

# *High ionic conduction in tetragonal solid solution of the system $\text{La}_2\text{O}_3\text{--MgF}_2$*

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LaOF-type tetragonal solid solution was found in the system  $\text{La}_2\text{O}_3\text{--MgF}_2$ . This phase showed higher anionic conduction than the previously reported cubic solid solution in the system  $\text{La}_2\text{O}_3\text{--CaF}_2$ . Electrolysis by Tubandt's method showed that fluoride ion conduction was dominant in this solid solution. The fluoride ions were considered to be easily substituted by oxide ions through cathode reaction in the oxygen atmosphere.

## 1. Introduction

Among many fluoride-oxides, the fluoride-oxides 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 and the low temperature tetragonal and rhombohedral phases [1–4]. The anion sites of these structures are considered to be randomly occupied by oxide ions and fluoride ions [3, 4]. And, 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  $\text{PbF}_2\text{--KF}$  or  $\text{PbF}_2\text{--BiF}_3$  [5–7]. However, there appears to be little work on ionic conduction in the fluoride-oxide system [8].

In a previous paper the authors examined the system  $\text{La}_2\text{O}_3\text{--MF}_2$  ( $M = \text{Ca}, \text{Sr}$  and  $\text{Ba}$ ) and found that a LaOF-type cubic solid solution was formed in the system doped with  $\text{CaF}_2$  [9], and that the conduction in this phase was caused by fluoride ions. However, solid state reactions were not observed in the other systems. This shows that the LaOF-type solid solution forms in the fluoride-oxide system doped with the fluoride having a smaller cation. Therefore, in the work reported in this paper we directed our attention to the fact that  $\text{MgF}_2$  has a smaller cation than  $\text{CaF}_2$ , and studied the formation of

the crystal phase with LaOF-type structure in the system  $\text{La}_2\text{O}_3\text{--MgF}_2$  and the electrical properties in the resultant phase.

## 2. Experimental details

### 2.1. Preparation of specimens

The specimens were prepared from  $\text{La}_2\text{O}_3$  (99.99%) and  $\text{MgF}_2$  (Wako special grade). These materials were weighed in the defined molar ratios, mixed in an agate mortar and fired at 1100–1200°C in dry air for 10 h. NaOH and  $\text{P}_2\text{O}_5$  were used as the air drying agents. The fired products were ground, pressed hydrostatically ( $2 \text{ ton cm}^{-2}$ ) into rods (5 mm  $\phi$  by 5–10 mm length) or discs (10 mm  $\phi$  by 2–3 mm thick) and sintered again under the same condition as the first firing. X-ray diffraction was carried out using  $\text{CuK}\alpha$ -radiation to identify the crystal phase of the specimens prepared.

### 2.2. Measurement of ionic conduction

The electrical conductivity of specimens was determined by measuring their impedance using a universal a.c. bridge with a 10 kHz signal. Rod specimens were generally employed in this measurement. Platinum paste or silver paste was smeared on both ends of the rod samples and baked to serve as the electrodes.

The ionic transport number of specimens was determined by measuring the e.m.f. of an oxygen gas concentration cell constructed using a disc specimen as an electrolyte and comparing the value with the e.m.f. calculated from the Nernst equation.

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 electrolysed products were identified by X-ray diffraction and the resultant weight changes in the three specimens were measured.

### 3. Results and discussion

#### 3.1. The crystal phase formed

The sintered specimens containing more than 45 mol %  $\text{MgF}_2$  were so dense that there was no open pore structure to allow penetration of gas. However, in the specimens having less than 40 mol %  $\text{MgF}_2$ , the sintering density became obviously low as the content of  $\text{MgF}_2$  decreased. Fig. 1 shows X-ray diffraction patterns of the representative specimens in the system  $\text{LaO}_{1.5}\text{-MgF}_2$ . In all samples, small diffraction lines assigned to  $\text{MgO}$  were additionally observed. The specimens containing less than 40 mol %  $\text{MgF}_2$  showed a mixed phase with the

