2U3UUSUUP 2UUFUՊԵՏՈՒԹՅԱՆ ԳԻՏՈՒԹՅՈՒՆՆԵՐԻ ԱՁԳԱՅԻՆ ԱԿԱԴԵՄԻԱ НАЦИОНАЛЬНАЯ АКАДЕМИЯ НАУК РЕСПУБЛИКИ АРМЕНИЯ

Հայաստանի քիմիական հանդես 60, №2, 2007 Химический журнал Армении

THE SYNTHESES AND INVESTIGATION OF THE SYSTEM CaTiSiO₅ - CaSnSiO₅

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It was installed that at ≥ 700 °C the system CaTiSiO₅ - CaSnSiO₅ is single-phase [1]. In the persisting message are brought results x-rays, UR studies of the multi-components system CaTiSiO₅ - CaSnSiO₅ at 1173 K and electro physical characteristics of formed hard solutions. Samples of CaTi₁_xSn_xSiO₅ (0 \leq x \leq 1,0; Δ x = 0,05) ware synthesized from oxides of appropriate metals in hydrogen - oxygen flames low temperature plasma [2] and classical ceramic technology.

The X-ray data identification, which was realized with use parameters, provided in work [3], shows, the CaTiSiO₅ (x = 0) crystallizes in monoclinic structure. The Ca²⁺ Ions are located inwardly polyhedral emptiness formed by seven oxygen atoms, formed by oxygen atoms of the octahedral TiO₆ and tetrahedral SiO₄.

In structure of titanite crystallize as well as formed hard solutions composition $CaTi_{1-x}Sn_xSiO_5$. Partial or full change Ti^{4+} ion by Sn^{4+} ion in titanite lattice at the temperature 1173K does not bring phase conversions. Entering Sn^{4+} ions occupy the inwardly octahedral emptiness of oxygen packing, ear earlier occupied Ti^{4+} ions. The parameters of an elementary cell are determined. The results were provided in table 1.

Состав	a	b	с	β, °
CaTiSiO ₅	7,061±0,004	8,710±0,005	6,568±0,005	$113,86 \pm 0,04$
CaTi _{0,9} Sn _{0,1} SiO ₅	$7,06 \pm 0,01$	$8,72 \pm 0,01$	$6,57 \pm 0,01$	$113,84 \pm 0,05$
CaTi _{0,8} Sn _{0,2} SiO ₅	$7,06 \pm 0,01$	$8,74 \pm 0,01$	6,57±0,01	$113,83 \pm 0,05$
CaTi _{0,7} Sn _{0,3} SiO ₅	7,06±0,01	$8,76 \pm 0,01$	$6,57 \pm 0,01$	$113,83 \pm 0,05$
CaTi _{0,6} Sn _{0,4} SiO ₅	$7,07 \pm 0,01$	$8,78 \pm 0,01$	$6,57 \pm 0,01$	$113,72\pm0,05$
CaTi _{0,5} Sn _{0,5} SiO ₅	$7,07 \pm 0,01$	$8,80 \pm 0,01$	6,57±0,01	$113,82 \pm 0,05$
CaTi _{0,4} Sn _{0,6} SiO ₅	$7,07 \pm 0,01$	8,82±0,01	$6,57 \pm 0,01$	113,82±0,05
CaTi _{0,3} Sn _{0,7} SiO ₅	7,07±0,01	8,84±0,01	6,57±0,01	$113,80\pm 0,05$
CaTi _{0,2} Sn _{0,8} SiO ₅	$7,08 \pm 0,01$	$8,85 \pm 0,01$	$6,58 \pm 0,01$	$113,78 \pm 0,05$
CaTi _{0,1} Sn _{0,9} SiO ₅	7,08±0,01	$8,86 \pm 0,01$	6,58±0,01	$113,78 \pm 0,05$
CaSnSiO ₅	$7,08 \pm 0,01$	$8,88 \pm 0,01$	$6,58 \pm 0.01$	$113,77\pm0,05$

Table 1. The parameters of an elementary cells of CaTi_{1x}Sn_xSiO₅ hard solutions

Herewith exists the linear growing a parameter elementary cell, given big, than beside changed titanium ion, radius tin ion. The parameters of an elementary cell vary unsignificantly and are in rectilinear dependence on structure (figure 1).

Using offered author [4, 5] acceptance to got by us parameter brings about conclusion that in synthesized us sample possible to expect that as a result silicon - a deficit in tetrahedral position are found ~ 4 % atoms of titanium. However result of the chemical analysis synthesized us sample [SAO - (28,8 0,3)%, TiO₂ - (40,2 0,3)%, SiO₂ - (30,6 0,4)%, [SAO] : [TiO₂] : [SiO₂] = (0,977 ± 0,007) : (1,000 ± 0,004) : (0,985 ± 0,004)] point to not more than 1,5% silicon deficit.

