

Polymorphism in rare earth sesquioxides: Dependence on pressure and cationic radii

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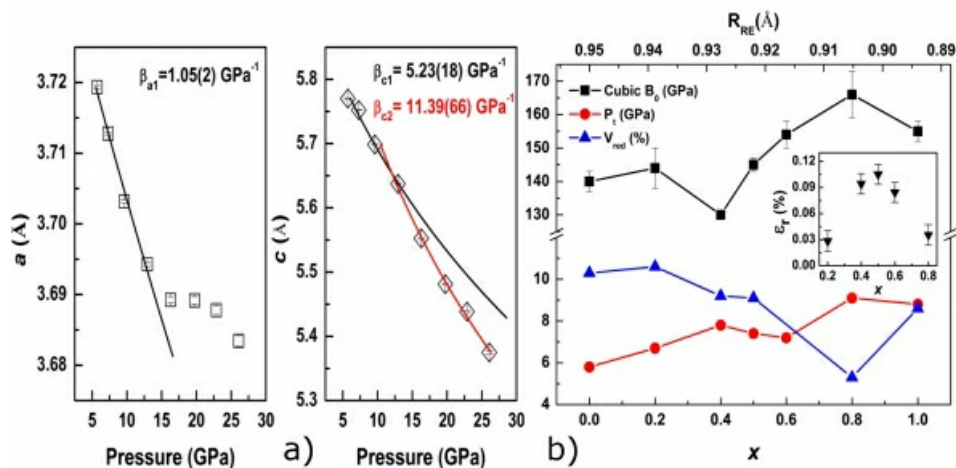
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Rare earth oxide ceramics have applications in nuclear reactors because of their high thermal neutron absorption coefficient. Crystal structural stability and phase diagram of these oxides are of technological interest. Depending on their cationic radii, rare earth sesquioxides (RES) exist in three different polymorphic modifications such as type-A(hexagonal), type-B(monoclinic) and type-C(cubic). Although the cation radii increases in the sequence C→B→A, the molar volumes are observed to be decreasing in the same sequence. Considering this fact, a structural sequence of C→B→A is expected to occur under high pressure. But the medium size RES do not obey this sequence. Instead, they go through a direct C→A transition and the reason for this is uncertain. The effect of cationic radii in preferring a particular structure type over the other and its influence in dictating the structural stability and phase transition in these RES need to be addressed. In order to understand the structural stability and phase transition, some of the selected oxides are investigated using high pressure X-ray diffraction (HPXRD) technique. Contrary to the available reports, monoclinic Eu₂O₃ shows anomalous lattice compressibility for the HP hexagonal phase. The pronounced hardening of a axis in the pressure range 15-25 GPa is found to be compensated by doubling the compressibility along the c axis (see Fig.1a). This atypical behavior may have its origin in an electronic transition. Nonetheless, more studies have to be carried out to clarify this aspect. Further, HPXRD measurements of (Eu_{1-x}Ho_x)₂O₃ have been carried out using Indus-2 synchrotron facility at RRCAT, India. In order to understand the phase transition behaviour with cationic radii, an average cationic radius has been calculated from the individual ionic radii of Eu³⁺ and Ho³⁺: $RRE = xR_{Ho} + (1-x)R_{Eu}$ and the structural evolution is investigated. Fig. 1b shows the, cubic bulk moduli, transition pressure and the volume reduction as a function of RRE. It is clearly seen that the bulk modulus is minimum for $RRE = 0.927 \text{ \AA}$ and the transition pressure shows a slight decreasing trend for $0.916 \text{ \AA} \leq RRE \leq 0.927 \text{ \AA}$. Further structural analysis, by employing Rietveld refinement, shows that, the reduction in transition pressure in the aforementioned region is due to the increased microstrain (ϵ_r) developed by the difference in cationic radii upon doping. This microstrain manifests as an internal pressure in the crystal structure and is responsible for the reduction in the bulk modulus and the transition pressure in this region. Also, the range of RRE which lies within 0.916 \AA

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