Thermal expansion of Cd- and Sr-containing NZP-related solid solutions

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Framework phosphates with crystal structure related to $NaZr_2(PO_4)_3$ (NZP) are characterized by resistance to high temperatures, aggressive media and radiation. One of practically important properties of the NZP-materials is their controlled thermal expansion. The behavior of the NZP-structure as a whole under thermal effects depends on the nature, the ratio of the sizes and the number of cations filling the crystallographic positions of various types, as well as the number of vacant positions and the symmetry of the unit cell.

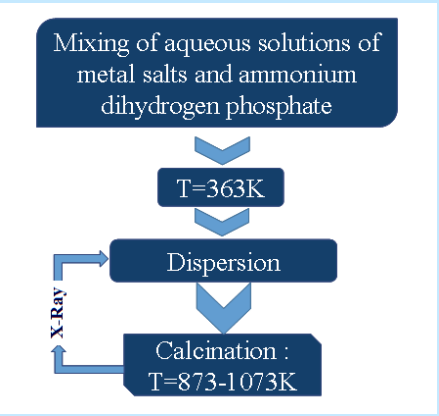
Objects of the study

$Cd_{0.5+x}Mg_xZr_{2-x}(PO_4)_3$ and $Sr_{0.5+x}Mg_xZr_{2-x}(PO_4)_3$ $(0 \le x \le 2.0)$

Methods

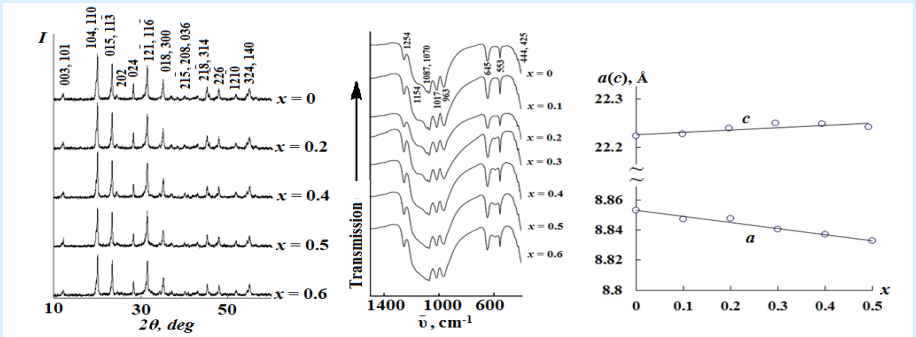
- ✓ X-ray diffraction (including Rietveld method and temperature studies)
- ✓ IR-spectroscopy
- ✓ Electron microscopy and microprobe analysis

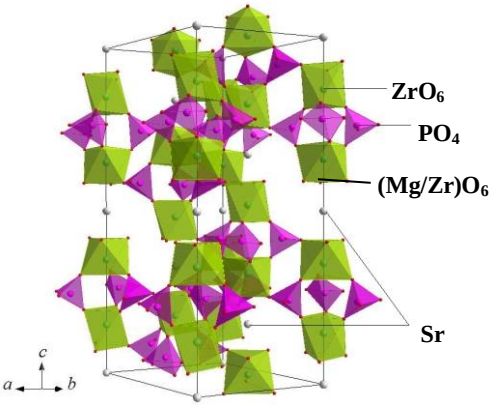
Synthesis



Phase formation in the system $Cd_{0.5+x}Mg_xZr_{2-x}(PO_4)_3$

XRD patterns | IR-spectra | Crystallographic characteristics

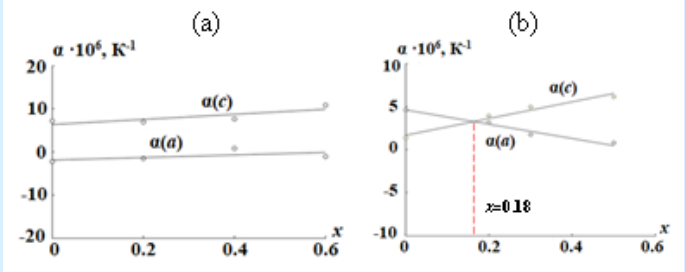




Structure of the phosphate $SrMg_{0.5}Zr_{1.5}(PO_4)_3$ (NZP)

Linear thermal expansion coefficients (LTEC) for the phosphates in the temperature range 173–473 K

$Cd_{0.5+x}Mg_xZr_{2-x}(PO_4)_3$ (a) $Sr_{0.5+x}Mg_xZr_{2-x}(PO_4)_3$ (b)



Composition	Thermal expansion coefficients ·10⁶, K⁻¹			
	α_a	α_c	α_{av}	anisotropy $\lvert\alpha_a-\alpha_c\rvert$
$Cd_{0.5}Zr_2(PO_4)_3$ (x=0)	-2.26	7.16	0.88	9.42
$Cd_{1.1}Mg_{0.6}Zr_{1.4}(PO_4)_3$($x$=0.6)	-1.02	10.80	2.92	11.82
$Sr_{0.5}Zr_2(PO_4)_3$ (x=0)	4.60	0.85	3.35	3.75
$SrMg_{0.5}Zr_{1.5}(PO_4)_3$($x$=0.5)	0.80	5.57	2.39	4.77

Temperature dependence of thermal expansion coefficients for the phosphates $Sr_{0.5+x}Mg_xZr_{2-x}(PO_4)_3$ allowed us to predict the composition of the solid solution (x = 0.18) with near-zero anisotropy, keeping small average expansion coefficient. The thermal expansion coefficients of the phosphate $Sr_{0.7}Mg_{0.2}Zr_{1.8}(PO_4)_3$ (x = 0.2) of the nearest composition were $\alpha_a = 3.73\cdot10^{-6}$, $\alpha_c = 4.28\cdot10^{-6}$, $\alpha_{av} = 3.92\cdot10^{-6}$, $|\alpha_a - \alpha_c| = 0.55\cdot10^{-6}$ K^{-1}.Thus, the studied phosphates $M_{0.5+x}Mg_xZr_{2-x}(PO_4)_3$ (M – Cd, Sr) are characterized by low values of the average coefficients of thermal expansion, which allow us to hope for success in the development of ceramics based on them that are resistant to thermal shock.

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