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Electrical Conductivity of $CaMoO_4$

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The electrical conductivity and ionic transport number of $CaMoO_4$ has been measured as a function of the partial pressure of oxygen (1–10^{-18} atm) at 750, 800, and 850°C. Two sets of samples were studied: (1) $CaMoO_4$ annealed at 1100°C in the presence of CaO, and (2) $CaMoO_4$ annealed in MoO_3 vapor at 1100°C. Sample 1 is a mixed ionic/electronic conductor while Sample 2 is essentially an electronic conductor. A defect structure model is proposed to explain the results.

Introduction

Studies of electrical conductivity and transport numbers as a function of temperature and ambient partial pressure of oxygen are much-used methods for studying defect structures and transport properties of oxide phases (*1*). In this work these methods have been used in studies of calcium molybdate, $CaMoO_4$.

An earlier study (*2, 3*) of molybdates of calcium and strontium at 700–800°C and in the oxygen pressure range 0.01–1.0 atm has shown that these oxide phases possess mixed electron hole–ion conductivity with an ionic transport number of 0.2–0.3. It was suggested that the predominating defects were oxygen and molybdenum vacancies. However, in view of the rather narrow temperature and oxygen pressure ranges at which the studies were conducted it was not possible to give a more general and detailed analysis of defect-formation processes in scheelite-type molybdates.

Rigdon and Grace (*4*) studied the electrical conductivity of $CaWO_4$ at 900–1300°C and partial pressures of oxygen from 10^{-9} to 10^{-14} atm. The tungstate was found to be an *n*-type semiconductor, and the isothermal dependence of the electrical conductivity, σ, as a function of the partial pressure of oxygen, P_{O_2}, was described by the equation $\sigma = \text{const}\ P_{O_2}{}^{-1/4}$. The ionic transport number was estimated to be 0.08–0.01. The defect structure was interpreted in terms of oxygen vacancies and interstitials. The authors did not take into consideration that molybdenum and tungsten show relatively high mobility in molybdates and tungstates, respectively (*5*).

A more general analysis of the defect structure of molybdates and tungstates of divalent metals of the type $Me^{\cdot}MO_{3+n}$ has recently been advanced (*6*). Five types of defects are considered: $V_M^{6'}$, $V_O^{2\cdot}$, $V_{Me}^{2'}$, $M_i^{6\cdot}$, and Me_i^2, and the authors illustrate possible defect structure by considering $PbMoO_4$ (scheelite-type structure) and Sr_3MoO_6 (perovskite-type structure) as examples.

An important aspect to consider in high-temperature studies of molybdates and tungstates is the relatively high volatility of MoO_3 and WO_3. During specimen

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preparation and during the measurements this may lead to loss of these components in the molybdates and tungstates and change their composition. This has not been considered in the above studies.

Experimental Methods and Materials

Measurements of electrical conductivity and transport numbers were made on flat, circular oxide specimens. In the experimental setup different partial pressures of oxygen could be maintained on each side of the specimen. The oxygen partial pressures were fixed by use of $Ar–O_2$ or $CO–CO_2$ mixtures, and the relative amounts of the gases in the two mixtures were determined by flow meters. The total gas pressure on each side was always equal (1 atm). During measurements the temperature was maintained at ± 1°C.

The electrical conductivity was measured by the two-point method using an ac bridge. During these measurements the same partial pressure of oxygen was maintained at both sides of the specimen.

The total ionic transport number was determined by measuring the EMF across the specimen (the electrolyte) while different partial pressures of oxygen were maintained at opposite sides of the specimen. As a rule the difference in partial pressure of oxygen was 0.5–0.7 atm, but differences as high as 1.2 atm were used. Measurements of the electrical conductivity and transport numbers were done under isothermal conditions with both increasing and decreasing partial pressure in order to ensure as far as possible that equilibrium conditions were reached.

