

**Limits of replacement of Zr and Ti for Al in kosnarite solid solution
including alkali and alkaline earth charge-compensating cations**

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Limits of replacement of framework forming octahedral cations: Ti^{4+} and Zr^{4+} for Al^{3+} in kosnarite were studied by a method of high-temperature solid phase synthesis at atmospheric pressure. Influence of various types of replacements in solid solution $Me^{n+}_{(1+X)/n}Al_x(Ti,Zr)_{2-X}(PO_4)_3$, where Me^{n+} is Na^+ , K^+ , Cs^+ , Ca^{2+} , Sr^{2+} , Ba^{2+} , for the sizes of a crystal cell and limitations of an isomorphous substitutions within kosnarite structure were interpreted by the crystal-chemical analysis.

Key words: kosnarite, solid solution, isomorphism, crystal-chemical analysis

Citation: Martynov, K. V., T. S. Lapitskaya, I. G. Tananaev, A. M. Kovalsky (2012), Limits of replacement of Zr and Ti for Al in kosnarite solid solution including alkali and alkaline earth charge-compensating cations, *Vestn. Otd. nauk Zemle*, 4, NZ9001, doi:10.2205/2012NZ_ASEMPG.

The mineral kosnarite, opened two decades ago, on a chemical composition is complex orthophosphate $KZr_2(PO_4)_3$ and crystallizes in a trigonal crystal system (s.g. R -3 c, Z=6). Thanks to the properties, synthetic analogs of kosnarite were known long before its discovery. NaSiCon ($Na_{1+x}Zr_2Si_xP_{3-x}O_{12}$) was studied as solid electrolytes, and NZP ($NaZr_2(PO_4)_3$) – as matrixes for components of radioactive waste and catalysts for organic synthesis. Thus, kosnarite is natural analogue of the most important in the technological relation of chemical compounds just as a pyrochlore, a perovskite, zeolites and other mineral types. Therefore, as it is accepted in other cases, all compounds and solid solutions having kosnarite's chemical composition and structure, we will call his name.

Despite simplicity of a chemical composition given above compounds, kosnarite represents the multicomponent solid solution possessing wide isomorphism of all types of cations entering into it. Its crystal-chemical formula can be presented as $(^{VI}M1)(^{VIII}M2)_3\{^{VI}L_2(^{IV}TO_4)_3\}$, where ^{IV}T is framework forming tetrahedral cations with charge $n = +4 - +6$: Si, Ge, Sn, P, V, As, Sb, S, Se, Mo, etc., ^{VI}L is framework forming octahedral cations with charge $n = +3 - +5$: Al, Ga, In, Cr, Fe, Ti, Zr, Hf, Nb, etc. These two types of polyhedra (TO_4 and LO_6), linking by corner atoms of oxygen, built the three-dimensional framework possessing a negative charge which is compensated by the cations located in $^{VI}M1$ and $^{VIII}M2$ cavities of a framework. $^{VI}M1$ position is preferable and only after its settling, cations occupy $^{VIII}M2$ position. Thus, extra frame positions can be vacant ($\square$) or are occupied with cations with charge $n = +1 - +4$, for example: alkali, alkaline earth, rare-earth metals, actinides, etc.

Ionic conductivity, "zeolitic" properties, ability to connect toxic and radioactive elements and other useful qualities of kosnarite correlate with the nature of extra frame positions settling. Thanks to its predisposition to isomorphism it is possible to change purposefully composition and properties of kosnarite. Isomorphous replacements in kosnarite are possible in all crystal-chemical positions, and all of them can influence filling of frame cavities. First, it is actually isomorphism of extra frame cations which can be described by replacement reaction: $mM^{n+} = nM^{m+} + (m-n)\square$; crystal-chemical formula of this type of solid solution is $(M^{n+}_{(m/n)X}M^{m+}_{1-X})_{1/m}L_2(TO_4)_3$, where the end-member fraction changes within $X=0-1$. Replacement of cations being in a tetrahedral position is described by reaction: $kT^{n+} + (n-m)\square = kT^{m+} + (n-m)M^{k+}$, crystal-chemical formula is $M^{k+}_{\{3(5-n)+X(n-m)+1\}/k}L_2T^{m+}_XT^{n+}_{3-X}O_{12}$, where $X=0-3$. At last, isomorphism of octahedral cations - $kL^{n+} + (n-m)\square = kL^{m+} + (n-m)M^{k+}$, crystal-chemical formula is $M^{k+}_{\{2(4-n)+X(n-m)+1\}/k}L^{m+}_XL^{n+}_{2-X}(PO_4)_3$, where $X=0-2$. To compensate of a framework charge during heterovalent replacements of framework forming cations it needs to change of an extra frame vacancies/cations ratio. It also is the main mechanism of updating of composition and properties of kosnarite.

