et al. have measured the relative responses to hydrogen on both the inside and outside of a cylindrical hollow thick film SnO₂ sensor. When hydrogen was applied from the outside, it was found that the interior exhibited a much higher hydrogen sensitivity than the surface. It was also found that the oxygen concentration was lower in the interior. It was suggested that the low interior oxygen concentration was due to the larger molecular size of oxygen and its reaction with the hydrogen on the outside during combustion. The higher hydrogen sensitivity on the inside was interpreted as being due to a reduced concentration of oxygen species in the centre leading to a higher carrier concentration. Thus the relative rates of diffusion played an important role in the gas response. The authors concluded that the key factors controlling sensor response were microstructure, thickness, catalytic activity and electrode position.

Figure 1.7  Cylindrical hollow thick film SnO₂ sensor, from Shimizu et al.
1.5 Outline of this thesis

The objectives behind this thesis are twofold; Firstly it was required that a suitable material be found and characterized that was capable of detecting propane in the presence of carbon monoxide, for potential application in the monitoring of car-exhaust emissions. In addition, the second aim was to establish and characterize a material capable of detecting carbon monoxide, with a view to general environmental monitoring applications.

This work is based on two parent systems, both of which are currently believed to conduct electronically. Both of these materials have not been routinely used for gas-sensing applications before in the general literature, although their gas sensing properties have been briefly reported. In addition, they both offer opportunities for manipulating the stoichiometry in order to attempt to tailor the gas-sensing properties. The families of compounds synthesized in this thesis were

(a) $\text{Ba}_x\text{Fe}_y\text{Nb}_{10-x}\text{O}_{30}$ (Chapter 3),
(b) $\text{Cr}_x\text{Fe}_{1-y}\text{NbO}_4$ (Chapter 4) and $\text{Fe}_y\text{Nb}_{1-x}\text{O}_4$ (Chapter 5), derived from the parent compounds $\text{Ba}_x\text{Fe}_y\text{NbO}_{30}$ for (a) and $\text{FeNbO}_4$ for (b) and (c).

Parent compound (a) was chosen for this study as it has been shown, in previous work, to exhibit an anomalous property (to be later discussed in chapter 3). Compound (b) also gave encouraging results in previous (unpublished) work.

In series (a), it was attempted to alter the electron-donor density by changing the stoichiometry of the parent compound. Theoretically, this could have been achieved by altering the Fe/Nb ratio. The relationship between stoichiometry and gas adsorption properties in oxides has not, to date, been characterized extensively in gas-sensing devices. However, there has been work published on the adsorption of $\text{CO}_2$ on Sr/Ca hydroxyapatites of varying Sr/Ca ratio.

For series (b), a solid solution was prepared by systematically substituting
increasing quantities of Cr$_2$O$_3$ for Fe$_2$O$_3$ in the initial oxide mixture. Cr$^{3+}$ was chosen for the substitution as it was expected to readily replace Fe$^{3+}$ in the host lattice, the ionic radii of Cr$^{3+}$ and Fe$^{3+}$ being 0.63 Å and 0.64 Å respectively. As for series (a) and series (c) it was also attempted to alter the donor density by changing the Fe/Nb ratio.

All compounds were prepared by solid state reaction of the oxides. In all cases, the materials were characterized by scanning-electron microscopy (SEM), X-ray powder diffraction (XRD) and in some cases, Mössbauer Spectroscopy and / or electron microprobe analysis (EPMA). Electrical properties such as resistivity and activation energy were determined and the responses to carbon monoxide and propane investigated.

It is postulated in this work that three major factors influence the gas selectivity and sensitivity of these materials: (1) the relative combustion temperatures of the gases in the atmosphere surrounding a particular material (2) grain size and porosity resulting from sintering; and (3) species desorbed from the surface of the material. It appears that ion substitution plays a relatively minor role.
Appendix 1.1

Windischmann and Mark\textsuperscript{71} and also Williams\textsuperscript{61} developed a model of 'surface-trap limited' conductivity. In this case, all of the electrons from donor states in the oxide are trapped on surface species, the sensitizer \( A \) (negatively charged oxygen species). For the adsorption of sensitizer onto empty surface sites:

\[
\text{A}(g) + S_A(\cdot) + n' \xrightarrow{k_s} S_A(A^-)
\]

and for the combination of the sensitizer with the reactant gas (CO, for example):

\[
S_A(A^-) + R \xrightarrow{k_R} RO + S_A(\cdot) + n'
\]

The rate at which conduction electrons are formed is represented by the equation:

\[
d(n')/dt = k_2P_RS_A(A^-) + k_3S_A(A^-) - k_4(n')S_A(\cdot)P_A
\]

They assume that the rate of dissociation of adsorbed sensitizer is much less than its rate of formation

(a) \( k_3S_A(A^-) \ll k_4(n')S_A(\cdot)P_A \)

and that the number of vacant sites is much less than the number with adsorbed sensitizer

(b) \( S_A(\cdot) \ll S_A(A^-) \)

so that \( S_A(A^-) \) may be considered constant\textsuperscript{3}.

All the electrons from the donor state are trapped as \( S(A^-) \) so that the surface concentration of this adsorbed surface species is determined by the thickness of the oxide film and the donor density of this film. The authors assumed that the change in surface coverage caused by the reaction is negligible. Simplifying equation (1) with these assumptions,

\[
d(n')/dt = \alpha P_R - \beta(n')S_A(\cdot)
\]

\textsuperscript{3} It may be noted that Windischmann and Mark assumed that most of the surface sites were occupied by \( A^- \) in the absence of reactant gas. However, Williams assumed that the surface coverage of the sensitizer is small, due to the formation of potential barriers at the surface on adsorption of the sensitizer. As a result, Williams showed that in order to have a response that was proportional to the square root of the gas concentration, the sensitizing species must be \( O^2^- \). This was ruled out on energetic grounds by Windischmann and Mark, who postulated a singly charged oxygen species.
where $\alpha = k_2S_A(A^\cdot)$ and $\beta = k_iP_A$

At the steady state, $dn'/dt = 0$ and thus $\alpha P_R = \beta(n')S_A(\ )$ \hspace{1cm} (2).

Since all the electrons are considered to be trapped in surface states and for every vacant site created, one conduction electron is released, the number of conduction electrons is equal to that of vacant surface sites i.e. $(n') = S_A(\ )$

From equation (2),

$\alpha P_R = \beta(n')^2$

and thus $n' = (\alpha/\beta P_R)^{1/2}$

The authors assumed no effects from the ionization of bulk donors.
Appendix 1.2

\((R_{\text{air}} - R_{\text{gas}})/R_{\text{gas}}\) was chosen as the definition of response for an n-type semiconductor. This allows for the conductance/resistance to have a positive value when the gas concentration is zero, with \(\sigma\) increasing with increasing gas concentration. This can be modelled simplistically as

\[\sigma_g = \sigma_0 (1 + f[\text{gas}])\]

\[\sigma_g/\sigma_0 - 1 = f[\text{gas}]\]

and \((\sigma_g - \sigma_0)/\sigma_0 = \Delta\sigma/\sigma_0 = f[\text{gas}]\)

but as \(\sigma \propto 1/R\)

\[\Delta\sigma/\sigma_0 = (R_{\text{air}} - R_{\text{gas}})/R_{\text{gas}}\]

Similarly, for a p-type material, the resistance increases with increasing (reducing) gas concentration and to allow the resistance/conductivity to have a positive value when the gas concentration is zero,

\[R_s = R_0(1+f[\text{gas}])\]

\[R_s/R_0 = 1 + f[\text{gas}]\]

\[R_s/R_0 - 1 = f[\text{gas}]\]

\[(R_s - R_0)/R_0 = f[\text{gas}]\]
Chapter 2: Experimental
Chapter 2: Experimental

2.1 Preparation of compounds

Compounds in all series were prepared by solid state reaction: the untreated oxides (Fe$_2$O$_3$ Fluka > 99.0 %, Cr$_2$O$_3$ Fluka > 99 %, Nb$_2$O$_5$ Fluka > 99.9 % (later changed to Johnson Matthey Grade 1) and, in the case of the barium iron niobates, BaCO$_3$ Fluka > 99 %) in the relevant stoichiometries, were milled with ceramic (steatite for series (a) and (b) and zirconia for series (c)) beads in a ball mill. The solvent was then evaporated and the resulting powder cake fired for 12 hours. The solid produced was ground for 5 mins. in a mechanical grinder, pressed into 13mm diameter pellets of approx. 3-4 mm thickness, using pressures 1-2 tons (0.75 - 1.5 ton cm$^{-2}$) and then re-fired at the same temperature for another 12 hours. Preparation conditions are shown in table 2.1 (exceptions are shown in appendix 2.1). The phases in these materials were identified using powder X-ray diffraction and their microstructures were characterized by scanning-electron microscopy (SEM). In some cases, the compositions were confirmed by electron probe microanalysis (EPMA) and also in some cases, the Mössbauer spectra at 77 K were recorded.

Table 2.1 Preparation conditions

<table>
<thead>
<tr>
<th>series</th>
<th>milling time (hours)</th>
<th>pressing pressure (tons)</th>
<th>firing temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) Ba$<em>6$Fe$<em>x$Nb$</em>{10-x}$O$</em>{30}$</td>
<td>9</td>
<td>1.5 - 2 (1.125-1.5 ton cm$^{-2}$)</td>
<td>1200</td>
</tr>
<tr>
<td>(b) Cr$<em>x$Fe$</em>{1-x}$NbO$_4$</td>
<td>18-24</td>
<td>1-2 (0.75-1.5 ton cm$^{-2}$)</td>
<td>1200</td>
</tr>
<tr>
<td>(c) Fe$<em>x$Nb$</em>{1-x}$O$_4$</td>
<td>24</td>
<td>1 (0.75 ton cm$^{-2}$)</td>
<td>1100</td>
</tr>
</tbody>
</table>
2.2 Scanning-electron microscopy

The microstructures of the compounds were examined under a Hitachi S-570 model SEM. Initially, samples were carbon coated. However, this soon proved to be unnecessary, and most of the samples in this work were used as pellets with no preparation. The instrument was operated at 25 kV and 60-80 mA (beam diameter of a few microns (dependent on aperture size)).

2.3 X-ray diffractometry

In all cases, powders made from the pellets were used. For series (a) (on a Philips PW1050 diffractometer), films were examined in reflection geometry mounted on a glass / metal slide. Co-K$_\alpha$ radiation was used (operating at 35 kV, 40 mA, scanning 5 to 90 °, with a 2Θ step of 0.05 °min$^{-1}$, counting for 3 seconds per point and with a Ni filter).

For series (b) and (c) (on a Siemens D5000), the samples were examined in transmission geometry, spread onto adhesive tape and placed in the middle of a circular sample holder. Monochromated Cu-K$_\alpha$ radiation was used (10-90 °, scan step of 0.02 °, sampling time 2s and sample spin at 60 rpm).

2.4 Electron probe microanalysis

Electron probe microanalysis (EPMA) linescans (Fe and Nb in series (a), Cr and Nb in series (b)) were carried out simultaneously on a JEOL Superprobe JXA-8600 equipped with twin wavelength-dispersive X-ray detectors (beam size of 5μm, scanning over approx. 4.5 mm). Sample pellets were set in resin and well polished prior to use.

2.5 Mössbauer spectroscopy

Mössbauer spectroscopy involves the recoil-less emission (by the source) and resonant reabsorption (by the sample) of $\gamma$ radiation$^{1,2}$. It is used to probe the energy states at the nucleus via the interaction between the nucleus and the surrounding electron density. The source provides a monochromatic beam of $\gamma$-rays, the frequency of which may be modulated by supplying a small relative motion, the Doppler velocity, between the source and absorber. The source is held rigidly in a crystal lattice so that
during emission, the momentum can be taken up by the whole crystal, leading to a small recoil velocity and small Doppler broadening. When the γ rays from the source have the exact energy to match the energy gap (ground state to excited (usually the first excited state)) of the sample nuclei, the γ ray is absorbed and immediately re-emitted as resonance fluorescence.

The Mössbauer technique is sensitive to the s electron density, as only the s electrons have a finite probability of occurring at the nucleus. The Mössbauer spectrum is obtained by plotting the percentage transmission (number of counts) of the γ rays transmitted by the sample at each instant as the Doppler velocity (mm s\(^{-1}\)) varies. A line in the spectrum occurs when the energy of the source is equal to that of the absorber, so that resonant reabsorption may occur (fig. 2.1). If the source is identical to the sample, the maximum resonance will occur where velocity = 0.

\[
\delta \propto (\Delta R/R) \Delta |\psi_0|^2
\]

Figure 2.1 Typical single line spectrum obtained when source and sample are identical from A.R. West*1

Upon excitation, the radius of the nucleus changes, leading to a change in s-electron density. For most isotopes, that of the excited state is largest. However, in some cases, for example \(^{57}\)Fe, the ground state has the largest radius. The isomer shift, \(\delta\), measures the difference between the valence s orbital populations of the Mössbauer atom in the sample and the source.
where $R$ and $\Delta R$ are the nuclear radius and its change upon excitation and $\Delta |\psi(0)|^2$ is the change in electron density of the sample upon excitation. In most cases, where the radius of the ground state is less than that of the excited state, $\Delta R/R$ is positive and an increase in electron density will lead to an increase in $\delta$. However, where $\Delta R/R$ is negative, such as in $^{57}\text{Fe}$, an increase in electron density will be seen as a decrease in $\delta$.

$^{57}\text{Co}$ undergoes spontaneous electron capture to give a metastable state of $^{57}\text{Fe}$ which in turn decays to the ground state via gamma ray emission, which includes the 14.4 keV Mössbauer gamma ray$^3$. $^{57}\text{Fe}$ has an excited state of $I = 3/2$ where $I$ is the nuclear angular momentum quantum number. However, for $I > 1/2$, there is nonspherical charge distribution which is characterized by a nuclear quadrupole moment. When this experiences asymmetrical electronic charge distribution, an electric field gradient (EFG) is produced, which splits the nuclear substate into two substates, characterized by $m_L = \pm 1/2$ and $m_L = \pm 3/2$ (figure 2.2). This leads to a doublet, with a quadrupole splitting, $\Delta$.

When there is a magnetic field at the nucleus, Zeeman splitting occurs$^4$. The field can originate either within the atom itself, within the crystal via exchange interactions, or as a result of the interaction of the compound being placed in an externally applied magnetic field. The magnetic field at the nucleus is dependent on a number of factors, including $H_s$, the Fermi contact term, which arises as a result of the interaction of the nucleus with an imbalance in the s-electron spin density. In $^{57}\text{Fe}$, $H_s$ is the most significant term contributing to the magnetic hyperfine splitting. The origin of $H_s$ may be unpaired s-electrons, or indirectly as a result of polarization effects on filled s orbitals. These can occur if the atom has unpaired electrons in the d- or f-orbitals, or if it is chemically bonded to such an atom. The interaction of an unpaired d-electron with s-electrons of parallel spins will be different to that with s-electrons of opposed spins, leading to a slight imbalance of spin density at the nucleus and a magnetic field.

Most compounds containing unpaired valence electrons show a hyperfine magnetic
splitting. However, the magnetic splitting is also dependent upon the spin relaxation. Generally, in paramagnetic compounds, the spin relaxation is usually rapid and no magnetic splitting is seen. In cases of ferromagnetism and antiferromagnetism, the relaxation rates are slower and a splitting will be observed. The internal fields found in iron compounds and alloys are generally strong enough to generate clear, six-line spectra.

For nuclear states with \( I > 0 \), \( 2I + 1 \) substates are produced, so that the ground state with \( I = 1/2 \) splits into 2 substates and the excited state of \( I = 3/2 \) splits into four substates. Due to the selection rule \( \Delta m_I = 0, \pm 1 \), six transitions are possible (figure 2.3) and a sextet is observed. If the sample is composed of randomly oriented crystallites, the intensities of the lines are 3:2:1:1:2:3. However, magnetic hyperfine splitting is often only observed at low temperatures as lowering of the temperature increases the recoil-free fraction.

![Figure 2.2 Mössbauer transitions of \(^{57}\text{Fe}\) from R.V. Parish](image)

![Figure 2.3 Zeeman splitting of energy levels in \(^{57}\text{Fe}\) from R.V. Parish](image)
Thus if iron is present in both the +3 and +4 oxidation states in the sample at 4.2 K, two different sextuplets should be observed with separate values for their isomer shift (proportional to the apparent s-electron density (change in atomic radius ΔR/R) and quadrupole splitting (measure of the asymmetry around the nucleus) and it should be possible to estimate the relative amounts of these species by integrating the respective areas under the peaks.

The Mössbauer spectrum of BaFeO$_{2.72}$, a compound containing iron in both the +3 and +4 oxidation states, has been reported in the literature. At 293 K, a broad asymmetric peak was produced (fig. 2.4). However, at 4.2 K, two different sextuplets were observed (fig. 2.5) as a result of magnetic ordering and the relative quantities of the iron species were estimated.

In the present work, experiments were carried out on a Driver-Transducer-MS2000 (ES Technology) with data buffer, gas-filled proportional counter and single channel analyzer (SCA) Canberra 2030. $^{57}$Co in a Rh matrix was used as the source.

![Figure 2.4](image)

**Figure 2.4** Mössbauer spectrum of BaFeO$_{2.72}$ at 293K, from Grenier et al.$^{6}$

![Figure 2.5](image)

**Figure 2.5** Mössbauer spectrum of BaFeO$_{2.72}$ at 4.2 K, from Grenier et al.$^{6}$
4.6 Instrumental: Electrical Measurements

For some of the very first experiments, a manual 4-pellet rig was used. However, the majority of the samples were tested in an automatic 4-pellet test rig. The test pellets were sandwiched between gold electrodes, which were separated by alumina spacers (fig. 2.6). Gold was chosen as an electrode material as it is not a known catalyst and there were no materials inside the furnace with known catalytic activity with respect to the gas mixtures. The sample was surrounded by a silica tube, with gas inlet and electrical connections at one end, and gas outlet at the other end. The electrode / pellet area (fig. 2.7) was surrounded by a tube furnace. Connections inside the furnace were with gold wires. A 2-point D.C. resistance measurement method was used. Resistances were measured by a digital multimeter and transferred to a 386 microcomputer via an IEEE 488 interface. The resistance measurement channels were selected using a relay multiplexer. The potential difference applied across the specimen (details in appendix 2.2) and the maximum current flowing depended upon the measurement range. The temperature inside the centre of the tube furnace was measured with a chromel / alumel thermocouple.

