

Cation size dependent phase structure of $(\text{Eu}_{1-x}\text{La}_x)_2\text{O}_3$ at high pressures

K. A. Irshad^{1*}, V. Srihari², S. Kalavathi¹ and N. V. Chandra Shekar¹

¹High Pressure Physics Section, Condensed Matter Physics Division, Materials Science Group, HBNI, Indira Gandhi Centre for Atomic Research, Kalpakkam 603102, India

²high Pressure & Synchrotron Radiation Physics Division, Physics Group, Bhabha Atomic Research Centre, 400085, Mumbai, India

Keywords: high pressure, crystal structure, phase diagram, rare earth oxides.

*e-mail: irshad@igcar.gov.in

Rare earth sesquioxides (RES) are known to be an important material owing to the wide spread applications in many of the fields like solid state lasers, solid oxide fuel cells, control rods in nuclear reactors, phosphors, wave guides, scintillating materials and so on[1]. They are also fundamentally interesting materials due to their existence in different polymorphic structures. Depending on the cation size, RESs are known to exist in any of the three polymorphic structures at ambient temperature and pressure (ATP)[1, 2]. The sesquioxides with small cation size (Dy-Lu) follows the C-type (cubic) structure whereas, the large cation sized RES (La-Nd) adopts the A-type (hexagonal) structure. Depending on the thermal history, the medium cation sized RES (Sm-Gd) crystallizes either in the B-type (monoclinic) or in the C-type. Although the cationic radii in the RES's increase in the sequence $C \rightarrow B \rightarrow A$, the molar volume is observed to be decreasing in the same sequence[2]. Considering this fact, a structural sequence of $C \rightarrow B \rightarrow A$ is expected to occur under high pressure (HP). Though the effects of cation size and pressure dependence are studied independently, there are no systematic studies revealing the role of cation size in preferring a particular structure type over the other at high pressures.

The effect of cation size and pressure on the phase structure and vibrational properties of solid solutions, $(\text{Eu}_{1-x}\text{Ho}_x)_2\text{O}_3$, with similar structure and very small difference in cationic radii has been reported earlier[3, 4]. The present study is intended to understand the simultaneous effect of cationic radii and pressure on the solid solutions of RESs with dissimilar structure and with significant difference in cationic radii. The medium cation sized RES Eu_2O_3 , crystallizing in the cubic structure at ATP, and the large cation sized RES La_2O_3 , crystallizing in the hexagonal structure at ATP, with the difference of cationic radii 0.15 \AA have been selected for the present study. When the difference in cationic radii exceeds the maximum that a particular structure can accommodate, a polymorphic structural phase transition is expected. The solid solutions, $(\text{Eu}_{1-x}\text{La}_x)_2\text{O}_3$ ($0 \leq x \leq 1$), have been prepared by simple soft chemistry approach. The composition, morphology and crystal structure evolution of the as synthesized oxides have been reported earlier in detail [5]. A $C \rightarrow B \rightarrow A$ structural phase transition have been observed with an increasing substitution of La[5]. The micro strain and substitutional disorder induced by the difference in the size of the rare earth ions are the key factors which drives the phase transitions in these oxides[5].

The structural stability and compression behaviour of these solid solutions have been investigated at high pressures. Cubic structure is found to be stable for $0.95 \text{ \AA} \leq R_{\text{RE}} < 0.98 \text{ \AA}$ at ATP and prefers $C \rightarrow A$ transition at high pressures. A biphasic region of cubic and monoclinic structure is stable for $0.98 \text{ \AA} \leq R_{\text{RE}} < 1.025 \text{ \AA}$ at ATP and a $C/B \rightarrow A$ transition is preferred under pressure. Further, a biphasic region of monoclinic and hexagonal structure is favoured for $1.025 \text{ \AA} \leq R_{\text{RE}} < 1.055 \text{ \AA}$ at ATP and the B phase progress towards the hexagonal A phase under pressure. A pure hexagonal phase have been obtained for $1.055 \text{ \AA} \leq R_{\text{RE}} \leq 1.10 \text{ \AA}$ at ATP and the system is structurally stable under pressure. The equation of state fit to the unit cell compressibility data indicated a monotonous decrease in the bulk modulus of hexagonal structure with the increasing R_{RE} except for $x=0.2$ and 0.6 . The results obtained from the high pressure structural investigations on $(\text{Eu}_{1-x}\text{La}_x)_2\text{O}_3$ are consolidated and a pressure concentration phase diagram is constructed upto a pressure of 25 GPa.

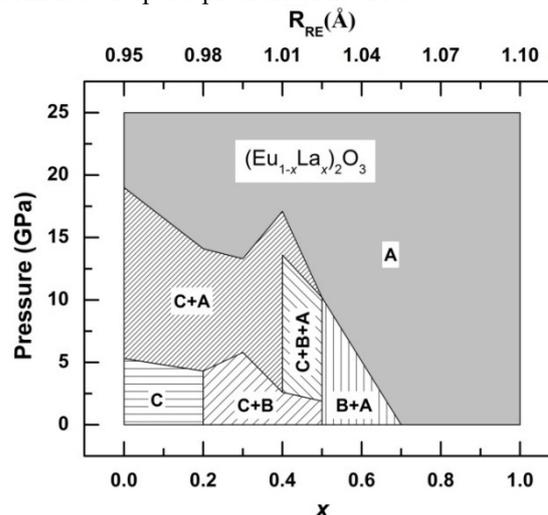


Figure 1. Pressure – concentration (P-x) phase diagram for the solid solution $(\text{Eu}_{1-x}\text{La}_x)_2\text{O}_3$.

Acknowledgments: This work was supported by Department of Atomic Energy, Government of India.

- [1] Eyring, L., *Handbook on the physics and chemistry of rare earths* 1979, **3**, 337.
- [2] Sahu, P.C., L. Dayana, and N.V. Chandra Shekar, *J Phys Conf Ser* 2012,**377**(1), 012015.
- [3] Irshad, K.A., et al., *J Mol Struct* 2017, **1128**, 325.
- [4] Irshad, K.A., et al., *J Alloys Compd* 2017,**725**, 911.
- [5] Irshad, K.A., et al., *J Appl Crystallogr* 2019,**52**(1),32.