Crystal Phase and Electrical Conductivity in the Pyrochlore-Type Composition Systems, $Ln_2Ce_2O_7$ ($Ln = La, Nd, Sm, Eu, Gd, Y$ and Yb)

Hiroshi YAMAMURA, Hanako NISHINO, Katsuyoshi KAKINUMA and Katsuhiro NOMURA*

Department of Applied Chemistry, Faculty of Engineering, Kanagawa University,
3-27-1, Rokkakubashi, Kanagawa-ku, Yokohama-shi 221-8686

*National Institute of Advanced Industrial Science and Technology, Kansai, 1-8-31, Midorigaoka, Ikeda-shi, Osaka 563-8577

パイロクロア型組成系 $Ln_2Ce_2O_7$ ($Ln = La, Nd, Sm, Eu, Gd, Y$ and Yb) の結晶相と電気伝導度

山村 博・西野華子・柿沼克良・野村勝裕*

神奈川大学工学部応用化学科, 221-8686 横浜市神奈川区六角橋 3-27-1

*産業総合研究所関西センター, 563-8577 池田市緑丘 1-8-31

The relationship between electrical conductivity and crystal structure in $Ln_2Ce_2O_7$ ($Ln = La, Nd, Sm, Eu, Gd, Y$ and Yb) systems was investigated. The crystal phases were assigned to a fluorite (F)-type phase accompanying the rare earth C-type superstructure, when the ionic radius ratio, $r(Ln^{3+})/r(Ce^{4+})$ were larger than 1.17. On the other hand, $La_2Ce_2O_7$ was the only F-type phase without the superstructure. The lattice constant increased linearly with increasing the ionic radius of Ln^{3+} independent of whether or not the superstructure was present. Oxygen partial pressure dependence of the electrical conductivity suggested that the charge carrier was oxide-ion, except for the Nd system. The electrical conductivity at 800°C in air for the $Ln_2Ce_2O_7$ systems also increased with increasing the ionic radius ratio. The activation energy for the conduction decreased remarkably in the fluorite-type phase region. The compositional change of the oxide-ion conductivity was understood by the introduction of an unit cell free volume. This result was also supported by Raman spectra.

[Received June 30, 2003; Accepted September 30, 2003]

Key-words: Fluorite-type structure, Rare earth C-type structure, Oxide-ion conductivity, Phase boundary, Rare earth ion

1. Introduction

Fluorite (F)-type and F-related oxides play an important role as oxide-ion conductors for various applications such as oxygen sensor, oxygen pump, solid oxide fuel cell, etc. Among the F-related oxides, there is a pyrochlore (P)-type oxide with a composition $A_2B_2O_7$, which can be recognized as an oxygen deficient fluorite oxide ($MO_{1.75}$) without any dopants. In the composition $A_2B_2O_7$, A^{3+} ion can be various rare earth ions and B^{4+} ion can be Zr, Ti, Sn and Hf. Therefore, too many P-type oxides have been prepared by the combination of the various A^{3+} and B^{4+} ions.¹⁾ Many workers have investigated the P-type oxides from viewpoints of both crystal chemistry and electrical conductivity by over the past several ten years.

Specially, the P-type oxides containing Zr^{4+} as B site, $Ln_2Zr_2O_7$ ($Ln = Gd, Sm, Nd$) systems, have been studied in order to clarify the relationship between the electrical conductivity and the cation and/or oxide-ion disordering.^{2)–6)} Minervini et al.⁷⁾ also discussed the relationship between the stability range to A^{3+} and B^{4+} cation sizes in the P-type structure with a general composition of $A_2B_2O_7$ and the disorder. Tuller et al.^{8),9)} have investigated the electrical conductivity of the P-type $Gd_2(M_{1-x}M'_x)_2O_7$ ($M, M' = Zr, Ti$ or Sn) systems and found that the high level of intrinsic anion disorder was consistent with the expectations based on the cation radius ratio, $r(A^{3+})/r(B^{4+})$, in the P-type compounds. Recently, the present authors have reported the electrical conductivity anomaly around fluorite-pyrochlore phase boundary in the $(Ln_{1-x}Ln'_x)_2Zr_2O_7$ systems.¹⁰⁾