The gases were switched on and off by solenoid valves and their flow regulated using Tylan model FC-260 mass flow controllers (MFCs) (fig. 2.8). Each mass flow controller was connected to a gas-control box (RO-28-RS Tylan) which was run from the computer via a Digital-analogue converter (DAC). The MFCs had a maximum flowrate of 500 cm³ (STP) min⁻¹ and a minimum rate of 6 cm³ (STP) min⁻¹, maintained with an accuracy of 1.0 % for nitrogen and 4 % for other gases*7.
Figure 2.6  General view of the pellet test rig
Figure 2.7 The electrode area of the test rig
Figure 2.8 Flow diagram for the multiple pellet rig
The concentration of test gas was regulated by mixing the test gas with pure air\(^1\). The MFC's produce a given concentration by adjusting the relative flowrates, and this in turn is based on properties such as the thermal conductivity and density of the gases. Since the MFC's were calibrated in nitrogen, correction factors for the flow rate must be applied to all other gases. As long as the same diluent is used in both channels, the concentration of the test gas will be correct, subject to a small correction outlined below. However, the flowrates will deviate from those specified in the program. The correction to the concentration may be computed as follows: If channel 1 = 20 % \(O_2\) / 80 % \(Ar\) and channel 2 = 1000 ppm propane (or CO) in 20 % \(O_2\) / 80 % \(Ar\), then the test gas would have slightly different properties to the diluent and a small correction to the concentration will be required. The conversion factor between control voltage and obtained flow rate for the oxygen / argon mixture has been given by the manufacturers as 1.305. The conversion factors for a) pure propane and b) pure CO have been given (same source) as 0.36 and 1.00 respectively. Thus assuming a linear relationship between the conversion factor for the propane/oxygen/argon mixture and the percentage propane in the mixture, a rough conversion factor for the mixture may be estimated (figure 2.9) and hence the relative flow rates for sample gas and diluent computed. It is evident from fig. 2.9 that the correction to the gas concentration caused by difference in calibration correction in the two channels may be neglected.

![Figure 2.9 Conversion factor for the test gas mixture](image)

---

1. either \(O_2/N_2\), \(O_2/Ar\) or dried lab air
Initially, gold contacts were evaporated onto the pellets (for the first pellets of series (a) and (b)). However, resistance graphs such as that in figure 2.10 were obtained, with random and wide variation in resistances. These were first attributed to poorly formed contacts between the pellets and the electrodes. However, it was later found that the 'spikes' were a) due to interference from the furnace controller, b) because the relay contacts had not settled before the measurement was taken and c) due to scaling errors in the DVM. It was later found that the evaporated gold contacts were unnecessary.

Figure 2.10  FeNbO₄ fired twice at 1200 °C, in Ar/O₂ mixture and 1000 ppm propane
Appendix 2.1

Exceptions to table 2.1.1

Milling:

series (a) - one preparation of Ba$_6$Fe$_{1.6}$Nb$_{8.4}$O$_{30}$ - milled for 17.5 hours, a second preparation of Ba$_6$Fe$_{1.6}$Nb$_{8.4}$O$_{30}$ and one preparation of Ba$_6$FeNb$_9$O$_{30}$ - milled for 7 hrs

series (b) - FeNbO$_4$ (9 hrs), Cr$_{0.6}$Fe$_{0.4}$NbO$_4$ (12 hrs)

Pressing:

series (a) - one preparation of Ba$_6$FeNb$_9$O$_{30}$ - 3 tons (2.3 ton cm$^{-2}$)

series (b) - Cr$_{0.1}$Fe$_{0.9}$NbO$_4$ and Cr$_{0.2}$Fe$_{0.8}$NbO$_4$ (5 tons (3.8 ton cm$^{-2}$)), FeNbO$_4$ (3 tons (2.3 ton cm$^{-2}$))

Firing:

series (a) - one preparation of Ba$_6$Fe$_{1.4}$Nb$_{8.6}$O$_{30}$ (fired 4 times at 1200 °C and once at 1100 °C when the compound fused to the crucible), one preparation of Ba$_6$Fe$_{0.8}$Nb$_{9.2}$O$_{30}$, fired 4 times at 1200 °C (for the same reason) and one preparation of Ba$_6$Fe$_{0.6}$Nb$_{9.4}$O$_{30}$ fired once at 1200 °C for 12 hrs and once at 1200 °C for 44 hrs (error in the temperature programme).
Appendix 2.2

Model 175 A Keithley Autoranging DMM*8

Ohms

<table>
<thead>
<tr>
<th>range</th>
<th>resolution</th>
<th>accuracy (1yr) 18-28 °C, (%rdg + counts)</th>
<th>max voltage across unknown on range</th>
</tr>
</thead>
<tbody>
<tr>
<td>200 Ω</td>
<td>10 mΩ</td>
<td>0.05 + 2*</td>
<td>0.2 V</td>
</tr>
<tr>
<td>2 kΩ</td>
<td>100 mΩ</td>
<td>0.05 + 1</td>
<td>2.0 V</td>
</tr>
<tr>
<td>20 kΩ</td>
<td>1 Ω</td>
<td>0.05 + 2</td>
<td>0.2 V</td>
</tr>
<tr>
<td>200 kΩ</td>
<td>10 Ω</td>
<td>0.05 + 1</td>
<td>2.0 V</td>
</tr>
<tr>
<td>2 MΩ**</td>
<td>100 Ω</td>
<td>0.05 + 2</td>
<td>0.2 V</td>
</tr>
<tr>
<td>20 MΩ**</td>
<td>1 kΩ</td>
<td>0.2 + 1</td>
<td>2.0 V</td>
</tr>
<tr>
<td>200 MΩ**</td>
<td>100 kΩ</td>
<td>2.0 + 1</td>
<td>2.0 V</td>
</tr>
</tbody>
</table>

* when correctly zeroed  ** appropriate range selected automatically

(current drawn for each resistance not explicitly stated by manufacturers)
Chapter 3: Tetragonal Tungsten Bronze-Type Niobates
Chapter 3: Tetragonal Tungsten Bronze-Type Niobates

3.1 Introduction

The monitoring of car-exhaust emissions is a major environmental concern of today. The chief combustion products of car engines are unburnt hydrocarbons, oxides of nitrogen and carbon monoxide. The emissions of these compounds are controlled by the use of a catalytic converter mounted in the exhaust pipe. Long chain hydrocarbons from the petrol should be broken down during the catalyzed combustion process. However, the efficiency of the catalyst must be monitored, as failure of the catalyst will result in their emission, which in the past, has lead to smog (the result of photochemically induced oxidation of unburnt hydrocarbons from automobile exhausts and the production of ozone, details of which may be found in appendix 3.1). Thus, for the monitoring of hydrocarbons, it is necessary to have a material that is selective to these over CO and oxides of nitrogen. It is envisaged that for such application, the operating temperatures would be high (400 - 500 °C).

Materials of the tetragonal tungsten bronze structure have not, to date (with the exception of two brief reports\textsuperscript{1,2}), been explored for gas sensor application. Barium iron niobate was chosen as a starting material for this series of compounds because previous work\textsuperscript{1} has shown that it exhibits an anomalous property: in the presence of two oxidizing gases, it gave different responses (fig. 3.1). When chlorine was applied, a resistance increase was observed as expected, yet in NO\textsubscript{2}, a resistance decrease was produced. In the same work, it was postulated that oxidizing/reducing power of the applied gas can determine the nature of the charge carriers in the oxide and thus, if NO\textsubscript{2} is a stronger oxidant than chlorine, for chlorine the response would be that normally observed for an n-type oxide, but NO\textsubscript{2} would be strong enough to cause the majority charge carriers to become holes (due to electron abstraction), leading to an apparent p-type response.
Figure 3.1  Resistance response of a pellet of Ba₂FeNb₃O₁₀ to reducing and oxidizing gases in air at 500 °C, from Williams and Moseley.

Ba₂FeNb₃O₁₀ has been characterized structurally in work by Krainik and Isupov. Similar niobates with the tetragonal tungsten bronze structure have been documented in works by other authors. In Ba₂FeNb₃O₁₀, the lattice, of general formula A₂B₆O₁₆, is composed of MO₆ octahedra (M = Fe or Nb, which are randomly distributed) joined together at their apices, forming trigonal, square and pentagonal tunnels, which lie parallel to the c axis (figure 3.2). The large Ba²⁺ cations occupy the pentagonal and square sites. As a result of the channels through the crystal, there will also be 5, 4 and 3-coordinated empty sites on the surface, which, due to their different sizes and repulsion energies with respect to entering gas molecules, may offer opportunity for selective adsorption (assuming that there is some adsorption of the gas onto the oxide surface).
As already mentioned in chapter 1, the conductivity depends on the number of electron-donor and acceptor states in the material. In compounds where the number of donors is much greater than the number of acceptors, the conduction will clearly be n-
type and for those where the number of acceptors is much greater than the number of donors, clearly, p-type will occur. However, there is the possibility that the number of acceptors is very close to the number of donors, in which case a changeover in conduction type may be induced by small variations in the number of these states. Williams and Moseley found that

\[ \sigma / e = \mu K_3 N_D / N_A + \mu K_1 N_A / K_3 N_D \]

(definitions of symbols given in chapter 1). The conductivity rises as \( N_A \) becomes larger if \( N_A \) is greater than \( N_D \) but also rises if \( N_A \) becomes smaller if \( N_A \) is less than \( N_D \), so that there is a conductance minimum fig. 3.3. Therefore, it is possible under these conditions for a small change in the number of surface acceptors (oxygen species) to cause a transition from n-type to p-type if the material is operating in the vicinity of the conductance minimum. Hence, it was proposed that by varying the Fe/Nb ratio, the acceptor / donor ratio would also be altered and there would be a corresponding change from n to p-type with increasing iron concentration and that in the vicinity of this transition, the material would be very sensitive to the relative oxidizing / reducing strength of gases.

Figure 3.3  A transition from p to n-type behaviour on increasing concentration of reducing gas, after Williams and Moseley.
Barium iron niobate, $\text{Ba}_6\text{FeNb}_9\text{O}_{30}$, is formed by substituting $\text{Ba}_6\text{Nb}_{10}\text{O}_{30}$ (in which Nb is in both the +4 and +5 oxidation states) with $\text{Fe}^{3+}$. A more accurate representation of the unsubstituted compound is $\text{Ba}_6\text{Nb}^{IV}_2\text{Nb}^{V}_8\text{O}_{30}$. This material conducts via 'polaron hopping'. In such mixed valence oxides, the element that is represented by two oxidation states has a non-integral charge (the net charge is not a whole number and there is transfer of charge between oxidation states). If there are different oxidation states of the same element, there are extra electrons in the solid with a small polaron trapping. This trapping is due to the difference in the ionic radii between the oxidation states, ($\text{Nb}^{4+} = 0.74 \text{ Å}$ and $\text{Nb}^{5+} = 0.69 \text{ Å}$) which cause local lattice distortions. Extra electrons or holes can also be introduced by changing the stoichiometry. Shannon gives the ionic radii of $\text{Fe}^{3+}$ (low spin), $\text{Fe}^{4+}$, and $\text{Nb}^{5+}$ as 0.55, 0.59 and 0.64 Å respectively. $\text{Ba}_6\text{FeNb}_9\text{O}_{30}$ has all the niobium in the +5 oxidation state. In the present work, it was proposed that if extra iron was introduced, it may be possible that $\text{Fe}^{3+}$ oxidizes to $\text{Fe}^{4+}$ to make up the charge balance and that it would substitute for $\text{Nb}^{5+}$, due to the similarity in their size. Alternatively, charge balance may be achieved by the formation of oxygen vacancies and / or secondary phases. Thus, if Fe is oxidised to a higher oxidation state, one would expect to see the material to increase in p-type characteristics. An increase in conductivity should be observed. For $x < 1$, it would be necessary for either the reduction $\text{Fe}^{3+} \rightarrow \text{Fe}^{2+}$ or $\text{Nb}^{5+} \rightarrow \text{Nb}^{4+}$ to occur. According to Shannon, the ionic radius of $\text{Nb}^{4+}$ is 0.68 Å. Considering the ionic radii, the reduction $\text{Nb}^{5+} \rightarrow \text{Nb}^{4+}$ would be more likely. Here, the conductivity would increase with decreasing $x$ and the material would remain n-type. There would also be energetic requirements for these oxidation / reduction reactions. In theory, it should therefore be possible to induce an n to p-type transition by modulating the electron-donor density. In this way it was hoped that it would be possible to modify the gas response.

$\text{Ba}_6\text{FeNb}_9\text{O}_{30}$ is an n-type extrinsic semiconductor. However, this conduction type has only been classified using the operational definition and the origin of the donor states has not been investigated. It should also be possible to define the conductivity type of an oxide by observing the effect on the conductance of changing the oxygen partial pressure. This experiment should also provide information about the type of
defect involved in electrical conduction\textsuperscript{13}. In addition, if the donor states are due to presence of oxygen vacancies, it should be possible to heat the sample in oxygen and observe a weight gain by thermogravimetric analysis (TG). Alternatively, the n-type conductivity could be the result of trace amounts of impurities such as alkali metals, donating electrons, or if the material were intrinsic, n-type conduction could be possible by thermal promotion of electrons from localized d states to delocalized states in the conduction band.

Here it was attempted to make a solid solution by increasing the relative iron content in Ba\textsubscript{x}Fe\textsubscript{10-x}O\textsubscript{30} (1 ≤ x ≤ 2). It was hoped that there would be a consistent trend in the corresponding gas-sensing properties of the material.

3.2 Experimental

A series of compounds, Ba\textsubscript{x}Fe\textsubscript{10-x}O\textsubscript{30} (1 ≤ x ≤ 2) was made using the method in chapter 2. For Ba\textsubscript{x}Fe\textsubscript{8}O\textsubscript{30}, the reaction may be written:

\[ 12 \text{ BaCO}_3 + \text{Fe}_2\text{O}_3 + 9\text{Nb}_2\text{O}_5 \longrightarrow 2\text{Ba}_6\text{FeNb}_9\text{O}_{30} + 12 \text{CO}_2 \]

Pellets were stabilized in 'zero grade air' (21 % oxygen : 79 % nitrogen) for two hours and exposed to increasing concentrations (160, 260, 400, 600 and 1000 ppm respectively) of test gas (propane and carbon monoxide), recovered in air, and then exposed again to the same concentrations, in the reverse order. Constant temperature experiments were run in the range 465 - 475 °C. In addition, the effect of variation in oxygen partial pressure was examined: a pellet of x = 1.6 was exposed to oxygen in nitrogen, continuously increasing the oxygen content from 0.2 % (2,000 ppm) to 20 % (200,000 ppm) at 700 °C over a period of 12 hours.

In order to investigate the possibility of the presence of oxygen vacancies, powders of x = 1.0 and x = 1.6 were heated in oxygen at a rate of 10 °C per minute from room temperature to 900 °C. However, only a very small weight loss was shown (approx. 0.1% of the pellet weight) for both samples.
3.3 Materials characterization

3.3.1 Scanning-electron microscopy

Generally, the materials showed a wide variety of crystallite shapes and sizes. The grains showed varying degrees of sintering. In some cases, there were masses of grains which had fused together. A typical example is shown in fig. 3.4. In addition, four pellets of the same composition, \( \text{Ba}_6\text{Fe}_{1.6}\text{Nb}_{8.4}\text{O}_{30} \), were made, firing at different temperatures (1100, 1125, 1150 and 1175 °C respectively). It could be observed from the SEM’s (fig. 3.5) that the sintering and grain size increased from 1100 °C until at 1175 °C, there was very little space in between the grains and the porosity had almost been removed.

Figure 3.4 A typical example of a pellet of \( \text{Ba}_6\text{Fe}_{1.6}\text{Nb}_{8.4}\text{O}_{30} \) fired at 1200 °C

with gold remaining from sputtered electrodes
3.3.2 X-ray diffractometry

All of the compounds were found to have the tetragonal tungsten bronze structure as in section 3.1. The parent compound, $\text{BaFeNb}_0\text{O}_{30}$ (space group P4bm) was not recorded in the powder diffraction literature. However, the experimental pattern (fig. 3.6 (a)) matched that simulated (fig. 3.6 (b) and table 3.1) using the program LAZY-PULVERIX (simulation by R.H. Jones, Royal Institution, London). It also matched the literature pattern (JCPDS 31-158) of $\text{Ba}_2\text{Nb}_2\text{O}_{15}$. Some compounds of lower Fe/Nb ratio were also prepared. However, although still containing the TTB, these were
mixed phases and did not respond to CO or propane. For iron-rich preparations, there was a small amount (up to ca. 20%) of secondary phase \( \text{BaFeO}_3 \) (possibly with some Nb substitution present), which generally disappeared as the iron content was decreased.

![Experimental XRD pattern of \( \text{Ba}_x\text{FeNb}_y\text{O}_{30} \)](image1)

![XRD pattern of \( \text{Ba}_x\text{FeNb}_y\text{O}_{30} \) simulated using LAZY-PULVERIX](image2)
Table 3.1  Agreement of experimental with simulated data (most intense peaks)

<table>
<thead>
<tr>
<th>2θ</th>
<th>Experimental</th>
<th>simulated</th>
<th>I (relative)</th>
<th>Experimental</th>
<th>simulated</th>
</tr>
</thead>
<tbody>
<tr>
<td>29.75</td>
<td>29.6</td>
<td>0.219</td>
<td>0.181</td>
<td></td>
<td></td>
</tr>
<tr>
<td>31.95</td>
<td>32.0</td>
<td>0.559</td>
<td>0.525</td>
<td></td>
<td></td>
</tr>
<tr>
<td>34.10</td>
<td>34.0</td>
<td>0.562</td>
<td>0.511</td>
<td></td>
<td></td>
</tr>
<tr>
<td>35.1</td>
<td>35.0</td>
<td>0.306</td>
<td>0.244</td>
<td></td>
<td></td>
</tr>
<tr>
<td>37.05</td>
<td>37.0</td>
<td>1.000</td>
<td>1.000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>53.30</td>
<td>53.4</td>
<td>0.209</td>
<td>0.212</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The lattice parameters (in Å) were calculated for the TTB in each case, and these remained the same from one end of the series to the other. This was verified by refining the lattice parameters using the Rietveld program OHPM1 (I.G. Wood, UCL Geology Department) for the compositions x = 1.6, x = 1 and x = 0.6. The results are shown in table 3.2:

Table 3.2  Lattice parameters for barium iron niobate

<table>
<thead>
<tr>
<th>x</th>
<th>calculated manually</th>
<th>Rietveld</th>
<th>Literature*</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.6</td>
<td>a = 12.60(1)</td>
<td>a = 12.587(1)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>c = 3.99(2)</td>
<td>c = 3.9921(5)</td>
<td></td>
</tr>
<tr>
<td>1.0</td>
<td>a = 12.58(1)</td>
<td>a = 12.592(1)</td>
<td>a = 12.60</td>
</tr>
<tr>
<td></td>
<td>c = 4.00(1)</td>
<td>c = 3.9898(5)</td>
<td>c = 3.99</td>
</tr>
<tr>
<td>0.6</td>
<td>a = 12.59(1)</td>
<td>a = 12.579(2)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>c = 3.99(1)</td>
<td>c = 3.9886(6)</td>
<td></td>
</tr>
</tbody>
</table>

* ICSD (Inorganic Crystal Structure Database) Daresbury, Entry no. 26095
3.3.3 Electron-probe microanalysis

The homogeneity of the material on the micrometer scale was examined using electron probe microanalysis. A Jeol Superprobe JXA - 8600 equipped with twin energy dispersive X-ray detectors was employed, with a beam size of 5 \( \mu \text{m} \) scanning over lengths of approx. 4.5 mm.