There are bands of the absorption IR spectrum all synthesized composition with maximum at frequency 465 - 470 cm⁻¹ and 495 - 500 cm⁻¹, referred fluctuations of SiO₄ tetrahedron. The maximum in the field of 555 - 565 cm⁻¹ were referred to oscillatory absorption of SnO₆ and TiO₆ octahedrons. On measure of the increase the contents tin on UR spectrum appears clearly denominated maximum under 565 cm⁻¹, referred oscillatory absorption SnO₆ octahedron, which already under x = 0.4 masks weakly denominated maximum (565 cm⁻¹), belong to TiO₆ octahedron. they was determined factors of the refraction hard solutions



Figure 1. The dependency of parameters of elementary cells of CaTi_{1-x}Sn_xSiO₅ hard solutions



Figure 2. Infra-red spectra of (1) $CaSnSiO_5$, (2) $CaTi_{0,7}Sn_{0,3}SiO_5$ and (3) $CaTiSiO_5$

Parameters of refractions of the hard solutions were installed. The results were provided in table 2.

Состав	n _g	n _p	
CaTiSiO ₅	~1,876		
CaTi _{0,8} Sn _{0,2} SiO ₅	1,862	~2,37	
CaTi _{0,6} Sn _{0,4} SiO ₅	1,855	~2,37	
CaTi _{0,4} Sn _{0,6} SiO ₅	1,862	~2,37	
CaTi _{0,2} Sn _{0,8} SiO ₅	≤1,890	1,869	
CaSnSiO ₅	2,08	≤2,68	

Table 2. Parameters of refractions of the CaTi_{1-x}Sn_xSiO₅ hard solutions

Table 2. Specific electro-conductivity (σ), dielectric permeability (ϵ), width of the forbidden zone (energy of activation DE), molar polarization (P) and molecular polarizability (α) of hard solutions CaTi_{1-x}Sn_xSiO₅

	$\sigma (om^{-1}.cm^{-1})$	ε	ΔE (ev)	Р	$\alpha . 10^{23}$
CaTiSiO ₅	3,802.10 ⁻¹²	39	0,973	51,62	2,0472
CaTi _{0,9} Sn _{0,1} SiO ₅	$2,884.\ 10^{-12}$	43	0,970	52,09	2,0659
CaTi _{0,8} 8Sn _{0,2} SiO ₅	$2,239.10^{-12}$	43	0,983	52,27	2,073
CaTi _{0,7} Sn _{0,3} SiO ₅	$1,905.10^{-12}$	48	1,005	52,65	2,088
CaTi _{0,6} Sn _{0,4} SiO ₅	$1,489.10^{-12}$	53	1,028	53,30	2,114
CaTi _{0,5} Sn _{0,5} SiO ₅	1,318.10 ⁻¹²	56	1,055	53,53	2,123
CaTi _{0,4} Sn _{0,6} 6SiO ₅	$1,000.10^{-12}$	62	1,073	54,00	2,142
CaTi _{0,3} Sn _{0,7} 7SiO ₅	$7,244.10^{-13}$	65	1,097	54,19	2,149
CaTi _{0,2} Sn _{0,8} SiO ₅	$4,721.10^{-13}$	70	1,118	54,30	2,154
CaTi _{0,1} Sn _{0,9} SiO ₅	$2,884.10^{-13}$	75	1,144	54,63	2,1667
CaSnSiO ₅	2,366.10 ⁻¹³	79	1,165	54,91	2,178

All of synthesized solid solutions are dielectrics with semiconductor nature of conduction. Change ion Ti^{4+} on Sn^{4+} brings the small reduction the specific conductivity.



Figure 2. The specific conductivity, width of the forbidden zone (energy of activation) and dielectric permeability of the $CaTi_{1-x}Sn_xSiO_5$ hard solutions.

Under full change ion Ti^{4+} on ions Sn^{4+} conduction sample decreases on one order. Herewith exists small increase the width of the forbidden zone, dialectical permeability and molecular polarization.

References

- Takenouchi S., Hydrothermal Synthesis and Consideration of Genesis of Malayaite. Mineral. Deposita, 1971, V. 6, P.335 – 347
- [2] Grigoryan R.A., Grigoryan L.A., Babayan G.G. Synthesis of ZnFe₂O₄ Zn₂ZrO₄ Solid Solutions. Inorganic Materials, 2001 V. 37, No. 3, p. 298.
- [3] Speer J.A., Gibbs G.V. The crystal structure of sinthetic titanite, CaTiOSiO₄, and the domain texture of natural titanite. Am. Minreral., 1976, V. 61, P. 238 247.
- [4] Hollanbaugh C.L., Rosenberg P.E. Substition of Ti for Si in Titanite and New End-member Cell Dimension for Titanit. Am. Mineralogist, 1983, V. 68, № 1-2, P. 177 – 180.
- [5] Buison G. J. Etude Par rayon's X at Neutrons de la Isomorphe ATiTO₅. Phys. Chem. Solids, 1970, V. 3, № 5, P. 1171 –1183.