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Ionic conduction in solid solution of the system La_2O_3–CaF_2

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The crystal phase and the electrical conduction in sesquioxide–alkaline earth difluoride systems were investigated. LaOF-type cubic solid solution was found in the system La_2O_3–CaF_2. This phase showed anion conductivity comparable to that of YF_3–doped CaF_2. Electrolysis by Tubandt's method showed that the conduction was predominantly attributed to fluoride ions. In this solid electrolyte, the fluoride ion is easily substituted by oxide ion through cathode reaction in the oxygen atmosphere.

1. Introduction

Numerous studies of the anion conduction in oxides as well as halides at high temperatures have been reported in the literature [1–8], but there appears to be little work on oxyhalides which have oxide ions and halide ions in a lattice [9]. Among many oxyhalides, the oxyfluorides of rare earth elements (LnOF) having comparatively large cationic radii are reported to have three types of crystal phase. These are the high temperature cubic phase with a fluorite-type structure, and the low temperature tetragonal and rhombohedral phases [10–13]. The latter two phases are also postulated to be pseudocubic [12]. The anion sites of these structures are considered to be occupied by the oxide ions and the fluoride ions randomly. In this case, if we can retain a defect structure having anion vacancies or interstitials by doping another compound, high anion conduction will be expected as in the sinters of the system PbF_2–KF or PbF_2–BiF_3 [14–16].

Pelloux *et al.* [17] studied the system La_2O_3–LaF_3, and reported oxide ion conduction in the solid solution of $LaO_{1-x}F_{1+2x}$. Similar oxyfluorides may be formed by the solid state reaction between sesquioxides and difluorides. If it is possible, anion conduction will be also observed.

From this point of view, we directed our attention initially to the Ln_2O_3–MF_3 system (Ln = La, Y M = Ca, Sr, Ba), and studied the formation of the crystal phase with LaOF-type structure and the electrical properties in the resultant phase.

2. Experimental details

2.1. *Preparation of specimens*

The specimens were prepared from sesquioxide (99.99% La_2O_3, 99.99% Y_2O_3) and difluoride (CaF_2, SrF_2, BaF_2). In the following studies, we use the expression $LaO_{1.5}$ instead of La_2O_3 to match the cation number of oxide with that of fluoride. These materials were weighed in the defined molar ratios, mixed in an agate mortar, and fired at 1100–1200° C in dry air for 5–10 hr. The fired products were ground, pressed hydrostatically (2 ton cm^{-2}) into rods (5 mm $\phi \times$ 5–10 mm length) or discs (10 mm $\phi \times$ 2–3 mm thick), and sintered, again at 1200° C in air for 10 hr. In the special case, specimens were obtained

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by sintering in dry nitrogen gas and compared with the specimens fired in dry air.

X-ray diffraction was carried out using CuK_α-radiation to identify the crystal phase of the specimens prepared. These specimens were cooled slowly (about 2° C min^{-1}) from sintering temperature to room temperature to avoid freezing of the high temperature forms. Densities of the powdered specimens were determined by the standard pycnometer method using *n*-butanol.

2.2. *Measurement of ionic conduction*

Electrical conductivity of specimens was determined by measuring their impedance using a universal AC bridge with a 10 kHz signal. Rod specimens were generally employed in this measurement. Platinum powder paste was smeared on both ends of the rod samples and fired to serve as the electrodes.

The ionic transport number of specimens was determined from the e.m.f. of an oxygen gas concentration cell constructed using a disc specimen as an electrolyte under various conditions. If the conduction in the specimen is purely ionic, the e.m.f. E_0 of the cell

$$\text{Gas}\ I\ (P_{O_2}, a),\ \text{Pt/specimen disc/Pt, Gas II}\ (P_{O_2}, c) \qquad (1)$$

is given by Equation 2

$$E_0 = (RT/4F)\ln\,[(P_{O_2}, c)/(P_{O_2}, a)] \qquad (2)$$

where R, T and F have their usual meanings. In an ion and electron mixed conductor, the e.m.f. E is lowered from E_0. In such a case, the ratio of the ionic conductivity σ_i to the total conductivity σ_t, that is, the ionic transport number t_i, can be given as the following equation, if the electrode reaction is sufficiently reversible,

$$t_i = \sigma_i/\sigma_t = \sigma_i/(\sigma_i + \sigma_e) = E/E_0 \qquad (3)$$

where σ_e is the electronic conductivity.

Ionic conduction was also investigated by electrolysis using Tubandt's method. In this method, three disc-shaped specimens (catholyte, bulk and anolyte) were contacted face-to-face. The electrolysis products were identified by X-ray diffraction and the resultant weight changes in the three specimens were measured.