The linescans were generally very irregular, due to the physical morphology of the samples. In all cases, there were areas of high iron concentration. The majority of these corresponded to decreases in the niobium concentration. It was assumed that these corresponded to the impurity phase, \( \text{BaFeO}_{2+x} \), detected in the X-ray diffraction patterns. Fig. 3.7 shows a typical EPMA linescan.

The apparent iron content of the major phase was examined by using the average Fe/Nb intensities recorded for the TTB phase, and using \( \text{Ba}_6\text{FeNb}_8\text{O}_{30} \) as a standard (assuming Fe = 1.0 for the stoichiometric compound). As can be seen in fig. 3.8, there appeared to be substitution of Fe for Nb in that the experimental \( x \) (experimental Fe content of the TTB matrix) increased with increasing Fe content in the starting mixture. However, it appeared that the theoretical value was not always entirely achieved and that the substitution was, in some cases, incomplete.

![Figure 3.7 EPMA linescan of \( \text{Ba}_6\text{Fe}_{1.6}\text{Nb}_{8.4}\text{O}_{30} \)](image-url)
3.3.4 Mössbauer spectra

Initial spectra were recorded for \( x = 1.0, 1.4 \) and \( x = 1.6 \), at 77K. In all cases, a symmetrical doublet was produced (table 3.3), thus showing the presence of low spin Fe\(^{3+}\). A typical example is shown in fig. 3.9. Thus at 77 K, there was no oxidation of Fe\(^{3+}\) to Fe\(^{4+}\).
3.4 Electrical characterization and gas response

3.4.1 Resistivities and Activation Energies

The resistance in 'air' was measured as a function of temperature. The pellets were heated from 400 to 800 °C over a period of 6 hours (1.1° min⁻¹) in Ar / O₂ mixture (80% / 20%) and cooled down again from 800 to 400 °C over the same time period, in the same mixture. Fig. 3.10 shows a typical resistance curve. Each pellet showed an initial shallow decrease followed by a sharp increase in resistance, due to desorption of moisture and carbon dioxide (the desorption of water and carbon dioxide will be shown in the following chapter). All pellets showed very little hysteresis. The resistivities at 450 °C are shown in table 3.4.:

Table 3.4 Resistivities of barium iron niobates

<table>
<thead>
<tr>
<th>x</th>
<th>resistivity (Ω cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.6</td>
<td>4.7 × 10⁷</td>
</tr>
<tr>
<td>1.4</td>
<td>1.1 × 10⁸</td>
</tr>
<tr>
<td>1.2</td>
<td>6.0 × 10⁷</td>
</tr>
<tr>
<td>1.0</td>
<td>3.9 × 10⁷</td>
</tr>
</tbody>
</table>

The activation energies for conduction were estimated from fig. 3.10 by plotting ln R vs 1/T (an example is shown in fig. 3.11) and by using the equation

\[ \ln R = \ln R_0 - \frac{E_a}{RT} \]
Figure 3.10 Resistance vs temperature for a pellet of Ba$_6$Fe$_{1.4}$Nb$_{8.6}$O$_{30}$ (in synthetic air)

$\ln R$ vs $1/T$ for Ba$_6$Fe$_{1.4}$Nb$_{8.6}$O$_{30}$ fired at 1200 °C

Figure 3.11 $\ln R$ vs $1/T$ for a pellet of Ba$_6$Fe$_{1.4}$Nb$_{8.6}$O$_{30}$ (in synthetic air)
The activation energies were as follows (table 3.5):

Table 3.5 Activation energies for barium iron niobates

<table>
<thead>
<tr>
<th>x</th>
<th>E_a (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.6</td>
<td>1.08</td>
</tr>
<tr>
<td>1.4</td>
<td>1.13</td>
</tr>
<tr>
<td>1.2</td>
<td>1.16</td>
</tr>
<tr>
<td>1.0</td>
<td>0.92</td>
</tr>
</tbody>
</table>

As the activation energies and resistivities did not differ significantly across the series, it was suspected that the materials were predominantly TTB, with intergrowths of a phase such as BaFe$_2$O$_4$, as intergrowths (typically on the Å scale) would not be seen under an SEM (resolution in the order of µm) or detected by X-ray diffraction. An attempt to confirm the presence if this phase using Mössbauer spectroscopy (K. Knight, University of Greenwich) was inconclusive.

3.4.2 Effect of increasing oxygen partial pressure

As expected, increasing oxygen partial pressure lead to an increase in resistance. This is shown in figure 3.12. From a plot of ln R vs ln p(O$_2$) (figure 3.13), it could be seen that the conductivity was roughly proportional to p(O$_2$)$^{-1/10}$. This is much smaller than typical values for other semiconducting oxides (of between -1/4 and -1/6 for the equilibration of O$_2$(g) with lattice oxygen $^{14}$ and of between -1/2 and - 1/4 for the equilibration of O$_2$(g) with surface oxygen$^{15}$). This low dependence on the oxygen partial pressure implies that the observed changes were due to the movement of lattice oxygen and that the rate of equilibration of this with oxygen gas was slow. It can be deduced that at 700 °C, conduction no longer takes place via anionic chemisorption at the surface, but at this temperature, defect migration in the bulk is slow. In addition, the slope changed during the course of the experiment. This indicated that the oxide had not equilibrated with its surroundings at the time the experiment began.
Increasing the oxygen partial pressure over the duration of the experiment may be seen as the equivalent of recovery from exposure to a reducing gas, in that on removal of the reducing gas, the oxygen partial pressure would be increased. During this experiment, an increase in $p(O_2)$ from 0.02 to 0.2 atmospheres over a period of 12 hours caused a drop in resistance from 140 kΩ to 110 kΩ. However, in 160 ppm propane at 467 °C, the resistance of the same pellet dropped from 1.1 MΩ to 0.32 MΩ over a period of 10 minutes. The change in resistance caused by exposure to propane was thus much more rapid than that caused by deliberately increasing the oxygen partial pressure, to the extent that it indicated that the mechanisms involved were different. It may be suggested that at 700 °C, the change in resistance was not due to gaseous oxygen equilibrating with the oxide surface but with lattice oxygen.
Figure 3.12 The effect of increasing oxygen partial pressure (oxygen/nitrogen mixture) on a pellet of Ba$_4$Fe$_{1.8}$Nb$_{0.2}$O$_{30}$ fired at 1200 °C

Figure 3.13 ln R plotted as a function of ln (p(O$_2$))
3.4.3 Response measurements

Preliminary experiments, showed that at 400 °C, $x = 1.0$ and $x = 1.4$ had almost zero response to $\text{H}_2\text{O}$, $\text{CH}_4$ and $\text{CO}_2$. Only small responses were observed to CO and in the case of $x = 1.4$, to $\text{H}_2$.

The principal experiments showed that all compounds gave decreases in resistance when exposed to reducing gases, typical of n-type semiconductors. A typical result is shown in figs. 3.14 (a) and (b). Many pellets were highly selective to propane. However, there was no pattern across the series in selectivity and there was little reproducibility within pellets of the same composition. Selectivities varied between 1 and 7 (where the selectivity ($S$) is defined as propane sensitivity / CO sensitivity). A typical example of the response of a selective pellet is shown in fig. 3.15. In agreement with Windischmann and Mark* (discussed in chapter 1), the CO response was proportional to the square root of the gas concentration and $(R_{\text{air}} - R_{\text{gas}})/R_{\text{gas}}$ (or $\Delta \sigma/\sigma_0$) vs $[\text{gas}]^{1/2}$ gave a linear graph. It was noted that for many pellets, the propane response cut approximately through the origin, whereas there was a large positive intercept for CO. In addition, a set of compounds fired at 1050 °C was also prepared. These had a much finer and more porous grain structure (a typical example is shown in fig. 3.16) than those fired at 1200 °C but they were not selective to propane. Other than this, there was no obvious difference in the nature of the response of those pellets fired at 1200 °C and those fired at the lower temperature. Further work concentrated on pellets fired at the higher temperature.

It appeared that the reactivity and selectivity was related to the porosity of the pellets: those that were too porous showed little selectivity, those that had no gas access as a result of over-sintering were not reactive at all and those that were very well-sintered but still retained some porosity showed high selectivity. This is illustrated in figure 3.17
Figure 3.14 (a) Response of $\text{Ba}_2\text{FeNb}_5\text{O}_{19}$ (modified sintering conditions) to propane

Figure 3.14 (b) Response of $\text{Ba}_2\text{FeNb}_5\text{O}_{19}$ (modified sintering conditions) to CO
Figure 3.15 Response at 467 °C vs \([\text{gas}]^{1/2}\) of a pellet of Ba$_6$Fe$_{1.6}$Nb$_{4.4}$O$_{39}$ fired at 1200 °C

Figure 3.16 Typical example of a pellet of Ba$_6$FeNb$_7$O$_{39}$ fired at 1050 °C
In order to observe the effects of sintering and the resulting microstructure on the selectivity, the responses of the pellets of $\text{Ba}_6\text{Fe}_{1.6}\text{Nb}_{8.4}\text{O}_{30}$ fired at different temperatures were examined. The selectivities were $S = 4, 6, 23$ and 4 for pellets fired at 1100, 1125, 1150 and 1175 °C respectively, showing that there was an optimum porosity for high propane selectivity. Hence, it would seem reasonable that in the previous pellets, the grains were of different shapes and sizes giving different degrees of sintering, leading to large variation in the subsequent response magnitude and selectivity.

Figure 3.17  SEM micrographs of pellets of $\text{Ba}_6\text{Fe}_{1.6}\text{Nb}_{8.4}\text{O}_{30}$ fired at 1200 °C (showing the selectivities (S) and sensitivities)

(a) low selectivity  \hspace{1cm} (b) high selectivity  \hspace{1cm} (c) unreactive

\begin{align*}
\text{S} & = 1.3 \\
\text{C}_3\text{H}_8 & = 0.152 \\
\text{CO} & = 0.048 \\
\text{S} & = 6.8 \\
\text{C}_3\text{H}_8 & = 0.328 \\
\text{CO} & = 0.115 
\end{align*}
In an effort to eliminate the erratic results produced using pellets, thick films were made, which, it was hoped, would avoid the partial grain fusion during the second firing and also prevent the formation of air pockets during compaction.

Thick film devices were successfully fabricated from 3 of the powders of \( \text{Ba}_x\text{Fe}_{1-y}\text{Nb}_y\text{O}_{30} \) that had been subject to only one sintering at 1200 °C. Three other materials were attempted, but these failed due to crumbling of the test material and very high resistances.

For each material, the powder was mixed with a small quantity of acetone and deposited on an alumina substrate with platinum interdigitate electrodes. On the reverse side of the substrate was a Pt heater. The substrates had been ultrasonically cleaned in acetone.

These thick films were exposed to 200, 400, 600, 800 and 1000 ppm CO, recovered in air, and then exposed to the same concentrations of propane. The materials in this form responded almost instantaneously. Although the magnitudes of the responses were comparatively small, two of the materials were reasonably selective to propane, whilst the other was less selective. The selectivities are shown in table 3.6

<table>
<thead>
<tr>
<th>film</th>
<th>( \Delta \sigma/\sigma_0 ) propane</th>
<th>( \Delta \sigma/\sigma_{CO} )</th>
<th>S</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a)</td>
<td>0.048</td>
<td>0.010</td>
<td>4.8</td>
</tr>
<tr>
<td>(b)</td>
<td>0.038</td>
<td>0.015</td>
<td>2.5</td>
</tr>
<tr>
<td>(c)</td>
<td>0.048</td>
<td>0.012</td>
<td>4.0</td>
</tr>
</tbody>
</table>

Following this, the temperature dependence of the relative responses to propane and carbon monoxide was examined. The pellets were heated from 100 to 700 °C over
a period of 6 hrs in zero grade air, then cooled down from 700 to 100 °C over the same time period. They were then heated back to 700°C in 1000 ppm CO and cooled down again. The experiment was repeated in air and then in 1000 ppm propane. It was evident that the selectivity was highly temperature dependent. The CO response decreased with increasing temperature, cutting off at ca. 560 °C. It was thus confirmed that (fig. 3.18) at the temperatures used in these experiments, the propane response was much larger than that of CO.

Figure 3.18  Ba₉Fe₁₀Nb₄O₉₅ in air, 1000 ppm carbon monoxide and 1000 ppm propane
3.5 Combustion studies on \( \text{Ba}_6\text{Fe}_{1.6}\text{Nb}_{8.4}\text{O}_{30} \)

A common reaction product of both propane and carbon monoxide over \( \text{Ba}_6\text{Fe}_{1.6}\text{Nb}_{8.4}\text{O}_{30} \) was carbon dioxide. The reaction of each gas over \( \text{Ba}_6\text{Fe}_{1.6}\text{Nb}_{8.4}\text{O}_{30} \) was monitored by inspection of the mass 44 intensity as a function of temperature. Fig. 3.19 shows that the onset of carbon monoxide oxidation to carbon dioxide occurred at ca. 310 °C whereas propane combustion began at ca. 420 °C. It should be noted that propane also exhibits a \( \text{C}_3\text{H}_7^+ \) peak at mass 44. However, the major propane peak was at mass 43 (\( \text{C}_3\text{H}_7^+ \)), the intensity of which decreased at the same temperature at which the mass 44 signal increased. The mass 44 peak would be expected to be more sensitive to \( \text{CO}_2 \) concentration since 3 molecules of \( \text{CO}_2 \) were produced for the complete combustion of 1 mole of propane.

![Graph showing mass 44 (CO₂⁺) intensity vs reactor temperature for the reaction of 1000 ppm CO and 1000 ppm propane over Ba₆Fe₁.₆Nb₈.₄O₃₀](image)

Figure 3.19  Graph showing mass 44 (CO₂⁺) intensity vs reactor temperature for the reaction of 1000 ppm CO and 1000 ppm propane over \( \text{Ba}_6\text{Fe}_{1.6}\text{Nb}_{8.4}\text{O}_{30} \)
3.6 Discussion

It was found that at the operating temperature (465-475 °C), carbon monoxide burns at a much faster rate than propane. Thus it was proposed that carbon monoxide burns within the outer shell of the pellet, having, as a consequence, a diminished effect on the conductivity.

This is in agreement with the gas composition profile for a porous pellet depicted in previous work by McAleer et al.\textsuperscript{17} (also discussed in chapter 1) where it was stated that as the operating temperature increases, the combustion zone becomes narrower and hence the measured response decreases. In the present work, CO burns before it can reach the interior of the pellet and hence the apparent selectivity\textsuperscript{18,19}. In addition, is postulated that the large positive intercept for the CO response shown in figure 3.15 is also a consequence of the combustion of CO on the outer part of the pellet. Thus, in agreement with McAleer\textsuperscript{17} et al and Komori et al\textsuperscript{20}, it was possible to have selectivity to a less reactive gas (propane) over a more reactive one (CO).

Thus, this work showed that the major factor influencing the response of the barium iron niobates is the microstructure. It appears that structural variations on a small (Å) scale (intergrowths) have little effect whereas structural variations on the micron scale have profound effects. The presence of intergrowths has not been conclusively confirmed. Recurrent intergrowths occur in hexagonal tungsten oxide bronzes (HTB), where slabs of WO\textsubscript{3} intergrow with the HTB. For example, an intergrowth tungsten oxide bronze (ITB) is formed in Bi\textsubscript{y}Ti\textsubscript{6}CrO\textsubscript{27}\textsuperscript{21}. Intergrowths also occur in non-stoichiometric compounds\textsuperscript{22}.

It was not possible to show any effect of change in the donor density with doping as complete substitution was not achieved and the responses were not composition dependent. Thus, as far as these results show, compositional changes have only little effect on the response compared to microstructural changes.

Results from film devices provided some evidence that the reproducibility might
be improved by this form of fabrication, although many more films would be needed in order to reach any firm conclusion. Film data showed two other things: Firstly, that a greater surface area (film vs. pellet) improves the rate of reaction and increases the response rate dramatically. Secondly, the same response as that achieved with powders fired twice can be achieved by only one firing. Thus, any later firings only modified the compound physically and caused no chemical changes.

The dependence of the selectivity on the microstructure is in agreement with the theory published by Williams\textsuperscript{**15}, it which he showed that the relative sensitivities are influenced by surface area, rate constant for combustion and the geometry of the pore sizes of the material. Williams showed that the gas concentration found at the centre of a pellet is determined by the ratio $k'r'^2/D'$ where $k'$ is the rate constant for combustion of the gas, $r$ is the pellet radius and $D'$ is the diffusivity of the gas within the pellet. $K'$ is directly proportional to the surface area of the material and $D'$ is directly proportional to the porosity. Thus the factor determining pellet response is the ratio of $1/k'(\text{reaction time})$ to $r^2/D'$ (diffusion time). For each gas, these will be different, so that this will determine the selectivity. In this case, $k'/D'$ is small for propane and large for carbon monoxide. In theory, it should be possible to calculate this ratio for a variety of gases of different oxides and predict the selectivity.

It has also been shown, by the oxygen partial pressure dependence, that the mechanisms responsible for conduction are different at 460 °C and at 700 °C. It may be suggested that at the lower temperature, conduction takes place on the oxide surface as described earlier, via charged oxygen species, but at 700 °C, conduction occurs via migration of lattice oxygen, which is slow at this temperature.

3.7 Conclusion

The combustion studies showed that the selectivity to propane at the operating temperature of 465-475 °C was due to the fact that in this temperature range, most of the CO had burned away whereas the propane combustion was very much incomplete. Effectively, only propane diffuses into the pellet whilst the CO burns on the outside
before it is able to penetrate the sensitive element. Thus the reactive element only
detects the propane. If selectivity is determined by the relative rates of combustion and
diffusion of the gases, it is not surprising that the porosity and microstructure play a
crucial role in determining the gas response. It has been shown that the effects of
microstructure are crucial in determining the gas response whereas ion substitution (and
structural changes on the Å scale) have little effect.

3.9 Suggestions for future work

In future work, as it has been shown that control of the microstructure is of
paramount importance in regulating and reproducing pellet responses, it might be
advantageous to use an alternative method of preparation such as precipitation\textsuperscript{23} or the
sol-gel process\textsuperscript{24} which would be more likely to produce more uniform starting
materials. Ritland and Readey\textsuperscript{25} showed that it was possible to control the pore size and
porosity of alumina ceramics by vapour phase sintering, firing alumina in a reactive gas
(HCl) atmosphere. Other methods of preparation may also be necessary to achieve
complete substitution and obtain the desired stoichiometry. Only when the desired
stoichiometry has been achieved will it be possible to verify conclusively the hypothesis
concerning modulation of the donor density by ion substitution. If the present method
of preparation were to be used, it may be advantageous to work at slightly lower firing
temperature (1150 or 1175 °C for example) in order to avoid agglomeration.

