

Heavy Ln-phosphate - unexpected glue of octahedron-like ceria based mixed oxides.

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This work presents the results of the studies on synthesis and characterization of $Ce_{1-x}Yb_xO_{2-(x/2)}$ nanocrystals (where $x=0-0.05$) with octahedron-like (defined by the eight (111) crystal planes) and cube-like (defined by the six (100) planes) morphology. The $Ce_{1-x}Yb_xO_{2-(x/2)}$ nanocrystals were synthesized by the hydrothermal method. To the aqueous solution of Ce- and Yb-nitrates mixture, with suitable Ce:Yb ratio, the appropriate amount of aqueous solution of NaOH (for cubic-like crystals) or $Na_3PO_4 \cdot 12H_2O$ (for octahedral crystals) was added. The final solution was transferred into the stainless steel, Teflon-lined autoclave and treated at 220 or 170°C for 24 or 12h under autogenously pressure to obtain cubic-like and octahedral crystals, respectively. Clearly visible differences in the aggregations and shapes of the formed particles were detected as a function of the Yb-content and morphology of the oxide crystals. As has been presented in this work, individual crystallites of pure ceria and $Ce_{1-x}Yb_xO_{2-(x/2)}$ with cube-like shapes were observed on TEM images. On the other hand, in case of the octahedral crystals of oxides with the same nominal compositions, individual crystallites were observed only for pure CeO_2 , in contrast to the $Ce_{1-x}Yb_xO_{2-(x/2)}$, where large agglomerates with octahedral shapes (built from smaller octahedral crystals of the mixed oxides) were observed (confirmed by comparison XRD and TEM data). One of the most interesting observation connected with the formation of octahedral agglomerates of the mixed Ce - Yb oxides is the very similar orientations of the crystals which make up the large agglomerates. While the arrangement of the large, octahedron-like the $Ce_{1-x}Yb_xO_{2-x/2}$ mixed oxides particles, visible on TEM images, was completely random.

Unexpected, aggregation effect observed for the octahedron-like mixed oxides ($Ce_{1-x}Ln_xO_{2-x/2}$), but unobserved for pure ceria crystals, has been described for the first time. As has been presented in this work, it is probably due to presence of $Na_3PO_4 \cdot 12H_2O$ as a base agent and Yb-ions in the reaction (octahedrons synthesis) mixture. During the hydrothermal synthesis process, the octahedron-like mixed oxide crystals undergo the aggregation process, but in very specified way (called by author "making sandwiches"). In pure ceria samples, the octahedral crystals of CeO_2 and rod-like crystals of cerium phosphate have been observed on HRTEM images. On the other hand, on HRTEM images collected for Ce-Yb mixed oxides, only octahedral aggregates of octahedron-like crystals (without Ln-phosphate phase or very slight part) have been found. The EDX measurements show that amount of phosphor on doped and pure ceria is very similar. On HRTEM images of high doped ceria octahedrons (more than 30%), the crystallization of the $YbPO_4 \cdot 3H_2O$ rice-like crystals on the mixed oxide octahedrons external surface have been observed. So, the thin, amorphous layer of Ln-phosphate phase ($YbPO_4 \cdot 3H_2O$) must play a role the unexpected "glue" of octahedron-like ceria based mixed oxides crystals while $CePO_4 \cdot H_2O$ phase is only a by-product of the octahedral $Ce_{1-x}Yb_xO_{2-(x/2)}$ synthesis reaction.

The author thank Mrs. Zofia Mazurkiewicz for valuable help with preparation of the samples and Mrs. Ewa Bukowska for XRD measurements. This work was supported by the National Science Centre (Grant No. UMO-2016/21/D/ST5/01640).