The $CaMoO_4$ was prepared by solid state reaction from stoichiometric amounts of CaO and MoO_3 powders. The powder mixtures were first heated for 3 hr at 550°C, then ground down to fine powder, and finally heated for 4 hr at 650°C. The specimens were prepared as pressed tablets 2–3 mm thick and with a 20-mm diameter. The tablets were baked at 1000°C for 3 hr.

Two sets of specimens, Samples 1 and 2, were prepared with different relative contents of CaO and MoO_3. Sample 1 was annealed for 8 hr at 1100°C in a sealed quartz ampoule with air pressure of 100 Torr and containing calcium oxide powder. These $CaMoO_4$ tablets were thus equilibrated with CaO; this yields specimens with a small deficit of MoO_3.

Sample 2 was annealed in a quartz ampoule at the same temperature but in equilibrium with MoO_3. The vapor pressure of MoO_3 was estimated to be 110 Torr during annealing.

The density of Sample 1 as measured with a pycnometer was $3.634\ g/cm^3$ and that of Sample 2 was $3.787\ g/cm^3$. By comparison with the measured density of the starting powder of $CaMoO_4$, it is concluded that the polycrystalline tablet specimens were 87–89% dense.

X-Ray diffraction measurements on the samples gave no indication of the presence of CaO or MoO_3 as separate phases. Within the accuracy of the measurements no difference in lattice parameters could be found for the different samples.

For the measurements of electrical conductivity and transport number the flat, polished surfaces of the tablet specimens were platinized for contact to the platinum lead wires. All measurements were conducted at temperatures more than 250°C lower than that of the prior thermal treatment (1100°C) in order to keep an evaporative loss of MoO_3 at a low level.

Experimental Results

Figure 1 shows the temperature dependence of the electrical conductivity at 1 atm O_2 for the two types of samples. Sample 1 ($CaMoO_4$ equilibrated with CaO) exhibited the larger electrical conductivity.

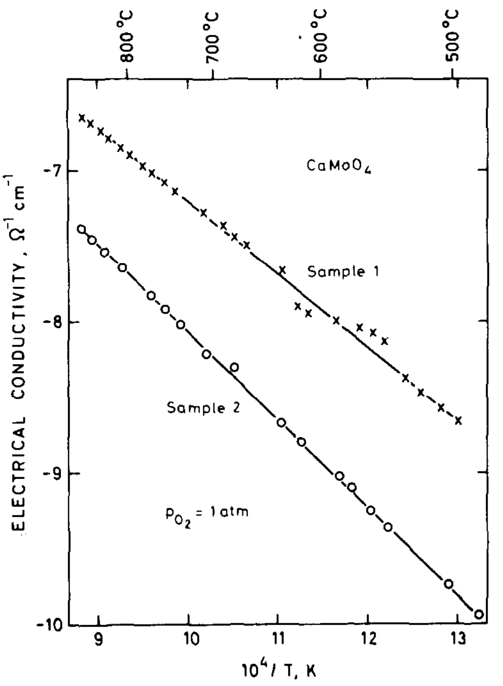

FIG. 1. The logarithm of the electrical conductivity of Samples 1 and 2 at 1 atm O_2 as a function of the reciprocal absolute temperature.

The activation energy of the electrical conductivity for Sample 1 under these conditions was 1 eV (or 96 kJ/mole) and for Sample 2 was 1.15 eV (or 110 kJ/mole).

The electrical conductivity and the ionic transport number of Sample 1 as a function of the partial pressure of oxygen under isothermal conditions (750, 800, and 850°C) are shown in Fig. 2. The results show that the sample is a mixed ionic–electronic conductor. Furthermore, the total ionic transport number goes through a maximum at an oxygen pressure range of about 10^{-6}–10^{-8} atm, and in the same pressure range the electrical conductivity goes through a minimum.

The corresponding results for Sample 2 are shown in Fig. 3. For this sample electronic conductivity predominates, and in the low-pressure range the ionic transport number is essentially equal to zero.

