SYNTHESIS AND X-RAY STUDY OF SOLID SOLUTIONS $(Ca,Sr)_{0.5}Zr_2(PO_4)_3$

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Introduction

Calcium-strontium zirconium-phosphates concern to orthophosphate group and are characterized by the wide development of isomorphic replacement of various groups of elements [1]. The general formula of an orthophosphate group is:
$(A_x^{I}B_y^{II}R_z^{III}M_v^{IV}C_w^{V})(XO_4)_n$,
Where n = 1, 2, 3, 4...., and x, y, z, v, w can accept both whole, and fractional meanings, and also zero.
(A) - one - valence elements - H, Li, Na, K, Rb, Cs, Cu, Ag, Tl;
(B) - two- valence elements - Be, Ca, Sr, Ba, Cu, Cd, Pb, Mn, Fe, Co, Ni, Eu;
(R) - three- valence elements - Sc, Y, La, Al, Ga, In, Bi, Cr, Fe, Co, Ce-Lu, Pu-Cm;
(M) - four- valence elements - Ti, Zr, Hf, Ge, Sn, Ce, Th, U, Np, Pu;
(C) - five- valence elements - Nb, Ta, Sb.
X - P, As, V.

The study of zirconium- phosphate solid solutions is of interest for study of thermodynamics of isomorphic replacements in various positions (within the framework of one structure). Besides zirconium-phosphate solid solutions are a perspective matrix material for radioactive waste elements immobilization, that is determined both wide development of isomorphic replacements, and high stability of the these solid solutions to processes of leaching. The aim of our work was experimental study of isomorphic replacements of Ca and Sr in zirconium- phosphate solid solutions: $(Ca, Sr)_{0.5}Zr_2(PO_4)_3$.

Experimental study of solid solutions $(Ca, Sr)_{0.5}Zr_2(PO_4)_3$

Starting materials. The mechanical mixtures of $Ca_{0.5}Zr_2(PO_4)_3$ and $Sr_{0.5}Zr_2(PO_4)_3$, prepared by zol-gel method and synthered at 800-1000°C during 1-3 days. On the basis of X-ray study data zirconium- phosphate were corresponded to described in PDF JCPDS zirconium- phosphate solid solutions (space group R3c, Z=6).

Experimental technique and procedure. The runs were carried out in the welded platinum ampoules which put in high pressure hydrothermal cold seal vessels with external heating. 80-100 mg starting materials (mixtures of $Ca_{0.5}Zr_2(PO_4)_3$ and $Sr_{0.5}Zr_2(PO_4)_3$) were loaded into capsules, necessary amount of distilled water added. In each run solid reagents were represented of $Ca_{0.5}Zr_2(PO_4)_3$ and $Sr_{0.5}Zr_2(PO_4)_3$ mixtures, taken in various ratio. The experiences carried out at 750°C and water pressure 2 kbar. The accuracy of temperature control was not worse 5°C, pressure control was not worse 50bars. The run duration was 15-20 days.

Analytical methods. X-ray study of zirconium-phosphate solid solutions was carried out by the powder diffractometer HZG-4 in a mode of constant scanning. Si of spectral cleanliness used as the internal standard. Calculation of the unit cell parameters was carried out till 12-17 reflections from the angle range 7-39°(Θ). Cell parameters refinement was carried out with use of the programs LCC, PUDI [2], REFLAT [3].
Microprobe analysis carried out on the device "Camebax" with energydispersive detector Link AN-10000; the method of ZAF-correction was used for determination of the composition of zirconium-phosphate solid solutions. The accuracy of microprobe analysis of solid solution composition was 2.5 mol.%.

Results of experiments

As has shown the analysis of the solid products of experiments, (Ca, Sr) - zirconium- phosphate solid solutions form at 750°C and P=2kbar a continuous series of solid solutions. The variations of grains compositions in one experience do not exceed 3-4 mol.%. The investigated phases of zirconium-phosphate solid solutions on the data X-ray study form a series of structural analogues described in space group. R3c. In tab. 1 The results of cell parameters refinement of zirconium- phosphate solid solutions are listed in table 1.

Table 1

Unit cell parameters of (Ca, Sr)- of zirconium- phosphate solid solutions

X_{Sr}	a, [A]	c, [A]	V, $[A]^3$	Reference
0.0	8.772(2)[1)]	22.766(6)	1517.2(4)	1
0.0	8.772(1)	22.759(4)	1516.9(3)	1
0.12(3)	8.757(1)	22.881(5)	1519.9(4)	1
0.24(2)	8.744(2)	23.034(5)	1525.1(5)	1
0.64(3)	8.722(1)	23.149(6)	1525.0(6)	1
0.93(4)	8.696(1)	23.315(5)	1526.9(3)	1
1.00	8.700(1)	23.330(4)	1529.9(3)	1
0.0	8.785	22.680	1516.1	2
1.0	8.693	23.380	1530.8	2

1) The standard errors of calculation are given in brackets and refer to last decimal place.
Reference: 1 - this work; 2 - PDF JCPDS data.

The concentration dependences of the unit cell parameters of the solid solutions $(Ca, Sr)_{0.5}Zr_2(PO_4)_3$ are characterized by nonlinear curves and can be described following equations of the 3-rd order:

$a = 8.7723 - 0.13776*X + 0.129335*X^2 - -0.067508*X^3$ [A] (±0.003) (1)

$c = 22.757 + 1.45150* X - 2.00305* X^2 + + 1.139735* X^3$ [A] (±0.021) (2)

$V = 1516.75 + 49.24236* X - 93.24639* X^2 + + 56.7028* X^3$ $[A]^3$ (±0.9) (3)

where X - mole fraaction of Sr in solid solution of (Ca, Sr)- zirconium- phosphate. On the basis of the equations (1) - (3) excess volume of solid solutions $(Ca, Sr)_{0.5}Zr_2(PO_4)_3$ was designed. The compositional dependence of excess volume was approximated by the following equation:

$V^e = -0.008544 + 36.567* X - 95.4772* X^2 + +58.8625* X^3$ [A^3/mole] (±0.6) (4)

The excess functions of solid solutions are convenient for describing within the framework of Margules model: $F^e = X_1* X_2* (W1* X_2 + W2* X_2)$, where F^e - appropriate function of mixture (excess volume or excess energy etc.); X_1 and X_2 - mole fractions of components of a binary solid solution 1-2; and W1 and W2 - constant of the equation of Margules (Saxena, 1975, [4]). The designed Margules parameters for the description of excess volume of (Ca, Sr)- zirconium- phosphate are equal: W1 = -2.25 (55); W2 = 3.67 (41) cm^3/mol.

$V^e = X*(1-X)*[-2.25*X + 3.67*(1-X)]$ (5)

The equation (5) describes excess volume of mixture with accuracy 0.2 cm^3/mol.

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