Synthesis, Structure and Thermophysical Properties of Phosphates $MNi_{0.5}Zr_{1.5}(PO_4)_3$ (M = Mg, Ca, Sr)

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Abstract

New phosphates $MNi_{0.5}Zr_{1.5}(PO_4)_3$ (M = Mg, Ca, Sr) were prepared by the precipitating method. Phosphates were characterized using X-ray powder diffraction, IR-spectroscopy and electron microprobe analyses. The crystal structure of phosphates was refined by the Rietveld method. Phosphates $CaNi_{0.5}Zr_{1.5}(PO_4)_3$ and $SrNi_{0.5}Zr_{1.5}(PO_4)_3$ are shown to have been crystallized in the $NaZr_2(PO_4)_3$-type structure and the phosphate $MgNi_{0.5}Zr_{1.5}(PO_4)_3$ was obtained as a single-phase with $Sc_2(WO_4)_3$-type structure. Heat capacity of phosphate $CaNi_{0.5}Zr_{1.5}(PO_4)_3$ was measured in the range 7 – 650 K and increased monotonically over the entire temperature range studied. Thermal expansion of phosphate $CaNi_{0.5}Zr_{1.5}(PO_4)_3$ was studied in the interval 295-1073 K by the high temperature X-ray diffraction. This phosphate is similar to the best low-expansion ceramics, such as zircon, cordierite and silica glass in thermal expansion behavior.

Introduction

Framework phosphates with $NaZr_2(PO_4)_3$ (NZP) and $Sc_2(WO_4)_3$ (SW) type structures due to their structural peculiarities have high useful properties among them there is thermal stability, low thermal expansion behavior and thermal conduction etc. A wide variety of iso- and heterovalent chemical substitutions at all crystallographic positions of these structures allows to prepare a large number of closely related compounds and to select NZP- and SW-compositions to create new materials with desired properties, including thermophysical (thermal expansion, heat capacity, thermal conduction). There are great possibilities of preparing new compounds and solid solutions (e. g., $M^{2+}_{0.5+x}M'^{2+}_{x}M^{4+}_{2-x}(PO_4)_3$, where M^{2+} is a lager sized cation compared with M'^{2+} and M^{4+}), whose thermophysical properties can be predicted on crystal-chemical principles [1, 2].

Compounds of the NZP family may be represented by the general crystal chemical formulae $(M1)_{0\rightarrow1}(M2)_{0\rightarrow3}\{[L_2(TO_4)_3]^{p-}\}_{3\infty}$ with the structure containing a three-dimensionalnetwork of corner-sharing LO_6 octahedra and TO_4 tetrahedra (Figure 1). Structural units consisting of two octahedra and three tetrahedra $[L_2(TO_4)_3]^{p-}$ are connected to form ribbons parallel to the *c* axis of the unit cell. These ribbons are linked together perpendicular to the *c* axis by TO_4 tetrahedra to build the three-dimensional framework. Two kinds of cavities within this framework of ribbons are formed: the first cavity, which is a strongly distorted octahedral site, M1, is located between $[L_2(TO_4)_3]^{p-}$ units of the ribbons. The other site, M2, is located between the ribbons. In the prototypical NZP structure, $NaZr_2(PO_4)_3$, the M1 site is occupied by sodium ions Na^+, the M2 site remains vacant, the L site is occupied by Zr^{4+} and the T site is occupied by P^{5+}. Four crystallographic sites with different coordination numbers allow substitutions by a variety of cations. Two L positions can be populated either with the same three- or the same tetravalent cations. The number of individual phases considerably increases due to

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the ability of different cations to occupy the L positions. The valences of cations can be the same (either +3 or +4) or different (for example, +1 and +4, +2 and +3, +2 and +4, +3 and +4, +4 and +5). The replacing atoms in the center of the LO_6 octahedra and the TO_4 tetrahedra (a tetrahedral site normally occupied by P^{5+}) cause changes in the negative charge of the framework. This charge is compensated by the substitutions in positions M1 and M2. These positions can be filled with cations with valences ranging from +1 to +4.

