

Revised phase stability diagram of rare earth sesquioxides

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Below 2000°C rare earth sesquioxides (RESOX) have three crystal structures: hexagonal, cubic and monoclinic, designated as A, C and B respectively [1-3]. Early studies, based on low temperature (LT) synthesis, suggested that RESOX phase stability versus temperature is a function of the metallic ion radii (MIR). La_2O_3 , Ce_2O_3 and Nd_2O_3 with the highest MIR are A-type, while for Sm_2O_3 , Eu_2O_3 and Gd_2O_3 with intermediate MIR the structure is C-type at LT and B-type at high temperature (HT) [1-3]. All other RESOX including Y_2O_3 and Sc_2O_3 were assumed to be cubic (C-type) at all temperatures below 2000°C. The transformation from LT cubic to high temperature (HT) monoclinic structure in Sm_2O_3 , Eu_2O_3 and Gd_2O_3 is unusual and therefore Brauer [4] and Yokogawa et al. [5] suggested that the stable phase is monoclinic at all temperatures below 2000°C. To resolve the controversy, we have demonstrated that slowing down grain growth of Sm_2O_3 and Gd_2O_3 [9] prevented transition from C to B-types in the expected temperatures (1100 and 1300°C respectively). Hence, we suggest that the surface

energy plays an important role in determining the structure of nanomaterials [6,7]. The monoclinic Sm_2O_3 , Eu_2O_3 and Gd_2O_3 is the stable structure at all temperatures below 2000 °C when the grain size is large in the nanoscale. However, for smaller nanocrystals the stable structure is cubic since it has a lower surface energy than the monoclinic phase. In addition, Kimmel et al. [9] suggested that for all RESOX with MIR lower than Gd^{3+} (except Sc_2O_3) obtained by HT synthesis [10-17] or under high pressure [18-20] the monoclinic phase is the stable phase also at LT. Figure 1 shows the transition from LT monoclinic to the HT cubic phase according to Sato et al. [17]. Figure 2 shows the suggested RESOX stability diagram as function of temperature versus MIR. In *sol-gel* production the formation of C-type structures is due to the formation of nano-crystals. Subsequent firing at high temperatures yields the HT cubic phase. Thus, the assumption of a continuous cubic structure at all temperatures is wrong. As seen in Figure 1, in Sc_2O_3 the monoclinic to cubic transition is below room temperature, in agreement with the fact that HT synthesis yields cubic Sc_2O_3 [17]. (The ion radius of Sc^{3+} is 0.087 nm [21,22]).

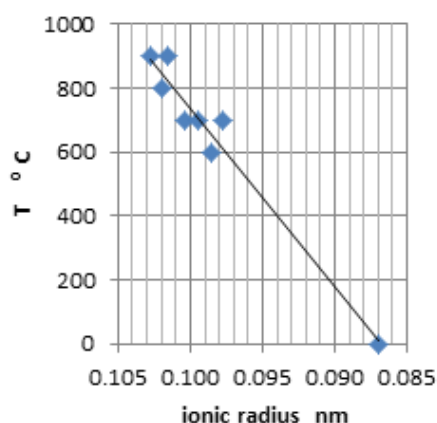


Figure 1. Extrapolation of B→C transition temperature values for RESOX with MIR between 0.103 (Dy^{3+}) to 0.097 (Lu^{3+}) [17] out to Sc_2O_3 with MIR = 0.087 nm).

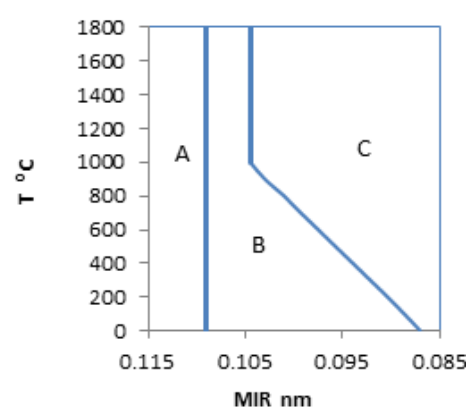


Figure 2. Revised T versus MIR phase stability diagram for bulk RESOX.

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