Characterization and solubility of mixed lanthanide oxides, $(L_1,L_2)_2O_3$ (L_1, L_2 = La, Nd, Eu, Tm)

*Md. Moniruzzaman [1], Taishi Kobayashi[1] and Takayuki Sasaki[1]
[1] Graduate School of Engineering, Kyoto Univ.

Binary components of $(L_1,L_2)_2O_3$ (L_1, L_2 = La, Nd, Eu, Tm) were successfully synthesized at 1000°C followed by a systematic solubility experiment by undersaturation method. The solid phases before and after the solubility experiments were characterized by XRD to clarify the attribution of obtained solubility products.

Keywords: Lanthanides, binary components, oxides and hydroxides, characterization, solubility products

1. Introduction Many of the previous studies have focused on the solubility of trivalent lanthanides as analogous of trivalent actinides, however, characterization of solubility limiting solid phases were not well investigated. For the prediction of the migration behavior of trivalent actinides, it is more relevant to investigate the solid phases, i.e. hydroxides and oxides of multicomponent elements under nuclear waste repository conditions along with their solubility. Therefore, this study focused on the characterization of lanthanide hydroxides and oxides of binary components using powder X-ray diffraction (XRD) technique to ascertain the exact solubility controlling solid phases. Furthermore, the obtained structures of the solid phases were discussed along with their thermodynamic data i.e. solubility products, determined by a systematic solubility experiment.

2. Experimental The mixed lanthanide oxides of $(L_1,L_2)_2O_3$ (L_1, L_2 = La, Nd; La, Eu & Eu,Tm) were synthesized from La, Nd, Eu, and Tm nitrate stock solutions. For La-Nd system, aliquots of 0.2 M La and Nd nitrate stock solutions were mixed at the molar ratios of 1:9, 3:7, 4:6, 5:5, 7:3 and 9:1. Aliquots of 5% PVA (polyvinyl alcohol) solution was added to the mixed solutions and heated up to 200 °C to dryness. The precipitates were then heated in a muffle furnace at 1000 °C to obtain the mixed oxides. The mixed oxides of $(La,Eu)_2O_3$ and $(Eu,Tm)_2O_3$ were synthesized in the same manner. For the solubility experiment, a certain amount of the mixed oxides was added into sample solutions at $6 < pH_c < 10$ and ionic strength (I) = 0.1 M by $NaClO_4$. The sample solutions were aged at 60 °C for 8 weeks and filtration (3kDa) of supernatants were performed at 60, 50, 40 and 25 °C. The XRD patterns of the solid phases before and after the solubility experiments were collected using MiniFlex600 (RIGAKU).

3. Results and discussion The XRD patterns of synthesized (La, Nd)$_2O_3$ along with La_2O_3 and Nd_2O_3 are shown in Fig.1. The peaks corresponding to those of La_2O_3 shifted rightward as decreasing the La mixing ratio from 9:1 to 1:9. These peak shifts were considered to be due to lowering distances between atomic planes by incorporating Nd into the host crystal lattice La_2O_3(cr), indicating the formation of solid solutions. Solubilities of the $(L_1,L_2)_2O_3$ solid solutions combined with the XRD patterns after the solubility experiments will be discussed and presented along with their thermodynamic analyses.

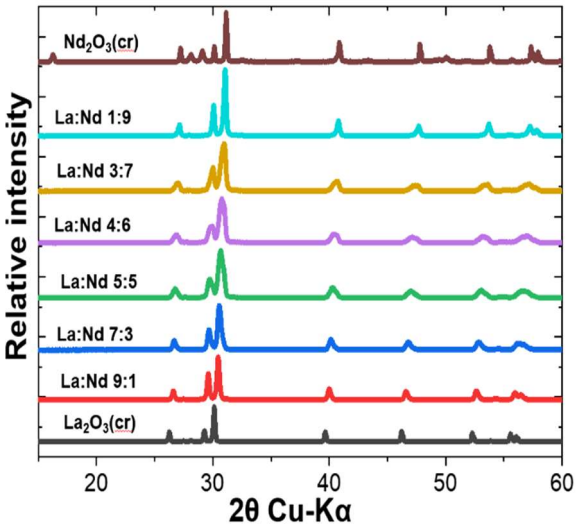

Fig.1 XRD pattern of $(La,Nd)_2O_3$ along with La_2O_3 and Nd_2O_3