The presence of intergrowths would be confirmed conclusively if lattice imaging
electron microscopy was used. It would also be interesting to examine the electrical
properties of other intergrowth tungsten bronze oxides and to compare the tetragonal
tungsten bronzes with some examples of the hexagonal type.

It was not possible, during the course of this work, to investigate the Mössbauer
spectra of the barium iron niobates at 4.2 K. This could show whether or not it is
possible to have mixed valence iron in this compound. If two separate types of iron
were found, a temperature study would illustrate the interchange of the oxidation
states.
Future work could also focus on examining the relative rates of combustion of other gases and over other materials and correlating them to the gas selectivity, in order to explore further the possibility of obtaining selectivity by utilizing combustion-induced composition gradients. In addition, the rate constants for combustion, together with microstructural data should allow the prediction of gas selectivity.

In addition, tetragonal and hexagonal tungsten bronze-type niobates may offer opportunity for selective adsorption due to their channels of different coordinations. It may be possible, on energetic grounds, to predict gas selectivity by considering the sizes of the gas molecules, the surface sites and the repulsion energies which must be overcome in order to dock a molecule at the channel entrance.
Appendix 3.1

Photochemical smog is a secondary air pollutant, formed when hydrocarbons, nitrogen oxides and atmospheric oxygen interact under the influence of ultraviolet radiation from the sun and under stagnant air conditions.

NO is produced by combustion in the car engine:

\[
N_2 + O_2 \rightarrow 2NO
\]

and on release into the atmosphere,

\[
NO + \frac{1}{2} O_2 \rightarrow NO_2
\]

Oxygen radicals are then formed by photolytic reaction with light energy:

\[
NO_2 + hv \rightarrow NO + O^* \\
O_2 + hv \rightarrow O^* + O^*
\]

and ozone is formed on combination of molecular oxygen and oxygen radicals

\[
O_2 + O^* \rightarrow O_3 \text{ (oxidant)}
\]

In addition, hydroxyl radicals are also produced by reaction of water with oxygen radicals

\[
H_2O + O \rightarrow 2OH \text{ (oxidant)}
\]

The oxidants react with hydrocarbons in various chain reactions to create smog.
Chapter 4: Chromium iron niobates
Chapter 4: Chromium Iron Niobates

4.1 Introduction

The effects on the gas sensing properties of changes in microstructure and ion substitution in chromium iron niobates were examined for the system $\text{Cr}_x\text{Fe}_{1-x}\text{NbO}_4$, and the chromium iron niobates were compared with iron niobate. Moseley et al. briefly reported the gas-sensing properties of $\text{FeNbO}_4$. It has been reported by Goldschmidt that $\text{Nb}_2\text{O}_5$ forms solid solutions with both $\text{Fe}_2\text{O}_3$ and $\text{Cr}_2\text{O}_3$. Later work stated that titania forms a rutile solid solution with $\text{FeNbO}_4$ and also with $\text{CrNbO}_4$. As mentioned previously in chapter 1, $\text{Cr}^{3+}$ and $\text{Fe}^{3+}$ have almost identical ionic radii. Thus it was proposed that $\text{CrNbO}_4$ would form a solid solution with $\text{FeNbO}_4$. It was hoped that there would be a trend in the gas sensing properties of the materials that corresponded to the increase in chromium content.

Chen and Colbow studied the variation in sensitivity to ethanol with MgO doping of $\text{Cr}_2\text{O}_3$. By using the sol-gel method, they prepared a solid solution with a solubility limit of 2.5 mol % MgO. The conductance of films of the material was measured at 350 °C. Above 2.5 mol % MgO, a spinel phase began to appear in addition to the Mg-substituted $\text{Cr}_2\text{O}_3$. The authors showed that the ethanol sensitivity decreased with increasing MgO content within the solubility limit, peaked at the boundary of the solid solution range and then decreased dramatically before levelling off and finally decreasing again at 50 mol % MgO, where a single spinel phase was formed. The conductance in air also peaked in the same place.

It was postulated that Mg$^{2+}$ substitutes for Cr$^{3+}$, creating local negatively charged sites in the lattice, with charge balance obtained by the formation of holes in the valence band. When the spinel phase appears, it surrounds the grains, blocking the diffusion of the holes. Thus, the spinel phase causes a drop in the conductance and also decreases the ethanol sensitivity. However, the reason for the ethanol sensitivity and the

---

1 The holes may alternatively be written as a local oxidation of Cr$^{3+}$
conductance peaking at just over the solubility limit was not established.

FeNbO₄ is an n-type semiconductor and CrNbO₄ (in preliminary work for this thesis) was found to be p-type. Obviously, somewhere in the solid solution range there will be an n/p type transition. If CrNbO₄ is p-type, one would expect to see a decrease in n-type character as this is added to the iron niobate.

Cr₂O₃ has been reported to be a sintering promoter. Cheon et al. found that Cr₂O₃ acted as a sintering promoter in PZT ceramics. Wu et al. also found Cr₂O₃ to be a grain growth promoter that accelerated densification in PNT (Pb₀.₈₈Nd₀.₀₈(Ti₀.₉₈Mn₀.₀₂)O₃). However, it was suggested in other work that in SnO₂, Cr₂O₃ prevents sintering and decreases the response to CO and H₂. In the same work it was suggested that Cr₂O₃ modifies the surface of tin dioxide, to form differently coordinated Cr species. In addition, Ouchi et al. reported that in Pb(Mn₁/₃Nb₂/₃)₀.₃₇₅Ti₀.₇₅Zr₀.₂₅O₃ solid solution piezoelectric ceramics, Cr₂O₃ retarded grain growth although it apparently promoted densification.

In this work, it is proposed that on substitution of Cr³⁺ for Fe³⁺ (increasing the quantity of Cr₂O₃ and decreasing that of Fe₂O₃), two changes might take place: firstly, there might be an electronic / compositional effect due to the substitution of Cr³⁺ for Fe³⁺ and also a microstructural change if Cr₂O₃ acts as a sintering agent. Whatever the sintering modifications caused by the addition of Cr₂O₃, it is proposed, in this work, that there should be a trend in the gas response that correlated with the microstructural variations.

4.2 Experimental

Compounds in the series CrₓFe₁₋ₓNbO₄, 0 ≤ x ≤ 1, were made using the method outlined in chapter 2. The pellets were sandwiched between gold electrodes in the automatic 4-pellet test rig described in chapter 2. For initial experiments, their resistance was recorded as a function of temperature in ‘zero grade’ air (21 % oxygen, 79 % nitrogen) and 1000 ppm CO in air, alternately, with 15 minutes per exposure, starting at 25 °C, ramping the temperature up to 700 °C over a period of 10 hrs and
then returning from 700 to 25 °C over the same time period. The initial switching experiments were then repeated using propane instead of CO.

The surface of one of the compounds (x = 0.20) was studied using Diffuse Reflectance Infra-Red Fourier Transform Spectroscopy (DRIFTS). The difference between a) a raw sample and b) a heat-treated sample of Cr$_{0.2}$Fe$_{0.8}$NbO$_4$ powder was examined using a Nicolet 510 FTIR spectrometer, which had been specially fitted with a gas cell, with a circular sample holder incorporating a heater and also inlet and outlet gas lines allowing flow of air and/or test gas to the sample. Sample (b) had been heated overnight at 700 °C in the furnace.

4.3 Materials characterization
4.3.1 Scanning-electron microscopy

From the SEM micrographs (fig. 4.1 (a)-(f)) it could be seen that the grain size increased on addition of Cr$_2$O$_3$. At x = 0.10, the grain size and also the degree of sintering/necking between grains increased. This became more obvious at x = 0.15, where some grains had fused together completely, and even more so at x = 0.20. It was noted that the larger grained materials were still very porous. Thus, the SEM micrographs indicated that Cr$_2$O$_3$ promotes grain growth and sintering.

In addition, EPMA linescans of a selection of these compounds indicated that both the chromium and the iron were uniformly distributed, although attempts at quantification were unsuccessful. A typical linescan is shown in figure 4.2.
Figure 4.1  SEM micrographs of $\text{Cr}_x\text{Fe}_{1-x}\text{NbO}_4$

(a) $\text{FeNbO}_4$
(b) $\text{Cr}_{0.1}\text{Fe}_{0.9}\text{NbO}_4$
(c) $\text{Cr}_{0.15}\text{Fe}_{0.85}\text{NbO}_4$
(d) $\text{Cr}_{0.2}\text{Fe}_{0.8}\text{NbO}_4$
(e) $\text{Cr}_{0.25}\text{Fe}_{0.75}\text{NbO}_4$
(f) $\text{Cr}_{0.3}\text{Fe}_{0.7}\text{NbO}_4$

$^2$ with Au remaining from deposited electrodes
4.3.2 X-ray diffractometry

XRD showed that it was possible to substitute FeNbO$_4$ with chromium up to $x = 0.08$ in Cr$_x$Fe$_{1-x}$NbO$_4$ and still retain the original (monoclinic) phase (figs. 4.3 (a) and (b)). However, $x = 0.10$ caused the formation of mixed phases (fig. 4.3 (c)). At $x = 0.20$, there was a change to the tetragonal phase, which was that of CrNbO$_4$ (fig. 4.3 (d)). X-ray diffraction patterns are also shown in Appendix 4.1. All tetragonal members of the series were found to be pure. On traversing the tetragonal part of the series, the lattice parameters decreased (c only very slightly) on increasing the chromium content (table 4.1 and figure 4.4). This decrease in the cell parameters was assigned to the formation of a solid solution:
Figure 4.3 Experimental X-ray diffraction patterns showing the transition from monoclinic to tetragonal phase.

Figure 4.4 Change in lattice parameters for the series Cr$_x$Fe$_{1-x}$NbO$_4$. 
Table 4.1  Lattice parameters for the tetragonal part of the series Cr$_x$Fe$_{1-x}$NbO$_4$ (standard deviations given in parentheses)

<table>
<thead>
<tr>
<th>[Cr]</th>
<th>a</th>
<th>c</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2</td>
<td>4.6801(8)</td>
<td>3.0446(5)</td>
</tr>
<tr>
<td>0.3</td>
<td>4.684(1)</td>
<td>3.047(2)</td>
</tr>
<tr>
<td>0.4</td>
<td>4.6784(4)</td>
<td>3.0458(7)</td>
</tr>
<tr>
<td>0.5</td>
<td>4.672(1)</td>
<td>3.0364(9)</td>
</tr>
<tr>
<td>0.6</td>
<td>4.679(1)</td>
<td>3.050(3)</td>
</tr>
<tr>
<td>0.7</td>
<td>4.6672(7)</td>
<td>3.037(1)</td>
</tr>
<tr>
<td>0.8</td>
<td>4.6689(9)</td>
<td>3.041(3)</td>
</tr>
<tr>
<td>0.9</td>
<td>4.669(1)</td>
<td>3.042(2)</td>
</tr>
<tr>
<td>1.0</td>
<td>4.6519(3)</td>
<td>3.024(1)</td>
</tr>
<tr>
<td>literature</td>
<td>4.6443(2)</td>
<td>3.0125(3)</td>
</tr>
</tbody>
</table>

* literature values for CrNbO$_4$ from JCPDS no. 34-366

4.3.3 Mössbauer spectroscopy

The Mössbauer spectra of the compounds Cr 0.0 to Cr 0.6 were recorded at 77K. In each case, a symmetrical doublet representing low spin Fe$^{2+}$ was produced. The spectrum of the compound with x = 0.4 was, however, highly asymmetrical. There was also, arguably, a small asymmetry observable in the spectrum of the compound with x = 0.2. This could indicate that either one transition was favoured over the other or that there were other peaks hidden beneath these spectra. The spectra are shown in fig. 4.5 (a)-(g) and also in Appendix 4.2. The chemical shifts and splittings are illustrated in figures 4.6 (a) and (b) and in table 4.2
Figure 4.5  Mössbauer spectra at 77 K of Cr$_3$Fe$_{13}$NbO$_4$
Figure 4.6 (a) Change in chemical shift on traversing the series Cr$_x$Fe$_{1-x}$NbO$_4$

These figures can be considered to be accurate to ± 0.15 mm s$^{-1}$ (this includes calibration errors of approx. 0.01 mm s$^{-1}$ and fitting errors of a) 0.001 and 0.003 mm s$^{-1}$ for δ and b) between 0.001 and 0.004 mm s$^{-1}$ for Δ).
It was not possible to repeat the Mössbauer measurement for the $x = 0.2$ compound. At this composition, a small increase in the quadrupole splitting, $\Delta$, was evident. FeNbO$_4$ is monoclinic, with space group P2$_1$/a$^3$ and CrNbO$_4$ is tetragonal, S.G. P4$_1$/mmm$^4$, so it is not obvious why an increase in $\Delta$ should be observed on the transition from $x = 0$ to $x = 0.6$. However, the Fe-Fe bond lengths are 3.132 Å and 3.011 Å for the iron niobate and the chromium iron niobate structure (using the Cr-Cr bond distance for CrNbO$_4$) respectively$^5$, so that a local distortion from increased intermetallic bonding may have caused this apparent decrease of symmetry. The Mössbauer spectra also proved that no other phases were present in the compounds.

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**Table 4.2** Mössbauer data for members of the series

<table>
<thead>
<tr>
<th>Cr</th>
<th>$\delta$</th>
<th>$\Delta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>0.50</td>
<td>0.41</td>
</tr>
<tr>
<td>0.1</td>
<td>0.50</td>
<td>0.43</td>
</tr>
<tr>
<td>0.2</td>
<td>0.44</td>
<td>0.50</td>
</tr>
<tr>
<td>0.3</td>
<td>0.52</td>
<td>0.48</td>
</tr>
<tr>
<td>0.4</td>
<td>0.51</td>
<td>0.47</td>
</tr>
<tr>
<td>0.5</td>
<td>0.51</td>
<td>0.49</td>
</tr>
<tr>
<td>0.6</td>
<td>0.52</td>
<td>0.48</td>
</tr>
</tbody>
</table>

---

$^3$ R.S.Roth and J.L.Waring, Amer Mineral., 49 (1964) 242-246

$^4$ JCPDS card no. 34-366

$^5$ ICSD Daresbury, nos. 4858 and 13050
4.4 Electrical characterization and gas response

4.4.1 Resistivities and Activation Energies

From fig. 4.7, it can be seen that the resistivities rose slowly for $x > 0.3$ and steeply for $x > 0.7$. The activation energies were roughly estimated using the data obtained from the air / CO switching experiments from plots of $\ln R$ vs $1/T$ (an example is shown in figure 4.8). The activation energy was approx. 0.3 eV for $x \leq 0.2$ and approx. 0.7 eV for $x \geq 0.5$ (fig 4.9). The change in activation energy (and the rise in resistance) was roughly in the region of the n/p transition, indicated by the change in sign of the response around $x = 0.5$.

Figure 4.7 Resistivity vs chromium content for the series $\text{Cr}_x\text{Fe}_{1-x}\text{NbO}_4$
Figure 4.8  In R vs 1/T for Cr_{0.2}Fe_{0.8}NbO_4 fired at 1200 °C

Figure 4.9  Activation energies for the series Cr_xFe_{1-x}NbO_4
4.4.2 Seebeck voltage measurements

A pellet of $\text{Cr}_{0.2}\text{Fe}_{0.8}\text{NbO}_4$ was heated from 100 °C to 700 °C over a period of 6 hours (ramp rate of 1.7°C per minute) and cooled back down over the same temperature interval. The potential difference developed across the pellet as a consequence of the small temperature gradient present in the furnace was monitored as a function of time.

A graph of potential difference against time is shown in figure 4.10. Two features were noted. Firstly, with increasing temperature, the voltage first increased and then decreased to zero. In addition, the potential differences produced on decreasing the temperature were smaller than those produced during heating. The sign and approximate magnitude of the Seebeck coefficient was obtained by measurement of the temperature profile in the furnace across the pellet position, with gas flowing. The temperature difference between the two sides of the pellet was approximately 1°C throughout the temperature range 100-700 °C. The maximum value attained by the Seebeck coefficient was estimated to be - 0.5 mV °C⁻¹, which is in the order expected for semiconductors (up to 1 mV °C⁻¹⁰).

Figure 4.10 Potential difference produced on heating a pellet of $\text{Cr}_{0.2}\text{Fe}_{0.8}\text{NbO}_4$
4.4.3 Response measurements

The conductance type of FeNbO₄ was found to be in agreement with that reported in the literature. All compositions from x = 0.0 to x = 0.4 showed decreases in resistance on exposure to CO, typical of n-type semiconductors (fig. 4.11 (a) - (f)). However, at x = 0.5, this response disappeared, and became a small increase in compositions with higher chromium content (Appendix 4.3). Poor data were obtained for CrNbO₄ due to the high resistances involved (not shown in fig. 4.11 ((a) - (f)). For propane, the same n/p transition was observed at x = 0.5. However, the propane responses were very small (Appendix 4.4).

It appeared that the response to CO reached a maximum at the composition Cr₀.₂Fe₀.₈NbO₄. It was also apparent that there was a noticeable difference in the response with temperature rising compared to that observed with decreasing temperature: after the specimen had been exposed to elevated temperatures, the CO responses were increased and extended to lower temperatures. In addition, it was noted that on initial heating, there was a sharp drop (rather than a steady decrease) in the resistance.

With the exception of Cr₀.₁Fe₀.₉NbO₄, all compounds showed some hysteresis in the resistance-temperature diagrams, although in most cases this was not pronounced (fig. 4.12). It was also observed that in all cases, for the heating part of the cycle, the responses began at ca. 250-300 °C, until after ca. 500 °C, there were no responses at all. In the latter half of the cycle, there was little response below ca. 150 °C. It could also be noted, that the response onset temperature became lower with increasing chromium content.

In contrast, in the case of propane, the responses were symmetrical in that they were identical in both the heating and cooling cycles, with only the expected uniform decrease in resistance on heating. This can be seen in figures 4.13 (a) to (d). The responses to propane only began to appear at around 300 °C and continued until nearly 650 °C. Thus the onset temperature for propane response was higher than that for CO.
In addition, in contrast to the CO response, the propane response appeared to go through a minimum at ca. $x = 0.2$.

