Crystallographic comparison of zirconium and molybdenum dioxide-based pyrochlores

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For $AO_{1.5}-MoO_2$ and $-ZrO_2$ equimolar systems (A = La, Nd, Sm, Gd, Dy, Y, Er, Lu), oxide compounds samples were prepared by solid-state sintering at 1673 K–1873 K in argon and air, respectively. In addition, oxide samples of $y NdO_{1.5} - (1 - y)ZrO_2$ with $y = 0.3-0.7$ were prepared to investigate the pyrochlore–fluorite (P–F) phase transition. X-ray diffraction measurements clarified that molybdenum oxides formed cubic-pyrochlore phase except for A = La, and zirconate pyrochlores formed for A = La, Nd, Sm, Gd, whereas other zirconium oxides exhibited the defect-fluorite structure. With decreasing ionic radius of A^{3+}, the broadening of Raman bands were observed for both pyrochlore systems. This might be due to the decrease of energy for defect cluster formation, i.e. cation antisite reaction and oxygen Frenkel defect formation. Especially for molybdate pyrochlores, it might be also attributed to the fact that the ionic charge of molybdenum was likely to be changeable. The P–F phase transition of the $y NdO_{1.5} - (1 - y)ZrO_2$ system was clearly confirmed by Raman spectroscopy, and the changes in band shape were influenced mainly by the oxygen environment around Zr, which was elucidated by molecular dynamics calculations.

1. Introduction

Pyrochlore oxides, $A_2B_2O_7$, (A = lanthanides, actinides, B = Ti, Zr), have been studied to immobilize radioactive nuclides in a ceramic waste form (Ewing et al., 2004) and to burn out actinides with long half-life in an inert matrix fuel as commercial reactors (Lutique et al., 2003; Imaura et al., 2009). Especially, zirconate pyrochlore as well as stabilized zirconia exhibits the excellent radiation tolerance and the chemical stability (Lian et al., 2002), compared to titanate pyrochlore (Ewing et al., 2004; Lian et al., 2003). So, these pyrochlore and fluorite oxides are attractive materials for the nuclear fuel cycle system. On the other hand, from the crystallographic view, zirconate pyrochlore and fluorite structures were very similar to each other. The lattice parameter of zirconate pyrochlore corresponds to two times of unit cell length of fluorite, and in pyrochlores trivalent A and tetravalent B cations, which have 8 and 6 oxygen co-ordinations, respectively, are regularly arranged on cation sublattice sites. Concerning oxygen ions, $48f$ oxygen having $(x, 1/8, 1/8)$ partial position in the unit cell is surrounded by two A and two B cations and $8a$ oxygen having $(1/8, 1/8, 1/8)$ partial position is surrounded by four A cations. For instance, in the

$y NdO_{1.5} - (1 - y)ZrO_2$ system, pyrochlore phase forms at the vicinity of $y = 0.5$ and fluorite phase appears with an increase in deviation from $y = 0.5$. Furthermore, even though the oxide compound is the isomeric pyrochlore, $Nd_2Zr_2O_7$, the phase transition from pyrochlore to fluorite occurs above ~2600 K (Wang et al., 2007). Such phase transitions depending on composition and temperature are different for different A cation (Wang et al., 2007; Ohtani et al., 2005) and are also related to the phase stability under the irradiation field (Sickafus et al., 2000).

However, compared to zirconate pyrochlores, others, e.g. molybdate and ruthenate pyrochlores have attracted little interest as the nuclear-related materials (Subramanian et al., 1980, 1983). In the low-temperature physics, the magnetic properties of molybdate pyrochlores have been extensively explored (Sato et al., 1986; Ali et al., 1989). Currently it is well known that molybdenum and ruthenium elements have been released in large quantity from the reprocessing process of spent fuel and are considered to be unwanted elements as undissolved residue (or yellow phase) especially for the vitrification process. Hence, we focused on molybdate pyrochlores as an effective use of molybdenum. Furthermore, molybdenum ionic radius lies between titanium and zirconium ones, and thus molybdate pyrochlore might exhibit intermediate properties between titanate and zirconate pyrochlores (Minervini and Grimes, 2000). In the present study, the crystallographic properties of both zirconate and molybdate pyrochlores were

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evaluated by X-ray diffraction measurement and Raman spectroscopy. The sintering condition was also discussed for the molybdenum oxide system. With respect to the zirconium oxide system, the pyrochlore–fluorite (P–F) phase transition due to the variation of the chemical composition was discussed especially for the yNdO$_{1.5}$ − $(1 − y)$ZrO$_2$ system by means of the classical molecular dynamics (MD) simulation.

