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New mixed rare earth orthophosphates with monazite and zircon types of structure

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Our special thanks to the HEROIC SOLDERS of the Ukraine Army, who protect us from russian aggressors at the cost of their lives

Introduction

Due to combination of diverse interesting physical and chemical properties (high fusion temperature, optical emissivity, high resistance to aqueous and molten glass corrosion or to radiation damage), rare earth (RE) orthophosphates RPO_4 have found diverse application. Among the main applications of these materials are: coatings and diffusion barrier, ionic conductors and matrixes for radioactive waste management. Besides, RE orthophosphates with efficient emission in Vis and IR spectral ranges are promising phosphors, scintillator and laser materials and are used in modern lighting and display fields, fluorescent and phototherapy lamps, optically pumped solid-state lasers, plasma display panels, and so on.

Motivation

Crystal structure engineering is a very powerful tool for purposed tuning of functional properties of the materials. Application of chemical pressure caused by rare earth cation substitution in the orthophosphate lattice allows impact in prognoses way on structural parameters of the monoclinic and tetragonal phases and energy band gap and hence on the important physical properties of the materials. In this respect over 35 new mixed RE orthophosphates from 25 different RPO_4–$R'PO_4$ pseudo-binary systems have been synthesized and their structural parameters were analyzed.

Experimental

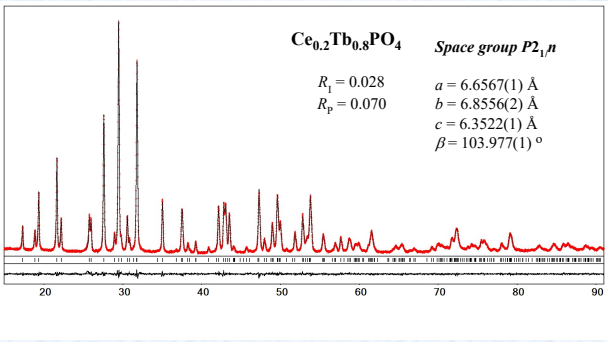
Single phase nanocrystalline $R_{1-x}R'_xPO_4$ powders with average grain size of 21-31 nm were obtained by solid state reactions in air by sequential calcination of appropriate mixtures of corresponding RE oxides and $(NH_4)_2HPO_4$ at 1473-1673 K.

In order to improve crystallinity of the materials, two series of the samples - $La_{1-x}Dy_xPO_4$ and $Ce_{1-x}Tb_xPO_4$ - were obtained by co-precipitation method. Appropriate aliquots of RE metal nitrates solutions were mixed together under continuous stirring, after that an excess of phosphoric acid was added. The solutions were boiled for 5-10 min until precipitate formation, cooled up to 348 K, and filtered thru ashless filter. After washing the sediments were annealed at 1373 K for 6 hours. Thus, single phase powders with average grain size of 120-160 nm and microstrains values of 0.01–0.05 % were obtained. The last data testify that co-precipitation technique favour more uniform distribution of different RE cations in mixed RE orthophosphates structures comparing with solid state synthesis route.

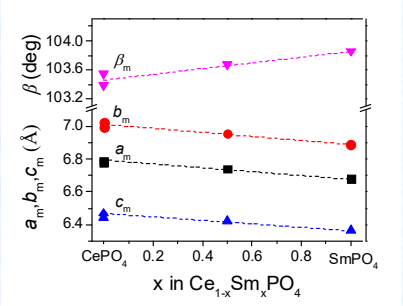
Phase and structural characterization of the synthesized materials was performed by using Aeris X-ray powder diffractometer (Malvern Panalytical) equipped with PIXcel^{1D} strip detector. Crystal structure parameters were derived from experimental XRD patterns by full profile Rietveld refinement. Rietveld technique was also used for the evaluation of average crystallite sizes and microstrain values from an analysis of angular dependence of Bragg's peaks profile.

Results

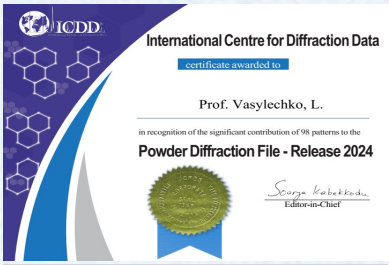
It was established that the monazite type of structure is inherent for the RPO_4–$R'PO_4$ systems with "light" RE, namely $La_{1-x}R_xPO_4$ (R=Nd, Sm, Eu), $Ce_{1-x}R_xPO_4$ (R=Pr, Nd, Sm, Tb), $Pr_{1-x}R_xPO_4$ (R=Nd, Sm, Eu, Gd) and $Nd_{1-x}R_xPO_4$ (R=Sm, Eu). In contrast, mixed phosphates with tetragonal zircon type of structure are formed in the systems of "heavy" RE and yttrium, e.g., $Dy_{1-x}R_xPO_4$ (R=Ho, Yb), $Ho_{1-x}R_xPO_4$ (R=Er, Yb, Lu) and $Y_{1-x}R_xPO_4$ (R=Tb, Dy, Ho, Er, Tm, Lu). In the mixed systems of "light" and "heavy" RE phosphates, two kinds of solid solutions are formed, as it was confirmed for $La_{1-x}Dy_xPO_4$ system, in which an immiscibility range between monoclinic and tetragonal phase was found at $0.6<x<0.97$.



Graphical results of Rietveld refinement of the monoclinic $Ce_{0.2}Tb_{0.8}PO_4$ and tetragonal $Er_{0.5}Yb_{0.5}PO_4$ structures. X-ray powder diffraction patterns (Cu Ka radiation, red and blue dots) are shown in comparison with calculated ones (black lines).



Evolution of the lattice parameters and monoclinic angle vs samarium content in $Ce_{1-x}Sm_xPO_4$ system



Diffractometric data and structural parameters over 25 new mixed phosphates with monazite and zircon types of structure are included by International Centre for Diffraction Data (ICDD) as standard reference data in PDF-4 database.

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