To show that the CO response maximum at $x = 0.2$ was reproducible, a second set of materials (shown earlier in fig. 4.1) was prepared in the same manner as the previous set of chromium iron niobates. These were of compositions $x = 0.1$, 0.15, 0.2, 0.25, and 0.3. The responses were generally largest in the temperature range 200-300 °C and the magnitude of the response was largest for $x = 0.2$ (Appendix 4.5). The responses (estimated from the raw data) are shown in figure 4.14. As previously mentioned, the substitution by Cr$^{3+}$ appeared to shift the response to lower temperature. Table 4.3 shows the numerical values for the responses at 250 °C:

<table>
<thead>
<tr>
<th>$x$</th>
<th>$(R_{\text{air}} - R_{\text{gas}}) / R_{\text{gas}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.10</td>
<td>0.08</td>
</tr>
<tr>
<td>0.15</td>
<td>0.36</td>
</tr>
<tr>
<td>0.20</td>
<td>1.46</td>
</tr>
<tr>
<td>0.25</td>
<td>0.76</td>
</tr>
<tr>
<td>0.30</td>
<td>0.30</td>
</tr>
</tbody>
</table>

The resistances are shown graphically in figures 4.15 (a) to (e).
Figure 4.11  Response to 1000 ppm CO for the series Cr$_x$Fe$_{1-x}$NbO$_4$
Figure 4.12 Resistance as a function of temperature for Cr$_{0.2}$Fe$_{0.8}$NbO$_4$ in air and 1000 ppm CO
Figure 4.13  Response to 1000 ppm propane for the series Cr$_x$Fe$_{1-x}$NbO$_4$

(a)  Cr$_{0.1}$Fe$_{0.9}$NbO$_4$
(b)  Cr$_{0.2}$Fe$_{0.8}$NbO$_4$
(c)  Cr$_{0.3}$Fe$_{0.7}$NbO$_4$
(d)  Cr$_{0.4}$Fe$_{0.6}$NbO$_4$
Figure 4.14 Response to 1000 ppm CO at selected temperatures for the series Cr$_x$Fe$_{1-x}$NbO$_4$.
Figure 4.15  Response to 1000 ppm CO for the second preparation of Cr$_x$Fe$_{1-x}$NbO$_4$
4.4.4 Effect of moisture

Initially, it was suspected that the difference in responses of pellets before and after heating to 700 °C was due to adsorbed moisture. The effect of moisture was examined. Two pellets, x = 0.1 and x = 0.2 were subjected to the program shown in table 4.4:

<table>
<thead>
<tr>
<th>Table 4.4 Program for comparison of CO response in dry and moist air</th>
</tr>
</thead>
<tbody>
<tr>
<td>Interval</td>
</tr>
<tr>
<td>1</td>
</tr>
<tr>
<td>2</td>
</tr>
<tr>
<td>3</td>
</tr>
<tr>
<td>4</td>
</tr>
<tr>
<td>5</td>
</tr>
<tr>
<td>6</td>
</tr>
<tr>
<td>7</td>
</tr>
<tr>
<td>8</td>
</tr>
</tbody>
</table>

It was observed (fig 4.16 (a) and (b)) that in one case (Cr$_{0.1}$Fe$_{0.9}$NbO$_4$) there was no difference in the CO response in both wet and dry air ($\Delta \sigma/\sigma_0 = 0.50$ in dry air and 0.49 in moist air) and in the other case (Cr$_{0.2}$Fe$_{0.8}$NbO$_4$) the response was enhanced considerably in wet air ($\Delta \sigma/\sigma_0 = 1.77$ in dry air and 3.14 in moist air).
Figure 4.16 (a) Response of Cr_{0.1}Fe_{0.9}NbO_{4} to dry and moist CO

Figure 4.16 (b) Response of Cr_{0.2}Fe_{0.8}NbO_{4} to dry and moist CO
In addition, two pellets of $x = 0.2$ were subjected to the regime shown in table 4.5:

**Table 4.5  Program for the effect of repeated exposures to CO in moist air**

<table>
<thead>
<tr>
<th>Interval</th>
<th>Gas</th>
<th>Temp / °C</th>
<th>Time / hrs</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>dry air</td>
<td>500</td>
<td>2</td>
</tr>
<tr>
<td>2</td>
<td>dry air</td>
<td>500-250</td>
<td>2</td>
</tr>
<tr>
<td>3</td>
<td>100 % moist air</td>
<td>250</td>
<td>2</td>
</tr>
<tr>
<td>4</td>
<td>500 ppm CO in 50 % moist air</td>
<td>250</td>
<td>0.5</td>
</tr>
<tr>
<td>5</td>
<td>100 % moist air</td>
<td>250</td>
<td>2</td>
</tr>
<tr>
<td>6</td>
<td>500 ppm CO in 50 %, moist air</td>
<td>250</td>
<td>0.5</td>
</tr>
<tr>
<td>7</td>
<td>100 % moist air</td>
<td>250</td>
<td>2</td>
</tr>
<tr>
<td>8</td>
<td>500 ppm CO in 50 % moist air</td>
<td>250</td>
<td>0.5</td>
</tr>
<tr>
<td>9</td>
<td>100 % moist air</td>
<td>250</td>
<td>2</td>
</tr>
<tr>
<td>10</td>
<td>500 ppm CO in 50 % moist air</td>
<td>250</td>
<td>0.5</td>
</tr>
<tr>
<td>11</td>
<td>100 % moist air</td>
<td>250</td>
<td>2</td>
</tr>
</tbody>
</table>

It was noted, that for two pellets of the same composition (different preparations) the magnitudes of the responses were different ($\sigma/\sigma_0 = 1.54$ for preparation A and 0.62 for preparation B) . From the SEM micrographs in figs. 4.17 (a) and (b) it can be seen that the grain size and the porosity were different in each case. The first preparation had much smaller grains and was much more porous. This showed the higher of the responses.
In both cases (figs. 4.18 (a) and (b)), there was a complete and rapid recovery throughout and the magnitude of the responses were not diminished by exposure to moisture at 250 °C. Thus it appeared that rehydroxylation was slow at this temperature or that some species other than that associated with moisture might have been responsible for the absence of response in the previous (unheated) pellets.

**Figure 4.17 (a)** SEM micrograph of preparation A of Cr$_{0.2}$Fe$_{0.8}$NbO$_4$

**Figure 4.17 (b)** SEM micrograph of preparation B of Cr$_{0.2}$Fe$_{0.8}$NbO$_4$
Figure 4.18 (a) Response of preparation A of \( \text{Cr}_{0.2}\text{Fe}_{0.8}\text{NbO}_4 \) to repeated exposures of moist CO

Figure 4.18 (b) Response of preparation B of \( \text{Cr}_{0.2}\text{Fe}_{0.8}\text{NbO}_4 \) to repeated exposures of moist CO
At this stage it was proposed that hydroxylation of the surface of unheated pellets (caused by the presence of moisture) inhibited the response to CO and that by heating the pellet, the surface hydroxyl groups were removed so that the response appeared. It would then appear that, at 250 °C, re-hydroxylation was slow. The following experiment addresses this problem.

To verify whether or not moisture could have been responsible for destroying the response, pellets were exposed to the regime as follows, this time applying the moisture at 25 °C, so that the pellet should be fully hydroxylated.

Table 4.6  Program for the effect on the CO response of moisture adsorption at low temperature

<table>
<thead>
<tr>
<th>Interval</th>
<th>Gas</th>
<th>Temp / °C</th>
<th>Time / hrs</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>dry air</td>
<td>700</td>
<td>5</td>
</tr>
<tr>
<td>2</td>
<td>1000 ppm dry CO / air (alternately)</td>
<td>700-25</td>
<td>20</td>
</tr>
<tr>
<td>3</td>
<td>100 % moist air</td>
<td>25</td>
<td>3</td>
</tr>
<tr>
<td>4</td>
<td>1000 ppm dry CO / air (alternately)</td>
<td>25-700</td>
<td>20</td>
</tr>
</tbody>
</table>

It can be seen (figs. 4.19 and 4.20 (a)) that at lower temperatures, the response was greatly diminished by the presence of water vapour ($\Delta \sigma/\sigma_0$ at 250 °C = 2.09 before and 1.02 after exposure to moisture at 25 °C). However, the response was not completely destroyed and not greatly affected at temperatures above ca. 350 °C. Figure 4.20 (b) shows, for comparison, the response on temperature cycling in a dry atmosphere of a pellet that had not been pre-heated at high temperature. It can be seen by inspection of the first halves of the data, that the pretreatment in table 4.6 brought about a response, whereas there was no response in the first half of the cycle for the pellet that had not had a prolonged exposure to high temperature.
Figure 4.19 Response of $\text{Cr}_{3.2}\text{Fe}_{6.8}\text{NbO}_4$ to 1000 ppm CO before and after exposure to moist air
Figure 4.20 (a) Resistance as a function of temperature for \( \text{Cr}_{0.2}\text{Fe}_{0.8}\text{NbO}_4 \) before and after exposure to moisture (prior heat treatment).

Figure 4.20 (b) Resistance as a function of temperature for \( \text{Cr}_{0.2}\text{Fe}_{0.8}\text{NbO}_4 \) in a dry atmosphere (no pretreatment).
These results lead to the conclusion that hydroxylation of the surface indeed destroyed the response at lower temperatures. There was a further possibility that another species was also responsible. De-hydroxylation required temperatures in excess of 400 °C and rehydroxylation was slow at room temperature. It was suspected that carbonate was present, in addition to surface hydroxyl groups.

4.4.5 Selectivity

In contrast to the TTB materials, the experiments in this chapter indicated that chromium iron niobates selectively detected CO in the presence of propane at ca. 250 °C (as opposed to ca. 470 °C for propane detection in the TTBs). Three different pellets of Cr_{0.2}Fe_{0.8}NbO_4 were exposed, at constant temperature, in dry air, to CO (as in table 4.7), and then the whole experiment was repeated in propane using the same concentrations.

Table 4.7 Gas sensitivity program - steps in gas concentration

<table>
<thead>
<tr>
<th>Interval</th>
<th>Gas</th>
<th>Temp / °C</th>
<th>Time / hrs</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>dry air</td>
<td>500</td>
<td>3</td>
</tr>
<tr>
<td>2</td>
<td>dry air</td>
<td>500-250</td>
<td>1.5</td>
</tr>
<tr>
<td>3</td>
<td>dry air</td>
<td>250</td>
<td>3</td>
</tr>
<tr>
<td>4</td>
<td>200 ppm CO in dry air</td>
<td>250</td>
<td>15 mins</td>
</tr>
<tr>
<td>5</td>
<td>400 ppm CO in dry air</td>
<td>250</td>
<td>15 mins</td>
</tr>
<tr>
<td>6</td>
<td>600 ppm CO in dry air</td>
<td>250</td>
<td>15 mins</td>
</tr>
<tr>
<td>7</td>
<td>800 ppm CO in dry air</td>
<td>250</td>
<td>15 mins</td>
</tr>
<tr>
<td>8</td>
<td>1000 ppm CO in dry air</td>
<td>250</td>
<td>15 mins</td>
</tr>
<tr>
<td>9</td>
<td>dry air</td>
<td>250</td>
<td>1</td>
</tr>
<tr>
<td>10</td>
<td>1000 ppm CO in dry air</td>
<td>250</td>
<td>15 mins</td>
</tr>
<tr>
<td>11</td>
<td>800 ppm CO in dry air</td>
<td>250</td>
<td>15 mins</td>
</tr>
<tr>
<td>12</td>
<td>600 ppm CO in dry air</td>
<td>250</td>
<td>15 mins</td>
</tr>
<tr>
<td>13</td>
<td>400 ppm CO in dry air</td>
<td>250</td>
<td>15 mins</td>
</tr>
<tr>
<td>14</td>
<td>200 ppm CO in dry air</td>
<td>250</td>
<td>15 mins</td>
</tr>
</tbody>
</table>
Before exposure to CO, all three pellets showed good stability in their baselines (fig. 4.21). As expected, at 250 °C, there was a reasonably large response to CO (fig. 4.22 (a)). Figure 4.22 (b) shows the response to CO plotted against the square root of the gas concentration. It can be seen that in the range 200 - 1000 ppm, the response was approximately linear and that there was no response hysteresis compared to that illustrated in section 4.4.3. These data thus showed that by high temperature heat treatment, it was possible to remove any response hysteresis. However, in propane, no response was visible (fig. 4.22 (c)). The recovery from CO exposure was very slow.

Thus it was illustrated that using this compound, it was possible selectively to detect CO in the presence of propane.
Figure 4.21  $\text{Cr}_6\text{Fe}_{12}\text{NbO}_4$ (first preparation) in air and CO
Figure 4.22 (a)  
Cr_{0.2}Fe_{0.8}NbO_4 (first preparation) in air and CO (expanded scale)

Figure 4.22 (b)  
Response vs $[\text{gas}]^{1/2}$ for a pellet of Cr_{0.2}Fe_{0.8}NbO_4 (first preparation)
4.4.6 Temperature dependence of selectivity

4.4.6 (i) Preliminary experiments

In order to examine how the relative responses to CO and propane changed with temperature, a pellet of \( \text{Cr}_{0.2}\text{Fe}_{0.8}\text{NbO}_4 \) (which had shown high selectivity) was treated as follows: the temperature was ramped up from 100 to 700 °C in dry air over a period of 6 hours. The temperature was then ramped back down again over the same time period. It was taken up again, in 1000 ppm CO, and finally brought back down. The experiment was repeated, using 1000 ppm propane instead of CO. This is represented in scheme 1:

![Scheme 1](image)
The materials in the chromium iron niobate series showed hysteresis in temperature cycling, both in gas response (section 4.4.3) and of the conductivity in a constant gas atmosphere. This hysteresis appeared to be caused by the thermal desorption of some surface species (attributed to adsorbed moisture and carbon dioxide).

After heating in air (figure 23 (a)), the resistance rose. On exposure to CO, the response was largest at the lower temperatures, in agreement with the results in section 4.4.3. On the decreasing temperature cycle, the CO response was increased and a pronounced minimum (section ABC) in resistance was clearly visible in the high temperature range (figure 23 (b)). On decreasing the temperature in CO, this minimum became larger and the CO line crossed over the air line at the higher temperature end. However, after cycling in CO, the baseline did not recover (figure 23 (c)) to its original value. Still, a small inflexion was visible at high temperature. After cooling in air, the response recovered (figure 23 (d)) to its original value, eventually becoming slightly higher than the original baseline. As expected, the propane responses were smaller than those of CO. Even at this stage (figure 23 (e)), small inflexions in the resistance were visible.
$\ln R$ vs. $1/T(K^{-1})$

1 = $T$ increasing
2 = $T$ decreasing

Figure 23 (a)  $\text{Cr}_{0.2}\text{Fe}_{0.8}\text{NbO}_4$ in air, before exposure to CO (first experiment)
Figure 23 (b)  \(Cr_{0.2}Fe_{0.8}NbO_4\) in air and 1000 ppm CO (first experiment)

2 = air (T decreasing)
3 = CO (T increasing)
4 = CO (T decreasing)
Figure 23 (c) $\text{Cr}_{0.2}\text{Fe}_{0.8}\text{NbO}_4$ before and after exposure to 1000 ppm CO (first experiment)

$2 = \text{air}_1$ (T decreasing)

$3 = \text{CO}$ (T increasing)

$5 = \text{air}_2$ (T increasing)
Figure 23 (d) \( \text{Cr}_{26.3}\text{Fe}_{0.8}\text{NbO}_{4} \) before and after exposure to 1000 ppm CO (first experiment)
Figure 23 (e) \( \text{Cr}_{0.2}\text{Fe}_{0.8}\text{NbO}_4 \) in air and 1000 ppm propane (first experiment)

2 = air (T decreasing)
7 = propane (T increasing)
8 = propane (T decreasing)
The experiment was repeated. Difficulties with poor contacts were experienced in the increasing temperature cycle. On heating in air (figure 24 (a)), the resistance rose, as in the previous experiment. However, the minimum was much stronger. Again, after heating in CO, the minimum became more pronounced (figure 24 (b)). After cycling in CO, the baseline did not recover to its original value (figure 24 (c)). After heating in air, however, the original baseline value was recovered (figure 24 (d)) and the new baseline was above the value of the resistance prior to CO exposure. Again, the resistance minimum was clearly visible during the propane exposures (figure 24 (e)). The peaks in resistance with temperature cycling are equivalent to variation of resistance with time at constant temperature: a resistance peak with decreasing temperature is equivalent to a decay in resistance with time at constant temperature, the timescale for the resistance change at a temperature in the range of the peak being comparable with the timescale for the change of temperature during the ramp.

Figure 24 (a)  \( \text{Cr}_{0.2}\text{Fe}_{0.8}\text{NbO}_4 \) in air before exposure to CO (repeat experiment)
Figure 24 (b)  
Cr$_{0.2}$Fe$_{0.8}$NbO$_4$ in air and 1000 ppm CO  
(repeat experiment)
Figure 24 (c) $\text{Cr}_{0.2}\text{Fe}_{0.8}\text{NbO}_4$ before and after exposure to 1000 ppm CO (repeat experiment)
Figure 24 (d) $\text{Cr}_{0.2}\text{Fe}_{0.8}\text{NbO}_4$ before and after exposure to 1000 ppm CO

$2 = \text{air}_1$ (T decreasing)
$6 = \text{air}_2$ (T decreasing)
$2 = \text{air}_1$ (T decreasing)
$7 = \text{propane (T increasing)}$
$8 = \text{propane (T decreasing)}$

Figure 24 (e) $\text{Cr}_{0.2}\text{Fe}_{0.8}\text{NbO}_4$ in propane (repeat experiment)
The increase in the air baseline resistance after the initial heating cycle was consistent with the removal of OH. Its removal as H₂O would cause it to act as an acceptor and thus increase the resistance of the pellet. On prolonged exposure to CO, heating to high temperature, the resistance minimum grew larger and the pellet was poisoned by CO. The baseline only recovered its original resistance after cycling in air. It was speculated that at high temperature, CO reacts with the oxide to remove lattice oxygen, thereby creating vacancies and that the high temperature resistance minimum was due to a carbonate species. When compared to previous data (sections 4.4 and 4.5), it may be deduced that chromium iron niobate of x = 0.2 is not modified by short exposures to CO (either in alternate pulses with air during temperature ramp experiments or in steps at a constant temperature of 250 °C), but prolonged continuous exposure to CO in temperature ramp experiments causes a modification of the surface.

4.4.6 (ii) Effects of heat treatment

In order to eliminate any possible effects of moisture, the experiment was again repeated, but this time heating for 5 hours, first, at 700 °C, before decreasing the temperature to 100 °C and beginning the cooling / heating cycle. In addition, the CO and propane cycles were included in this (one continuous) experiment and between each cycle, the pellets were stabilized for 2 hours in dry air. This is represented by scheme 2 and detailed in table 4.8:

![Scheme 2](image)
This time, resistance minima at high temperature were not observed (fig. 4.25). This could be interpreted in one of two ways: either the pellet had dried out completely and the effects previously observed were due to some interaction with moisture, or with sufficient heating time, some other unknown species was being driven off the surface. The same experiment was then repeated, but with exposures to air (first and second cycles), CO (third cycle) and air again (fourth cycle), to see if the CO had any effect on the baseline. This is represented by Scheme 3:
In both the increasing and decreasing temperature directions, the baseline stayed constant, showing that CO had no effect. However, at high temperature (ca. 600 °C), for all except the first air line, there appeared to be a small inflexion. This was much larger on the decreasing temperature cycle (fig. 4.26 (a)) than on the increasing temperature section (fig. 4.26 (b)), showing that with sufficient heating, the species responsible for the observed minima could be desorbed.

