SYNTHESIS, ELECTRICAL PROPERTIES AND DEFECT CHEMISTRY OF Ti-DOPED NdCrO3

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ABSTRACT

Synthesis, defect chemistry and electrical properties of Ti-doped NdCrO3 have been studied at different oxygen partial pressures at 1000 and 1200 °C. Both the citric acid and glycine/nitrate method have been used for preparation of the specimens. The electrical conductivity has been measured by a four probe measurement technique and the Seebeck coefficient by a two point technique. The specimens used for measuring the electrical properties have been characterised by X-ray diffraction and scanning electron microscopy. The solubility of titanium in NdCr1-xTiO3 is found to be about 20 atom %. The results from the electrical conductivity and Seebeck coefficient measurements showed a p-type conductivity at high po2 and an n-type conductivity at low po2. At low oxygen partial pressures the concentration of electrons decreased by a slope of - 1/4 with increasing oxygen partial pressure and at high oxygen partial pressure the electron holes increased by a slope of 1/4 with increasing oxygen partial pressure. The concentration and the mobility of the electronic defects have been calculated at 1000 °C as function of oxygen partial pressure. A model calculation of the defect concentration in NdCr1-xTiO3 is presented.

INTRODUCTION

There is today an intensive research in developing new anode materials for use in solid oxide fuel cells (SOFC) to increase the performance and the life time. Recent research on nickel-cermet anodes has shown promising results in uses where hydrogen serves as fuel. A problem with the nickel-cermet anode when methane is used as fuel, is that the nickel metal catalyses the dehydrogenation reaction of methane to form a layer of carbon between the zirconia and the nickel and thereby inhibits the anode reaction and a good performance of the SOFC. It is therefore necessary to develop new anode materials if methane is to be used directly as fuel in the SOFC. This work has investigated possible candidates in the NdCrO3 - NdTiO3 system.

Thermodynamic data are not available for the NdCrO3 - NdTiO3 system, but it is suggested that these ternary oxides are at least as stable as the most unstable binary component oxides. Cr2O3 is calculated to be stable down to an oxygen partial pressure of about 10^-22 atm and for TiO2 down to about 10^-20 atm at 1000 °C (1,2).
Palguev et al. (3) have measured the thermal expansion coefficient of NdCrO₃ to be 7.8 × 10⁻⁶ K⁻¹. Previously, electrical conductivity of NdCrO₃ has been measured by Tripathi (4) and Palguev et al. to be in the range of 0.1 to 0.2 S/cm at 1000 °C in air. Palguev et al. also measured the electrical conductivity as function of oxygen partial pressure at 1000 °C to be constant down to 10⁻¹³ atmospheres, below which it decreases with decreasing oxygen partial pressures. The observed constant electrical conductivity at high oxygen partial pressure indicates that the main defect situation is controlled by lower valent impurities and electron holes, \( p = [M_{f\text{Cr}}] \).

The idea for the present work was to substitute chromium with titanium in NdCrO₃ to obtain high electrical conductivity at oxygen pressures equal to the operation conditions of the anode. This idea is clarified in a Kroger Vink diagram which shows the different concentrations of defects in NdCr₁₋ₓTiₓO₃ at different oxygen partial pressures, shown in figure 1. \( [V_{\text{Cr}}'''] \) denotes chromium and neodymium vacancies, \( [V_{\text{O}}] \) oxygen vacancies, \( [\text{Ti}_{\text{Cr}}] \) titanium on chromium sites, \( p \) electron holes and \( n \) electrons, respectively. A desirable defect situation is in the region where the free electron concentration is equal to the doping concentration, \([\text{Ti}_{\text{Cr}}] = n\).