On the other hand, although there are many papers concerning trivalent cation-doped CeO_2 systems,¹¹⁾ the oxides with $B^{4+} = Ce^{4+}$ in the pyrochlore-type composition, $A_2B_2O_7$ have not been studied in detail. In the present study, we found that the F-type phase in the $Ln_2Ce_2O_7$ ($Ln^{3+} = La^{3+}$,

Nd^{3+} , Sm^{3+} , Eu^{3+} , Gd^{3+} , Y^{3+} or Yb^{3+}) systems accompanied the superstructure of the rare earth C (C)-type phases, and that their electrical properties were investigated. The C-type phase with cubic symmetry belongs to space group $Ia\bar{3}$ (T_h^7), $Z=16$, which can be derived from the F-type structure due to the ordering of oxygen vacancies on the anionic sublattice. High oxide-ion conductors need the disordered arrangement of oxygen vacancies through an order-disorder transition. However, the order-disorder transition of the C-type oxide is prevented because of the strong coulomb repulsion between vacancies.¹²⁾ Therefore, the electrical properties of the C-type oxides have not been studied. The present paper reports the electrical conductivity of the C-type phase in the relation with the F-type one.

2. Experimental procedures

Powder samples of the present systems, $Ln_2Ce_2O_7$ ($Ln = La, Nd, Sm, Eu, Gd, Y$ or Yb) were synthesized by means of a solid-state reaction method, using CeO_2 (99.99%, High Purity Chemicals Co.), La_2O_3 (99.99%, Wako Chemicals Co.), Nd_2O_3 (99.9%, Mitsuwa Chemicals Co.), Gd_2O_3 (99.9%, High Purity Chemicals Co.), Eu_2O_3 (99.9%, Mitsuwa Chemicals Co.), Sm_2O_3 (99.9%, Huruuchi Chemicals Co.), Y_2O_3 (99.9%, High Purity Chemicals Co.) and Yb_2O_3 (99.99%, High Purity Chemicals Co.) as starting materials.

The weighed powders were wet ball-milled for 16 h, using a milling pot made of synthetic resin and resin-coated balls, and ethanol as the dispersion reagent. After drying, the powder mixtures were calcined at 1100°C for 5 h in air. After sieving under 53 μm in mesh size, the powder samples were molded uniaxially under the pressure of 50 MPa and subjected to rubber press at 200 MPa. The compacts thus obtained were sintered at 1600°C for 10 h in air. The relative

density of the sintered specimens, which was estimated from the geometrical dimensions and weight, was over 95%.

The powdered samples were characterized by means of an X-ray diffraction (XRD) (model: RAD-A, Rigaku Co.) with monochromated Cu K α radiation. The lattice constant was determined from the XRD peaks by the least square method, using Si powder as the external standard.

Raman spectra were measured with JASCO NRS-1000 model at room temperature in order to obtain information about a local structure. A liquid nitrogen cooled CCD detector was used. The excitation source was 532 nm line transformed from 1064 nm line of Nd:YVO₄ laser by non-linear crystal.

The electrical conductivity of the sintered specimens was mainly measured by a dc four-probe method in the temperature range of 600 to 1000°C in air. Oxygen partial pressure P_{O_2} dependence of the electrical conductivity was also measured in the range of 1.013×10^5 to 32.0 Pa. The detail of the electrical conductivity measurements was reported elsewhere.¹⁰⁾

