

## Electronic conductivity of LaCrO<sub>3</sub> ceramics prepared by self-propagating high temperature synthesis

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### Abstract

Lanthanide orthochromite materials have been widely studied as refractory conducting ceramics because of their electrical conductivity, oxidation resistance and high melting points. In this paper theoretical and experimental analysis about electric conductivity of the SHS prepared ceramics was carried out. The usefulness of the Seebeck-coefficient measurements as a function of P(O<sub>2</sub>) is emphasized. Electronic conduction was found to be n-type in the lower P(O<sub>2</sub>) range, and p-type in the higher P(O<sub>2</sub>) range. The carrier concentrations were calculated as a function of P(O<sub>2</sub>) and defect structure.

**Key Words** : LaCrO<sub>3</sub>, SHS, electrical conductivity, Seebeck coefficient, n type and p type

### I. Introduction

Lanthanide orthochromites have the general formula LaCrO<sub>3</sub> and adopt the perovskite crystal structure [1]. These materials have been widely studied as refractory conducting ceramics because of their electrical conductivity, oxidation resistance and high melting points (>2400 °C). These properties have lead to applications in high-temperature furnace heating elements and interconnect in solid oxide fuel cells. Substituted also show potential in gas sensing application [2]. There are so many methods of synthesis such materials. All of these reactions give some improvement in synthesis time and product quality by allowing mixing of the precursors at the molecular level. Here we report the rapid synthesis of lanthanide orthochromites by self-propagating high-temperature synthesis (SHS). SHS is the name given to a general process where an exothermic chemical reaction replaces

the requirement to heat the reagents. Energy for the transformation primarily comes from the reaction enthalpy. The present study was undertaken to calculate the high-temperature cation distribution from Seebeck coefficient measurements for LaCrO<sub>3</sub> system.

### II. Experimental Part

#### a) Samples.

All reagents (La<sub>2</sub>O<sub>3</sub> and chromium metal) were obtained from Aldrich (U.K.) and used as supplied. Milling operations were carried out in a FRITSCH 05.102 ball mill (Germany). The mixture was pressed (30 kg/cm<sup>2</sup>) into cylindrical pellet. The pellet was supported on a ceramic boat and the reaction ignited by an electrically heated nichrome wire filament at one end. This produces a solid flame that moves out from point of initiation through the whole material. Oxygen was admitted through the tube (10 l/min) This produce an white-yellow propagation wave that proceeds through the solid at the velocity 3-4 mm/s. The X-ray analysis of this powder showed LaCrO<sub>3</sub>

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single phase (  $a=5.500 \text{ \AA}$ ,  $b=5.480 \text{ \AA}$ ,  $c= 7.762 \text{ \AA}$ ;  $\gamma=89.46$ ). Rectangular samples (0.25 by 0.25 cm in cross section and 1.5 cm long) were cut from the sintered  $\text{LaCrO}_3$  for electron conductivity and Seebeck coefficient measurements.

*b) Conductivity measurements.*

The standard dc four-probe method was used. Current was applied through probes consisting of several turns (2 mm wide) of Pt wire wound tightly around the sample at each end. Voltages were measured between two single turns of Pt wire 4.5 mm from the ends and 6 mm apart. To avoid the electrochemical effects the potentials across the voltage measuring electrodes was always  $< 10 \text{ mV}$ . The sample was connecting in series with a standard resistor and a variable resistor. The sample current was measured from the Ohmic drop across a standard resistor (either 100  $\Omega$  or 1 k $\Omega$ ) and the potential across the sample was controlled by the variable resistor. Voltage was measured with a high impedance digital voltmeter. The sample was placed horizontally in a vertical Mo-wound tube furnace. Ar/O<sub>2</sub> or CO/CO<sub>2</sub> gas mixtures were used to control the P(O<sub>2</sub>) in the ambient atmosphere. The P(O<sub>2</sub>) was measured by a zirconia cell (at 800 °C down stream from the furnace) The difference between log P(O<sub>2</sub>) obtained from the zirconia cell and that calculated from the CO/CO<sub>2</sub> relations was less than 0.1. The temperature of the furnace was controlled within 2 °C and the measurements were made at 1000 °C to 1300 °C.

