SYNTHESIS AND PROPERTIES OF SYNTHETIC ZIRCONATES

V.A.Suvorova, A.R.Kotelnikov
Institute of Experimental Mineralogy, RAS, Chernogolovka, Moscow Region, Russia

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The main problem of this investigation is a study chemical and physical properties and definition of the parameters of the elementary cell (PEC) of synthesized accesory minerals (zirconate type). Mainly, these minerals are solid solutions and potential matrices for the fixation alkaline, alkaline- and rare-earth elements (Cs, Sr, Ba, Ce, Eu etc) which can enter the crystalline lattice of minerals as isomorphous impurities replacing the atoms Ca, Ba and partially Zr. A high stability for a physico-cyemical effect makes it possible to consider this material as perspective for the use as matrix to displase RAW-elements.

Mineral synthesis is performed by hot pressing method in to 3 stages: 1) drying of charge in vacuum during 0.5 hour; 2) pressing at 1350°C and axis pressure of 300 bar during 0.5 hour; 3) completing synthesis at 1350°C and remaining axis pressure (50 bar) during 4 hours [1]. Synthesized solid solution of zirconates represent the samples of poly- and monomineral ceramics with the density of 88-98% from the theoretical one. Chemical composition, equations of synthesized matrices and stable phases of the stadied part of the system CaO - (SrO) - (EuO) - TiO - CeO_2 are given in Tabl.1 (according to the microprobe data).

For some of these synthesized zirconolite the parameters of the elementary cell (PEC) are calculated. The results of the calculations are given in tabl.2 (the errors of some more exact definitions are given in brackets and refer to the last decimal sihgs).

These samples of zirconates were subjected by us to leaching of Sr, Ca, Zr and Eu. The velocities of leaching V g/(m^2·day) after 28 days are equel to $1.2\cdot10^{-2} \div 8.4\cdot10^{-2}$ for Ca, $3.9\cdot10^{-2} \div 9.5\cdot10^{-2}$ for Sr, $5.1\cdot10^{-4} \div 6.7\cdot10^{-2}$ for Zr and $2.1\cdot10^{-4} \div 5.5\cdot10^{-5}$ for Eu, comparable with the stability of Sinrok-C [4] and natural monocrystals of plagioclase [5]. The data on the leaching testify to zirconates applicability as matrices, keeping these elements.

1. *Martjnov K.V. et al.* Synthesis and study of the composition and properties of ceramic matrices on basic of minerals of complex oxide group bearing elements-imitators RAW // 4th Annual Scientific & Technical Conference of the Nuclear Society «Nuclear Energy and Man Security NE-93» June 28- Jule 2, 1993, Nizhni Novgorod, Abs. of Conf, part.II, pp.968 - 969 (in Russian).
2. PDF, N 34-167.
3. PDF, N 35-790.
4. *Kotelnikov A.R., Akhmedzhanova G.M. and Suvorova V.A.* Minerals and their solid solution - matrices for immobilization radioactive waste // Geochemistry, 1999, № 2, pp.1-9, (in Russian).
5. *Ringwood A.E et al.* SYNROC. In: Radioactive waste forms for the future (eds. Lutze and Ewing). 1988, ch.4, p.232-334.

Table 1

Contens of oxides (wt%) and eguation of samples

N sample	Mineral phase	CaO	SrO	TiO_2	ZrO_2	Формула
1101/1	Zrnlt[a]	47.00	-	50.53	2.47	$Ca_{1.1}(Ti_{0.81}Zr_{0.20})_{2.9}O_{6.9}$
	Prv[b]		-	59.58	13.12	$Ca_{1.9}(Ti_{0.94}Zr_{0.06})_{2.1}O_{6.1}$
1102/1	SrZrnlt[c]	18.47	8.067	54.27	19.20	$(Ca_{0.7}Sr_{0.3})_{1.1}(Ti_{0.7}Zr_{0.3})_{2.9}O_{6.9}$
	SrPrv [d]	7.976	14.81	87.42	2.05	$(Ca_{0.7}Sr_{0.3})_2(Ti_{0.94}Zr_{0.06})_{2.1}O_{6.1}$
1106/1	Zr-Prv [e]	41.21	-	-	58.79	$Ca_{1.98}Zr_{2.02}O_{6.02}$
	Tzr[f]	21.95	-	-	78.05	$Ca_{0.9}Zr_{3.1}O_{7.1}$
1103/1			Eu_2O_3			
	EuZrnlt[g]	26.36	1.991	50.16	20.99	$(Ca_{0.93}Eu_{0.07})_{1.2}(Ti_{0.7}Zr_{0.3})_{2.9}O_{6.9}$
	EuPrv [h]	48.16	1.564	49.29	0.72	$(Ca_{0.96}Eu_{0.04})_2(Ti_{0.99}Zr_{0.01})_2O_{6.0}$
1126/1	EuZr-Prv [i]	36.88	11.05	-	52.25	$(Ca_{0.74}Eu_{0.26})_{1.99}Zr_{2.01}O_{6.01}$
	EuTzr[j]	37.38	10.55	-	51.75	$(Ca_{0.8}Eu_{0.2})_{0.91}Zr_{3.09}O_{7.09}$
Ст		SrO				
17/2	SrZr-Prv[k]	43.44	0.522	-	56.01	$(Sr_{1.89}Eu_{0.018})_{1.908}Zr_{2.04}O_{6.0}$
1130/1	EuCrt[l]	6.676	3.630	41.55	48.14	$(Ca_{0.6}Eu_{0.4})_{1.2}(Ti_{0.43}Zr_{0.57})_{2.57}O_{7.57}$
	EuZr-Prv	22.36	0.462	-	76.18	$(Ca_{0.56}Eu_{0.04})_{1.98}Zr_{2.02}O_{6.02}$

[a] - zirconolite; [b] - perovskite; [c] - Sr-bearing zirconolite; [d] - Sr-bearing perovskite; [e] - zircon perovskite; [f] - tazheranite; [g] - Eu-bearing zirconolite; [h] - Eu-bearing perovskite; [i] - Eu-bearing zirconium perovskite; [j] - Eu-bearing tazheranite; [k] - Sr-bearing zirconium perovskite; [l] - Eu-bearing calzitrite.

Table 2

Parameters of the elementary cell of the number of some zirconates

N sample	Basic phase	a, Å	b, Å	c, Å	α, °	β, °	γ, °	V, (Å)^3
1101/1	Zrnlt mono*[2]	12.436 (2)**	7.220 (1)	11.480 (1)	90.00	100.27 (1)	90.00	1014.3 (2)
1102/1	SrZrnlt mono*[2]	12.428 (8)	7.224 (4)	11.480 (6)	90.00	100.07 (6)	90.00	1015.4 (9)
1103/1	EuZrnlt mono*[2]	12.443 (3)	7.228 (3)	11.476 (4)	90.00	100.31 (3)	90.00	1015.4 (5)
1106/1	Zr-Prv orto*[3]	5.757 (2)	8.012 (2)	5.592 (1)	90.00	9 0.00	90.00	257.9 (09)
1126/1	EuZr-Prv orto*[3]	5.742 (8)	7.921 (9)	5.924 (8)	90.00	90.00	90.00	269.5 (5)
Ст 17/2	SrZr-Prv orto*[3]	5.807 (1)	8.195 (2)	5.804 (1)	90.03 (1)	90.46 (1)	89.76 (1)	276.24 (6)
1130/1	EuCrt mono*[2]	12.445 (7)	7.225 (2)	11.483 (3)	90.00	100.32 (2)	90.00	1015.8 (7)

* - structure in the approximation of which the calculation was made.