3. Results and discussion

Figure 1 shows XRD patterns of the $Ln_2Ce_2O_7$ systems. We must emphasize that several weak extra diffraction lines were detected beside those of the cubic F-type phase, which were indexed well on a basis of the superlattice lines of F-type structure, as shown in Fig. 1. It was found that the superlattice lines were assigned to rare earth C-type phase. However, the C-type superstructure may be incomplete because of the very weakness of the superlattice lines. Though no systematic characteristic of their superlattice lines was found among the various compounds, the superstructure of the Yb compound seemed to be the most incomplete structure because of the obscure lines. The C-type superstructure was found when Yb³⁺, Y³⁺, Gd³⁺, Eu³⁺,

Sm³⁺, Nd³⁺ was used as Ln^{3+} of $Ln_2Ce_2O_7$, while only the F-type one was obtained when Ln^{3+} was La³⁺. This means that when the ionic radius ratio, $r(Ln^{3+})/r(Ce^{4+})$, is smaller than 1.17, the C-type phase can be stabilized. The P-type composition $(Ln, Ce)O_{1.75}$ can be considered to be an oxygen excess compound of the C-type sesquioxides having a composition $AO_{1.5}$ such as $YO_{1.5}$ and $YbO_{1.5}$. Husson et al.¹³⁾ reported that the rare earth sesquioxides had the monoclinic B-type from Sm³⁺ (0.109 nm) to Gd³⁺ (0.106 nm) and the cubic C-type for other sesquioxides such as Y³⁺ (0.1015 nm) and Yb³⁺ (0.098 nm), where the number in parenthesis denotes the ionic radius, which was the oxygen 8-coordinated value of Shannon and Prewitt.¹⁴⁾ The values of ionic radius of the various elements used in the present study were summarized in Table 1. We confirmed also that Sm₂O₃ had the B-type structure but Eu₂O₃ ($r_{Eu^{3+}} = 0.107$ nm) and Gd₂O₃ had the C-type one. Anyway, it means that the C-type structure can be stable for the cation ionic radius smaller than 0.107 nm. The calculated values of the average ionic radii of the component cations in the $Ln_2Ce_2O_7$ systems were 0.108 and 0.105 nm for the La and Nd systems, respectively. The occurrence of the C-type superstructure can be understood by introduction of the average ionic radii of the component cations.

Figure 2 shows lattice constants of the $Ln_2Ce_2O_7$ systems as a function of the ionic radius ratio, where the lattice constants of the F-type phase were doubled for convenience

Table 1. Ionic Radius (nm) of the Various Elements Used in the Present Study*

Ce ⁴⁺	La ³⁺	Nd ³⁺	Sm ³⁺	Eu ³⁺	Gd ³⁺	Y ³⁺	Yb ³⁺
0.097	0.118	0.112	0.109	0.107	0.106	0.1015	0.098

*Data was cited from Ref. 14.

Fig. 1. X-ray diffraction patterns for $Ln_2Ce_2O_7$ systems.

Fig. 2. Lattice constant as a function of ionic radius ratio for $Ln_2Ce_2O_7$ systems. Lattice constant of the F-type phase is doubled.

Fig. 3. Oxygen partial pressure dependence of the electrical conductivity for the $Ln_2Ce_2O_7$ systems.

in order to compare with those of the C-type one. The lattice constant increased linearly with increasing the ionic radii of Ln^{3+} without any irregularity at the phase boundary of the F- and C-type phases. The lattice constant of the F-type phase was calculated on the basis of a following equation, according to the method of Hong and Virkar,¹⁵⁾

$$a = (4/\sqrt{3})[0.5r(Ln^{3+}) + 0.5r(Ce^{4+}) + 0.875r(O) + 0.125r(V_O)] \quad (1)$$

where $r(Ce^{4+})$, $r(O)$ and $r(V_O)$ are the radius of Ce^{4+} (0.097 nm), oxide-ion (0.1380 nm) and oxygen vacancy (0.0164 nm), respectively. The estimated values are also shown as a broken line in Fig. 2, where the doubled values of lattice constant estimated using the Eq. (1) are given. The observed values of lattice constant were smaller than those of the calculated ones in either the F-type or the C-type phases. We speculated that the difference between the observed lattice-constant and the calculated one can be ascribed to the use of the value of the ionic radius of 8-oxygen coordinated Ce^{4+} . The oxygen coordination number of Ce^{4+} must be lower than 8 due to the oxygen vacancy. The ionic radius of Ce^{4+} estimated conversely from the observed lattice constant was 0.094 nm, which was positioned between 6-coordinated radius (0.080 nm) and 8-coordinated one (0.097 nm).