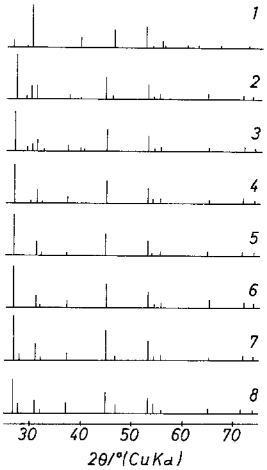

Fig. 1. X-ray diffraction patterns of $(\text{LaO}_{1.5})_{1-x}(\text{CaF}_2)_x$: 1. $x = 0.0$; 2. $x = 0.25$; 3. $x = 0.33$; 4. $x = 0.37$; 5. $x = 0.40$; 6. $x = 0.46$; 7. $x = 0.50$; 8. $x = 0.60$.

3. Results and discussion

3.1. *The crystal phase formed*

The sintered specimens thus prepared were so dense that there were no open pores to allow penetration of the gas. Fig. 1 shows the X-ray diffraction patterns of the specimens in the system $\text{LaO}_{1.5}$–CaF_2. The specimens including 36–45 mol % CaF_2 show the diffraction patterns of the LaOF-type cubic phase, although small diffraction lines assigned to CaO were, in addition, observed in all the cases examined. Each peak assigned to the LaOF-type structure shifted toward a higher angle as compared with the pure cubic LaOF crystal, which indicates a smaller lattice constant (5.714 Å for $x = 0.43$) than for the pure LaOF crystal (5.76 Å in [10]). The specimens containing less than 36 mol % CaF_2 showed mixed phases with LaOF-type cubic and La_2O_3, and the specimens having more than 45 mol % CaF_2 were mixed phases with LaOF-type cubic and CaF_2.

Any other systems examined here did not exhibit the crystal phases corresponding to LaOF modifications and remained in mixed phases of original oxide and fluoride. Gorbulev *et al.* [18] studied the phase relation between LaOF and MF_2 (M = Ca, Sr, Ba). They reported that the fluorite-type solid solution regions and high temperature modification of LaOF were observed and that these regions narrowed sharply with decreasing temperature. In the present system, however, it was considered that the solid state reaction differs from the previous systems, and that it is not the compound LaOF but the solid solution that is formed according to Equation 4.

$$(1-x)LaO_{1.5} + xCaF_2 \rightarrow La_{1-x}Ca_xO^{1}_{1.5-1.5x}F_{2x} \qquad (4)$$

In order to explain this, the following arguments are presented in addition to the above X-ray results.

(a) CaF_2, SrF_2 and BaF_2 have almost the same free enthalpies of formation (ΔG_f) over a wide range of temperatures. But, in the system $LaO_{1.5}$–MF_2, LaOF-type cubic phase appeared only in the case of CaF_2 whose cationic radius is smaller than that of the other doping fluorides.

(b) In the system based on Y_2O_3, which has a smaller cationic radius than La_2O_3, no LaOF-type crystal phase was formed even when CaF_2 was doped.

(c) If a compound, LaOF, was only formed by the following reaction,

$$(1-x)LaO_{1.5} + xCaF_2 \rightarrow (1-x)LaOF + [(1-x)/2]CaO + [(3x-1)/2]CaF_2, \quad x > 0.33 \qquad (5)$$

or

$$(1-x)LaO_{1.5} + xCaF_2 \rightarrow 2xLaOF + xCaO + (1-3x)LaO_{1.5}, \quad x < 0.33 \qquad (5')$$

the amount of LaOF must be maximal at $x = 0.33$. However, in this composition, the mixed phase containing unreacted La_2O_3 was observed.

(d) The CaO-free specimens could be obtained by washing the specimen powder with 2N HNO_3. The powder densities were lower than those calculated for pure LaOF and decreased with increasing content of CaF_2.

3.2. *Conductivity*

Attention was focused on the electrical properties of the LaOF-type phase in the system $LaO_{1.5}$–CaF_2, since no other new phases were observed in the system examined. Arrhenius plots of conductivity of $(LaO_{1.5})_{1-x}(CaF_2)_x$ are presented in Fig. 2 for the representative compositions. As the conductivity of each specimen measured below 800° C was time dependent and poor in reproducibility, only the data above 800° C are shown in this figure. The conductivity of these specimens was almost comparable to that of CaO-stabilized ZrO_2 [19, 20] and YF_3-doped CaF_2 [21] above 800° C. The conductivities increased with addition of CaF_2 to $LaO_{1.5}$ and maximum conductivity lay at $x = 0.5$, where excess CaF_2 was mixed in the LaOF-type phase (see Fig. 1). This result suggests that the solid solution formation range becomes wide at high temperatures. When more than 53 mol % CaF_2 was added to $LaO_{1.5}$, the conductivity was lowered. The poor reproducibility in conductivity at lower temperatures could not be explained easily. At the least it could not be attributed to the phase transition, since any thermal phase transition was not detected by the DTA in this temperature range.