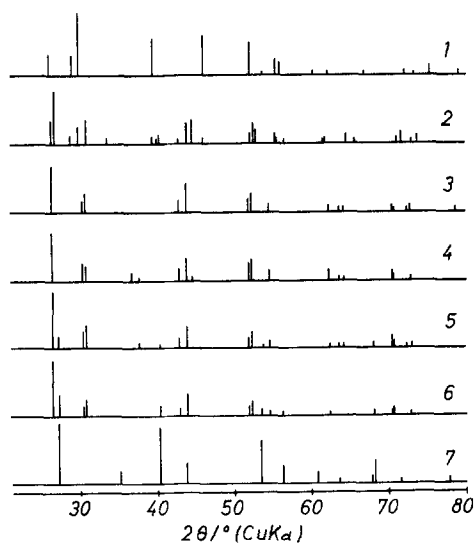


Fig. 1. X-ray diffraction patterns of  $(\text{LaO}_{1.5})_{1-x}(\text{MgF}_2)_x$  where values of  $x$  are: 1, 0.0; 2, 0.33; 3, 0.44; 4, 0.53; 5, 0.56; 6, 0.67; 7, 1.0.

$\text{LaOF}$ -type rhombohedral phase and  $\text{La}_2\text{O}_3$ . As the content of  $\text{MgF}_2$  increased, the mixed phase disappeared and a tetragonal phase was formed in the composition range 44–53 mol %  $\text{MgF}_2$ . This phase was considered to correspond to the  $\text{LaOF}$ -type tetragonal phase. However, some small diffraction lines indicated on the ASTM card (NO. 5–470) could not be detected. This might show the disorder of the anion coordination in the  $\text{MgF}_2$ -doped tetragonal crystal. We have observed such a phenomenon between tetragonal  $\beta\text{-Bi}_2\text{O}_3$  (ordered) and 25 mol %  $\text{MoO}_3$ -doped  $\text{Bi}_2\text{O}_3$  (disordered) [10]. The rhombohedral single phase was not observed in the composition range examined. This was considered to be due to the fact that the crystal form of the  $\text{LaOF}$ -type compounds is easy to change (cubic  $\rightleftharpoons$  tetragonal  $\rightleftharpoons$  rhombohedral) according to the variation of fluorine content [3, 4]. Formation of the tetragonal phase in 44–53 mol %  $\text{MgF}_2$  was a reproducible phenomenon. The specimens containing more than 56 mol %  $\text{MgF}_2$  showed a mixed phase with the  $\text{LaOF}$ -type tetragonal phase and  $\text{MgF}_2$ .

#### 3.2. Conductivity

Arrhenius plots of conductivity in air for  $(\text{LaO}_{1.5})_{1-x}(\text{MgF}_2)_x$  are shown in Fig. 2 for the representative compositions. As reported previously, the data in the specimen of the system  $\text{LaO}_{1.5}\text{-CaF}_2$  were time-dependent and poor in reproducibility below  $800^\circ\text{C}$  [9]. In the present system, conduction was stable over a wide temperature range investigated and did not show dependence on oxygen partial pressures. The conductivities increased by adding  $\text{MgF}_2$  to  $\text{LaO}_{1.5}$  and maximum conductivity lay in the tetragonal sample of  $x = 0.47$ . The activation energy of conduction was  $70\text{ kJ mol}^{-1}$  at high temperatures above  $500^\circ\text{C}$ . Conductivity of this specimen was almost one order of magnitude higher than that of  $\text{CaO}$ -stabilized  $\text{ZrO}_2$  [11, 12] and  $\text{YF}_3$ -doped  $\text{CaF}_2$  [13]. When more  $\text{MgF}_2$  was added to  $\text{LaO}_{1.5}$  the conductivity was lowered.