From these temperature ramp experiments, it appeared that some (unknown) species was being driven off the surface when the pellet was exposed to long heating cycles. However, not all the results were in agreement. In the cases of no pretreatment, their effect was much greater for CO, apparently indicating some reaction involving CO.
Figure 4.25   \( \text{Cr}_{0.2}\text{Fe}_{0.8}\text{NbO}_4 \) in air, 1000 ppm CO and 1000 ppm propane after 5 hours at 700 °C (increasing temperature)

Figure 4.26 (a)   \( \text{Cr}_{0.2}\text{Fe}_{0.8}\text{NbO}_4 \) in air, 1000 ppm CO and then air (temperature decreasing)
Figure 2 (b) \( \text{Cr}_{0.2}\text{Fe}_{0.8}\text{NbO}_4 \) in air, 1000 ppm CO and then air (temperature increasing)

4.7 Stepped temperature in CO

It was postulated that the resistance minimum observed (section ABC of figure 4.23) in an atmosphere containing CO, was due to the thermal desorption of a surface species formed as a consequence of the reaction between CO and the oxide surface. In order to detect the resistance minimum of the CO response, a pellet \( \text{Cr}_{0.2}\text{Fe}_{0.8}\text{NbO}_4 \) was heated to 700 °C for 5 hours, brought down to 600 °C, stabilized, and then taken down to 350 °C. After a two hour interval, the temperature was raised again to 600 °C. This process was repeated for successive temperature intervals, each one 50 °C smaller than the last. The whole experiment was performed with 1000 ppm CO in dry air.
Table 4.9 Program for temperature steps in constant CO atmosphere

<table>
<thead>
<tr>
<th>Interval</th>
<th>Temp / °C</th>
<th>Time / hrs</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>700</td>
<td>5</td>
</tr>
<tr>
<td>2</td>
<td>700-600</td>
<td>2</td>
</tr>
<tr>
<td>3</td>
<td>600</td>
<td>2</td>
</tr>
<tr>
<td>4</td>
<td>600-350</td>
<td>3</td>
</tr>
<tr>
<td>5</td>
<td>350</td>
<td>2</td>
</tr>
<tr>
<td>6</td>
<td>350-600</td>
<td>3</td>
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<td>7</td>
<td>600</td>
<td>2</td>
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<td>8</td>
<td>600-400</td>
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<td>11</td>
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</tr>
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<td>2</td>
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<td>18</td>
<td>500-600</td>
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<td>19</td>
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<td>2</td>
</tr>
<tr>
<td>20</td>
<td>600-550</td>
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<tr>
<td>21</td>
<td>550</td>
<td>2</td>
</tr>
<tr>
<td>22</td>
<td>550-600</td>
<td>3</td>
</tr>
</tbody>
</table>

The experiment failed to show any effect other than the expected monotonic decrease in resistance with increasing temperature (fig.4.27).
The two experiments described in section 4.4.6 (ii) and in this section, together demonstrate that the key element in removing the unusual transient behaviour which gave rise to the peaks in resistance as a function of temperature is the heating of the surface to a sufficiently high temperature (600-700°C) for an adequate length of time. Other experiments on related oxides\textsuperscript{11} have shown that the response to CO comprises two elements: a fast initial response and a slow subsequent drift in resistance over a period of hours before a stable state is achieved. In these experiments also, if the material was preheated at 700 °C in a dry atmosphere, the slow element in the response was eliminated and the signal on response to the presence of CO changed rapidly to the final state, otherwise only obtained after some hours.

Figure 4.27  \( \text{Cr}_{0.2}\text{Fe}_{0.8}\text{NbO}_4 \) in 1000 ppm CO (stepped temperature)
4.5 The effect of gross substitution of Ti$^{4+}$ in chromium iron niobate

4.5.1 Philosophy of these experiments

The sizes of Cr$^{3+}$, Fe$^{3+}$, Nb$^{5+}$ and Ti$^{4+}$ are 0.63 Å, 0.64 Å, 0.69 Å and 0.68 Å respectively. Therefore, it would seem logical to expect Ti$^{4+}$ to substitute for Nb$^{5+}$ due to the similarity in their sizes. Andrade et al. found that it was possible to substitute at least half the Ti$^{4+}$ ions in rutile with other cations. In addition, Khazai et al. synthesized rutile solid solutions in which both iron and niobium were substituted for titanium. Furthermore, Cr$_{0.2}$Fe$_{0.8}$NbO$_4$ was found in the early stages of this work to have the rutile structure. Thus it also seems logical to expect TiO$_2$ (rutile) to form a solid solution with the chromium iron niobate. The compound (Cr$_{0.2}$Fe$_{0.8}$NbO$_4$)$_{0.5}$(TiO$_2$)$_{0.5}$ was prepared and its response to CO compared with that of the parent material (Cr$_{0.2}$Fe$_{0.8}$)NbO$_4$.

XRD (fig. 4.28) showed the compound to be pure, with the same rutile structure as chromium niobate and similar lattice parameters (a = 4.6547(5)) and c = 3.019(1) Å, compared to 4.6443(2) Å for a and 3.0125(3) Å for c in CrNbO$_4$ (4.3.2). Three pellets (shown in figures 4.29 (a), (b) and (c)) of the compound, were examined under the SEM. The structure was similar to the chromium iron niobates, with large well-sintered grains in all three cases.

4.5.2 CO response vs temperature

The pellets were subjected to the same air / CO switching experiment as in section 4.2. The responses of the three pellets at 250 °C were 1.57, 1.60 and 0.68 respectively, compared to a response of 1.53 for Cr$_{0.2}$Fe$_{0.8}$NbO$_4$. A number of points were noted in the resistance plots (two examples are shown in figures 4.30 (a) and (b)).

1. In the initial stage, there was a very pronounced minimum in the resistance with decreasing temperature. The hysteresis in the resistance-temperature diagram was much more marked than for Cr$_{0.2}$Fe$_{0.8}$NbO$_4$.

2. Comparison of increasing and decreasing temperature cycles produced highly asymmetrical graphs (fig. 4.31), with temperature increasing from room temperature on the first cycle, in which the hysteresis of response
much greater than that of Cr$_{0.2}$Fe$_{0.8}$NbO$_4$.

(3) The responses were only very small, but in the second half of the cycle, with temperature decreasing, appreciable responses were observed at lower temperature. As in the chromium iron niobates, these were maximum at around 250 °C, but here they continued as low as 100 °C. In addition, two of these ((a) (which is shown in figure 30 (b)) and (b)), on the final part of the decreasing temperature cycle, showed a sigmoidal loop in the resistance at low temperature, reminiscent of those produced by SnO$_2^{15}$ (shown later in section 4.10). It was assumed that this difference on the decreasing temperature cycle was due to moisture remaining in the pellet and that the moisture level was slightly different for each pellet.
Figure 4.29 SEM micrographs of pellets (a), (b) and (c) of 
$(\text{Cr}_{0.2}\text{Fe}_{0.8}\text{NbO}_4)_{0.5}(\text{TiO}_2)_{0.5}$

Figure 4.30 (a) $(\text{Cr}_{0.2}\text{Fe}_{0.8}\text{NbO}_4)_{0.5}(\text{TiO}_2)_{0.5}$ in air and 1000 ppm CO, pellet (c)
Figure 4.30 (b) \((\text{Cr}_0.2\text{Fe}_{0.8}\text{NbO}_4)_{0.5}(\text{TiO}_2)_{0.5}\) in air and 1000 ppm CO, pellet (a)

Figure 4.31 \((\text{Cr}_0.2\text{Fe}_{0.8}\text{NbO}_4)_{0.5}(\text{TiO}_2)_{0.5}\) in air and 1000 ppm CO, plotted as a function of temperature (pellet (c))
4.5.3 Effect of pretreatment

In order to verify that pretreatment (prolonged heating) was necessary to develop a gas response, the pellets were (i) exposed to 1000 ppm CO at 250 °C with stabilization only, at that temperature and (ii) exposed to CO as in (i), but with a pretreatment of 5 hours at 700 °C in dry synthetic air. An example is shown in figures 4.32 (a) and (b).

It was evident that in two cases, (a) and (b), those pellets that had not been heated initially to 700 °C did not respond, whereas those that had been heat-treated did. In the third case in section 4.8.1, there was no response. This suggested that it was possible, with sufficient heat treatment, to drive off some surface species which was acting to inhibit the response. In this respect the solid solution $(\text{Cr}_{0.2}\text{Fe}_{0.8}\text{NbO}_4)_{0.3}(\text{TiO}_2)_{0.7}$ behaved in the same way as $\text{Cr}_{0.2}\text{Fe}_{0.8}\text{NbO}_4$. If anything, the effect of the inhibiting surface species was more marked in the Ti-substituted composition.

![Figure 4.32 (a)](image-url) (Cr$_{0.2}$Fe$_{0.8}$NbO$_4$)$_{0.5}$(TiO$_2$)$_{0.5}$ pellet (a) in air and 1000 ppm CO, with 5 hours' pretreatment at 700 °C
4.6 Study of the surface of Cr$_{0.2}$Fe$_{0.8}$NbO$_4$ by DRIFTS

Figures 4.32 (a) and (b) show the difference between the raw and heat-treated samples. Spectra were measured at 250 °C. A mirror was used as the background. It was observed that in the untreated sample (fig. 4.33 (a)), that there was broad maximum centred at 3400 cm$^{-1}$ which was assigned to the stretching vibration of OH bonded to the surface of the oxide. This peak was greatly reduced for the heat-treated sample (fig. 4.33 (b)). Both preheated and raw samples exposed to 10,000 ppm CO at 250 °C, using the raw sample in air as the background, showed no additional peaks associated with carbonate or other such surface species.

These spectra provided clear evidence for 1) the hydroxylation of the oxide surface in untreated samples and 2) that there is no direct adsorption of CO onto the oxide surface during gas-sensing, as no carbonate peaks were observed.
Figure 4.33 (a) FTIR spectrum of untreated Cr$_{0.2}$Fe$_{0.8}$Nb$_4$O$_4$ at 250 °C, in air

Figure 4.33 (b) FTIR spectrum of heat-treated Cr$_{0.2}$Fe$_{0.8}$Nb$_4$O$_4$ at 250 °C, in air
4.7 Discussion

From the resistivity data and the phase purity, it was deduced that from $x = 0.2$ to $x = 1.0$, a solid solution was formed and that Cr$^{3+}$ had substituted for Fe$^{3+}$ on the rutile lattice. The presence of only low spin Fe$^{3+}$ supported this assumption.

It was clear from the SEMs that Cr$_2$O$_3$ acted as a sintering agent, increasing the size of the grains. When compared to FeNbO$_4$, all n-type chromium iron niobates showed an increased sensitivity to CO. For example, at 250 °C, the responses ($\Delta \sigma/\sigma_0$) of FeNbO$_4$ and Cr$_{0.2}$Fe$_{0.8}$NbO$_4$ were 0.61 and 1.53 respectively on exposure to 1000 ppm CO.

It also appeared that there was an optimum grain size / porosity for good CO sensitivity. It was possible to have variation in sensitivity within the same composition as a consequence of variation in the microstructure. Some microstructural effects are important and cloud the obvious conclusion to be drawn from section 4.4.3 that the response is enhanced by limited substitution of Cr$^{3+}$ for Fe$^{3+}$. It appeared that the substitution of Fe$^{3+}$ by Cr$^{3+}$ did indeed lower the response temperature. Figures 4.18 (a) and (b) showed that two pellets of Cr$_{0.2}$Fe$_{0.8}$NbO$_4$ had different sized responses to CO in moist air. However, responses to dry air were very similar. It was also possible that the sensitivity maximum may have been related to the monoclinic-to-tetragonal phase transition.

Figure 4.10 showed that initially, as the temperature was increased, the Seebeck voltage rose. This is consistent with extrinsic conduction due to electron transfer to surface states, in agreement with McAleer et al.\textsuperscript{15}, who found that adsorbed water on SnO$_2$ pellets introduced a new electronic surface state, represented by OH$^-$. The sign of the Seebeck effect confirmed that electrons were the majority carriers. However, at higher temperatures, thermal promotion of electrons from the valence band to the conduction band takes place, causing intrinsic conduction to become dominant, resulting in a voltage decrease due to the generation of holes.

The second half of the experiment was not a mirror image of the first half,
showing lower voltages. This would have occurred if some of the surface species responsible for the extrinsic regime had been removed as a consequence of the excursion to high temperature.

McAleer et al.\textsuperscript{15} suggested that in SnO\textsubscript{2}, it is likely that water is bound to the surface as OH groups, and reported trace evidence of O-H absorption in the 3400 cm\textsuperscript{-1} region. Previous studies\textsuperscript{16} assigned a band at 3640 cm\textsuperscript{-1} to the stretching mode of surface hydroxy groups perturbed by hydrogen bonding. In addition, Petrosyan et al.\textsuperscript{17} reported an absorption at 3485 °C, for single crystals of lithium niobate, which they attributed to the stretching vibrations of OH groups.

McAleer et al.\textsuperscript{15} also showed that with SnO\textsubscript{2}, carbon monoxide may react with the oxygen surface states and with the electron associated with OH\textsuperscript{-}. However, they concluded that because of this, the conductance response of SnO\textsubscript{2} pellets extends to lower temperature in the presence of moisture than in the absence of moisture (fig. 4.34). They confirmed that moisture was necessary for the observation of a CO response at temperatures below ca. 350 °C.

**Figure 4.34** Resistivity-temperature profile for a porous pellet of SnO\textsubscript{2} (FEM) exposed to alternating gas atmosphere; 15 min in air, 15 in 1 % CO / 78 % N\textsubscript{2} / 21 % O\textsubscript{2} (a) T increasing (b) 1 % CO (c) air (d) T decreasing

(_____) Temperature increasing (initially wet pellet, dried)

(---) Temperature decreasing (dry pellet, dried air)

from McAleer et al.\textsuperscript{15}
Unlike SnO₂, it was shown in the present work, that for chromium iron niobates, hydroxylation of the surface prevents CO response. It is assumed that in this case, the general rise in resistivity after heating was due to the loss of OH as water, and its replacement by ionosorbed oxygen species. If in this case, adsorbed OH did not react with CO whilst adsorbed oxygen did, then the replacement of OH by adsorbed oxygen would result in an increase in response. This idea therefore rationalizes the observation that, in the chromium iron niobates, prolonged heat treatment at high temperatures (≥ 700 °C) is necessary to induce the response.

Here, it has been shown, within the limits of sensitivity of the I.R. measurement, that in the case of CO adsorption on Cr₀.₂Fe₀.₈NbO₄ at 250 °C, there is no direct bonding between the oxide surface and CO. This is in contrast to the results of Thornton and Harrison[16], who showed, using Mössbauer spectroscopy, that CO bonds to the surface of SnO₂, creating reduced Sn²⁺. One complication in interpretation is that the measurements of Thornton and Harrison were performed at ambient temperature, after exposure to CO and subsequent evacuation, whereas in the present work, observations were made directly on the surface in the gas stream at the above operating temperature.

In contrast to the TTB materials in chapter 3, the chromium iron niobates were selective to CO over propane. The different onset temperatures for responses lead to CO selectivity. In this case, the selectivity appears to have nothing to do with different combustion rates. Simply, a response to CO is obtained at low temperature if the surface is dry. No such response is observed for propane (unlike the TTB materials).

The chromium iron niobates show a variety of behaviour which can be rationalized in terms of the effects of surface hydroxyl groups on the response. Firstly, there is the response hysteresis induced by adsorption of water at a sufficiently low temperature (section 4.4.4). Heating to a sufficiently high temperature in a dry atmosphere restores the response to CO at low temperature; the response can again be inhibited by exposure to water vapour at sufficiently low temperature; infrared...
spectroscopy suggested that the species removed by the high temperature treatment are hydroxyls, OH. Therefore, it appears that tightly bound surface OH blocks the response to CO. The tightly bound OH can only be formed by an extended period of exposure to water vapour at low temperature. Replacement of this surface OH by oxygen, on heating at high temperature in a dry atmosphere, restores the response to CO.

In addition, it has been shown that prolonged continuous exposure to CO at high temperature (during temperature ramp experiments) modifies the resistance of the oxide. This does not occur in short CO / air exposures or in low temperature experiments. It may be speculatively suggested that after such prolonged high temperature exposure, CO reacts with lattice oxygen to create sub-surface vacancies, which are responsible for this modification. After cycling in air, these vacancies are filled and the original resistance is restored. Alternatively, one may speculate on a slow surface reaction between OH and CO, on a surface that has not completely dried, to form some new species, perhaps analogous to the formate species which are presumed to form and decompose readily on SnO$_2$\(^{18}\). In the chromium titanium iron niobates, it was shown that it was possible to substitute large quantities of Ti$^{4+}$ onto the rutile-type lattice, with relatively little effect on the CO sensitivity.

4.11 Conclusion

From this chapter, it may be concluded that the microstructure again appears to be one of the principal factors influencing the gas response. In addition, it has been shown that the response of the chromium iron niobates is inhibited by the presence of moisture, due to adsorbed hydroxyl groups on the oxide surface. In the case of CO on Cr$_{0.2}$Fe$_{0.8}$NbO$_4$, there is no direct adsorption of the gas onto the oxide surface. The response of the chromium iron niobates is also modified by prolonged, continuous exposure to carbon monoxide during temperature cycling. This had been attributed (speculatively) to the reaction of CO with lattice oxygen. In the case of substitution with Ti$^{4+}$, ion substitution plays a relatively minor role in controlling the gas response.
Suggestions for future work

To further examine the possibility of an optimum porosity for gas response, BET adsorption measurements could give accurate porosity data for repeated sets of sample preparations.

In this work, it appears that Cr\(^{3+}\) lowers the response temperature. This could also be investigated for other oxides, to see if it is possible to lower the response temperature with substitution by Cr\(^{3+}\). Other systems could be (CrNbO\(_4\))(SnO\(_2\)), for example.

In order to further prove the existence of surface hydroxyl species, D\(_2\)O exchange could be used in conjugation with FTIR spectroscopy. Thornton and Harrison have used such methods on SnO\(_2\)\(^{16}\).

For the chromium iron niobates, the distribution of chromium on the surface and in the bulk could be examined using X.P.S. in order to observe any segregation. It may be possible to show a link between surface segregation and gas response.

