Lanthanide contraction in mixed rare-earth orthovanadates

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A list of the mixed rare-earth orthovanadates $Lu_{0.5}R_{0.5}VO_{4s}$ (R = Pr, Nd, Eu, Tb, Dy, Ho, Er, Tm, Yb) have been synthesized and investigated in order to define the impact of the lanthanide contraction on the value of the electronic band gap.

Synthesis. The compounds $Lu_{0.5}R_{0.5}VO4$ (R = Pr, Nd, Eu, Tb, Dy, Ho, Er, Tm, Yb) have been prepared by a solid-state reaction method. Appropriate quantities of rare-earth oxides (Pr_6O_{11}, Tb_4O_7, Nd_2O_3, Eu_2O_3, Dy_2O_3, Ho_2O_3, Er_2O_3, Tm_2O_3, Yb_2O_3, 99.9% Alfa Aesar) and ammonium metavanadate NH4VO3 (99% Sfera Sim, Lviv, Ukraine) have been grinded in agate mortar and three-time passed through 60um polyamide mesh. The heat treatment procedure of the samples was performed in three stages at 900°C, 1200°C and 1400°C for 24h, 5h and 2h respectively.

X-ray diffraction and optical transmission measurements. X-ray diffraction powder patterns were collected on Aeris Research diffractometer (Malvern PANalytical, Netherlands) with Cu Kα-radiation (λ = 1.541854 Å) equipped by PIXcel 1D detector. Transmission spectra have been obtained using FS5 Spectrofluorometer (Edinburgh Instruments, Great British. Diffuse reflection spectra have been measured using Cary 5000 UV-Vis-NIR Spectrophotometer with the installed DRA 2500 UV-Vis-NIR External Diffuse Reflectance Attachment.

Calculations procedure. We used ABINIT code to perform first-principle calculations. Ground-state properties have been evaluated within PBE0 hybrid functional, based on the projector augmented waves (PAW).

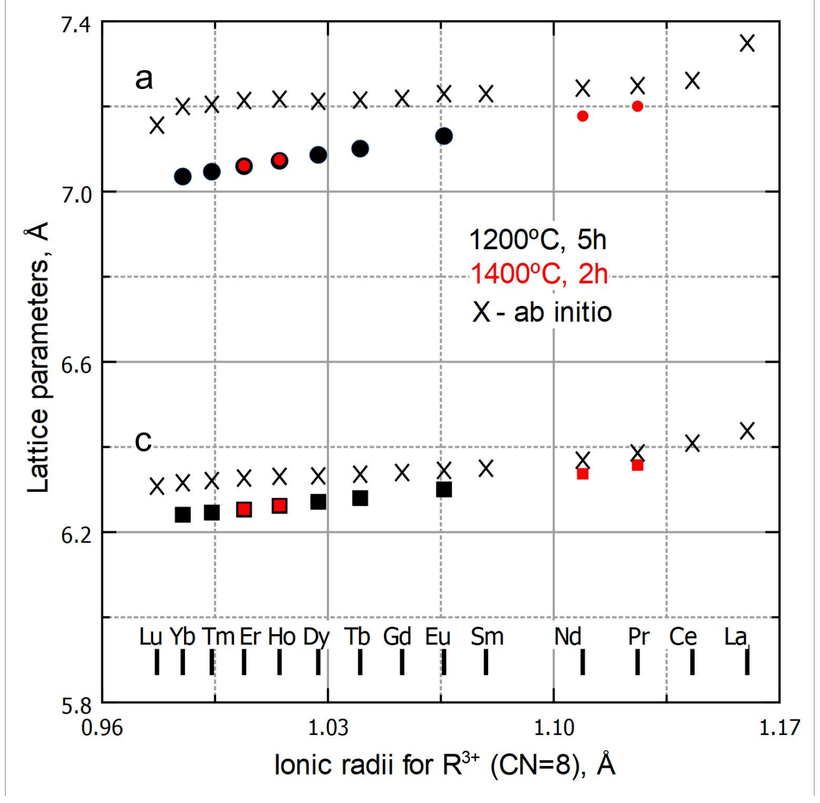

Fig.1. Lattice parameters and unit cell volumes of the $Lu_{0.5}R_{0.5}VO_4$ (R = Sm, Tb, Dy, Ho, Tm, Yb, Lu) powders