From given above reactions and crystal-chemical formulas for different types of replacements in

kosnarite solid solution it is possible to find stoichiometric constraints with heterovalent isomorphism. Since the substitution of Ti or Zr for Al which is accompanied by the filling of vacancies alkali and alkaline earth charge-compensating cations according to stoichiometric constraints X can change from 0 to 2. Actually, as showed by experiments [Mouahid, 2000; Sysoeva, 2009], limiting values $X_{\max}$ are much less. For definition of replacement limits of tetravalent octahedral cations for Al we have studied four pseudo-binary sections of multicomponent system $\text{Na}_2\text{O}-\text{CaO}-\text{Al}_2\text{O}_3-\text{TiO}_2(\text{ZrO}_2)-\text{P}_2\text{O}_5$ by a method of high-temperature solid phase synthesis at atmospheric pressure.

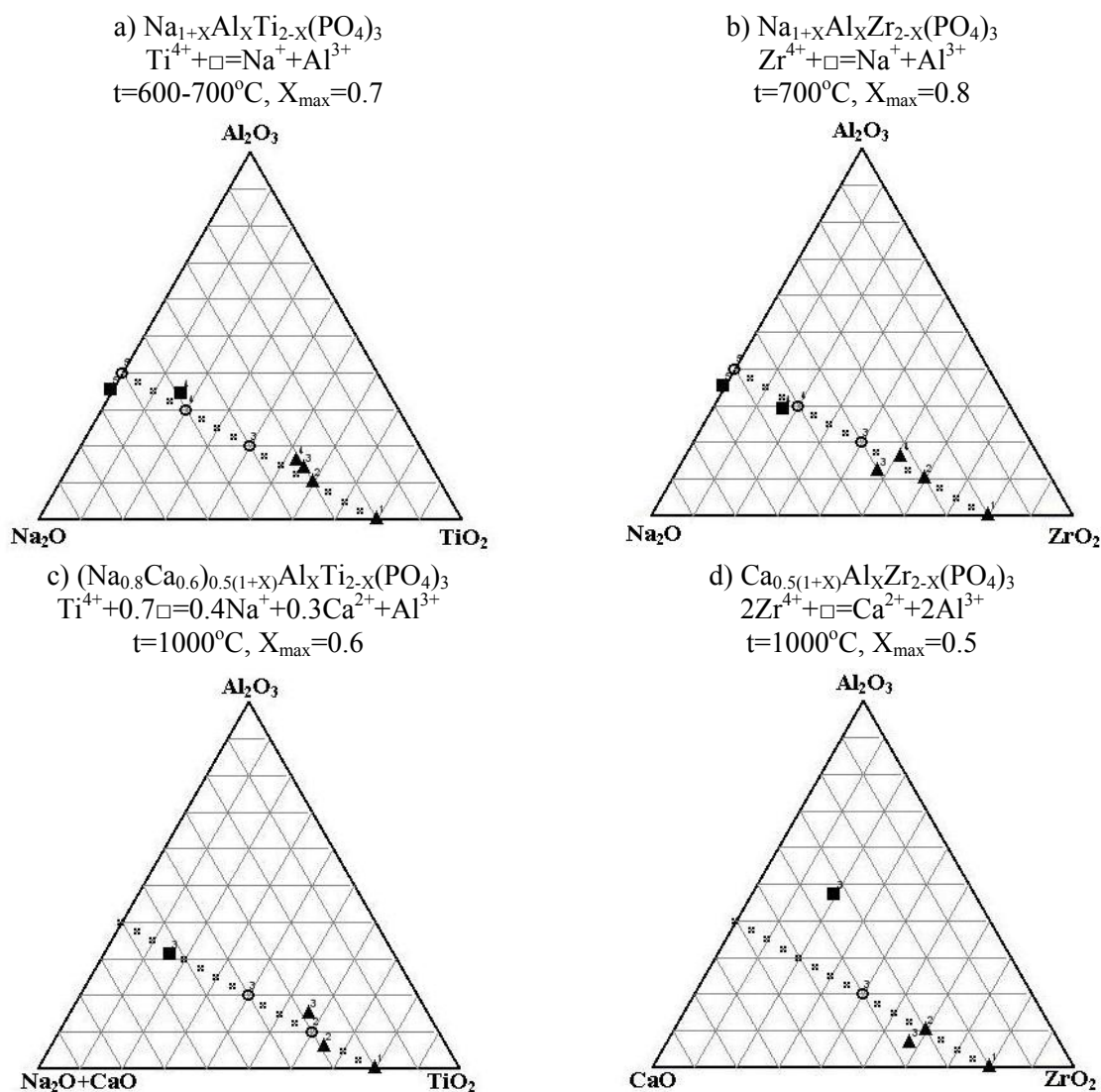


Fig. 1. Stability fields of kosnarite in the studied sections: *** – sections, ○ – compositions of initial mixtures, ▲ – kosnarite, ■ – tetragonal phase

Precursors for synthesis were prepared by sol-gel technique from starting reagents: NaNO_3 , CsNO_3 , $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{Zr}(\text{OH})_4$ и $\text{TiOC}_2\text{O}_4 \cdot \text{H}_2\text{O}$, 70% HNO_3 , 85% H_3PO_4 , 25% ammonia water, over some stages: 1) dissolution and mixing for sol production, 2) gel maturing at room temperature, 3) drying at 120°C for xerogel production, 4) calcinating at 300°C for removal of the flying. Synthesis was carried out at $600-700^\circ\text{C}$ for alkali kosnarites and $900-1000^\circ\text{C}$ for alkaline earth ones. Products of synthesis were studied by X-ray powder diffraction (XRPD) method and electron microprobe analysis (EMPA). For phase analysis XRPD patterns of the samples