It would also be informative to study systematically for other oxides the temperature cycling characteristics in air/gas exposure experiments as described here, for other oxides, and to correlate the results with the surface species observed by FTIR. Thus, it may be possible to establish the pretreatment conditions which improve the gas response of each sensor material. In order to prove that the surface poisoning effect of CO was due to the formation of a carbonate species, it would be necessary to repeat the FTIR experiment temperature cycling in situ, examine the spectrum with CO at high temperature (≥ 700 °C, for example) and compare this to the spectrum obtained after subsequent cycling in air.
Appendix 4.1  FeNbO$_4$

C:\LAURA\CRO00.RAW  CR00 (CT: 2.0s, SS: 0.020dg, WL: 1.5406Ao)
16-0374  FeNbO$_4$  Iron Niobium Oxide  (WL: 1.5406Ao)
Appendix 4.1  
Cr$_{0.08}$Fe$_{0.92}$NbO$_4$

![X-ray diffraction pattern for Cr$_{0.08}$Fe$_{0.92}$NbO$_4$](C:\LAURA\CR008_RAW CR008 (CT: 2.0s, SS: 0.020dg, ML: 1.5406Ao))

16-0374 1 FeNbO4 Iron Niobium Oxide (ML: 1.5406Ao)
Appendix 4.1 \( \text{Cr}_{0.2}\text{Fe}_{0.8}\text{NbO}_4 \)

Cr\text{O}_{0.2}\text{Fe}_{0.8}\text{NbO}_4 1200

C: \ LAURA\ CR02.RAW CR02 (CT: 2.0s, SS: 0.020dg, WL: 1.5406Ao)
34-0366 x CrNb04 Chromium Niobium Oxide (WL: 1.5406Ao)
Appendix 4.1  CrNbO₄
Appendix 4.2

FeNbO₄

Transmission

Source velocity (mm s⁻¹)

δ = 0.58 Å / 0.41 Å

Trends show results in response...
Appendix 4.2  \( \text{Cr}_{0.2}\text{Fe}_{0.8}\text{NbO}_4 \)
Appendix 4.2  \( \text{Cr}_{0.4}\text{Fe}_{0.6}\text{NbO}_4 \)

\[
\begin{array}{cccc}
\text{Source velocity (mm s\textsuperscript{-1})} & 96.0 & 96.5 & 97.0 \\
\text{Transmission (\%)} & 99.0 & 99.5 & 100.0 \\
\end{array}
\]

\( \delta = 0.51 \), \( \Delta = 0.47 \)
Appendix 4.2  \( \text{Cr}_{0.5}\text{Fe}_{0.5}\text{NbO}_4 \)

\[ \delta = 0.51, \Delta = 0.49 \]
Appendix 4.2  \( \text{Cr}_{0.6}\text{Fe}_{0.4}\text{NbO}_4 \)

\[
\begin{align*}
\delta &= 0.52 \\
\Delta &= 0.48
\end{align*}
\]

Transmission (%) vs. Source velocity (mm s\(^{-1}\))

![Graph showing transmission vs. source velocity with markers and line indicating the values for \( \delta \) and \( \Delta \).]
Appendix 4.3  Response of FeNbO$_4$ to 1000 ppm CO
Appendix 4.3  Response of $\text{Cr}_{0.1}\text{Fe}_{0.9}\text{NbO}_4$ to 1000 ppm CO
Appendix 4.3  
Response of Cr$_{0.2}$Fe$_{0.8}$NbO$_4$ to 1000 ppm CO
Appendix 4.3

Response of $\text{Cr}_0.3\text{Fe}_{0.7}\text{NbO}_4$ to 1000 ppm CO
Appendix 4.3  
Response of Cr$_{0.4}$Fe$_{0.6}$NbO$_4$ to 1000 ppm CO
Appendix 4.3  
Response of $\text{Cr}_{0.4}\text{Fe}_{0.4}\text{NbO}_4$ to 1000 ppm CO

![Graph showing the response of $\text{Cr}_{0.4}\text{Fe}_{0.4}\text{NbO}_4$ to 1000 ppm CO over time.](image-url)
Appendix 4.4  Response of $\text{Cr}_{0.1}\text{Fe}_{0.9}\text{NbO}_4$ to 1000 ppm propane
Appendix 4.4  Response of Cr$_{0.2}$Fe$_{0.8}$NbO$_4$ to 1000 ppm propane
Appendix 4.4  
Response of $\text{Cr}_3\text{Fe}_{0.7}\text{NbO}_4$ to 1000 ppm propane

![Graph showing response of $\text{Cr}_3\text{Fe}_{0.7}\text{NbO}_4$ to 1000 ppm propane. The plot includes axes for resistance ($\Omega$) and temperature ($^\circ\text{C}$) against time ($\text{s}$).]
Appendix 4.4  Response of Cr$_{0.4}$Fe$_{0.6}$NbO$_4$ to 1000 ppm propane
Appendix 4.5  
Response of Cr$_{2.1}$Fe$_{0.9}$NbO$_4$ to 1000 ppm CO (second preparation)
Appendix 4.5  Response of Cr$_{0.55}$Fe$_{0.55}$NbO$_4$ to 1000 ppm CO (second preparation)

![Graph showing the response of Cr$_{0.55}$Fe$_{0.55}$NbO$_4$ to 1000 ppm CO. The x-axis represents time in seconds, ranging from 0 to 80,000 seconds. The y-axis represents resistance in Ω, ranging from 1e+001 to 1e+008. The graph also shows the temperature in °C, ranging from 0 to 700 °C. The graph depicts a rapid increase and decrease in resistance with a corresponding increase and decrease in temperature.]
Appendix 4.5  Response of Cr$_{0.2}$Fe$_{0.8}$NbO$_4$ to 1000 ppm CO (second preparation)
Appendix 4.5  Response of Cr$_{0.25}$Fe$_{0.75}$NbO$_4$ to 1000 ppm CO (second preparation)

![Graph showing the response of Cr$_{0.25}$Fe$_{0.75}$NbO$_4$ to 1000 ppm CO.](image-url)
Appendix 4.5  Response of Cr$_{0.3}$Fe$_{0.7}$NbO$_4$ to 1000 ppm CO (second preparation)
Chapter 5: Iron niobates of variable stoichiometry
Chapter 5: Iron niobates of variable stoichiometry Fe$_n$Nb$_{3-n}$O$_5$

5.1 Introduction

FeNbO$_4$, together with CrNbO$_4$ and other ABO$_4$ compounds, was reported by Brandt$^1$ as having the rutile structure. Goldschmidt$^2$ showed the whole solid solution range in the system Nb$_2$O$_5$ - Fe$_2$O$_3$. Here it was stated that a rutile solid solution is formed at high temperature for approx. 35-50% Fe$_2$O$_3$, which transforms to an orthorhombic ‘columbite’ phase at lower temperature (800 °C) with a solubility range of 35-55 %. Outside these ranges, the oxide which is present in excess begins to appear, unreacted, in addition to the niobate.

Later work by Roth and Waring$^3$, showed FeNbO$_4$ to be polymorphic. Here it was shown that a reversible phase transition occurs at ca. 1085 °C from monoclinic to orthorhombic form. At 1380 °C, there is another phase transition, from orthorhombic to tetragonal (rutile) structure and above 1410 °C, a liquid begins to form with the rutile phase. All these phase changes are believed to be reversible.

For FeNbO$_4$ to be made non-stoichiometric (in the relative Fe/Nb ratio) there would have to be either some charge compensation or the formation of oxygen vacancies. If excess Nb were used, it would be expected to reduce Nb$^{5+}$ to Nb$^{4+}$, or iron from Fe$^{3+}$ to Fe$^{2+}$. However, if excess Fe were used, the Fe would have to oxidize to Fe$^{3+}$ as niobium does not form the +6 oxidation state. In either case, a trend in electrical conductivity should result. Alternatively, oxygen vacancies could be formed to create the donor states in the case of excess Fe, or a mixture could result.

In the present work it was chosen to investigate the solid solution range in relation to the gas sensing properties and also the effect of the phases formed on these properties.
5.2 Experimental

Compounds in the series Fe$_x$Nb$_{1-x}$O$_4$ (0.5 $\leq$ $x$ $\leq$ 1.5) were prepared as described in chapter 2. Pellets were exposed to alternate pulses of air and 1000 ppm CO as in chapter 4.

5.3 Materials characterization

5.3.1 Scanning-electron microscopy

It was found that all of the compounds had similar, fine, porous microstructures. Examples are shown in fig. 5.1 (a)-(c). However, there were regions of foreign particle formation in the compounds $x = 0.5$, $x = 0.7$ and $x = 1.5$. This appeared to indicate to presence of other phases in these compounds.

Figure 5.1 SEM micrographs of iron niobates fired at 1100 °C

(a) Fe$_{1.3}$Nb$_{0.7}$O$_4$  (b)Fe$_{0.9}$Nb$_{1.1}$O$_4$  (c) Fe$_{0.7}$Nb$_{1.3}$O$_4$
5.3.2 X-ray diffractometry

It was found that as the stoichiometry changed, different phases were formed. At \( x = 1.5 \), both monoclinic and orthorhombic phases were present, with the majority in the orthorhombic phase. On decreasing the iron content, the orthorhombic component decreased until at \( x = 1.05 \), pure monoclinic iron niobate was formed. On becoming sub-stoichiometric in iron content, a tetragonal phase began to appear at \( x = 0.90 \). The tetragonal component increased on decreasing the iron content. These phase changes are summarized in table 5.1. The 7 strongest peaks for compounds with \( x = 1.5, 1.0 \) and 0.5 are shown in Appendix 5.1 together with the literature values*\(^3\) for the principal peaks of these phases. Diffraction patterns are shown for each compound in appendix 5.2. The end members of the series also contained oxides of the element present in excess. Lattice parameters for the monoclinic phase, estimated from single points, are shown in table 5.2. These remained approximately constant throughout the series and thus it was deduced that there had been only limited substitution.

<table>
<thead>
<tr>
<th>( x )</th>
<th>iron niobate</th>
<th>oxide</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.5</td>
<td>monoclinic</td>
<td>orthorhombic</td>
</tr>
<tr>
<td>1.3</td>
<td>monoclinic</td>
<td>orthorhombic</td>
</tr>
<tr>
<td>1.1</td>
<td>monoclinic</td>
<td>orthorhombic</td>
</tr>
<tr>
<td>1.05</td>
<td>monoclinic</td>
<td>pure</td>
</tr>
<tr>
<td>1.0</td>
<td>monoclinic</td>
<td>pure</td>
</tr>
<tr>
<td>0.95</td>
<td>monoclinic</td>
<td>(pure)(^1)</td>
</tr>
<tr>
<td>0.9</td>
<td>monoclinic</td>
<td>( \underline{\text{---}} )</td>
</tr>
<tr>
<td>0.7</td>
<td>monoclinic</td>
<td>tetragonal</td>
</tr>
<tr>
<td>0.5</td>
<td>monoclinic</td>
<td>tetragonal</td>
</tr>
</tbody>
</table>

\(^{1}\) one extra peak, attributed to \( \text{NbO}_2 \)
Table 5.2  Lattice parameters for the monoclinic component of the series Fe$_x$Nb$_{2-x}$O$_4$

<table>
<thead>
<tr>
<th>x</th>
<th>a</th>
<th>b</th>
<th>c</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.5</td>
<td>5.00</td>
<td>5.63</td>
<td>4.65</td>
</tr>
<tr>
<td>1.3</td>
<td>5.01</td>
<td>5.63</td>
<td>4.66</td>
</tr>
<tr>
<td>1.1</td>
<td>4.97</td>
<td>5.64</td>
<td>4.62</td>
</tr>
<tr>
<td>1.05</td>
<td>5.00</td>
<td>5.63</td>
<td>4.61</td>
</tr>
<tr>
<td>1.0</td>
<td>5.01</td>
<td>5.64</td>
<td>4.67</td>
</tr>
<tr>
<td>0.95</td>
<td>5.02</td>
<td>5.65</td>
<td>4.68</td>
</tr>
<tr>
<td>0.9</td>
<td>5.01</td>
<td>5.64</td>
<td>4.66</td>
</tr>
<tr>
<td>0.7</td>
<td>5.01</td>
<td>5.63</td>
<td>4.66</td>
</tr>
<tr>
<td>0.5</td>
<td>5.02</td>
<td>5.64</td>
<td>4.67</td>
</tr>
<tr>
<td>literature</td>
<td>5.001</td>
<td>5.620</td>
<td>4.653</td>
</tr>
</tbody>
</table>

5.3.3 Mössbauer spectroscopy

The Mössbauer spectra of compounds $x = 1.5$, 1.0 and 0.5 were recorded at 77K (instrumentation as in section 2.5). In each of the spectra, a symmetrical doublet representing low spin Fe$^{3+}$ was produced. This feature was identical in all three compounds. However, at $x = 1.5$, a broad doublet at $\delta = 0.29$ and $\Delta = 2.77$ belonging (part of a sextet) to Fe$_2$O$_3$ appeared. The spectra are shown in figures 5.2 (a) - (c) and also separately in appendix 5.3. Parameters are given in table 5.3.

Table 5.3  Mössbauer data for the iron niobates

<table>
<thead>
<tr>
<th>x</th>
<th>$\delta$</th>
<th>$\Delta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.5</td>
<td>0.50</td>
<td>0.45</td>
</tr>
<tr>
<td>1.0</td>
<td>0.50</td>
<td>0.40</td>
</tr>
<tr>
<td>0.5</td>
<td>0.49</td>
<td>0.39</td>
</tr>
</tbody>
</table>

(These figures may be taken as accurate to 0.015 mm s$^{-1}$, which includes a calibration error of approx. 0.01 mm s$^{-1}$ and fitting errors of between 0.0001 and 0.002 mm s$^{-1}$ for $\delta$ and 0.001 and 0.004 mm s$^{-1}$ for $\Delta$).
Figure 5.2 Mössbauer spectra at 77 K of iron niobates fired at 1100 °C
5.4 Electrical characterization

5.4.1 Resistivities and Activation Energies

The resistivities (shown in table 5.4) were all very similar and were in the range 1-5 Ωm, with the exception of x = 0.5. The activation energies, roughly estimated, as for chapter 4, from plots of ln R vs 1/T (an example is given is figure 5.3) for the series (table 5.5) were also found to be similar and these ranged from 0.35 to 0.47 eV.

Table 5.4 Resistivities at 600 °C

<table>
<thead>
<tr>
<th>x</th>
<th>ρ (Ωm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>90.5</td>
</tr>
<tr>
<td>0.7</td>
<td>5.2</td>
</tr>
<tr>
<td>0.9</td>
<td>1.2</td>
</tr>
<tr>
<td>0.95</td>
<td>2.3</td>
</tr>
<tr>
<td>1.0</td>
<td>1.8</td>
</tr>
<tr>
<td>1.05</td>
<td>1.5</td>
</tr>
<tr>
<td>1.1</td>
<td>1.2</td>
</tr>
<tr>
<td>1.3</td>
<td>1.5</td>
</tr>
<tr>
<td>1.5</td>
<td>3.6</td>
</tr>
</tbody>
</table>
Table 5.5 Activation energies (in eV)

<table>
<thead>
<tr>
<th>x</th>
<th>$E_a$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>0.43</td>
</tr>
<tr>
<td>0.7</td>
<td>0.39</td>
</tr>
<tr>
<td>0.9</td>
<td>0.35</td>
</tr>
<tr>
<td>0.95</td>
<td>0.40</td>
</tr>
<tr>
<td>1.0</td>
<td>0.38</td>
</tr>
<tr>
<td>1.05</td>
<td>0.41</td>
</tr>
<tr>
<td>1.1</td>
<td>0.47</td>
</tr>
<tr>
<td>1.3</td>
<td>0.38</td>
</tr>
<tr>
<td>1.5</td>
<td>0.45</td>
</tr>
</tbody>
</table>

Figure 5.3 Plot of $\ln R$ vs $1/T$ for FeNbO$_4$
5.4.2 Preliminary response measurements

All materials gave n-type responses to CO. Some examples are shown in fig. 5.4 (a)-(f). Responses for the whole series are shown in appendix 5.4. All the responses were very similar (figure 5.5). As for the chromium iron niobates, it could be observed that there was a hysteresis in response on temperature cycling. However, as a generalization, this effect was much more noticeable in the iron-rich compounds. For example, there was no such effect observed for Fe$_{0.5}$Nb$_{1.5}$O$_4$. Similarly, it was noted that many of the plots showed the same initial sharp decrease in resistance observed for the chromium iron niobates. Figure 5.6 shows a typical response plotted as a function of temperature during heating. On heating, there were no responses at the lower temperature end until ca. 300 °C. On cooling, the responses continued until temperatures as low as 150 °C. In addition, there were negligible responses at temperature higher than ca. 500 °C. In general, all compounds except Fe$_{0.7}$Nb$_{1.3}$O$_4$ and Fe$_{0.5}$Nb$_{1.5}$O$_4$ showed little hysteresis in resistance. In the region where there were both responses on heating and cooling, the responses were almost mirror images of each other as expected.

The experiment was repeated in 1000 ppm propane. The responses were very similar in magnitude to those with CO. For example, the responses of Fe$_{0.9}$Nb$_{1.1}$O$_4$ in propane and CO were 0.25 (at 450 °C) and 0.18 (at 300 °C) respectively. However, like those for the chromium niobate series, there was generally little difference between the propane response during heating and cooling cycles. In one compound, the response was slightly diminished during the heating stage. However, this effect was very small. Figures 5.7 (a) to (e) show the propane responses (given separately in appendix 5.5). They are also shown graphically in figure 5.8. It could be noted that $x = 0.5$ showed a much larger response to propane that other materials ($\Delta \sigma/\sigma_o$ at 450 °C = 0.25 for $x = 0.9$ but for $x = 0.5$, $\Delta \sigma/\sigma_o = 0.85$). The maximum propane response was observed for the composition that showed the smallest CO response ($x = 0.5$). It appeared that the propane response became larger with deviation from stoichiometry. However, since the differences were only marginal, no firm conclusion could be reached. For $x = 0.5$, there was a large hysteresis in resistance. This is shown in
Figure 5.9. There was also some hysteresis for $x = 1.5$ and $0.7$. However, $x = 1.3$ and $x = 0.9$ showed no hysteresis at all. $x = 1.3$ is shown in figure 5.10.

Figure 5.4  Response to 1000 ppm CO of iron niobates
Figure 5.5  Response to 1000 ppm CO at 350 °C for iron niobates

Figure 5.6  Response of Fe$_{13}$Nb$_{6.7}$O$_4$ to 1000 ppm CO, plotted as a function of temperature
Figure 5.7  Response to 1000 ppm propane of iron niobates
Figure 5.8  Response to 1000 ppm propane at 450 °C for iron niobates

Figure 5.9  Response to 1000 ppm propane of Fe$_{0.5}$Nb$_{1.5}$O$_4$ plotted as a function of temperature
As with the CO experiments, the responses to propane did not begin until ca. 300 °C (with the exception of $x = 1.3$, which on the decreasing temperature cycle continued until ca. 200 °C). However, at the higher temperature end, these responses continued until ca. 600 °C in most cases ($x = 1.3$ responded only up to ca. 500 °C and $x = 0.5$ continued until ca. 650 °C).