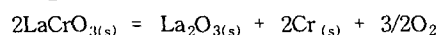
*c) Seebeck-coefficient measurements.*

For these measurements the sample was held by the Pt legs of two Pt-Pt10Rt thermocouple would near the two ends, spaced 13 mm apart. The sample was placed vertically in the lower part of the furnace where the temperature gradient was 15°C/cm Seebeck voltage were measured between the two Pt content points was determined from the two thermocouples. The P(O<sub>2</sub>) and current were controlled in the same way as they were for the conductivity measurements.

### III. Results and Discussion

Selection and evaluation of electrode materials is, therefore, aided by knowledge of the defect structure as a function of chemical potential which for oxides may be varied experimentally by varying the oxygen partial pressure, P(O<sub>2</sub>). However very little information exists on the defect structure of these materials as a function of P(O<sub>2</sub>) and temperature, T. Since we have proposed solid solution perovskite type oxides based on  $\text{LaCrO}_3$  as candidate for high-temperature furnace heating elements. The purpose of the present study was to determine the relation of electrical properties of  $\text{LaCrO}_3$  to P(O<sub>2</sub>) and T and relate the results to defect chemistry of SHS. Seebeck coefficient along with the electrical conductivity, were measured as a function of P(O<sub>2</sub>) and T and used in the calculations for the defect concentrations. In our experiments we did not independently fix the La and Cr activity, but instead kept the La/Cr ratio fixed for all experiments. If volatilization of these cations is insignificant, then the variation of the defects with the change in oxygen activity is defined.

Fig.1 shows electronic conductivity,  $\sigma$  vs log P(O<sub>2</sub>) for several temperatures. At each temperature, is independent of P(O<sub>2</sub>) in the highest P(O<sub>2</sub>) range. In the middle range decreases with decreasing P(O<sub>2</sub>). In the lowest range increases with decreasing P(O<sub>2</sub>). The conductivity passes through a minimum value,  $\sigma_{\text{min}}$ , at the P(O<sub>2</sub>,  $\sigma_{\text{min}}$ ). These values are listed in Table. Conductivity measurements could not be continued below the P(O<sub>2</sub>) values indicated in Fig.1, due to the erratic fluctuations in the dc conductivity, which presumably indicated decomposition of  $\text{LaCrO}_3$  according to the reaction



These P(O<sub>2</sub>) values are plotted in Fig.2. The plots of Seebeck coefficient, Q vs log P(O<sub>2</sub>) are shown in Fig.3. To calculate Q the following equations were used:

$$Q = Q_{s/Pt} - Q_{Pt} \quad (1)$$

$$\text{where } Q_{s/Pt} = E_{s/Pt} / (T_h - T_c) \quad (2)$$

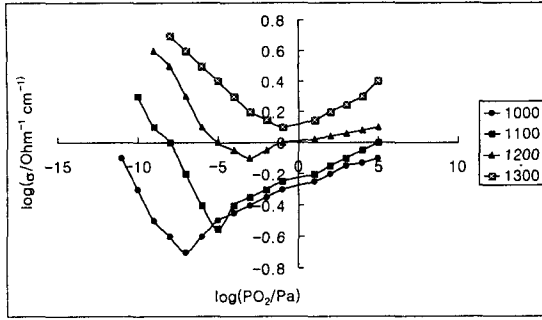


Fig.1. DC electrical conductivity,  $\sigma$  vs  $P(O_2)$  at temperature indicated. Solid line was calculated from  $K_i$ ,  $K_{ox}$ ,  $\mu_h$ ,  $\mu_e$  [ $V_{La}$ ] values.