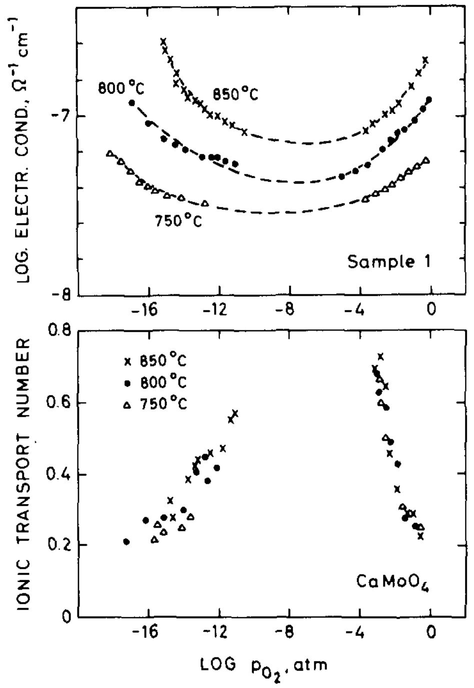

FIG. 2. The electrical conductivity and the ionic transport number of Sample 1 as a function of the partial pressure of oxygen under isothermal conditions (700, 750, and 800°C).

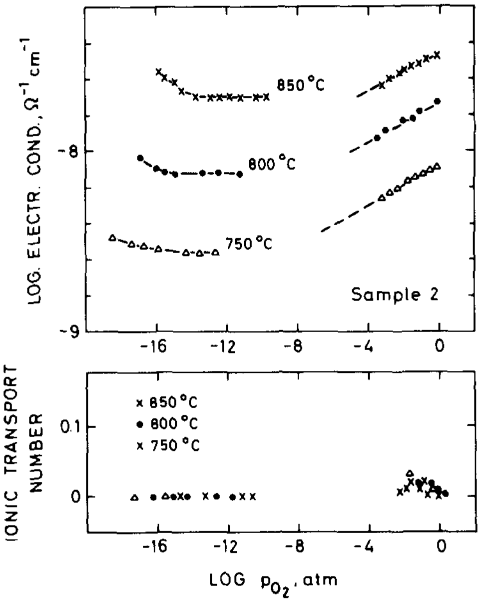

FIG. 3. The electrical conductivity and the ionic transport number of Sample 2 as a function of the partial pressure of oxygen under isothermal conditions (700, 750, and 800°C).

Discussion

For the interpretation of the results and of the defect structure of $\mathrm{CaMoO_4}$ it may be noted that previous tracer diffusion studies on $\mathrm{CaMoO_4}$ and $\mathrm{CaWO_4}$ have shown that diffusion of the isotope $^{185}\mathrm{W}$ is considerably faster than that of $^{45}\mathrm{Ca}$ (*5, 7, 8*). These results are summarized in Fig. 4. From studies of diffusion-controlled state synthesis of $\mathrm{CaMoO_4}$ it has furthermore been concluded that mass transfer of oxygen is faster than that of molybdenum, and thus that $D_\mathrm{O} > D_\mathrm{Mo}$ (*2, 3*). On this basis it will in the following be assumed that oxygen ions are the most mobile ionic species in $\mathrm{CaMoO_4}$.

For Sample 1 it is concluded that the annealing treatment has produced a deficit of $\mathrm{MoO_3}$ relative to the stoichiometric composition of $\mathrm{CaMoO_4}$:

$$\mathrm{CaMoO_4} = \mathrm{CaMo_{1-\mathit{y}}O_{4-3\mathit{y}}} + y\mathrm{MoO_3(g)}. \quad (1)$$

This nonstoichiometry is assumed to be equivalent to the presence of oxygen and molybdenum vacancies. If these can be considered to be fully ionized, they may be written as $V_\mathrm{O}^{2\cdot}$ and $V_\mathrm{Mo}^{6'}$, respectively. Their formation may correspondingly be written as

$$\mathrm{Mo_{Mo}} + 3\mathrm{O_O} = V_\mathrm{Mo}^{6'} + 3V_\mathrm{O}^{2\cdot} + \mathrm{MoO_3(g)}. \quad (2)$$

From Eqs. (1) and (2) it is qualitatively seen that the oxygen and molybdenum vacancy concentrations are relatively high at low activities of $\mathrm{MoO_3}$. Correspondingly, y is expected to be larger for Sample 1 than for Sample 2.