Oxygen partial pressure, P_{O_2} , dependence of the electrical conductivity was measured for the $Ln_2Ce_2O_7$ system in order to clarify conduction carrier. The conductivity of all the samples except $Ln = Nd$ were independent on the P_{O_2} between 1.013×10^5 and 10.0 Pa, suggesting an oxide-ion conduction, as shown in Fig. 3. The electrical conductivity of $Nd_2Ce_2O_7$ slightly increased in proportion to the P_{O_2} , indicating mixed conduction of oxide-ion and hole.

Figure 4 shows Arrhenius plots of the electrical conductivity of the $Ln_2Ce_2O_7$ systems measured in air. The temperature dependence of conductivity (σ) can be described by,

$$\sigma = \sigma_0 \exp(-E_a/RT) \quad (2)$$

where pre-exponential term (σ_0) is a measure of the

Fig. 4. Arrhenius plots of the electrical conductivity for the $Ln_2Ce_2O_7$ systems.

Table 2. Electrical Conductivity (σ) at 800°C, Activation Energy (E_a) and Unit Cell Free Volume (V_f) for $Ln_2Ce_2O_7$ Systems

Compound	σ at 800°C (mS cm ⁻¹)	E_a (kJ mol ⁻¹)	V_f (nm ³)
Yb ₂ Ce ₂ O ₇	2.52	128	0.0553
Y ₂ Ce ₂ O ₇	2.62	130	0.0582
Gd ₂ Ce ₂ O ₇	3.66	132	0.0611
Eu ₂ Ce ₂ O ₇	5.91	122	0.0619
Sm ₂ Ce ₂ O ₇	5.63	121	0.0637
Nd ₂ Ce ₂ O ₇	9.62	116	0.0654
La ₂ Ce ₂ O ₇	22.6	99	0.0698

number of mobile ions and E_a the activation energy. The σ at 800°C and E_a values for the $Ln_2Ce_2O_7$ systems are tabulated in Table 2. The activation energies for the electrical conduction of the samples containing the C-type phases were in the range of 116 to 132 kJ mol⁻¹, which have a tendency to decrease with increase in the ionic radii of Ln^{3+} , while that of $La_2Ce_2O_7$ (F-type phases) was around 99 kJ mol⁻¹.

Figure 5 shows the electrical conductivity at 800°C as a function of the ionic radius ratio, $r(Ln^{3+})/r(Ce^{4+})$, in the $Ln_2Ce_2O_7$ system, where the data of the $Ln_2Zr_2O_7$ system are also shown for comparison. The conductivity gradually increased with increasing the ionic radius ratio in the C-type phase region, and sharply did at the phase boundary of C-type and F-type phase. The maximum value of the conductivity was 22.6 mS·cm⁻¹ at 800°C for $La_2Ce_2O_7$. On the other hand, the oxide-ion conductivity of $Ln_2Zr_2O_7$ system showed the maximum value in the vicinity of the phase boundary between F- and P-type phases, as also shown in Fig. 5. This tendency of the compositional change in conductivity was maintained in the temperature range of

Fig. 5. Electrical conductivity at 800°C in air as a function of the ionic radius ratio for $\text{Ln}_2\text{Ce}_2\text{O}_7$ and $\text{Ln}_2\text{Zr}_2\text{O}_7$ systems.

Fig. 6. Electrical conductivity at 800°C as a function of unit cell free volume.

600 to 1000°C.