Table. Logarithm of  $P(O_2)$  corresponding to  $\sigma_{min}$ ,  $Q = 0$

T(°C)	log $P(O_2, min)$ /(Pa)	log $P(O_2, Q=0)$ /(Pa)
1000	-7.1	-6.9
1100	-5.1	-4.1
1200	-3.0	-2.9
1300	-1.1	-1.1

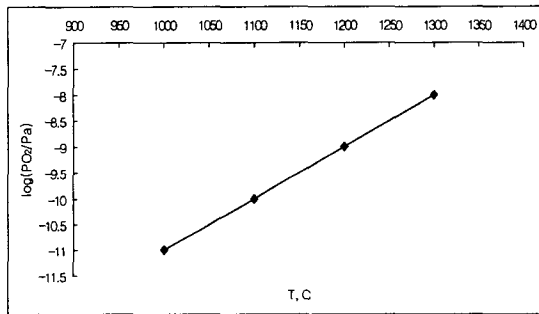


Fig.2. Decomposition  $P(O_2)$  of  $LaCrO_3$  vs temperature

$E_{s/Pt}$  is the observed Seebeck voltage,  $Q_{Pt}$  the Seebeck coefficient of platinum,  $T_h$  the temperature at the hot end of the sample, and  $T_c$  that at the cold end. For our calculation  $Q_{Pt}$  was taken from Ref.3. In the higher  $P(O_2)$  range,  $Q$  is positive, indicating p-type conduction, whereas in the lower range  $Q$  is negative, indicating n-type conduction.

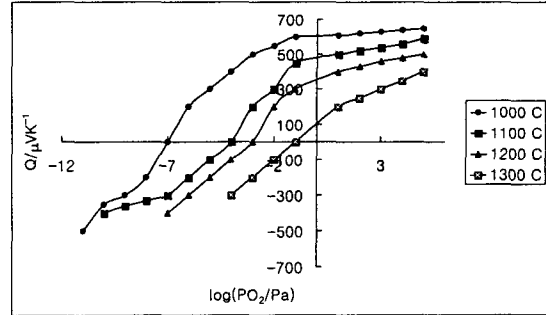


Fig.3. The plots of Seebeck coefficient  $Q$  vs  $\log P(O_2)/Pa$ .

Table contains the  $P(O_2)$  at which  $Q$  changes its sign,  $P(O_2, Q=0)$ . The  $\log P(O_2, Q=0)$  essentially agrees with  $\log P(O_2, min)$ . Thus the conductivity in the region  $P(O_2) > P(O_2, min)$  is mainly due to holes, whereas in the region  $P(O_2) < P(O_2, min)$  it is mainly due to electrons.

#### IV. Analysis of the results

##### A. Concentration and mobility of carriers

Electronic conductivity due to electrons,  $\sigma_e$  can be expressed by

$$\sigma_e = (N_A/V_m) \cdot n \cdot e \cdot \mu_e \quad (3)$$

and that to holes,  $\sigma_h$  is

$$\sigma_h = (N_A/V_m) \cdot p \cdot e \cdot \mu_p \quad (4)$$

where  $n$  is the molar fraction of electrons,  $p$  that of holes,  $N_A$  Avogadro's constant,  $V_m$  the molar volume of  $LaCrO_3$ ,  $e$  the magnitude of the charge on a single electron or hole,  $\mu_e$  the mobility of electrons,  $\mu_h$  that of holes. The equilibrium relation between electrons and holes is

$$\text{electron} + \text{hole} = \text{null} \quad (5)$$

$$n \cdot p = K_i \quad (6)$$

where  $K_i$  is a constant. When the molar fractions of  $n$ ,  $p$ , and other defects sensitive to  $P(O_2)$  are small enough, the change in  $\mu_e$ ,  $\mu_h$  and  $V_m$  with  $P(O_2)$  can be assumed negligible. The combinations of Eqs. (3), (4), (6) give

$$\begin{aligned} \sigma_e \cdot \sigma_h &= (N_A/V_m)^2 \cdot e^2 \cdot p \cdot \mu_h \cdot n \cdot \mu_e \\ &= K_i \cdot (N_A/V_m)^2 \cdot e^2 \cdot \mu_h \cdot \mu_e = K'_i \quad (7) \end{aligned}$$

where  $K_i$  is a constant.