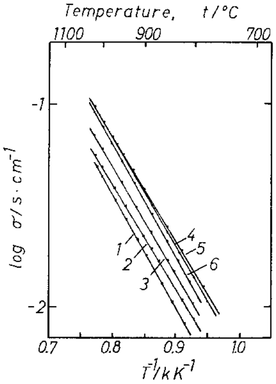

Fig. 2. Arrhenius plots of conductivity for $(LaO_{1.5})_{1-x}(CaF_2)_x$: 1. $x = 0.37$; 2. $x = 0.40$; 3. $x = 0.46$; 4. $x = 0.50$; 5. $x = 0.53$; 6. $x = 0.56$.

3.3. *Electrolytic properties*

Fig. 3 shows the measured e.m.f. of the oxygen gas concentration cell using specimen discs as electrolytes, and pure oxygen (1 atm) and air (1 atm) as cathode and anode gases, respectively. The e.m.f. calculated from Equation 2 is indicated as a solid line. The measured values are in good agreement with the calculated values over a wide temperature range. It was also possible to draw d.c. currents from the cells. These results denote

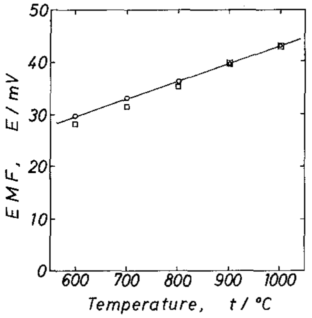

Fig. 3. E.m.f. of the following oxygen gas concentration cell. Gas I (P_{O_2}, a), Pt/$(LaO_{1.5})_{1-x}(CaF_2)_x$/Pt, Gas II ($P_{O_2}, c$) where $P_{O_2}, a = 0.21$ atm and $P_{O_2}, c = 1.0$ atm. ○ – $x = 0.43$; □ – $x = 0.50$. Solid line shows the e.m.f. calculated by Equation 2.

that the specimens are ionic conductors. However, these currents were lower than the value calculated from the e.m.f.s and the a.c. resistances of the electrolytes. Therefore, the true ionic charge carrier in the electrolyte cannot be concluded by the gas concentration cell method alone.

Fig. 4 shows the terminal voltage vs d.c. current relation at 800° C in dry air. The specimen was $(LaO_{1.5})_{0.57}(CaF_2)_{0.43}$, which contained a very small amount of CaO. A decomposition voltage was observed at about 5 V in air. In order to clarify the ionic charge carrier in the electrolyte, electrolysis was carried out using Tubandt's method, in which porous platinum electrodes were used. After electrolysis above the decomposition voltage of about 5 V by 165 C, the three specimen discs were analysed by X-ray diffraction. The bulk sample kept its original crystal phase. However, the catholyte surface was electrolysed to form La_2O_3 and CaO, and CaF_2 appeared on the anolyte surface. The results cannot be explained by considering oxide ions as the charge carriers, because both electrodes can be reversible for oxide ions. If fluoride ions are charge carriers in the specimens, the above results are explained by the following electrode reactions.

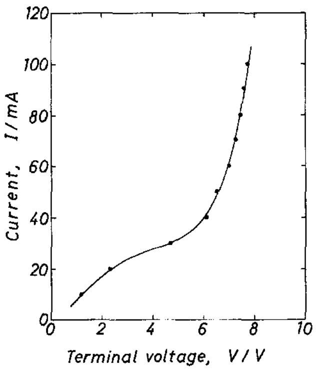

Fig. 4. Electrolysis curve of $(LaO_{1.5})_{0.57}(CaF_2)_{0.43}$ at 900° C in dry air.

Cathode:

$$LaCaO_{1.5}F_2 + 2e \rightarrow LaO_{1.5}(Ca) + 2F^- \qquad (6)$$

and

$$LaO_{1.5}(Ca) + 1/2O_2 \rightarrow LaO_{1.5}(CaO) \qquad (7)$$

Anode:

$$CaO + 2F^- \rightarrow CaF_2 + 1/2O_2 + 2e \qquad (8)$$

where the ratio of La to Ca in the specimen is made to be unity for convenience. In this case, the weight change in the specimens must be observed corresponding to the amount of electricity; – 18.8 mg in the catholyte and + 18.8 mg in the anolyte for 165 C. In this experiment, catholyte weight decreased by 19.2 mg which was close to the calculated value. This result obviously showed that the transport number of fluoride ions (t_{F^-}) was almost unity within experimental error. The weight change in anolyte (9.6 mg) was smaller than that in the catholyte suggesting that about half of the fluoride ions were dispersed from the anode as fluorine gas.