It was tried to explain the compositional change in the electrical conductivity on a basis of unit cell free volume. The free volume (V_f) was calculated using a following equation,

$$V_f = \left(\frac{a}{2} \right)^3 - 4 \times \frac{4}{3} \pi \left\{ \sum M_i r_{\text{cation}}^3 + 2 \times r_{\text{O}}^3 - 0.25 \times r_{\text{VO}}^3 \right\} \quad (4)$$

where a , M_i , r_{cation} , r_{O} and r_{VO} denote the lattice constant of pyrochlore phase, mol fraction of cations, ionic radii of oxygen and oxygen vacancy, respectively. For the ionic radii of oxygen and oxygen vacancy, the same values as in the calculation of lattice constant were also adopted. The estimated values of the V_f were summarized in Table 2. Figure 6 also shows the logarithmic value of the electrical

Fig. 7. Raman spectra at room temperature for the $\text{Ln}_2\text{Ce}_2\text{O}_7$ systems.

conductivity at 800°C as a function of the V_f in the $\text{Ln}_2\text{Ce}_2\text{O}_7$ system. The log value of conductivity linearly increased with increasing the V_f , in which the oxygen vacancy concentration was kept constant. This result means that the oxide-ion conductivity was not affected by the presence of the C-type phase in the P-type one, but only by the unit cell free volume. The free volume means a “free space” in the crystal structure. Therefore, it may be reasonable for oxide-ion to move more easily in the larger “space.” It has been reported that the oxide-ion conductivity of perovskite-type structure has a close relation with the unit cell free volume,^{16),17)} while we have also successfully applied the idea of unit cell free volume in the Y_3NbO_7 system, which is F-type solid-solution.¹⁸⁾

Figure 7 shows Raman spectra of the present system. All samples exhibited almost the same broad Raman spectra, suggesting the similar local structure among the oxides. Four Raman peaks were recognized for the C-type oxides in wave number range of 260–280, 360–380, 470–490 and 580–590 cm^{-1} . Among these peaks, the peak of wave number 470–490 cm^{-1} was the strongest. Michel et al.¹⁹⁾ reported Raman spectra of the F-related oxides, where that of Y_2O_3 with the C-type structure showed the strongest peak with 377 cm^{-1} and two weak peaks with 480 and 600 cm^{-1} . On the other hand, the Raman spectrum of $\text{La}_2\text{Ce}_2\text{O}_7$ was similar with that of the samples with the C-type superstructure, and also with 15 mol% Gd_2O_3 -doped ZrO_2 with cubic symmetry,²⁰⁾ which was characteristic to the oxygen deficient F-type structure. All peaks shifted to lower wave number when Ln^{3+} changed from Y^{3+} to La^{3+} , suggesting that the force constant, that is, the bonding strength decreased with increasing the free volume. These facts suggest that the arrangement of oxygen vacancy disordered in the F-type structure of the $\text{Ln}_2\text{Ce}_2\text{O}_7$ system, and also agreed with the results of both the conductivity measurement and the speculation on the basis of the free volume. An exception in the Raman shift of the Yb compound may have a close relation to the most incomplete superstructure in the Yb one.

4. Conclusions

In the present study concerning the crystal structure and electrical conductivity of the $Ln_2Ce_2O_7$ ($Ln = \text{La, Nd, Gd, Sm, Y and Yb}$) systems, the following conclusions were obtained.

(1) The crystal phases were assigned to the F-type phase accompanying the C-type one as superstructure, while $\text{La}_2\text{Ce}_2\text{O}_7$ was only the F-type phase.

(2) The lattice constant increased linearly with increasing the ionic radius of Ln^{3+} . Though the estimation result of the lattice constant did not agree with the observed one, it was ascribed to the presence of oxygen vacancy.

(3) The compositional change in the oxide-ion conductivity was understood by the introduction of the unit cell free volume.

(4) The measurement of Raman spectra revealed that the local structure of the present samples was almost the same as the oxygen deficient fluorite-type oxide.

Acknowledgments The financial support for the present work was partly provided by the High Tech. Research Project at Kanagawa University from the Ministry of Education, Science, Sports and Culture, Japan.

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