#### 3.3. Electrolytic properties

Fig. 3 shows the measured e.m.f. of the oxygen

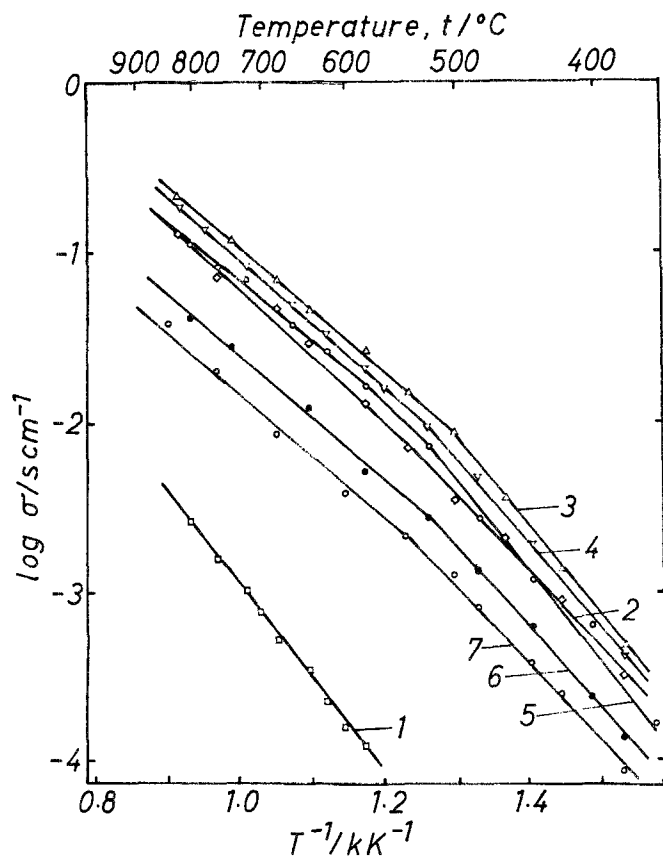


Fig. 2. Arrhenius plots of conductivity for  $(\text{LaO}_{1.5})_{1-x}(\text{MgF}_2)_x$  where values of  $x$  are: 1, 0.33; 2, 0.44; 3, 0.47; 4, 0.50; 5, 0.56; 6, 0.67; 7, 0.77.

gas concentration cell using specimen discs as electrolytes, where pure oxygen (1 atm) and air (1 atm) were used as cathode and anode gases, respectively. The e.m.f. calculated from the Nernst equation is indicated by the solid line.

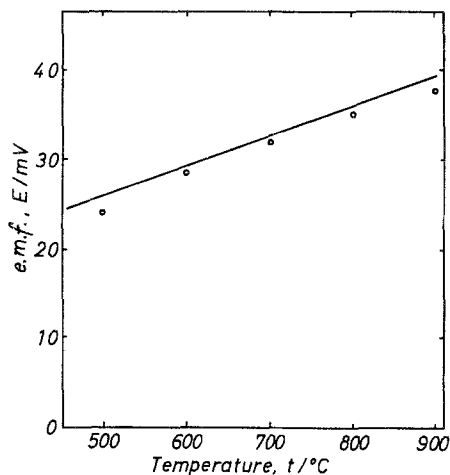


Fig. 3. Plot of e.m.f. of the following oxygen gas concentration cell: Gas I ( $P_{\text{O}_2}$ , a),  $\text{Pt}/(\text{LaO}_{1.5})_{0.5}(\text{MgF}_2)_{0.5}/\text{Pt}$ , Gas II ( $P_{\text{O}_2}$ , c), where  $P_{\text{O}_2}$ , a = 0.21 atm and  $P_{\text{O}_2}$ , c = 1.0 atm. The solid line shows the e.m.f. calculated by the Nernst equation.

The measured values are in fairly good agreement with the calculated values over the temperature range examined; d.c. current could also be drawn from the cells. These results denote that the specimens are ionic conductors. However, the true charge carrier in the electrolyte can not be concluded to be oxide ion by the gas concentration cell method only. In fact, the current drawn from the cell decreased with time and after a few minutes became about two orders of magnitude lower than the value calculated from the a.c. resistance of the electrolyte. This phenomenon demonstrates the existence of severe polarization.

Fig. 4 shows the electrode potential versus d.c. current relations at  $600^\circ\text{C}$  in dry air and in dry nitrogen gas for the specimen  $(\text{LaO}_{1.5})_{0.5}(\text{MgF}_2)_{0.5}$ . In order to study the electrode reaction taking place on this material the d.c. voltage was applied to the two end electrodes (silver) of the cell with a sweep rate of  $20 \text{ mV s}^{-1}$ , and the cathode and anode potentials were measured against a reference electrode

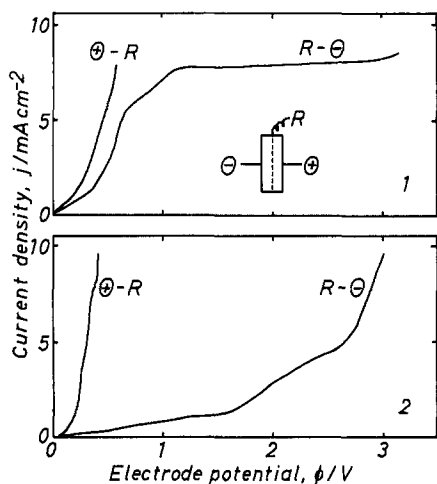
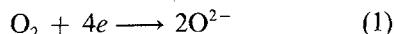


Fig. 4. Electrode potential versus d.c. current relations at 600°C for  $(\text{LaO}_{1.5})_{0.5}(\text{MgF}_2)_{0.5}$ . 1, in dry air; 2, in dry nitrogen gas.