The Kroger Vink diagram in figure 1 has been calculated by combining the equations for site- and mass-balances, electroneutrality condition and the equilibrium expressions of formation for the different defects by a computer program (5). The electroneutrality condition is described by

\[
3[V_{\text{Nd}}'''] + 3[V_{\text{Cr}}'''] + n = p + 2[V_{\text{O}}'] + [\text{Ti}_{\text{Cr}}'] \tag{1}
\]

The equilibrium expressions of formation for the different defects are given by equations 2, 3 and 4,

\[
\frac{1}{2}O_2 (g) + V_{\text{O}}' \rightarrow O_{\text{O}} + 2h' \Rightarrow K_{V_{\text{O}}} = \frac{[O_{\text{O}}']} {[V_{\text{O}}']} p_{O_2}^{1/2} \tag{2}
\]

\[
0 = V_{\text{Nd}}'''' + V_{\text{Cr}}'''' + 3 V_{\text{O}}' \Rightarrow K_S = [V_{\text{Nd}}''''][V_{\text{Cr}}''''][V_{\text{O}}']^3 \tag{3}
\]

\[
0 = e' + h' \Rightarrow K_i = np \tag{4}
\]

where \( K_{V_{\text{O}}} \) and \( K_i \) are equilibrium constants for formation of oxygen vacancies and the electronic defects and \( K_S \) is the equilibrium constants for formation of Schottky defects.

### MATERIALS AND METHODS

Both the citric acid and glycine/nitrate method have been successfully used in the preparation of NdCr₁₋ₓTiₓO₃ and Nd₂Ti₂O₇ powders.
Synthesis by the citric acid method

Four different specimens of NdCr_{1-x}Ti_xO_3 with composition x=0, x=0.1, x=0.2, x=0.4 and one specimen of Nd_2Ti_2O_7 have been prepared by the citric acid method (6). C_{15}H_{21}O_6Cr, C_{10}H_{14}O_5Ti, Nd_2O_3, HNO_3 and C_6H_8O_7 H_2O were used as precursor materials. Nd_2O_3 dissolves in HNO_3. C_{15}H_{21}O_6Cr and C_{10}H_{14}O_5Ti dissolved slowly under evaporation of water from the solution. After decomposition in the temperature range 100-130 °C the powders were calcined at 1000 °C for 4 hours. The colour of the oxide powders that contained both chromium and titanium was mainly green with a taste of a yellow. The NdCrO_3 powder had a green colour and Nd_2Ti_2O_7 was light blue with a red tint under certain light conditions. The size of the particles after calcining was approximately 0.1 μm, but mainly agglomerated into larger particles.

Synthesis by the glycine/nitrate method

Three different specimens of NdCr_{1-x}Ti_xO_3 with composition x=0, x=0.3 and x=0.6 have been prepared by the glycine/nitrate method (7). Cr(NO_3)_3 9H_2O, Ti[OCH(CH_3)_2]_4, Nd_2O_3 and HNO_3 were used as precursor materials.

Under addition of Ti[OCH(CH_3)_2]_4 a polymerisation occurred immediately and solid transparent flakes on the surface of the solution were formed. These flakes dissolved again under heating. The powder formed after the glycine-nitrate reaction was examined by X-ray diffraction and showed crystalline structures for all specimens. After calcination at 1300 °C in air the specimens were again examined by X-ray diffraction. Table I lists the colour and the crystal structure before and after calcination of the formed oxide powders.

From table I it can be seen that the NdCr_{1-x}Ti_xO_3 powders changed from single phase materials to two phase materials after calcination at 1300 °C in air. The formation of a single phase material directly from the glycine/nitrate syntheses at high titanium concentrations may indicate a higher solubility of titanium at lower temperatures. The results also indicate a change from orthorhombic to cubic crystal structure of NdCr_{1-x}Ti_xO_3 above a certain titanium concentration. The powders formed glycine-nitrate reaction were very airy and were easily broken down to smaller particles in a mortar.

Electrical conductivity measurements

The specimens used for electrical conductivity and Seebeck measurements were prepared by cold pressing NdCr_{1-x}Ti_xO_3 powder synthesised from the citric acid method to pellets at a pressure of 550 atmospheres with a diameter of 28 mm. The specimens were sintered at a temperature of 1500 °C for 10 hour in air after cold pressing. The porosity of the specimens, as determined by the weight and the geometrical size, was about 60% except for Nd_2Ti_2O_7 where the porosity was only about 6 %.