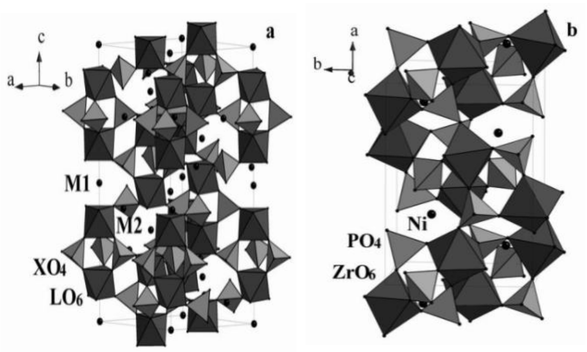

Fig. 1. a – NZP-type crystal structure; b – SW-type crystal structure.

NZP and SW structure types are closely related: they can be described as built up from the same type of $[L_2(TO_4)_3]^{p-}$ units [3]. They differ from each other by the packing of these groupings (Figure 1). As a result, holes formed in frameworks structure differ in shape and size.

Herein, synthesis, crystal structure and thermophysical data for the new complex $MNi_{0.5}Zr_{1.5}(PO_4)_3$ (M = Mg, Ca, Sr) are reported. The crystal chemical analysis gives us a possibility to propose that the framework phosphates $CaNi_{0.5}Zr_{1.5}(PO_4)_3$ and $SrNi_{0.5}Zr_{1.5}(PO_4)_3$ with $NaZr_2(PO_4)_3$-type structure. In these compounds the larger Ca and Sr atoms occupy the framework cavities and smaller Ni-atoms – framework positions (together with zirconium). In the phosphate $MgNi_{0.5}Zr_{1.5}(PO_4)_3$ with SW-structure Mg-atoms occupy the framework cavities with tetrahedral coordination.

Experimental

Preparation

New phosphates $MNi_{0.5}Zr_{1.5}(PO_4)_3$ (M = Mg, Ca, Sr) were prepared by the precipitating method starting from the following reagents: $Mg(NO_3)_2$, $CaCl_2$, $Sr(NO_3)_2$, $(CH_3COO)_2Ni\cdot4H_2O$, $ZrOCl_2\cdot8H_2O$ and H_3PO_4. Aqueous solutions of the salts, prepared with reagent grade chemicals, were mixed together, at room temperature. Some precipitates were dried at 353 K and thermally treated in the range from 473 to 1123 K during at 48 h with intermediate regrinding.

Techniques

Phase purity of the phosphates $MNi_{0.5}Zr_{1.5}(PO_4)_3$ (M = Mg, Ca, Sr) was established by powder X-ray diffraction (XRD) on a Shimadzu XRD-6000 type diffractometer using monochromatic CuK_α radiation. Data were recorded from 10 to 50 2θ at 1°·min^{-1}. The data allowed indexing and assessment of phase purity. Unit cell parameters were derived from least squares refinement of the powder diffraction data from single phases.

XRD data for the structure refinement of the $CaNi_{0.5}Zr_{1.5}(PO_4)_3$ phosphate as collected in the angular range 8-117° 2Θ with a step size of 0.01° and exposure times of 4800 s. The structures were refined with the WYRIET (version 3.3) software package [4]. For the high-temperature measurements (295-1073K), $CaNi_{0.5}Zr_{1.5}(PO_4)_3$ sample was held at the measurement temperatures for 1 h.

The M:Ni:Zr:P molar ratio (M = Mg, Ca, Sr) and homogeneity of the single phases were checked by electron microprobe analysis on a CamScan MV-2300 device with a Link INCA ENERGY 200C energy dispersion detector operated at 20.0 kV. The error in determining the sample composition was no more that 2.5 at %.

IR spectra were obtained by a Shimadzu FTIR-8400S spectrophotometer in the frequency range 1400-400 cm^{-1}. The samples were prepared by finely dispersing powder material on a ZnSe carier.