### 5.4.3 Effects of moisture

As in chapter 4, it appeared that some species present (associated with moisture) was inhibiting the CO responses until the pellets were heated to high temperatures. In order to investigate this, the effect of moisture was examined: Two pellets of $x = 1.3$ and $x = 1.1$ (those showing appreciable response inhibition) were subjected to the program shown in table 5.6:
Table 5.6  Program for comparison of CO response in dry and moist air

<table>
<thead>
<tr>
<th>Interval</th>
<th>Gas</th>
<th>Temp / °C</th>
<th>Time / hrs</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>dry air</td>
<td>500</td>
<td>2</td>
</tr>
<tr>
<td>2</td>
<td>dry air</td>
<td>500-250</td>
<td>2</td>
</tr>
<tr>
<td>3</td>
<td>dry air</td>
<td>250</td>
<td>1</td>
</tr>
<tr>
<td>4</td>
<td>dry 500 ppm CO</td>
<td>250</td>
<td>0.5</td>
</tr>
<tr>
<td>5</td>
<td>dry air</td>
<td>250</td>
<td>3</td>
</tr>
<tr>
<td>6</td>
<td>100 % moist air</td>
<td>250</td>
<td>1</td>
</tr>
<tr>
<td>7</td>
<td>500 ppm CO in 50 % moist air</td>
<td>250</td>
<td>0.5</td>
</tr>
<tr>
<td>8</td>
<td>dry air</td>
<td>250</td>
<td>3</td>
</tr>
</tbody>
</table>

On exposure to dry CO, baseline recovery was incomplete and very slow. On exposure to moist CO, in the case of $x = 1.3$ (figure 5.11 (a)), the response was reduced ($\sigma/\sigma_0 = 1.00$ in dry CO and 0.46 in moist CO). In the case of $x = 1.1$ (figure 5.11 (b)), the response magnitude remained almost the same ($\sigma/\sigma_0 = 1.18$ in dry CO and 1.10 in moist CO).
Figure 5.11 (a)  Response of Fe$_{1.3}$Nb$_{0.7}$O$_4$ to dry and moist 500 ppm CO

Figure 5.11 (b)  Response of Fe$_{1.5}$Nb$_{0.5}$O$_4$ to dry and moist 500 ppm CO
In addition, pellets of $x = 1.1$ and $x = 1.05$ were subjected to the regime shown in table 5.7:

<table>
<thead>
<tr>
<th>Interval</th>
<th>Gas</th>
<th>Temp /°C</th>
<th>Time / s</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>dry air</td>
<td>500</td>
<td>2</td>
</tr>
<tr>
<td>2</td>
<td>dry air</td>
<td>500-250</td>
<td>2</td>
</tr>
<tr>
<td>3</td>
<td>100% moist air</td>
<td>250</td>
<td>2</td>
</tr>
<tr>
<td>4</td>
<td>500 ppm CO in 50% moist air</td>
<td>250</td>
<td>0.5</td>
</tr>
<tr>
<td>5</td>
<td>100% moist air</td>
<td>250</td>
<td>2</td>
</tr>
<tr>
<td>6</td>
<td>500 ppm CO in 50% moist air</td>
<td>250</td>
<td>0.5</td>
</tr>
<tr>
<td>7</td>
<td>100% moist air</td>
<td>250</td>
<td>2</td>
</tr>
<tr>
<td>8</td>
<td>500 ppm CO in 50% moist air</td>
<td>250</td>
<td>0.5</td>
</tr>
<tr>
<td>9</td>
<td>100% moist air</td>
<td>250</td>
<td>2</td>
</tr>
<tr>
<td>10</td>
<td>500 ppm CO in 50% moist air</td>
<td>250</td>
<td>0.5</td>
</tr>
<tr>
<td>11</td>
<td>100% moist air</td>
<td>250</td>
<td>2</td>
</tr>
</tbody>
</table>

It could be seen (fig. 5.12 (a) and (b)) that for both pellets, the CO response was slightly reduced. For $x = 1.1$, the responses were 1.57 and 0.97 during the first and second exposures respectively. For $x = 1.05$, the responses were 0.86 and 0.72 during the first and second exposures. In addition, the baseline recoveries were very slow.
Figure 5.12 (a)  Response of Fe$_{1.1}$Nb$_{0.9}$O$_4$ to repeated exposures of moist 500 ppm CO

Figure 5.12 (b)  Response of Fe$_{1.05}$Nb$_{0.95}$O$_4$ to repeated exposures of moist 500 ppm CO
In order to observe the effect of exposure to moisture at low temperature, the experiment detailed in table 4.5 of chapter 4 (CO / air switch, with 3 hours exposure to 100 % moist air) was run on a pellet of \( x = 1.3 \). The results (figure 5.13) showed that with this material, the response at low temperature was diminished by the presence of moisture (\( \Delta \sigma / \sigma_0 \) at 250 °C = 1.47 before exposure to moisture and 1.03 at 250 °C after exposure to moisture), but the effect was much smaller than that observed for the chromium iron niobates.

**Figure 5.13** Effect of exposure to moisture at low temperature on the response of a pellet of Fe\(_{1.3}\)Nb\(_{0.7}\)O\(_4\)
5.4.4 Temperature dependence of the selectivity

A pellet of $x = 1.3$ was heated from 100 to 700 °C over a period of 6 hours (ramp rate of 1.7 °C per minute), cooled back down to 100 °C over the same temperature range in air, heated from 100 to 700 °C in 1000 ppm CO and then cooled down to 100 °C in CO as described in chapter 4 (section 4.4.6 (i), scheme 1). The experiment was then repeated in air and 1000 ppm propane.

As with the chromium iron niobates, there was an inflexion in the resistance plot in the higher temperature part of the cycle. The inflexion became smaller on decreasing the temperature. Again, as with the chromium iron niobates, the resistance increased after the pellet was heated and the baseline rose (figure 5.14 (a)). On heating in CO, there was a pronounced inflexion in the resistance, and this grew on the decreasing temperature half of the cycle (figure 5.14 (b)). Also, the response in the lower temperature range increased. After the CO cycle, the baseline did not recover to its original value (figure 5.14 (c)). However, after heating in air, the baseline recovered to just above its original level (figure 5.14 (d)). As expected, the propane response (figure 5.14 (e)) was smaller than that of CO. It also grew on the second half of the cycle. There was still a minimum in resistance at higher temperature.
Figure 5.14 (a) in air

1 = $T$ increasing

2 = $T$ decreasing

$\text{Fe}_{1.3}\text{Nb}_{0.7}\text{O}_4$ in air
Figure 5.14 (b) $\text{Fe}_{1.3}\text{Nb}_{0.7}\text{O}_4$ in air and 1000 ppm CO

2 = air (T decreasing)
3 = CO (T increasing)
4 = CO (T decreasing)
Figure 5.14 (c) \( \text{Fe}_{1.3}\text{Nb}_{0.7}\text{O}_4 \) before and after exposure to 1000 ppm CO

2 = air\(_1\) (T decreasing)
3 = CO (T increasing)
5 = air\(_2\) (T increasing)
Figure 5.14 (d) $\text{Fe}_{1.3}\text{Nb}_{6.7}\text{O}_4$ before and after exposure to 1000 ppm CO
Figure 5.14 (e) $\text{Fe}_{1.3}\text{Nb}_{6.3}\text{O}_4$ in air and 1000 ppm propane

$2 = \text{air}_1$ (T decreasing)
$7 = \text{propane}$ (T decreasing)
$8 = \text{propane}$ (T decreasing)
The same experiment was repeated on the same pellet a week later. The general resistance was much higher than in the first experiment. There was a very pronounced resistance minimum in both halves of the air cycle and after heating the baseline shifted upwards (figure 5.15 (a)). An even more pronounced minimum was observed in CO and the response was larger on the second half of the cycle than in the first half (figure 5.15 (b)). After CO exposure, the baseline did not recover to its original value (figure 5.15 (c)). However, after heating in air, the baseline recovered to just above its original level (figure 5.15 (d)). Pronounced minima were still observed in propane (figure 5.15 (e)).

Figure 5.15 (a) \( \text{Fe}_{1.3}\text{Nb}_{0.7}\text{O}_4 \) in air (repeat experiment)

--- = air of fig. 5.14 (a)
1 = T increasing
2 = T decreasing
Figure 5.15 (b) \( \text{Fe}_{13}\text{Nb}_{0.7}\text{O}_{4} \) in air and 1000 ppm CO (repeat experiment)
Figure 5.15 (c)  \( \text{Fe}_{1.3}\text{Nb}_{0.7}\text{O}_4 \) before, during and after exposure to 1000 ppm CO (repeat experiment)
Figure 5.15 (d) \( Fe_{1.3}Nb_{0.7}O_4 \) before and after exposure to 1000 ppm CO (repeat experiment)
Figure 5.15 (e) \( \text{Fe}_{1.3}\text{Nb}_{0.7}\text{O}_4 \) in air and 1000 ppm propane (repeat experiment)

\begin{align*}
2 &= \text{air}_1 \quad (T \text{ decreasing}) \\
7 &= \text{propane} \quad (T \text{ increasing}) \\
8 &= \text{propane} \quad (T \text{ decreasing})
\end{align*}
The data were consistent with the desorption of OH during the first cycle in air, as discussed in chapter 4. The smaller CO response on the increasing temperature half of the cycle was consistent with the inhibition of the CO response by residual moisture still on the pellets.

It appeared again, that the pellet had been poisoned by continuous exposure to CO during temperature cycling and that this effect was only removed once the pellet had been heated in air. As in chapter 4, it can be speculated that this poisoning was due to the formation of subsurface oxygen vacancies by the reaction of lattice oxygen with CO at high temperatures.

5.5 Discussion

It was only possible to vary the composition of FeNbO$_4$ in Fe$_x$Nb$_{3-x}$O$_4$ by $x = \pm 0.05$ without causing any phase changes. Any deviation from this stoichiometry caused the formation of mixed phases, in some cases, with oxide impurity. Thus it was not possible to make a whole solid solution of the same phase of Fe$_x$Nb$_{2.5}$O$_4$, although it seems reasonable to suggest that there was limited substitution of Fe$^{3+}$ into the lattice of the excess iron compositions as there was no evidence for the presence of Fe$^{2+}$ in the Mössbauer spectra and only a small number of the oxide peaks were observed in samples that were not single phase.

Generally, the iron niobates were slower to respond to CO in both dry and moist atmospheres than the chromium iron niobates. It appeared that the different phases had little effect on the gas response. The mixed phase $x = 0.5$, appeared to have a much larger propane response than the other members of the series. It could be possible that the presence of mixed phases enhances the gas response as reported by Daza$^5$ who showed that biphasic sensors of SnO$_2$ - Sb$_2$O$_4$ or WO$_3$ - Sb$_2$O$_4$$^2$ showed an enhanced

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$^2$ The authors stated that Sb$_2$O$_4$ was prepared from a solution containing Sb$^{3+}$ and Sb$^{5+}$ (obtained from the respective chlorides).
response to formaldehyde compared to the sum of the responses of the pure oxide components. In addition, the mixed phases $x = 0.7$ and $0.5$ showed large resistance hysteresis, but the other members of the series did not.

However, the CO response hysteresis present in the chromium iron niobates with temperature cycling was not so evident in the iron niobates for the experiments described in section 5.4.2. These materials only responded to CO appreciably after they had been heated to $700 \, ^\circ \text{C}$. Exposure to moisture led to a long and incomplete recovery. Temperature ramp experiments at constant gas concentration indicated that some (unknown) species was being desorbed from the surface of the materials at temperatures in the range $560$ to $440 \, ^\circ \text{C}$. No conclusion can be reached from this chapter alone to conclusively prove the nature of the species responsible for the observed phenomena. It can be reasonably suggested that this is due to the hydroxylation of the surface prior to heating as discussed in chapter 4. In addition, as in chapter 4, it was shown that prolonged exposure to CO during temperature cycling modifies the surface and that subsequent cycling in air reverses this change. Again, it may be speculated that this was due to reaction of CO with lattice oxygen.

5.6 Conclusion

It was concluded that limited substitution of iron and niobium had no effect on the gas sensitivity of iron niobate and that the presence of different phases of the niobate also had little effect. It was also shown that the moisture response was diminished by a surface species, which can reasonably be assumed to be hydroxyl groups. It was also shown that prolonged continuous exposure to carbon monoxide poisons the surface of the iron niobates. This was speculatively attributed to the formation of subsurface oxygen vacancies.
### Appendix 5.1

Principal peaks and literature values\(^5\) for selected members of the series Fe\(_x\)Nb\(_{1-x}\)O\(_4\)

<table>
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<th>literature values</th>
<th>monoclinic</th>
<th>orthorhombic</th>
<th>tetragonal</th>
</tr>
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<tr>
<td>d</td>
<td>hkl</td>
<td>d</td>
<td>hkl</td>
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<td>---</td>
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<td>1.432</td>
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</table>

<table>
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<th>x = 1.0</th>
<th>x = 0.5</th>
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<tr>
<td>d</td>
<td>hkl</td>
<td>d</td>
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<td>-----</td>
<td>---</td>
<td>-----</td>
</tr>
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<td>2.9166</td>
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<td>111 (m+o)</td>
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<td>2</td>
<td>2.7024</td>
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<td>FeO3 104</td>
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<td>3</td>
<td>3.5893</td>
<td>56</td>
<td>011 (m+o)</td>
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<td>53</td>
<td>2007 (m+o)</td>
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<tr>
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<td>122(m+o)</td>
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<tr>
<td>7</td>
<td>3.6923</td>
<td>42</td>
<td>FeO3 012</td>
</tr>
</tbody>
</table>

**peaks of x = 0.5 assigned to the tetragonal phase**

<table>
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<th>d</th>
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<th>d</th>
<th>hkl</th>
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<td>1.4038</td>
<td>14</td>
<td>1.396</td>
<td>12</td>
</tr>
</tbody>
</table>
Appendix 5.2  \( \text{Fe}_{1.5}\text{Nb}_{0.5}\text{O}_4 \)

2-Theta – Scale

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C:\LAURA\FE15F.RAW FE15F (CT: 2.08, SS: 0.020dg, WL: 1.5406A0)
16-0374 Iron NbO4 Iron Niobium Oxide (WL: 1.5406A0)
Appendix 5.2 \( \text{Fe}_{1.1}\text{Nb}_{0.9}\text{O}_4 \)
Appendix 5.2

Fe$_{1.05}$Nb$_{0.95}$O$_4$
Appendix 5.2  \( \text{Fe}_{0.9}\text{Nb}_{1.1}\text{O}_4 \)
Appendix 5.3  Mössbauer spectrum at 77 K of Fe$_{1.5}$Nb$_{0.5}$O$_4$
Appendix 5.3 Mössbauer spectrum at 77 K of FeNbO$_4$
Appendix 5.3  Mössbauer spectrum at 77 K of $\text{Fe}_{0.5}\text{Nb}_{1.5}\text{O}_4$

![Mössbauer spectrum graph]

Transmission (%) vs. Source velocity (mm s$^{-1}$)

$\delta = 0.49, \Delta = 0.39$
Appendix 5.4  \( \text{Fe}_{1.5}\text{Nb}_{0.5}\text{O}_4 \) in air and 1000 ppm CO
Appendix 5.4 \quad \text{Fe}_{1.3}\text{Nb}_{0.7}\text{O}_4 \text{ in air and 1000 ppm CO}
Appendix 5.4  $\text{Fe}_{1.1}\text{Nb}_{0.9}\text{O}_4$ in air and 1000 ppm CO
Appendix 5.4  \( \text{Fe}_{1.05}\text{Nb}_{0.95}\text{O}_4 \) in air and 1000 ppm CO
Appendix 5.4  FeNbO$_4$ in air and 1000 ppm CO
Appendix 5.4  \( \text{Fe}_{2.95}\text{Nb}_{1.05}\text{O}_4 \) \( \text{in air and 1000 ppm CO} \)
Appendix 5.4  \( \text{Fe}_{0.8}\text{Nb}_{1.2}\text{O}_4 \) in air and 1000 ppm CO

![Graph showing resistance and temperature over time for \( \text{Fe}_{0.8}\text{Nb}_{1.2}\text{O}_4 \) in air and 1000 ppm CO.]
Appendix 5.4  Fe$_{8.5}$Nb$_{1.5}$O$_4$ in air and 1000 ppm CO
Appendix 5.4  Fe$_{0.3}$Nb$_{1.5}$O$_4$ in air and 1000 ppm CO
Appendix 5.5  \( \text{Fe}_{1.5}\text{Nb}_{2.5}\text{O}_4 \) in air and 1000 ppm propane
Appendix 5.5 \( \text{Fe}_{1.3}\text{Nb}_{0.7}\text{O}_4 \) in air and 1000 ppm propane
Appendix 5.5 Fe₀.₉Nb₁.₁O₄ in air and 1000 ppm propane
Appendix 5.5  
$\text{Fe}_{5.7}\text{Nb}_{1.3}\text{O}_4$ in air and 1000 ppm propane
Appendix 5.5  \( \text{Fe}_{0.5}\text{Nb}_{1.5}\text{O}_4 \) in air and 1000 ppm propane

![Graph](image_url)

- **Time (s)**
- **Temperature (°C)**
- **Resistance (Ω)**
General Conclusion

The theme of the work undertaken has been the selectivity and sensitivity of the electrical resistance response of certain complex niobates to carbon monoxide and propane.

Experimental results on complex chromium/iron, barium/iron and iron niobates have shown electrical resistance responses that are not simple, but explicable in terms of porosity of the materials, the presence of moisture and (speculatively) the formation of oxygen vacancies.

The barium iron niobates were particularly selective to propane. For these materials, it may be concluded that the difference in combustion temperatures of the surrounding gases and the microstructure are the principal factors determining the response and selectivity. In these compounds, ion substitution is of relatively minor importance.

In the chromium iron niobates, it is possible to achieve a clear n/p type transition in the middle of the series CrFe$_{1-x}$NbO$_4$, $0 \leq x \leq 1$ and it appears that there is a CO response maximum at $x = 0.2$. Thus it appears that limited substitution of Cr$^{3+}$ for Fe$^{3+}$ enhances the response. In addition, the response temperature was lowered. However, in this system also, variations in microstructure had a profound influence on the carbon monoxide response.

In the chromium iron niobates, it was found that surface hydroxyl groups prevented the response to carbon monoxide at low temperature. It was shown in the case of CO adsorption on Cr$_{0.2}$Fe$_{0.8}$NbO$_4$, that there is no direct bonding between CO and the oxide surface at 250 °C. It has also been shown for both iron niobates and chromium iron niobates, that prolonged exposure to CO at elevated temperature causes a modification of the surface. This poisoning has been speculatively attributed to the formation of subsurface oxygen vacancies as a consequence of the removal of lattice oxygen by carbon monoxide.
In the case of Ti$^{4+}$ substitution in Cr$_{0.2}$Fe$_{0.8}$NbO$_4$ and in the case of limited substitution of iron niobate by excess niobium or iron, ion substitution appeared to have little effect on the gas response.

It may be suggested that for the barium iron niobates, the gas sensitivity and selectivity are essentially physically determined parameters which may be predictable from microstructural and combustion data. However, for chromium and iron niobates, the gas sensitivity is also strongly influenced by the presence of adsorbed surface species.
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