# Size effects in rare earth sesquioxides

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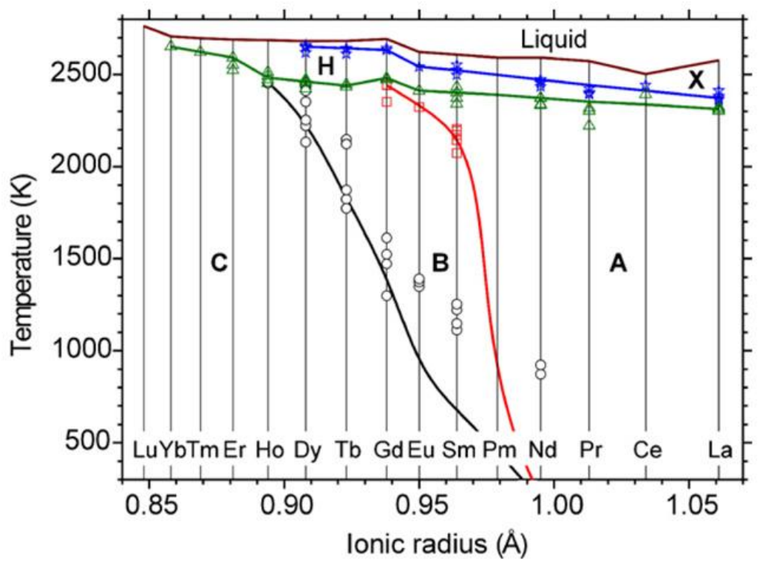
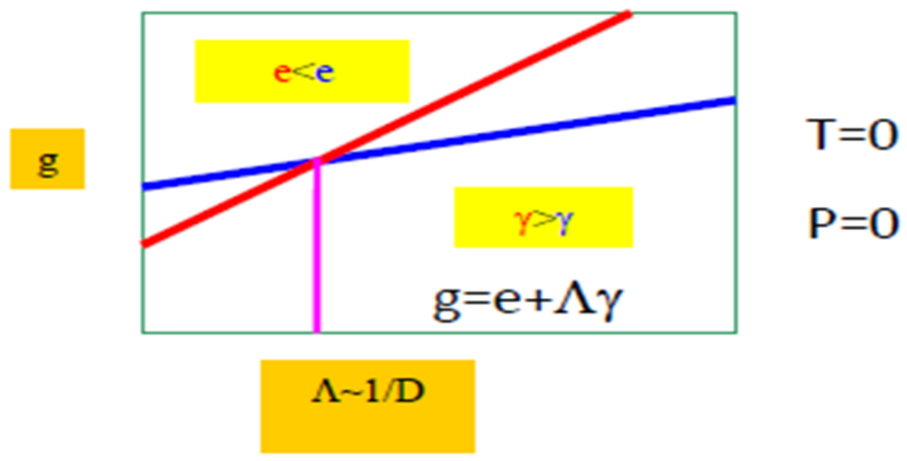
Below 2000 °C rare earth sesquioxides (RESOX) have three crystal structures: hexagonal , cubic and monoclinic, **designated as A, C and B respectively**. Early studies, based on low temperature (LT) synthesis, suggested that RESOX phase stability versus temperature is a function of the metallic ion radii (MIR) only. $La_2O_3$ $Ce_2O_3$ 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). 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 and Yokogawa et al. 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 $Gd_2O_3$ prevented transition from C to B-types in the expected temperatures (1100 and 1300 °C respectively). Hence, we suggest that the grain size plays an important role in determining the structure of nano-REOXs. The monoclinic $Sm_2O_3$, $Eu_2O_3$ and $Gd_2O_3$ is the stable structure at all temperatures below 2000 °C when the grains are large. However, for small nano-crystals the stable structure is cubic since it has a lower surface energy than the monoclinic phase. In addition, Kimmel et al. [1] suggested that for all RESOX with MIR lower than $Gd^{3+}$ (except $Sc_2O_3$) obtained by HT synthesis or under high pressure, the monoclinic phase is the stable phase at LT. Thus, for all RESOX with MIR lower than $Gd^{3+}$ except $Sc_2O_3$, the assumption of a continuous cubic structure at all temperatures is wrong.

