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Supporting information for article:

**Site-occupancy scheme in disordered $\text{Ca}_3\text{RE}_2(\text{BO}_3)_4$: a
dependence on rare-earth ionic radius**

**Katarzyna M. Kosyl, Wojciech Paszkowicz, Roman Minikayev, Alexey N.
Shekhovtsov, Miron B. Kosmyna, Maciej Chrunik and Andrew N. Fitch**

S1. Synthesis description – Pechini method

$\text{Ca}_3\text{Er}_2(\text{BO}_3)_4$ powder was synthesized by means of a modified Pechini method (Pechini, 1967). The following precursor materials were used for the synthesis, without additional purification: commercial calcium carbonate (CaCO_3 , SIAL, 99.9%), erbium oxide (Er_2O_3 , ALFA, 99.999%), boric acid (H_3BO_3 , STENMARK, 99.5%), citric acid ($\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$, POCH, 99.4%), mannitol ($\text{C}_6\text{H}_8(\text{OH})_6$, CHEMDREAMLAND, 99.5%), deionized water (MILIPORE, resistivity $\rho = 15 \text{ M}\Omega \cdot \text{cm}$) and nitric acid (HNO_3 , 65 % wt., POCH, pure p.a.). In order to prepare the initial solution, the proper quantities of metal precursors: CaCO_3 and Er_2O_3 were dissolved in a minimal volume of HNO_3 in the presence of citric acid (complexing agent) under stirring and heating at 80 °C. Citric acid was chosen as a complexing agent due to the fact that the citrate ligands form rather stable complexes of Ca^{2+} as well as of rare-earth ions in strongly acidic solutions. The molar ratio between citric acid and metal cations was set to be 3:1. Under these conditions, the complete dissolution of metal oxides was assured. When transparent and homogeneous solution containing metal complexes was obtained, a proper amount of H_3BO_3 was charged into the solution and the mixing was continued. The overall molar ratio of used CaCO_3 , Er_2O_3 and H_3BO_3 substrates was then as follows: 3:1:4. After secondary homogenization, the mannitol (polymeric agent) was added into the solution. The molar ratio of citric acid to mannitol was constant and set to 3:1. After dissolving of all the reagents, the solution mixing was continued for about 1 h at 90 °C in order to initialize the polyesterification. Prepared sol was then transferred into an alumina crucible (INCERAMICS S.A.) and put inside a furnace equipped with an EUROTHERM 906S temperature controller. The content was kept for about 24 h at 100 °C in order to evaporate the solvents (H_2O - HNO_3 azeotrope) and to accomplish the polyesterification. A yellowish, foamy-like viscous gel was obtained. The temperature was raised up to 350 °C for 4 h in order to remove the water residuals and dry the gel until it turned into black, brittle resin. To start the pyrolysis process and to get rid of the organic part, the temperature was gradually raised up to 1000 °C and kept at that value for 3 h. In between these stages and after finishing, the powder material was thoroughly ground in an agate mortar.

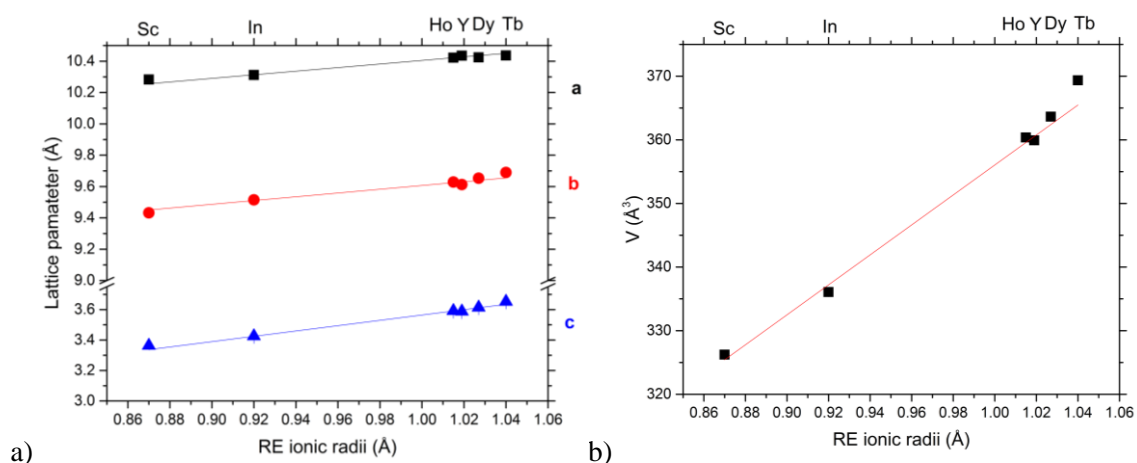


Figure S1 Lattice parameters (a) and unit cell volume (b) of RECa(BO₃)O minor phases found in Ca₃RE₂(BO₃)₄ samples, versus ionic radii of RE³⁺ (for CN = 8). For comparison, data for RE = Sc (Ma *et al.*, 2017), Y (Zhang *et al.*, 2001) and InCa(BO₃)O (Li *et al.*, 2012) are presented (in *Pnam* setting). Lines are linear fit to the data. Error bars are smaller than symbol size.