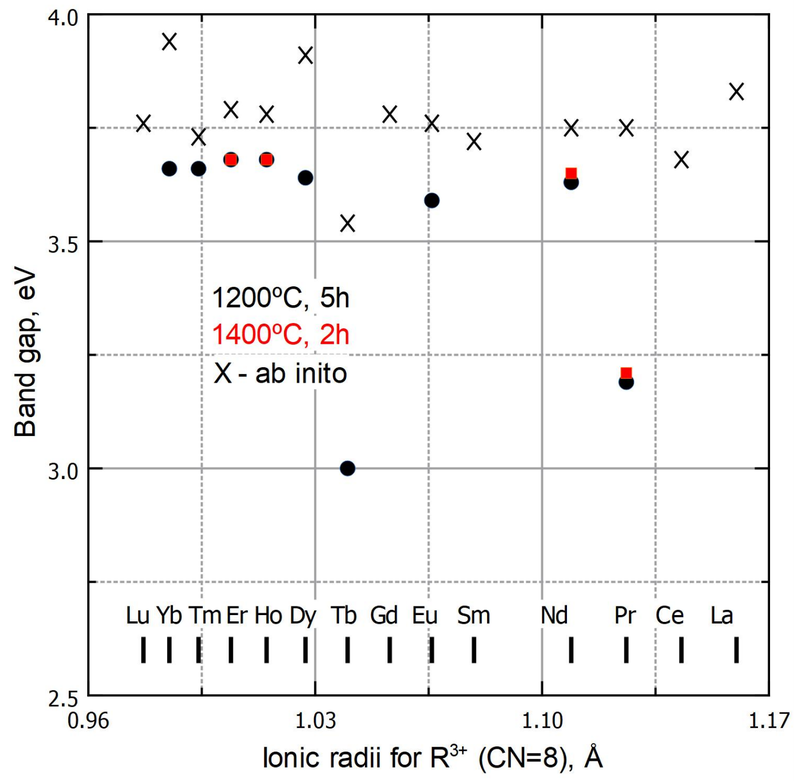

Fig.2. Bang gap energy in the $Lu_{0.5}R_{0.5}VO_4$ (R = Sm, Tb, Dy, Ho, Tm, Yb, Lu) powders

Results and Discussion. The crystal structure refinement of the mixed Lu-based vanadates was provided by Rietveld method in tetragonal space group I41/amd. Fig. 1 shows the linear evolution of the obtained lattice parameters of the $Lu_{0.5}R_{0.5}VO_4$ solid solutions as a function of average ionic radii of rare earth elements.

Increasing the annealing temperature leads to an improvement in the crystallinity of the structure, as a result, microstrains decrease, and the crystallite sizes increase, as estimated from the analysis of diffraction peaks.

Mixed orthovanadates $Lu_{0.5}R_{0.5}VO_4$ (R = Pr, Nd, Eu, Tb, Dy, Ho, Er, Tm, Yb) have been successfully synthesized by solid-state reaction method at annealing temperatures of 900° C, 1200° C and 1400° C. The materials have a zircon-type structure (space group $I4_1/amd$), and their cell parameters agree with literature data for the $Lu_{1-x}R_xVO_4$ systems, indicating the formation of continuous solid solutions.

The electronic and optical properties of $Lu_{0.5}R_{0.5}VO_4$ crystals have been calculated. It has been established that the presence of lanthanide compression does not affect the value of the bandgap. The positioning of f-states of lanthanides is the determining factor in the difference in the values of the bandgap.

Significant changes were observed in the transmission and diffuse reflection spectra of the samples that were additionally annealed at a temperature of 1400° C for two hours (Fig. 3). It is evident that these changes are caused by an improvement in the crystallinity of the structure – a reduction in defect density, grain growth, and their microstrains. The choice of synthesis methods, temperature treatment regimes, and changes in the nominal composition will allow modification of the functional properties of solid solutions of mixed rare-earth orthovanadates.