In order to explain the appreciable ionic conductivity, it is assumed that the concentrations of the oxygen and molybdenum vacancies are relatively large for Sample 1 and that the electroneutrality condition can be approximated by

$$[V_\mathrm{O}^{2\cdot}] = [3\,V_\mathrm{Mo}^{6'}]. \quad (3)$$

It is further assumed that the oxygen vacancies are the most mobile point defects. This condition may explain the appreciable ionic conductivity of the sample.

Additional minor variations in the nonstoichiometry may take place through changes in the ambient partial pressure of oxygen. If one assumes that the oxygen exchange between the gas and the molybdate principally changes the oxygen vacancy

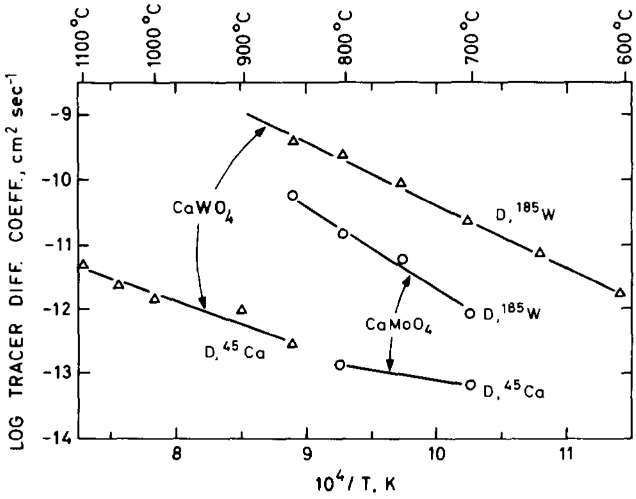

FIG. 4. Temperature dependence of the tracer diffusion coefficients for $^{185}\mathrm{W}$ and $^{45}\mathrm{Ca}$ in polycrystalline specimens of $\mathrm{CaMoO_4}$ and $\mathrm{CaWO_4}$ (*5, 7, 8*).

concentration, this can be expressed by the equation

$$\mathrm{CaMo}_{1-y}\mathrm{O}_{4-y} \pm \frac{\delta}{2}\mathrm{O}_2 = \mathrm{CaMo}_{1-y}\mathrm{O}_{4-3y\pm\delta}. \tag{4}$$

The oxygen vacancy equilibrium is further given by

$$[V_O^{2\cdot}]n^2 = K_{V_O^{2\cdot}} P_{O_2}^{-1/2} \tag{5}$$

and that of the intrinsic electronic equilibrium by

$$n \cdot p = K_i. \tag{6}$$

If the variation in the oxygen vacancy concentration with the partial pressure of oxygen, $\pm\delta$, can be considered to be small compared to that created by the MoO_3 deficit, y, i.e., $\delta \ll y$, the concentration of oxygen and molybdenum vacancies can be considered essentially constant under the experimental conditions:

$$3[V_{Mo}^{6'}]_{\mathrm{const}} \cong [V_O^{2\cdot}]_{\mathrm{const}}. \tag{7}$$

By combining Eqs. (5–7), the electron and electron hole concentration is given by

$$n = \left(\frac{K_{V_O^{2\cdot}}}{[V_O^{2\cdot}]_{\mathrm{const}}}\right)^{1/2} P_{O_2}^{-1/4}, \tag{8}$$

$$P = K_i\left(\frac{[V_O^{2\cdot}]_{\mathrm{const}}}{K_{V_O^{2\cdot}}}\right)^{1/2} P_{O_2}^{+1/4}. \tag{9}$$

In these terms the total electrical conductivity is given by

$$\sigma_{\mathrm{tot}} = \sigma_{\mathrm{ion}} + \sigma_{\mathrm{el}} = \sigma_{\mathrm{ion}} + \sigma_n^0 P_{O_2}^{-1/4} + \sigma_p^0 P_{O_2}^{+1/4}. \tag{10}$$

Accordingly, at high oxygen pressures the electrical conductivity will essentially constitute p-conductivity and at low oxygen pressure n-conductivity. In a middle-pressure region ionic conductivity may be important depending upon the relative concentrations of ionic and electronic defects.