[1] Kimmel G, Shneck RZ, Lojkowski,W, Porat Z, Chudoba T, Mogilyanski D, Gierlotka, S, Ezersky V |,Zabicky J. Phase stability of rare earth sesquioxides with grain size controlled in the nanoscale, J.Am. Ceram. Soc. 2019; **102**: 3829-3835.

Wrong stability phase diagram as obtain during xerogel firing
Grain size is grows along temperature of formation. At low temperature the grain size is small and the structure controlled by minimum surface energy



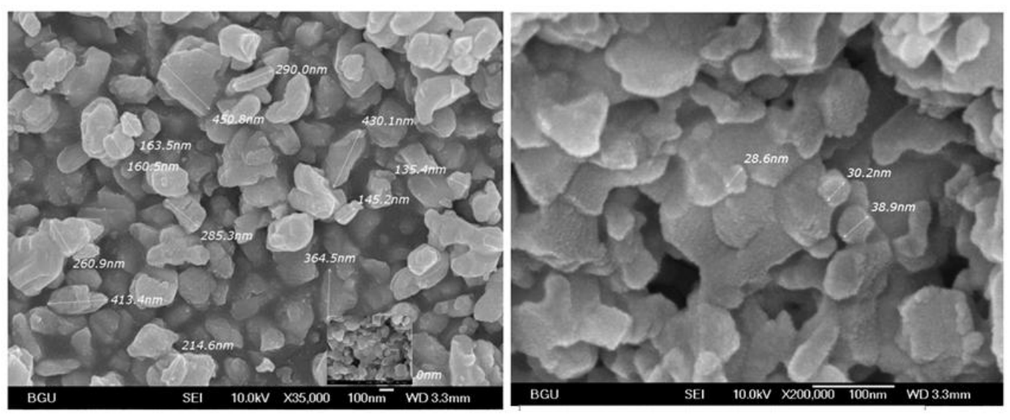

Grain size phase transformation



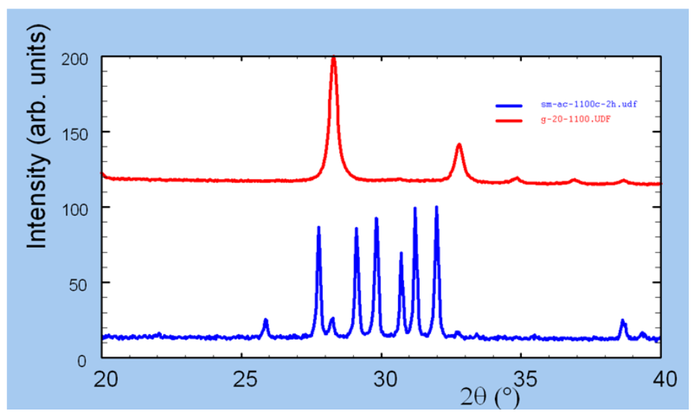

Solution: Formation of Sm and Gd oxides confined in MgO in order to prevent thermal growth

XRD patterns show that pure oxides (bottom) transformed into monoclinic structure. However oxides embedded in MgO (bottom) stay cubic.

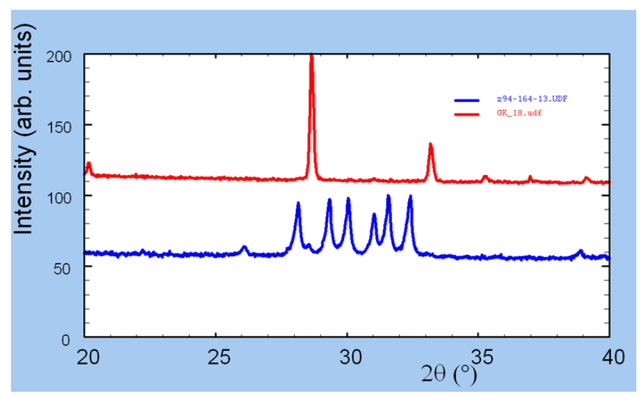
SEM photography of xerogels after treatment at 1100 °C for 3 h.
Left: pure $Sm_2O_3$ .- grain size ~300 nm.
Right 20 % vol. $Sm_2O_3$ in MgO - grain size ~30 nm..