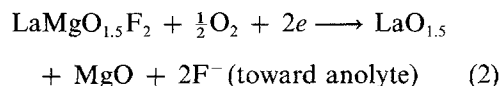
attached to the edge of the sample. In each atmosphere, a limiting current was observed at the cathode. In air, the limiting current was about  $7.4 \text{ mA cm}^{-2}$ , which is a larger value than that in nitrogen gas. This suggests that the following oxygen gas reaction at the cathode is limited by the diffusion rate of oxygen molecules which depends on the partial pressure of oxygen.



However, the limiting current was smaller than that in the case of oxide ion conductors [14].

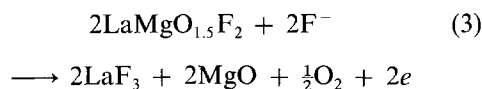
In order to clarify the ionic charge carrier in the electrolyte, electrolysis was carried out in dry air by way of Tubandt's method. The sample was  $(\text{LaO}_{1.5})_{0.5}(\text{MgF}_2)_{0.5}$ , which contained a small amount of MgO. After electrolysis at 146°C, applying a voltage higher than 3 V, the three specimen discs were analysed by X-ray diffraction. These results are indicated in Fig. 5. In the catholyte surface,  $\text{La}_2\text{O}_3$  and a small amount of the LaOF-type rhombohedral phase were newly observed and the diffraction lines of MgO became much higher than that of the original sample.  $\text{LaF}_3$  appeared on the anolyte surface. The bulk sample almost retained its original crystal phase, but showed some weak diffraction lines of  $\text{LaF}_3$ . These results can not be explained by considering oxide ions as the charge carriers. If fluoride ions are the charge carriers in the specimens, the above results are explained as follows.

**3.3.1. Cathode.** Due to the absence of fluorine gas, oxygen in the air is considered to act as the cathode reactant and fluoride ions at the surface of catholyte migrate toward the anolyte. As a result  $\text{La}_2\text{O}_3$  and MgO are formed in the catholyte.

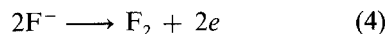


The rhombohedral phase in the catholyte was considered to be formed by depletion of fluorine due to electrolysis. This corresponded to the formation of a mixed phase with a rhombohedral phase and  $\text{La}_2\text{O}_3$  in the composition range less than 40 mol %  $\text{MgF}_2$ .

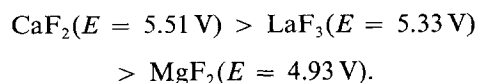
**3.3.2. Anode.** The anode reaction is considered to be



MgO was hardly observed in the X-ray diffraction pattern of the anolyte surface. This would be due to the formation of a  $\text{LaF}_3$  layer at the anolyte surface. When the carrier gas (air) from the anode surface was introduced into a 5%  $\text{CaCl}_2$  aqueous solution, white colloidal  $\text{CaF}_2$  was formed only during electrolysis. This phenomenon suggests evolution of fluorine gas from the anode. Therefore, the following reaction also proceeds in parallel,



In the LaOF-type cubic specimen of the previously reported  $\text{LaO}_{1.5}\text{-CaF}_2$  system,  $\text{CaF}_2$  was formed at the anode as a result of the reaction between evolving fluorine and CaO present in the specimen. In the present system, fluorine did not react with MgO present in the sample but with  $\text{LaMgO}_{1.5}\text{F}_2$  to form  $\text{LaF}_3$ . This difference arises from the theoretical decomposition voltages based on the free enthalpies of formation ( $\Delta G_f$ ), the values of which are as follows at 600°C,



**3.3.3. Bulk.** The same reaction as that for the

anode may take place in part. In fact, a small amount of  $\text{LaF}_3$  was also detected in the anode side of the catholyte and the cathode side of the anolyte. This can be explained by partial electronic conduction present in the specimen; catholyte and anolyte tablets are considered to behave as a partial electrode and electrolyse the bulk tablet to deposit  $\text{LaF}_3$  at the 'anode area' according to Equation 3. In this case, the bulk tablet electrolysed in dry nitrogen gas contained very little  $\text{LaF}_3$ . This shows that the electronic conductivity decreases at lower oxygen pressure. Therefore, the electronic conduction was considered to be p-type.