The specimens were formed to dimensions of 2-3 mm in thickness, 7-9 mm in width and about 28 mm in length with four notches on each side to attach the electrodes. Platinum wire was used as electrodes. The specific conductivity of the specimens was corrected for porosity by the equation

\[ \sigma_s = \frac{\sigma_m}{(1-v_p)^2} \]  \[5\]
where \( \sigma_s \) is the specific electrical conductivity, \( \sigma_m \) is the measured electrical conductivity and \( \nu_p \) is the volume fraction of pores. The error due to uncertainties in the corrections for porosity is estimated to be about 20%.

The electrical conductivity measurements were done by a Solartron 1260 impedance/gain phase analyser. The bulk conductivity was investigated by using four probe arrangements. Controlling and data acquisition was done by a HP BASIC compatible computer running the IS program (8). The electrical parameters for the measurements of the conductivity at a constant frequency were 1 Hz AC with an oscillating voltage of 1V. The oxygen partial pressure was controlled by mixing CO/CO₂, O₂/Ar or H₂/H₂O in different ratios by a gasmixer (9). The specimens were characterised by scanning electron microscopy (SEM). The crystal structure were determined by X-ray powder diffraction with CrKα radiation.

**Seebeck coefficient measurements**

The specimens used for the electrical conductivity measurements were also used for Seebeck measurements. The specimens were modified by a polish treatment to remove the notches used in the electrical conductivity measurements. Each short end of the specimens were formed to a slightly round shape to get as good contact as possible with the thermocouples/electrodes, which consisted of Pt / Pt+10%Rh. The Seebeck coefficient experiment was carried out by recording the voltage generated (\( \Delta E \)) over the specimens under an applied temperature gradient (\( \Delta T \)). The Pt-legs of the thermocouples were used as electrodes and the measured voltage was corrected for the Seebeck effect in the Pt-electrode wires (10). The Seebeck coefficient (\( Q \)) was calculated by

\[
Q = \frac{\Delta E}{\Delta T} \quad [6]
\]

For one specimen different temperature gradients were applied at constant oxygen partial pressure and average temperature to evaluate if the Seebeck coefficient was independent of the magnitude of the temperature gradient and to evaluate if there were any off-set voltage at origo due to small errors in the voltage or temperature measurements. The results showed a straight line in a \( \Delta E \) versus \( \Delta T \) plot passing through origo within the error of the measurements with values of \( \Delta T \) up to 30 °C.

**EXPERIMENTAL RESULTS AND DISCUSSION**

**X-ray diffraction**

The results from the X-ray diffraction of NdCr₁₋ₓTiₓO₃ showed for \( x \geq 0.2 \) a single phase of a distorted perovskite type structure (ABO₃). The crystal system is orthorhombic. Figure 2 shows the lattice parameters as function of the titanium content. The error in lattice parameters is calculated by the computer program CELLKANT (11). From figure 2 it can be seen that the lattice parameters vary up to Ti contents of about 20 %, for then to be approximately constant at higher contents. It is therefore concluded that the solubility of titanium is about 20% at 1500°C. This is also in agreement with X-ray diffraction spectra, which shows no peaks from the Nd₂CrₓTi₂₋ₓO₇ phase at 20 % titanium or less. Above
about 20% titanium Nd$_2$Cr$_x$Ti$_{2-x}$O$_7$ starts to form. This is a pyrochlore type structure (A$_2$B$_2$O$_7$), in this particular case of the monoclinic crystal system.

**Electrical conductivity**

In this study the electrical conductivity of four different specimens has been measured at 1000 °C and 1200 °C. At each temperature the electrical conductivity was measured as a function of oxygen partial pressure.