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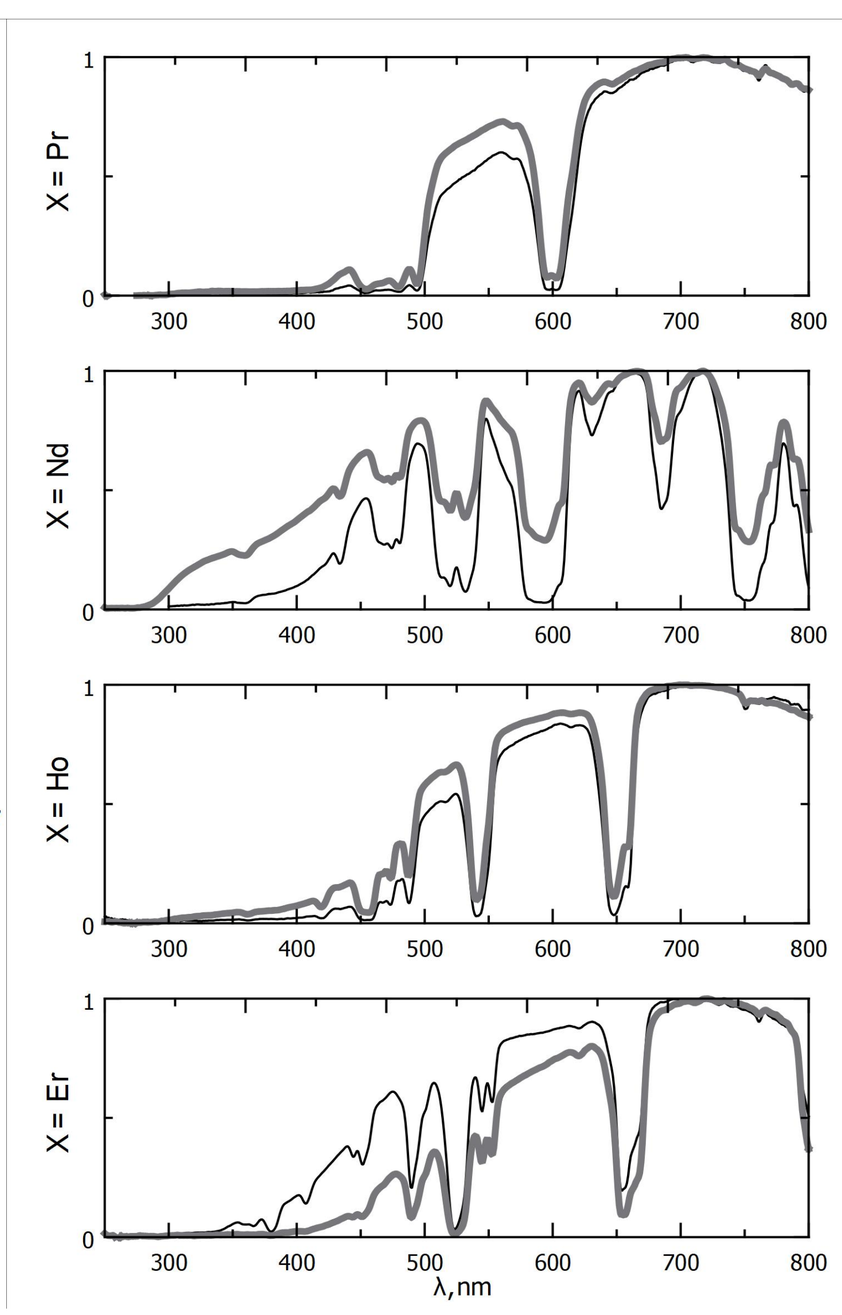

Fig.3. Transmission spectra of the $Lu_{0.5}R_{0.5}VO_4$ (R = Pr, Nd, Ho, Er) powders. Black thin curve - 1200°C, 5h, Grey bold curve - 1400°C, 2h.

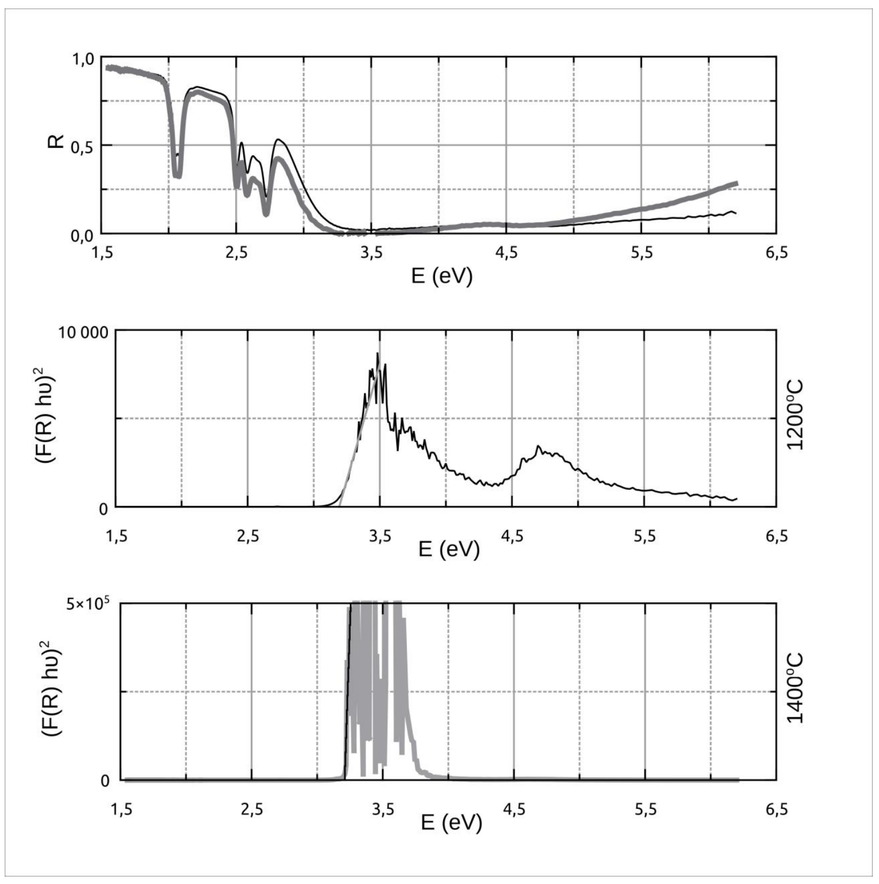

Fig.4. Diffuse reflectance spectra R and the Kubelka-Munk plot $(F(R)\ hv)^2$ for the material $Lu_{0.5}Pr_{0.5}VO_4$. Black thin curve - 1200°C, 5h, Grey bold curve - 1400°C, 2h