The heat capacity of the $CaNi_{0.5}Zr_{1.5}(PO_4)_3$ in the range from T=7 K to T=350 K was measured with a BCT-3 low-temperature adiabatic vacuum calorimeter. Its design and operational procedure were similar to those in reference [5]. An automated dynamic calorimeter (ADCTTB) operating by the principle of triple thermal bridge was used to measure the heat capacity in the range from T=330 K to T=665 K. The apparatus design and operational procedure were reported elsewhere [6]. From the calibration and testing results of the calorimeters it was established that the apparatus and the measurement procedure allowed us to obtain the $C^0_{p,\mathrm{m}}$ values of the substances in the crystalline state with an uncertainty of not more than 2 per cent from T=7 K to T=10 K, 0.5 per cent between T=10 and T=40 K, and within 0.2 per cent in the range from *T*=40 K to *T*=350 K and 1.5 per cent above 350 K.

Results and discussion

Powder XRD data of the thermally treated phosphates at the 1123 K (Fig. 2) showed that single-phase $CaNi_{0.5}Zr_{1.5}(PO_4)_3$ and $SrNi_{0.5}Zr_{1.5}(PO_4)_3$ were formed, which are isostructural to $NaZr_2(PO_4)_3$. These phases are rhombohedral and described by hexagonal cell parameters. The phosphate $MgNi_{0.5}Zr_{1.5}(PO_4)_3$ was obtained as a single-phase sample as isostructural to $Sc_2(WO_4)_3$. The presence of orthophosphate anions in the crystal structures was confirmed with IR spectroscopy. General view of the IR-spectra (Fig. 3) of the $CaNi_{0.5}Zr_{1.5}(PO_4)_3$ and $SrNi_{0.5}Zr_{1.5}(PO_4)$ phosphates was typical of $R\bar{3}c$ space group. At IR-spectra of the $MgNi_{0.5}Zr_{1.5}(PO_4)_3$ phosphate there were absorption bands which are characteristic of structure SW-type: 7 from 9 possible bands of absorption ν_3 with maxima at 1220, 1190, 1095, 1077, 1060, 1030 and 1005 sm^{-1}, all 3 possible bands ν_1 with maxima at 980, 960 and 945 sm^{-1} and 6 (from 9 possible) bands ν_4 with maxima at 650, 620, 610, 605, 575 and 560 sm^{-1}.

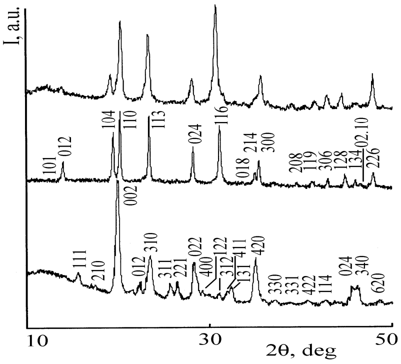

Fig.2. XRD patterns of $MNi_{0.5}Zr_{1.5}(PO_4)_3$ with different M: 1- M = Sr, 2 – M = Ca, 3 – M = Mg

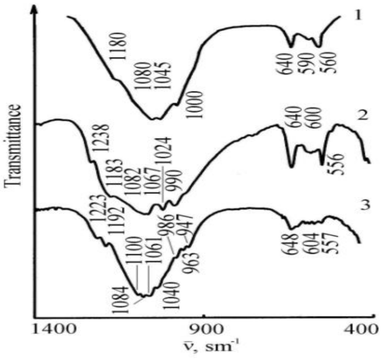

Fig.3. IR-spectra of $MNi_{0.5}Zr_{1.5}(PO_4)_3$ with different M: 1- M = Sr, 2 – M = Ca, 3 – M = Mg

The results of the electron microprobe analysis (Figure 4) have shown the homogeneity of the samples, their compositions were close to the theoretical values. For example, the stoichiometry of the Ca-containing sample is $Ca_{0.95(5)}Ni_{0.53(6)}Zr_{1.45(3)}P_{3.11(4)}O_{12}$ and is close to the theoretical composition $CaNi_{0.5}Zr_{1.5}(PO_4)_3$.