**Oxygen partial pressure dependence**

The results of the oxygen partial pressure dependence measurements of NdCr$_{1-x}$Ti$_x$O$_3$ at 1000 and 1200 °C are shown in figure 3. The results showed that the electrical conductivity at high oxygen partial pressure decreases with decreasing oxygen partial pressure with a slope of about 1/4 for then at intermediate oxygen partial pressures to go through a minimum. By a further decrease in the oxygen partial pressure the electrical conductivity starts to increase with a slope of -1/4. The minimum reflects a change from p-type conductivity at high p$_{O_2}$ to n-type at low p$_{O_2}$. This corresponds to the region in figure 1 where the main ionic defect is V$_{M^+}$. From this survey plot it can be seen that at very low oxygen partial pressure the electrical conductivity changes more steeply than the predicted -1/4 dependence. This may be due to a phase transition or phase change at a distinct oxygen partial pressure. The phase transition may be due to formation of another phase with lower oxygen content.

**Temperature dependence**

The electrical conductivity has been measured as a function of the temperature at constant oxygen partial pressure. At p$_{O_2}$ = 0.21 the activation energy is calculated to be in the range of 90-110 kJ/mol and at 10$^2$ atm to be in the range of 190-240 kJ/mol.

**Seebeck coefficient**

The Seebeck coefficient of two different specimens with composition NdCr$_{0.9}$Ti$_{0.1}$O$_3$ and NdCr$_{0.6}$Ti$_{0.4}$O$_3$ have been measured versus oxygen partial pressure at 1000°C. The results are shown in figure 4.

For NdCr$_{0.9}$Ti$_{0.1}$O$_3$ the results show that the Seebeck coefficient is positive at oxygen partial pressures higher than 10$^{-4}$ atmospheres. In this region it is concluded that the electron holes are the major mobile defects. The observed decrease in the Seebeck coefficient by decreasing oxygen partial pressure is due to a beginning of a turnover from electron holes to electrons as the major mobile defects. For NdCr$_{0.6}$Ti$_{0.4}$O$_3$ the Seebeck coefficient was positive at oxygen partial pressure higher than 10$^{-3}$ and increased with decreasing oxygen partial pressure. This is attributed to a decrease in electron hole concentration. At 10$^{-3}$ atm oxygen partial pressure a sharp shift from positive to negative values in the Seebeck coefficient was observed. At intermediate oxygen partial pressure (10$^{-5}$ to 10$^{-10}$ atm) the Seebeck coefficient shows approximately a constant negative value. In this region the Seebeck coefficient is suggested to be influenced by the second phase in the specimen, Nd$_2$Cr$_x$Ti$_{2-x}$O$_7$. At oxygen partial pressure lower than 10$^{-10}$ the absolute value of the Seebeck coefficient increases with decreasing oxygen partial pressure. This is concluded to be due to an increase in the electron concentration.
In view of this Heikes (12) has developed a relation between the Seebeck coefficient and the fraction of hopping sites for a semi conductor following the small polaron hopping mechanism. The relation is expressed by

\[ \text{Q} = \frac{k}{e} \left( \ln \frac{1-x}{x} + \frac{\Delta S^\prime}{k} \right) \]  

where Q is the Seebeck coefficient, k is the Boltzman constant, e is the elementary charge, x is the fraction of occupied hopping sites and \( \Delta S^\prime \) is the vibrational entropy associated with the local distortions around the polaron. The contribution by the \( \Delta S^\prime/k \) term to the Seebeck coefficient is less than 10 \( \mu \text{V/K} \) (13) and may therefore be regarded as insignificant and is therefore excluded in the calculations below. Inserting the measured Seebeck coefficients at different oxygen partial pressure in eq.7 the mole fraction of charge carrier can be calculated. The results are shown in figure 5.

The values at intermediate oxygen partial pressure is excluded due to interference by several types of charge carriers. For \( \text{NdCr}_{0.9}\text{Ti}_{0.1}\text{O}_3 \) at an oxygen partial pressure as low as 10\(^{-20}\) atm the electron concentration is still two decades below available hopping sites which correspond to the sum of the titanium and chromium sites. In other words the electron concentration corresponds to 10 % of the doping level at 10\(^{-20}\) atm oxygen partial pressure. The difference from a -1/4 slope is suggested to be due to too short equilibrium times. For \( \text{NdCr}_{0.6}\text{Ti}_{0.4}\text{O}_3 \) the concentrations of charge carrier concentrations is extrapolated to point where the electron and electron hole concentration are equal. From this point the electronic equilibrium constant \( (K_i) \) is calculated to be about 3\( \times 10^{-10} \) at 1000 °C.