have been removed on DRON-4 X-ray diffractometer, using $\text{CuK}\alpha$ radiation with Ni-filter ($\lambda=1.5418 \text{ \AA}$). For specification of crystal phases structures XRPD patterns of the samples have been removed at 25°C on Bruker D8 ADVANCE X-ray diffractometer, using $\text{CuK}\alpha_1$ radiation ($\lambda=1.5406 \text{ \AA}$) with step of $0.010^\circ 2\theta$. In this case angular positions of reflections were corrected by the internal standard (spectral pure Si, $a=5.4305 \text{ \AA}$). CRYSFIRE 2004 (TREOR90 procedure) and CHEKCELL computer programs

have been used for definition of reflection indexes and calculation of unit cell parameters. Chemical compositions of synthesized phases have been studied by a scanning electron microscope (SEM) 1) Tescan Vega II XMU combining with X-ray energy dispersive spectrometer INCAx-sight attached with BSE+SE detectors, 2) Jeol JSM-U3 with Getac Edison-32 system, which involved WinEDS digital scanner and Eumex X-ray energy dispersive spectrometer based on Si(Li) semiconductor detector equipped with an ultrathin polymer window. For EMPA the samples have been pressed in tablets from polystyrene, polished and covered graphite.

Results of experiments on kosnarite stability in the studied sections are shown in Fig. 1, together with the parameters of the synthesis, crystal-chemical formulas of the solid solutions and substitution reactions. The stability field of alkaline earth kosnarite compounds was more limited than for the alkali ones. For $X > X_{\max}$ decomposition of the solid solution is observed and in poor Ti or Zr field another phase crystallizes which is defined by us as a tetragonal, also forming a solid solution. Thus, the decomposition of solid solution in the studied sections was combined with the phase transition.

