Synthesis of perovskites and perovskite based technical stones

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Introduction

Perovskite group includes minerals with common formula $A_{2-x}B_2O_6$ where A — Ca, Na, Ce, etc, B — Ti, Nb, etc (Kostov, 1993). Perovskite $CaTiO_3$ at temperatures under 1380 K is orthorhombic, in the range 1380-1580 K — tetragonal, and above 1580 K — cubic (Zelezny, 2002; Romero, 2002). The substitution of Ca and Ti in the perovskite structure with other cations leads to ordering in calcium positions and to occurrence of defects in oxygen positions (Hazen, 1988), which is the reason for their unique properties. The oxygen vacancies cause deformation of the perovskite structure and arising antiferroelectric properties (Pollert, 1988).

Uhligite is a cubic mineral with cell parameter a_o 0,7654 nm (Feklichev, 1977). Dysanalite possesses orthorhombic structure and elementary cell parameters a_o 0,545 nm, b_o 0,778 nm and c_o 0,555 nm. According to Strunz (1977) it is cubic with cell parameter a_o 0,760 nm or 1,539 nm. Nioboloparite is cubic with parameter of the elementary cell a_o 0,3881 nm (Mirkin, 1961). Zirconolite is monoclinic below 973°C and pseudocubic at higher temperatures with parameters of the elementary cell a_o 1,243 nm, b_o 0,726 nm, c_o 1,135 nm and β 100,52° (Berejnoi, 1970). Freudenbergite is monoclinic with cell parameters a_o 1,230 nm, b_o 0,382 nm, c_o 0,650 nm and β 107,3° (Garin, 1981).

To the perovskite structure of some copper-containing oxide compounds is relevant one of the great discoveries of XX century — the high temperature superconductivity (Simeonov, 1991; Butckov, 1998). Magnesium silicate with perovskite structure ($MgSiO_3$ perovskite) is main component in the supposed composition of the Earth's lower mantle (Kamenov, 2003; Stixrude, 1993).

Experiment and discussion

For synthesis of the perovskites and the perovskite technical stones — perovskitites, oxides and carbonates with ***p*** and ***pa*** purity are used taken in amounts corresponding to the stoichiometric formulae of the relevant minerals of the perovskite group:

perovskite $CaTiO_3$,
tausonite $SrTiO_3$,
makedonite $PbTiO_3$,
latrapite $CaNbO_3$, lueshite $NaNbO_3$,
zirconolite $CaZrTi_2O_7$,
zirkelite $CaZr(Ti_{0,7}Nb_{0,15}Fe_{0,15})_2O_7$,
hawthorneite $BaTi_3Cr_4Fe_4MgO_{19}$,
freudenbergite $Na_2Fe_2Ti_7O_{18}$,
latrappite $(Ca_{0,7}Na_{0,3})(Nb_{0,7}Ti_{0,15}Fe_{0,15})O_3$,
jeppeite $(K_{0,7}Ba_{0,3})(Ti_{0,7}Fe_{0,3})_3O_6$,
priderite $(K_{0,7}Ba_{0,3})(Ti_{0,7}Fe_{0,3})_8O_{16}$,
loparite $NaCeTi_2O_6$, knopite $(Ca_{0,7}Ce_{0,3})TiO_3$,
dysanalite $Ca(Ti_{0,7}Nb_{0,3})O_3$,
nioboloparite $(Na_{0,7}Ca_{0,15}Ce_{0,15})(Ti_{0,7}Nb_{0,3})O_3$,
ankangite $Ba(Ti_{0,7}Cr_{0,3})O_3$
and uhligite $Ca(Ti_{0,7}Al_{0,15}Zr_{0,15})_3O_7$.

The technological scheme for preparation of the perovskite technical stones includes: grinding and homogenization of the starting powders → drying → preliminary thermal treatment → milling and preparation of perovskite press-powders → moulding of samples → annealing. The perovskites are synthesized at preliminary thermal treatment of the samples in the temperature range from 900 to 1300°C, for 30 min. Thus prepared perovskites are subjected to milling, moistening with water up to 8 % humectation, granulation through sieve 0,5 mm and placing in sealed polyethylene bags for 24 h. From these perovskite press-powders by means of semidry pressing at 50 MPa samples for annealing in the temperature range from 1250 to 1350°C for 30 min are prepared.