2. Experimental

2.1. Sample preparation

For preparation of molybdenum oxide-based samples, LaO$_{1.5}$ (Soekawa, 99.999%), NdO$_{1.5}$ (Kanto, 99.95%), SmO$_{1.5}$ (Kanto, 99.95%), GdO$_{1.5}$ (Kanto, 99.95%), DyO$_{1.5}$ (Kanto, 99.95%), YO$_{1.5}$ (Kojundo, 99.99%), ErO$_{1.5}$ (Kanto, 99.95%), LuO$_{1.5}$ (Kojundo, 99.9%) and MoO$_2$ (Soekawa, 99%) powders were used as purchased. On the other hand, CeO$_2$ (Kanto, 99.99%), NdO$_{1.5}$, ErO$_{1.5}$, LuO$_{1.5}$ and ZrO$_2$ (Tosoh, 99.9%) powders were used for preparation of zirconia-based samples, because other compositions were explored in our previous study (Shimamura et al., 2007). Especially for the neodymia–zirconia system, NdO$_{1.5}$ content varied from 30 mol% to 70 mol%. Pyrochlore samples were synthesized according to the following procedure. Equimolar powders of AO$_{1.5}$ and BO$_2$ were mixed with ethanol and zirconia balls in a planetary ball mill for 15 min. The dried mixture powder was uniaxially die-pressed at 200 MPa to form a small disk having ca. 6 mm in diameter and 3 mm in thickness. Then, MoO$_2$-based samples were sintered at 1673 K or 1873 K for 6 h in an inert gas atmosphere (argon) to keep the oxygen stoichiometry of MoO$_2$, whereas ZrO$_2$-based ones were sintered at 1873 K for 8 h in air. For Ce$_2$Zr$_2$O$_7$ sample, subsequently to sintering of CeO$_2$·ZrO$_2$ sample in air, the heat treatment was performed in argon gas at 1873 K for 6 h to control the oxygen stoichiometry.

2.2. X-ray diffraction measurement and Raman spectroscopy

X-ray diffraction (XRD) measurements (Rigaku, Multi-Flex) were conducted to confirm whether the pyrochlore phase was formed and to obtain the lattice parameters of pyrochlore and fluorite phases. Since the crystal structure of pyrochlore A$_2$B$_2$O$_7$ can be considered to be oxygen-defect fluorite with two different cations which are regularly arranged on cation sublattice sites, small diffraction peaks originated from such a superlattice appear on the diffraction pattern of pyrochlore structure as well as those from fluorite one. The diffraction patterns were measured in the 2θ range from 20° to 110° at room temperature with Cu Kα radiation under the condition of 30 mA and 40 kV, where θ is the diffraction angle.

Raman spectroscopy measurements (Horiba, LabRAM ARAMIS) were performed in the spectral range from 20 cm^{-1} to 1000 cm^{-1} with 532 nm excitation at room temperature. Raman spectroscopy can compensates for the XRD measurement because the XRD pattern of pyrochlore phase is almost identical to that of fluorite. Further, Raman spectrum reflects the crystallographic relationship between cation (A and/or B) and oxygen, whereas XRD patterns provide the information of cation arrangement in the crystal. As a result, pyrochlore oxide (e.g. La$_2$Zr$_2$O$_7$) exhibits specific narrow peaks and fluorite oxide (e.g. Y$_2$Zr$_2$O$_7$) exhibits broad ones on respective Raman spectra (Subramanian et al., 1983; Shimamura et al., 2007).