The electronic conductivity,  $\sigma$  is expressed by

$$\sigma = \sigma_e + \sigma_h \quad (8)$$

Combining Eqs. (7) and (8), we have

$$\sigma = \sigma_e + K_i' \sigma_e^{-1} \quad (9)$$

$$\text{At } \sigma = \sigma_{\min}, \Delta\sigma / \sigma_e = 0 \quad (10)$$

From Eqs. (9), (10),

$$\sigma_{\min} / 2 = \sigma_e(\sigma_{\min}) = \sigma_h(\sigma_{\min}) = K_i'^{1/2} \quad (11)$$

where  $\sigma_e(\sigma_{\min})$  denote  $\sigma_e$  at  $P(O_2, \min)$  and  $\sigma_h(\sigma_{\min})$  denote  $\sigma_h$  at  $P(O_2, \min)$ .

Thus  $K_i$  for each temperature can be calculated from  $\sigma_{\min}$ , using Eq. (1) and the data in Fig.1. From Eq.(9) we have

$$\sigma - \sigma_h = \sigma_e = [\sigma - (\sigma - 4K_i')^{1/2}] / 2 \quad (12a)$$

for  $\sigma_e < \sigma_h$

$$\sigma - \sigma_h = \sigma_e = [\sigma + (\sigma - 4K_i')^{1/2}] / 2 \quad (12b)$$

Using Eq. (8), (12a, 12b), and  $K_i'$  from Eq. (11),  $\sigma_e, \sigma_h$  were obtained. Figure 4 shows the calculated  $\sigma_e, \sigma_h$  at 1,200 °C.

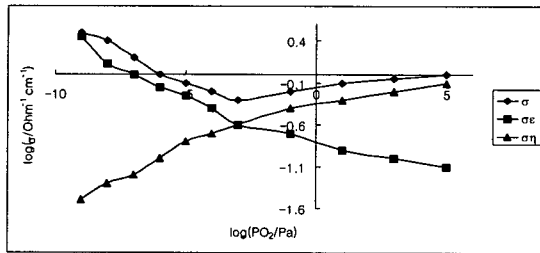


Fig 4. Calculated conductivity at 1,200 °C.

### B. Electrical properties and non-stoichiometry

In a perovskite type oxide represented by  $ABO_3$ , the  $BO_3$  portion is a stoichiometric  $ReO_3$  structure, whereas the A site may easily be deficient. Thus it is more probable that deficiencies in La exist in the sample. These deficiencies may have entered during sample preparation. Consequently,  $V_{La}^{III}$  is assumed to be the acceptor. The concentrations of the other

cations defects are assumed to be negligibly small compared to  $V_{La}^{III}$ . The proposed defect structure shows that variations in the electrical properties of  $LaCrO_3$  with  $P(O_2)$  changes are caused not only by oxygen vacancies but also by lanthanum vacancies. La vacancies result from a non-stoichiometric La/Cr ratio that is possibly introduced during the sample preparation. Small deviations from stoichiometry such as this cause marked changes in electrical conductivity in the highest  $P(O_2)$  region. For instance, if the samples were prepared closer to stoichiometry  $La/Cr < 1$ ,  $V_{La}^{III}$  would be smaller and  $p$  type conductivity in the highest  $P(O_2)$  range would be lower. If  $LaCrO_3$  were made stoichiometric, i.e.  $La/Cr=1$ , the carrier concentration in the highest  $P(O_2)$  range would be determined by Eq.(6), i.e.  $(p = n = K_i')^{1/2}$ .

### V. Conclusions

Electronic conductivity and Seebeck coefficients of  $LaCrO_3$  were measured as a function of temperature (1,000 to 1,300 °C) and  $P(O_2)$  ( $10^5$  to  $10^{-13}$ ). Electronic conduction was found to be  $n$  type in the lower  $P(O_2)$  range, and  $p$  type in the higher  $P(O_2)$  range. The carrier concentrations were calculated as a function of  $P(O_2)$  and defect structure was described.

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### References

- [1] Kilbourn B.T., *A Lanthanide Lanthology*. Molycorp. Inc., White Plains, NY, 1993.
- [2] Houg R.F. and Woung W.Y., *J. Mater. Res.*, 1996, vol. 11, p.3077.
- [3] Cusak N., Kendall P. Absolute Scale of Thermoelectric Power at High Temperature. *Proc. Phys. Soc. (London)*, vol. 72, N5, 1958, p.898-901.