The chemical composition of the starting powders, identical to the chemical composition of the corresponding perovskites, their temperatures of synthesis, the average crystal size and temperatures of annealing of the perovskite technical stones are presented in table 1. The theoretical density and characteristic interplanar spaces of the perovskites are given in table 2, and some physical-chemical and electrical properties of the technical stones in table 3.

At the two-staged ceramic technology of sintering of perovskite technical stones, at the first stage,

Table 1. Chemical composition of the starting perovskite samples, temperatures of synthesis of the perovskites (T_s), average crystal size (l_a) and annealing temperature (T_f) of the perovskite technical stones

№	Mineral	Oxides, wt.%	T_f, °C (T_s, °C) 30 min	l_a, µm
1	2	3	4	5
1	$CaTiO_3$ perovskite	CaO 41,24 TiO_2 58,76	1350 (1300)	3
2	$SrTiO_3$ tausonite	SrO 56,47 TiO_2 43,53	1350 (1300)	2
3	$PbTiO_3$ makedonite	PbO 73,64 TiO_2 26,36	1200 (900)	3
4	$CaNbO_3$ latrappite	CaO 29,67 Nb_2O_5 70,33	1300 (1200)	1
5	$NaNbO_3$ lueshite	Na_2O 18,90 Nb_2O_5 81,09	1250 (1200)	2
6	$CaZrTi_2O_7$ zirconolite	CaO 16,54 ZrO_2 36,34 TiO_2 47,12	1300 (1200)	3
7	$CaZrx(Ti_{0,70}Nb_{0,15}xFe_{0,15})_2O_7$ zirkelite	CaO 15,78 ZrO_2 34,66 TiO_2 31,46 Nb_2O_5 11,22 Fe_2O_3 6,47	1250 (1200)	2
8	$BaTi_3Cr_4xFe_4MgO_{19}$ hawthorneite	BaO 14,51 TiO_2 22,68 Cr_2O_3 28,77 Fe_2O_3 30,22 MgO 3,81	1350 (1300)	3
9	$Na_2Fe_2Ti_7O_{18}$ freudenbergite	Na_2O 7,94 Fe_2O_3 20,45 TiO_2 71,61	1250 (1150)	4
10	$(Ca_{0,7}Na_{0,3})x(Nb_{0,70}Ti_{0,15\,x}{}_xFe_{0,15})O_3$ latrappite	CaO 23,71 Na_2O 5,62 Nb_2O_5 56,20 TiO_2 7,24 Fe_2O_3 7,23	1300 (1200)	2

№	Mineral	Oxides, wt.%	T_f, °C (T_s, °C) 30 min	l_a, µm
1	2	3	4	5
11	$(K_{0,7}Ba_{0,3})(Ti_{0,7x}{}_xFe_{0,3})_3O_6$ jeppeite	K_2O 10,35 BaO 14,44 TiO_2 52,66 Fe_2O_3 22,56	1350 (1300)	25
12	$(K_{0,7}Ba_{0,3})(Ti_{0,7x}{}_xFe_{0,3})_8O_{16}$ priderite	K_2O 4,59 BaO 6,41 TiO_2 62,31 Fe_2O_3 26,69	1350 (1300)	2
13	$NaCeTi_2O_6$ loparite	Na_2O 8,54 CeO_2 47,43 TiO_2 44,02	1300 (1200)	2
14	$(Ca_{0,7}Ce_{0,3})TiO_3$ knopite	CaO 22,99 CeO_2 30,24 TiO_2 46,78	1250 (1150)	5
15	$Ca(Ti_{0,7}Nb_{0,3})O_3$ dysanalite	CaO 36,93 TiO_2 36,82 Nb_2O_5 26,25	1300 (1200)	5
16	$(Na_{0,70}Ca_{0,15}xCe_{0,15})(Ti_{0,70}xNb_{0,30})O_3$ niobloparite	Na_2O 14,30 CaO 5,54 CeO_2 17,02 TiO_2 36,86 Nb_2O_5 26,28	1250 (1150)	2
17	$Ba(Ti_{0,7}Cr_{0,3})_8O_{16}$ ankangite	BaO 19,58 TiO_2 57,13 Cr_2O_3 23,29	1350 (1300)	2
18	$Ca(Ti_{0,70}Al_{0,15x}{}_xZr_{0,15})_3O_6$ uhligite	CaO 18,56 TiO_2 55,51 Al_2O_3 7,59 ZrO_2 18,35	1250 (1150)	1

Table 2. Theoretical density (c_p) and characteristic interplanar d-spacings of the synthesized perovskites