3. Molecular dynamics simulation

For the system yNdO$_{1.5}$ − $(1 − y)$ZrO$_2$, the MD calculations were performed to understand the changes in these Raman spectra.

In the present study, the MXDORTO program was used with the Busing-Ida type interatomic potential function (Kawamura, 1992). The Busing-Ida type potential function with the partial ionic charge is given by

$$U(rij) = \frac{z_i z_j e^2}{r_{ij}} + f_0(b_i + b_i)\exp\left(\frac{a_i + a_j − r_{ij}}{b_i + b_j}\right) − \frac{c_i c_j}{r_{ij}^6}, \quad (1)$$

where f_0 (=4.186 × 10 J nm^{-1} mol^{-1}) is the adjustable parameter. Potential parameters, a_i, b_i, c_i are given to the ion of types i. In this potential function, the ionic bonding of 67.5% is assumed, e.g. for $z_{Zr} = 2.7$. The potential parameters of Nd^{3+} in the oxide system were determined based on the crystal structure and the thermal expansion of Nd$_2$O$_3$ (hexagonal), and others were obtained from previous studies (Inaba et al., 1999; Arima et al., 2006). These are summarized in Table 1. All calculations were performed at 300 K and 0.1 MPa.

4. Results and discussion

4.1. AO$_{1.5}$–MoO$_2$ system

The equimolar AO$_{1.5}$–MoO$_2$ samples were heated at 1673 K in argon to synthesize pyrochlore, however, the LuO$_{1.5}$–MoO$_2$ sample was not fully sintered. So, all samples were heated at 1873 K. As a result, the LaO$_{1.5}$- and NdO$_{1.5}$–MoO$_2$ samples were melted in the crucible. These results indicate that the equimolar AO$_{1.5}$–MoO$_2$ oxides, the A^{3+} ionic radius of which is large, have lower melting temperatures, i.e. structural instability in high temperature.

X-ray diffraction patterns of AO$_{1.5}$–MoO$_2$ system, where A = La, Nd, Sm, Gd, Dy, Y, Er, Lu, were shown in Fig. 1. The system LaO$_{1.5}$–MoO$_2$ showed two or more oxide compound phases, whereas others showed cubic pyrochlore phase (Fd$\overline{3}$m) whose composition was A$_2$B$_2$O$_7$. On the diffraction pattern of cubic pyrochlore, the diffraction peaks having indexes of 311 (small), 331, 511 and 531 could be found. Other peaks are identical to those of fluorite. In the system LaO$_{1.5}$–MoO$_2$, La$_2$Mo$_2$O$_7$ composition could be also found, however its crystal structure was orthorhombic (Pnnm) (Moini et al., 1987). The lattice parameter of cubic pyrochlore structure was obtained as follows:

(1) the lattice parameter corresponding to the spacing of the plane (hkl) was plotted as a function of $(\cos^2\theta)/\sin\theta + (\cos^2\theta)/\theta$;
(2) the lattice parameter at $2\theta = 180°$ was obtained from the extrapolation method.

The result thus obtained was shown in Fig. 2. This figure clearly shows that the lattice parameter increases with ionic radius of A^{3+}. Furthermore, the detailed observation reveals that this relationship between them is not linear but the increasing ratio changes around the ionic radius between Dy^{3+} and Gd^{3+}. The similar relationship was also obtained by Sato et al. (1986) and Ali et al. (1989), and they pointed out that the metallic ferromagnetic order occurred for A$_2$Mo$_2$O$_7$ (A = Nd, Sm, Gd) at the Curie temperature, and for A$_2$Mo$_2$O$_7$ (A = Y, Er, Dy) such magnetic ordering was not observed, i.e. semiconductor.

Table 1
Potential parameters of Busing-Ida type interatomic potential function.

Ion	z_i	a_i (nm)	b_i (nm)	c_i (J$^{-0.5}$ nm^3 mol$^{-0.5}$)	Source
Nd^{3+}	2.025	0.12154	0.00134	0.0	Present study
Zr^{4+}	2.70	0.10950	0.00254	0.0	Arima et al. (2006)
O^{2-}	−1.35	0.18470	0.01660	1.294	Inaba et al. (1999)