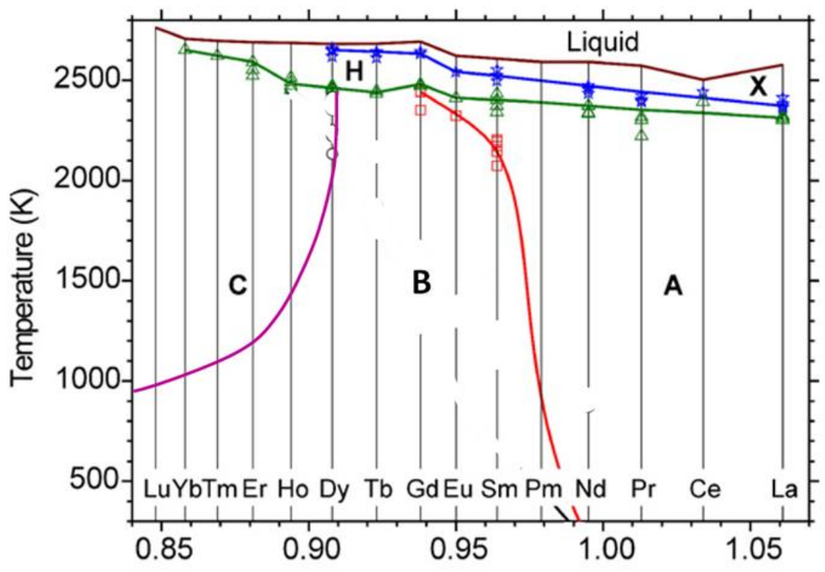

After treatment at 1100 °C for 3 h.
Bottom: pure $Sm_2O_3$.
Top 20 % vol. $Sm_2O_3$ in MgO



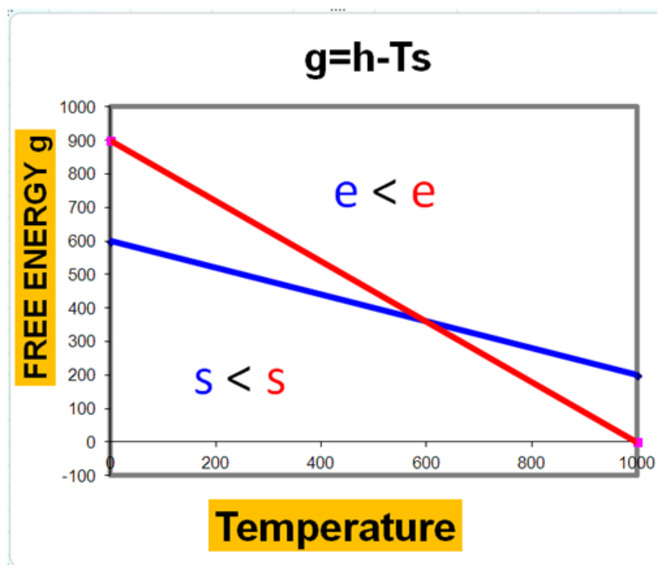

After treatment at 1300 °C for 3 h.
Bottom: pure $Gd_2O_3$.
Top 20 % vol. $Gd_2O_3$ in MgO




Correct stability phase diagram for bulk material




Phase transformation conrolled by temperature
(P=0; Λ =0)




$$g = e + Pv - Ts$$

$a$ = grain area

$v$ = grain volume

$$\text{Defining}: \Lambda = a / v \approx \frac{1}{D}$$

$$g = e + \Lambda\gamma + Pv - Ts$$

$$\text{Defining}: g_b = e + Pv - Ts$$

$$g = g_b + \Lambda\gamma$$

Summary: When the two parameters, grain size and temperature were separated as independent variables, a true phase stability diagram of the rare earth sesquioxides was obtained.