№	ρ_p, kg/m_3	d, nm	№	ρ_p, kg/m_3	d, nm
1	4040	0,270 - 0,191 - 0,156	10	4380	0,274 - 0,389 - 0,194
2	5110	0,283 - 0,231 - 0,200	11	3970	0,307 - 0,299 - 0,281
3	7950	0,390 - 0,284 - 0,276	12	3860	0,320 - 0,505 - 0,714
4	5330	0,274 - 0,389 - 0,194	13	4760	0,275 - 0,194 - 0,159
5	4280	0,276 - 0,390 - 0,195	14	4200	0,270 - 0,191 - 0,155
6	4800	0,293 - 0,190 - 0,180	15	4150	0,382 - 0,269 - 0,191
7	4740	0,293 - 0,282 - 0,251	16	4770	0,275 - 0,194 - 0,158
8	5020	0,277 - 0,241 - 0,147	17	4330	0,320 - 0,247 - 0,223
9	4340	0,363 - 0,310 - 0,191	18	4150	0,270 - 0,191 - 0,169

which is a preliminary thermal treatment in the temperature range 900—1300°C, the perovskites are synthesized, but in the second stage from 1250 to 1350°C the annealing of the perovskite ceramic samples takes place. The identification of the perovskite group of minerals is done using their characteristic d-spaces given in table 2.

Table 3. Apparent density (ρ_{ap}), shrinkage (S), water absorption (WA), dielectric constant (ε) and specific electrical resistivity (R) of the perovskite technical stones

№	ρ_{ap}, kg/m^3	S, %	WA, %	ε	R, Ω.cm
1	3640	3,50	0,98	201	$1,8.10^9$
2	4860	4,61	0,13	114	$4,8.10^8$
3	7550	9,28	0,13	235	$1,9.10^9$
4	4800	8,12	0,29	164	$5,0.10^9$
5	3850	7,43	0,32	170	$1,3.10^8$
6	4320	4,22	0,39	82	$1,2.10^9$
7	4270	4,24	0,44	65	$4,3.10^9$
8	4520	4,60	0,11	146	$1,3.10^8$
9	3910	4,01	0,24	105	$1,1.10^8$
10	3940	4,57	0,31	197	$1,1.10^8$
11	3900	10,2	0,34	230	$7,5.10^8$
12	3740	12,4	0,06	240	$1,3.10^6$
13	4280	6,57	0,18	306	$2,5.10^6$
14	4120	4,43	0,04	244	$3,0.10^8$
15	3730	3,97	0,31	250	$2,4.10^9$
16	4530	6,29	0,20	245	$2,5.10^7$
17	3900	4,37	0,42	237	$1,8.10^7$
18	3840	3,72	0,35	140	$3,8.10^8$

The perovskite technical stones have monophase composition and microgranular homeograinoblastic texture. Average crystal size varies from 1 to 5 μm with exception of jeppeite crystals with size of 25 μm (table 1). The apparent density of the technical stones ranges from 3640 to 7550 kg/m^3 being 90—98 % of the theoretical density (tables 2—3). They have shrinkage from 3,50 to 12,40 % and water absorption from 0,04 to 0,98 % (table 3). Their specific electrical resistivity varies from $1,3.10^6$ to $5,0.10^9$ Ω.cm indicating that many of these materials are semiconductors ($10^5 \div 10^{10}$ Ω.cm). On the semiconductive-dielectric boundary are positioned the samples of perovskite (1), makedonite and latrappite (3—4), zirconolite and zirkelite (6—7) and dysanalite (15). The relative dielectric constant of the technical stones is in the range from 65 to 306.

Conclusion

From synthetic perovskites by means of semidry pressing technique and annealing in the temperature range 1250—1350°C for 30 min perovskite technical stones — perovskitites are prepared. They have monophase composition and microgranular homeograinoblastic texture The perovskitites have high density, close to the theoretical and low water absorption. Their specific electrical resistivity $1,3.10^6$-$5,0.10^9$ Ω.cm indicates that some of these materials are semiconductors.

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Синтез на перовскити и технически камъни на тяхна основа

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Резюме. Посредством твърдофазов синтез в температурния интервал от 900 до 1300°C от вещества с квалификация р и ра са получени перовскит, таусонит, луешит, лопарит, кнопит, дизаналит, ниоболопарит, анкангит, фройденбергит, хоуторнеит, латрапит, джепеит и придерит. На основата на тези минерали са изготвени перовскитови технически камъни — перовскитити. Определени са някои техни физико-механични и електрични свойства.