Table 1. The unit cell volumes of Ti (a) and Zr (b) kosnarites according to our and literature data and calculated values of the reduced ionic radii of extra frame cations $R^* = (R_M^{n+} + (n-1) \cdot R_{\square})/n$

Cation	a) $M^{n+}_{1/n}Ti_2(PO_4)_3$, $R_{\square}=0.53 \text{ \AA}$				b) $M^{n+}_{1/n}Zr_2(PO_4)_3$, $R_{\square}=0.55 \text{ \AA}$			
	$R_M^{n+}, \text{ \AA}$	$R^*, \text{ \AA}$	$V, \text{ \AA}^3$	Source for V	$R_M^{n+}, \text{ \AA}$	$R^*, \text{ \AA}$	$V, \text{ \AA}^3$	Source for V
Na ⁺	0.95	0.95	1360	[Sysoeva, et al., 2009]	0.95	0.95	1528	[Kotelnikov, et al., 2000a]
K ⁺	1.33	1.33	1400	[Sysoeva, et al., 2009]	1.33	1.33	1573	[Kotelnikov, et al., 2000a]
Cs ⁺	1.68	1.68	1437	the equation shown in Fig. 2a	1.68	1.68	1582	our data
Ca ²⁺	1.01	0.78	1341	[Sysoeva, et al., 2009]	1.01	0.78	1517	[Kotelnikov, et al., 2000b]
Sr ²⁺	1.16	0.85	1349	[Sysoeva, et al., 2009]	1.16	0.86	1530	[Kotelnikov, et al., 2000b]
Ba ²⁺	1.36	0.95	1359	the equation shown in Fig. 2a	1.36	0.96	1534	the equation shown in Fig. 2b

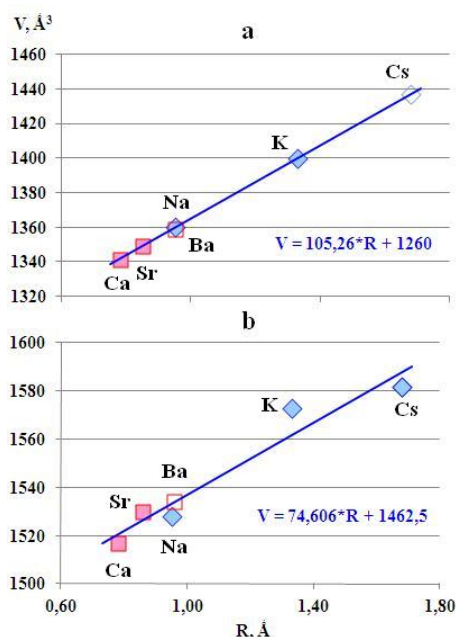


Fig. 2. The dependences of the unit cell volumes of $M^{n+}_{1/n}Ti_2(PO_4)_3$ (a) and $M^{n+}_{1/n}Zr_2(PO_4)_3$ (b) kosnarites from the reduced extra frame cation

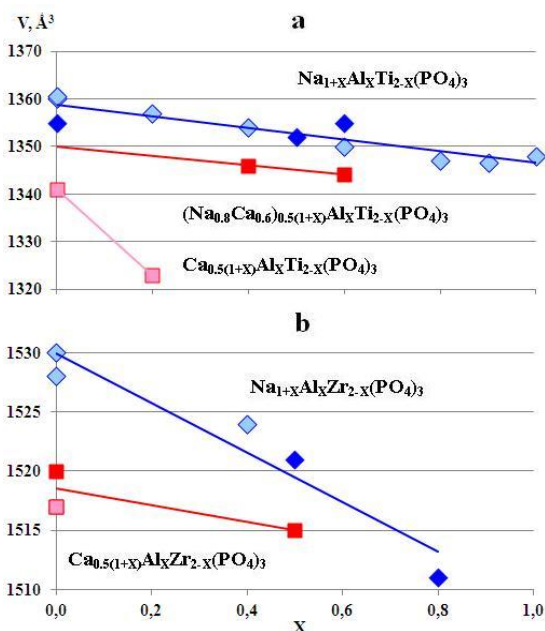


Fig. 3. The dependences of the unit cell volumes from the compositions of Al-containing Ti (a) and Zr (b) kosnarites according to our (filled symbols)

ionic radius $R^* = (R_M^{n+} + (n-1) \cdot R_{\square})/n$

and literature (open symbols) data

Conclusions

1. Installed directly proportional dependence of the unit cell volume of kosnarite solid solution from the reduced ionic radius of extra frame cations.
2. Limitation of miscibility in the replacement of Ti and Zr for Al in kosnarite solid solution due to the conflict consequences of this process: the compression of the crystal structure with increasing charge of the frame on one side and a positive volume effect accompanying the replacement of the other.
3. Both observed effects can be used to predict the properties of kosnarite solid solution for different types of isomorphous substitution.

This work was supported by The State Contract № 16.740.11.0538 from 16.05.2011.

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