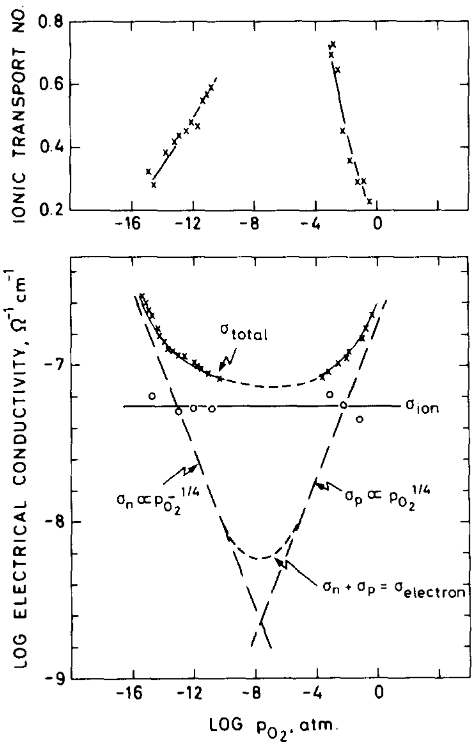

FIG. 5. The proposed model for the defect structure situation for Sample 1 applied to the experimental results at 850°C.

The proposed model is applied to the results on Sample 1 at 850°C in Fig. 5. The relative contributions of the conductivity due to electrons, electron holes, and ions are shown, and the model is in its main features in agreement with the results.

Similar analyses for the results at 800 and 750°C for Sample 1 show that the temperature dependence of the ionic conductivity is characterized by an activation energy of about 80 kJ/mole. In view of the higher diffusion rate of oxygen than of molybdenum in $CaMoO_4$ (*5, 7, 8*), this value is concluded to reflect the activation energy for the mobility of oxygen vacancies. The same approximate value has also been found for oxygen vacancy mobility in other oxide systems (*1*).

It may be noted that the same general model applies if it is assumed that the concentration of oxygen vacancies is fixed by the presence of lower-valent foreign cations (impurities) occupying Mo sites (*1, 9*).

For Sample 2 ($CaMoO_4$ annealed in MoO_3 vapor at 1100°C) the model suggests that the contribution of the ionic conductivity should be smaller than that for Sample 1. This is also borne out by the results which show that Sample 2 is essentially an electronic conductor. However, for this sample it has not been possible to determine the value of y or, for that matter, whether it is positive or negative. A more detailed interpretation is also difficult.

A possible interpretation of the results is that the oxygen pressure-independent electrical conductivity at oxygen pressures from about 10^{-9} to 10^{-12} atm reflects intrinsic electronic conductivity where $n = p = K_i^{1/2}$. The activation energy under these conditions amounts to 46 kcal/mole. At higher oxygen pressures ($P_{O_2} > \sim 10^{-4}$ atm) the electrical conductivity increases with increasing oxygen pressure and approximately $\sigma \propto P_{O_2}{}^{1/18}$. This may possibly reflect that molybdenum vacancies become of increasing relative importance. The increasing electrical conductivity at low oxygen pressures may correspondingly indicate the increased relative importance of oxygen vacancies. But without further studies no definite interpretation at high or low oxygen pressures can be offered for Sample 2.

All in all, the results clearly demonstrate that the exact composition and pretreatment of molybdate specimens is of decisive importance for the defect structure situations observed. The same will also apply to tungstates, although the volatility of WO_3 is smaller than for MoO_3 at the same temperature. These aspects should be given attention in future studies of transport properties of these types of compounds.

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