Results of structural study of the $CaNi_{0.5}Zr_{1.5}(PO_4)_3$ phosphate have confirmed its frame structure and belonging to NZP-family.

Octahedral atoms of zirconium and nickel, and phosphorus atoms tetrahedral participate the in formation anions a skeleton.

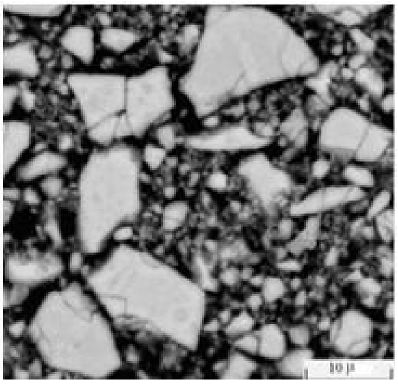

Fig. 4. Microstructure of $CaNi_{0.5}Zr_{1.5}(PO_4)_3$

Crystallographic positions M1 in crystal structure of calcium-nickel-zirconium phosphate are completely populated with atoms of calcium. The atomic coordinates, isotropic thermal parameters of atoms and occupation cationic positions are listed in Table 1. The structure is shown in Figure 5. The interatomic distances in coordination polyhedras are close to the usual: (Zr, Ni)–O 2.01 – 2.13, P–O 1.52 – 1.54 Å. The length of bond Ca–O is 2.52 Å.

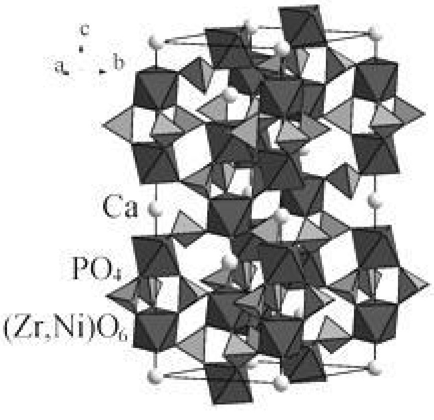

Fig. 5. Crystal structure of $CaNi_{0.5}Zr_{1.5}(PO_4)_3$

Table 1

Coordinates, thermal displacement parameters and site occupation (q) for the basic atoms in the structure of the $CaNi_{0.5}Zr_{1.5}(PO_4)_3$phosphate

atom	x	y	z	B_{iso}, $Å^2$	q
Ca	0	0	0	3.2(2)	1.00(1)
Ni	0	0	0.1459(1)	2.99(12)	0.25(9)
Zr	0	0	0.1459(1)	2.99(12)	0.75(3)
P	0.2878(6)	0	0.25	2.7(3)	1.0
O(1)	0.1774(8)	-0.025(1)	0.1944(4)	2.4(3)	1.0
O(2)	0.1983(8)	0.1689(8)	0.0850(4)	2.2(2)	1.0

The experimental values of the molar heat capacity of $CaNi_{0.5}Zr_{1.5}(PO_4)_3$ between T = 7 K and T = 650 K are presented in figure 6. It is seen that temperature dependence of heat capacity has no any special features: it gradually increases with rising temperature in the above temperature range. The thermodynamic functions of crystalline $CaNi_{0.5}Zr_{1.5}(PO_4)_3$ were calculated from the $C^0_{p,\mathrm{m}}$ (T) curve in the range $T \to 7$ K to T=650 K. The calculations of $\mathrm{H}^0_\mathrm{m}(T) - \mathrm{H}^0_\mathrm{m}(0)$ and $\mathrm{S}^0_\mathrm{m}(T)$ were made by numerical integration of the relations $C^0_{p,\mathrm{m}}$ = f(T) and $C^0_{p,\mathrm{m}}$ = f(ln$T$), respectively, and $\mathrm{G}^0_\mathrm{m}(T) - \mathrm{H}^0_\mathrm{m}(0)$ was evaluated from the corresponding values of $[\mathrm{H}^0_\mathrm{m}(T) - \mathrm{H}^0_\mathrm{m}(0)]$ and S^0_m (T) and by equation (1):

$$\mathrm{G}^0_\mathrm{m}(T) - \mathrm{H}^0_\mathrm{m}(0) = [\mathrm{H}^0_\mathrm{m}(T) - \mathrm{H}^0_\mathrm{m}(0)] - T\mathrm{S}^0_\mathrm{m}(T). \quad (1)$$