Knowing the electrical conductivity and the concentration of the main charge carrying species the mobility can be calculated. The mobility is calculated to be 25±2 \( 10^{-3} \) cm\(^2\)/Vsec for electron holes and for 16±6 \( 10^{-3} \) cm\(^2\)/Vsec for electrons.

**CONCLUSIONS**

The glycine/nitrate method has been found to be the most suitable method for preparing \( \text{NdCr}_{1-x}\text{Ti}_x\text{O}_3 \) powder due to the reduced preparation time, formation of the finale phase directly without formation of any intermediate products and finally due to less agglomeration of the powder.

The solubility of titanium in \( \text{NdCr}_{1-x}\text{Ti}_x\text{O}_3 \) has been found to be about 20%. The results from the electrical conductivity and Seebeck coefficient measurements showed a p-type conductivity at high \( \text{PO}_2 \) and a n-type conductivity at low \( \text{PO}_2 \). At low oxygen partial pressures the concentration of electrons decreased by a slope of -1/4 with increasing oxygen partial pressure and at high oxygen partial pressure the concentration of electron holes increased by a slope of 1/4 with increasing oxygen partial pressure. The mobility of the electronic defects have been calculated at 1000 °C as well as the defect concentration as function of oxygen partial pressure. The result showed that the desirable defect situation where \([\text{TiCr}] = n\) may is not satisfied before an oxygen partial pressure as low as about 10\(^{-24}\) atm.

It is therefore concluded that Ti-doped NdCrO\(_3\) is not suitable for use as an anode material in solid oxide fuel cells due to the low electrical conductivity in the region of...
interest. On the other hand, a substitution of chromium fully or partly with another d-element metal may lead to a shift in the high electron concentration in direction of higher oxygen partial pressures. To evaluate these further experiments are necessary.

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Table I Colour and crystal structure before and after calcination of the oxide powder.

| Compound         | Colour        | Crystal structure before calcination | Crystal structure after calcination |
|------------------|---------------|--------------------------------------|-----------------------------------|
| NdCrO₃           | Green         | Orthorhombic                         | Orthorhombic                      |
| NdCr₁₋₇Ti₁₋₃O₃  | Green-yellow  | Orthorhombic                         | Orthorhombic + monoclinic         |
| NdCr₀.₄Ti₀.₆O₃   | Green-yellow  | Cubic                                | Orthorhombic + monoclinic         |
Kroger Vink diagram showing how the different concentrations of defects in NdCr_{1-x}Ti_{x}O_{3} change with p_{O_{2}}. \( K_{i}=10^{-10}, K_{Vo}=3 \times 10^{-2}, K_{s}=1.111 \times 10^{-18} \) and \( x=0.1 \) have been used as input parameters.

Figure 1 Kröger Vink diagram showing how the different concentrations of defects in NdCr_{1-x}Ti_{x}O_{3} change with p_{O_{2}}. \( K_{i}=10^{-10}, K_{Vo}=3 \times 10^{-2}, K_{s}=1.111 \times 10^{-18} \) and \( x=0.1 \) have been used as input parameters.

Figure 2 The lattice parameters for NdCr_{1-x}Ti_{x}O_{3} as function of the titanium content. The crystal system is orthorhombic.
Figure 3  The electrical conductivity of NdCr\textsubscript{1-x}Ti\textsubscript{x}O\textsubscript{3} versus the oxygen pressure at 1000 and 1200 °C.
Figure 4  Seebeck coefficient of NdCr_{0.9}Ti_{0.1}O_{3} and NdCr_{0.6}Ti_{0.4}O_{3} at 1000 °C versus the oxygen partial pressure.

Figure 5  Concentration of electrons and electron holes on available hopping sites in NdCr_{0.9}Ti_{0.1}O_{3} and NdCr_{0.6}Ti_{0.4}O_{3} at 1000 °C versus the oxygen partial pressure.