The fluoride ion transport number ( $t_{\text{F}^-}$ ) was determined from the result of the electrolysis under a dry nitrogen atmosphere ( $P_{\text{O}_2} \approx 10^{-4}$  atm). The weight of catholyte decreased by 16.7 mg as a result of electrolysis at 170 C. The theoretical weight decrease calculated on the basis of Equation 2 was 19.4 mg in this condition. This result showed that  $t_{\text{F}^-}$  was about 0.9. The true fluoride ion transport number was, however, considered to be much closer to unity because formation of a small amount of  $\text{LaF}_3$ , which could not be detected by X-ray diffraction, would introduce an extra weight change of catholyte. The weight change in the anolyte (+14.8 mg) was smaller than that in the catholyte, suggesting that some of the fluoride ions were also dispersed from the anode as fluorine gas.

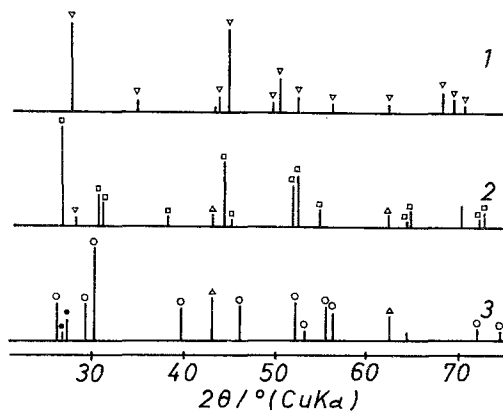


Fig. 5. X-ray diffraction patterns of  $(\text{LaO}_{1.5})_{0.5}(\text{MgF}_2)_{0.5}$  electrolysed by Tubandt's method. 1, anode; 2, bulk; 3, cathode. The symbols are as follows:  $\nabla$ ,  $\text{LaF}_3$ ;  $\square$ ,  $\text{LaOF}$  (tetragonal);  $\triangle$ ,  $\text{MgO}$ ;  $\circ$ ,  $\text{La}_2\text{O}_3$ ;  $\bullet$ ,  $\text{LaOF}$  (rhombohedral).

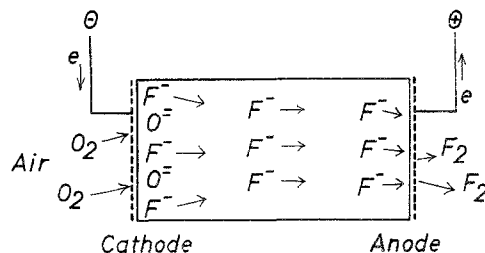
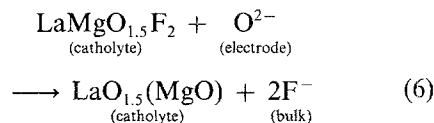
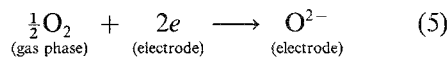


Fig. 6. Schematic diagram of fluoride ion conduction on electrolysis in air.

As is clear from Fig. 5 at lower cell voltages ( $< 1$  V), the d.c. current, which could be applied to the sample in air, was larger than that in nitrogen gas. Electrolysis in this low voltage range gave the same results as in the high voltage ( $> 3$  V) experiment described above. This suggests that the participant in the cathode reaction is oxygen (Equation 5) and that the oxide ion thus formed diffuses toward the bulk of the fluoride-oxide lattice. As a result, fluoride ion would easily be substituted by oxide ion once formed at the cathode surface as shown in Equations 5 and 6 and Fig. 6.



Considering that the cathode in this experiment is a blocking electrode for fluoride ion and that the charge density of the monovalent fluoride ion is smaller than that of the divalent oxide ion, these results seem to be reasonable.

#### 4. Conclusion

$\text{LaOF}$ -type tetragonal solid solution was found to be formed at the intermediate composition range in the systems  $\text{LaO}_{1.5}\text{-MgF}_2$ . This solid solution showed high anion conductivity, about one order of magnitude higher than that of  $\text{YF}_3$ -doped  $\text{CaF}_2$ . The conduction was predominantly due to the fluoride ion, the charge density of which is smaller than that of the oxide ion. In this solid solution, the fluoride ion is considered to be easily substituted by the oxide ion through the cathode reaction.

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