As is seen in Fig. 4, it was possible to pass an appreciable d.c. current through the sample below the decompoition voltage (about 5 V). In this condition, we obtained almost the same electrolysis results as those using Tubandt's method mentioned above. This suggests that fluoride ion is easily substituted by oxide ion at the cathode surface as shown in Equations 9 and 10, and that fluoride ion conduction is predominant.

$$\underset{\text{(gas phase)}}{1/2O_2} + \underset{\text{(electrode)}}{2e} \longrightarrow \underset{\text{(electrode)}}{O^{2-}} \qquad (9)$$

$$\underset{\text{(catholyte)}}{LaCaO_{1.5}F_2} + \underset{\text{(electrode)}}{O^{2-}} \longrightarrow \underset{\text{(catholyte)}}{LaO_{1.5}(CaO)} + \underset{\text{(bulk)}}{2F^-} \qquad (10)$$

Considering that the cathode in this experiment is a blocking electrode for fluoride ion and the

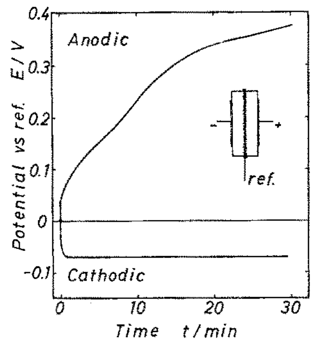

Fig. 5. Change in electrode potential with time at 800° C in air. Specimen: $(LaO_{1.5})_{0.57}(CaF_2)_{0.43}$; current: 1 mA.

charge density of monovalent fluoride ion is smaller than that of divalent oxide ion, these results would be reasonable.

The facility of reaction of Equation 10 was investigated by measuring the variation of electrode potential with time. A small d.c. voltage was applied galvanostatically between the two end electrodes of the disc specimen in air. The variation with time of the cathode and anode potentials was measured against a reference electrode attached laterally to the specimen. Fig. 5 shows the results obtained for $(LaO_{1.5})_{0.57}(CaF_2)_{0.43}$. The anode potential increased with time as in the case of charging a large capacitor, which shows that the anode reaction is not smooth. However, the cathode potential was stabilized within a minute suggesting that the cathode reaction corresponding to Equation 10 proceeds smoothly (fairly reversibly).

Fig. 6 shows the result of the d.c. four-probe method for $(LaO_{1.5})_{0.57}(CaF_2)_{0.43}$. A small d.c. voltage was applied galvanostatically between the two end electrodes of the cylindrical specimen in air. When a steady-state was reached, the current and the voltage between the two inner electrodes were measured. As mentioned above, the conduction in the specimen is due to fluoride ions. In this experiment, the voltage was stabilized in a few seconds and the relation between the voltage and current was linear. The conductivity calculated from the gradient of the lines corresponded to the values measured by an a.c. bridge at each temperature. Therefore, it was considered that fluoride ion conductivity of oxyfluoride can be measured stably using the usual d.c. four probe method.

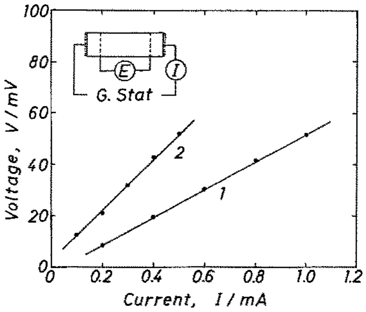

Fig. 6. Voltage between two inner electrode vs d.c. current relation for $(LaO_{1.5})_{0.57}(CaF_2)_{0.43}$ in dry air. 1. 900° C; 2. 800° C.

Pelloux *et al.* [17] reported oxide ion conduction in $LaO_{1-x}F_{1+2x}$. They favoured an oxide ion conduction mechanism in the specimens based only from the e.m.f. measurements of galvanic cells using metal and metal oxide mixtures. However, as the sample compositions are different from our case, we can not discuss the difference between the results in detail.

4. Conclusion

LaOF-type solid solution was found to be formed at the intermediate composition range in the system $LaO_{1.5}$–CaF_2. This solid solution showed high anion conductivity comparable to that of YF_3-doped CaF_2 above 800° C. The conduction was predominantly due to fluoride ion, the charge density of which is smaller than that of oxide ion. In this solid solution, fluoride ion is considered to be easily substituted by oxide ion through the electrode reaction.

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