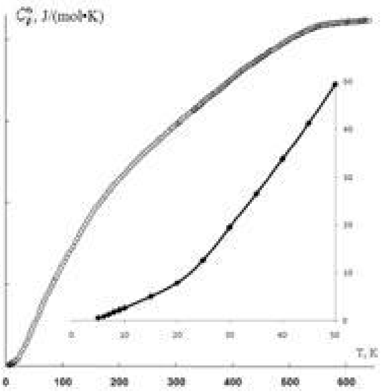

Fig. 6. Temperature dependence of the heat capacity of crystalline $CaNi_{0.5}Zr_{1.5}(PO_4)_3$

These functions of the investigated phosphate are given in Table 2.

Table 2

Thermodynamic functions of the crystalline $CaNi_{0.5}Zr_{1.5}(PO_4)_3$

T, K	$C^0_{p,\mathrm{m}}(T)$, J mol^{-1}K^{-1}	$[\mathrm{H}^0_\mathrm{m}(T)$-$\mathrm{H}^0_\mathrm{m}(0)]$, kJ mol^{-1}	$\mathrm{S}^0_\mathrm{m}(T)$, J mol^{-1}K^{-1}	-$[\mathrm{G}^0_\mathrm{m}(T)$-$\mathrm{H}^0_\mathrm{m}(0)]$, kJ mol^{-1}
0	0	0	0	0
100	123.0678	5.2883	84.7397	3.185708
200	229.0856	23.3929	205.9473	17.79657
298.15	294.1043	49.2002	310.0794	43.24993
300	295.2612	49.7454	311.9022	43.82526
400	352.8579	82.1535	404.7423	79.74346
500	400.4206	119.8969	488.7709	124.4886
600	420.75	161.2838	564.1726	177.2197
640	423.35	178.1628	591.4052	200.3365

The temperature dependences of the parameters of the rhombohedral unit cell in the structure of the $CaNi_{0.5}Zr_{1.5}(PO_4)_3$ phosphate (Figure 7) were used to calculate the components of the thermal strain tensor [7]. The termal expansion coefficient of $CaNi_{0.5}Zr_{1.5}(PO_4)_3$ phosphate are: $\alpha_a = 0.5\cdot10^{-6}$, $\alpha_c = 3.6\cdot10^{-6}$, $\alpha_{av} = 1.5\cdot10^{-6}$ K^{-1} (for the 295 K). This phosphate is similar to the best low-expansion ceramics, such as zircon, cordierite and silica glass in thermal expansion behavior

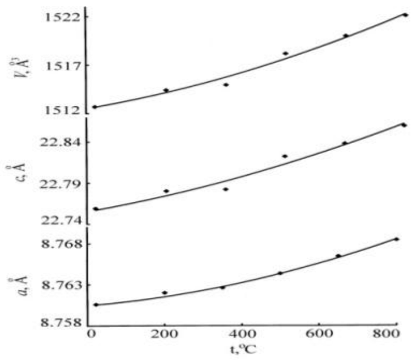

Fig. 7. Temperature dependencies of the unit cell parameters for the structure of the $CaNi_{0.5}Zr_{1.5}(PO_4)_3$ phosphate in the temperature range from (22-800°C)

Conclusion

From the results presented the following conclusions might be drawn:

- New framework phosphates $CaNi_{0.5}Zr_{1.5}(PO_4)_3$, $SrNi_{0.5}Zr_{1.5}(PO_4)_3$ and $MgNi_{0.5}Zr_{1.5}(PO_4)_3$ have been prepared and studied by X-ray powder diffraction, IR-spectroscopy and electron microprobe analyses
- Crystal structure, temperature dependence of the heat capacity and thermal expansion for phosphate $CaNi_{0.5}Zr_{1.5}(PO_4)_3$ were studied.

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