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A Thermal Study of the New Mineral Belomarinaite $KNaSO_4$

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Abstract—For the first time, the thermal behavior of a new mineral belomarinaite $KNaSO_4$ coming from volcanic exhalations (trigonal syngony, Sp. gr. $P3m1$, $a = 5.6072(3)$, $c = 7.1781(4)$ Å, $V = 195.45(2)$ Å^3) was studied on a natural sublimate sample from the 2012–2013 Tolbachik Fissure Eruption and its synthetic analogue, a low temperature (LT) polymorph of KNaSO4 (Sp. gr. P3m1) in the range 30–800°C (high-temperature X-ray diffraction) и 30–1000°C (DSC and TG). The mineral is stable up to a temperature of 475 ± 10°C, at which it has a polymorphic transformation into a high-temperature (HT) hexagonal polymorphic modification (Sp. gr. $P6_3/mmc$), which is stable until melted at 800°C based on DSC. The thermal expansion of both modifications is sharply anisotropic, and in the case of the HT phase the parameter a has a U-shape dependence with a minimum at T = 620°C. The volumetric expansion of the α_V HT phase is greater than that for the LT phase by factors of 2–2.5 on average.

Keywords: volcanic exhalations, new mineral, belomarinaite, Tolbachik volcano, 2012–2013 eruption, high-temperature anhydrous sulfate, thermal expansion

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INTRODUCTION

In recent years, an active study of minerals from volcanic exhalations has been carried out, including the search and identification of the conditions for their formation with changes in temperature and composition of gases. The eruptions of Tolbachik Volcano in 1975-1976 and 2012-2013 are among the most studied mafic eruptions (*Bolshoye treshchinnoe ...,* 1984; Belousov et al., 2015). New mineral species are often found in the exhalations of these eruptions. Anhydrous and aqueous sulfates occupy a special place among the minerals of volcanic exhalations of the 1975–1976 Great Tolbachik Fissure Eruption (GTFE) and the 2012–2013 Tolbachik Fissure Eruption (TFE). Among the anhydrous sulfates discovered in recent years, one can distinguish such minerals as 1 ivsite $Na_3H(SO_4)_2$ (Filatov et al., 2013), bubnovite $K_2Na_8Ca(SO_4)_6$ (Gorelova et al., 2016), puninite $Na_2Cu_3O(SO_4)_3$ (Siidra et al., 2017), dravertite $CuMg(SO_4)_2$ (Pekov et al., 2017), saranchinaite $Na_2Cu(SO_4)_2$ (Siidra et al., 2018), itelmenite $Na_2CuMg_2(SO_4)_4$ (Nazarchuk et al., 2018), belomarinaite $KNaSO_4$ (Filatov et al., 2019), koryakite $NaKMg_2Al_2(SO_4)_6$ (Siidra et al., 2020), natroaphthitalite $Na_3K(SO_4)_2$ (Pekov et al., 2020b), metathénardite (Pekov et al., 2020b), petrovite $Na_{10}CaCu_2(SO_4)_8$ (Filatov et al., 2020), and dobrovolskyite $Na_4Ca(SO_4)_3$ (Shablinskii et al., 2020). The most complete list of minerals found on Tolbachik Volcano is given in a review work (Pekov et al., 2020a).

The sample in which belomarinaite was found after cooling to atmospheric conditions (Filatov et al., 2019), was taken on May 27, 2013 at the Tolud lava field on the TFE lava flow, the temperature of which was about 1000°C. The sample is a product of degassing of an active lava flow of trachyandesite composition and turned out to be a new mineral species, which was named belomarinaite.

The mineral is a dendritic (skeletal) formation of a pale blue-green color, and belongs to the trigonal system ($P3m1$), unit cell parameters are $a = 5.6072$ (3), $c = 7.1781$ (4) Å, $V = 195.45$ (2) Å^3. The structure of the mineral was first described on a synthetic sample in (Okada and Osaka, 1980) and determined more accurately using a natural sample (Filatov et al., 2019). Comparison of crystallographic data for belomarinaite and similar minerals and chemical compounds is given in Table 1. The mineral was approved by the Commission on New Minerals, Names and Classifi-

Table 1. Crystallographic data on belomarinaite and similar minerals and chemical compounds

Mineral	Formula	sp. gr.	a, Å	c, Å	V, Å^3	Reference
Aphthitalite	$K_3Na(SO_4)_2$	$P{-}3m1$	5.680(1)	7.309(3)	204.2(1)	1
Belomarinaite	$KNa(SO_4)$	$P3m1$	5.6072(3)	7.1781(4)	195.45(2)	2
Natroaphthitalite	$KNa_3(SO_4)_2$	$P{-}3m1$	5.6014(3)	7.1507(5)	194.30(1)	3
Moenite	$(NH_4)K_2Na(SO_4)_2$	$P{-}3m1$	5.7402(3)	7.435(1)	212.16(1)	4
Metathénardite	Na_2SO_4	$P6_3/mmc$	5.347(1)	7.088 (2)	175.48(7)	5
	$\alpha{-}K_2SO_4$ (740°C)	$P6_3/mmc$	5.917(4)	8.182(4)	248.3(1)	6
Bubnovite	$K_2Na_8Ca(SO_4)_6$	$P31c$	10.804(3)	22.011(6)	2225(2)	7
Hanksite	$Na_{22}K(SO_4)_9(CO_3)_2Cl$	$P6_3/m$	10.490(1)	21.240(1)	2024(1)	8
Dobrovolskyite	$Na_4Ca(SO_4)_3$	$R3$	15.7223(2)	22.0160(5)	4713.1(2)	9

Note. 1 (Okada, Osaka, 1980); 2 (Filatov et al., 2019); 3 (Shchipalkina et al., 2018); 4 (Chukanov et al., 2015); 5 (Pekov et al., 2020b); 6 (Arnold et al., 1981); 7 (Gorelova et al., 2016); 8 (Kato and Saalfield, 1972); 9 (Shablinskii et al., 2020).

cation of Minerals of the International Mineralogical Association on April 4, 2018. The reference sample of the new mineral species was transferred to the Mineralogical Museum of St. Petersburg State University (catalog number 1/19678).

In the crystal structure of belomarinaite, there are two symmetrically independent positions of K atoms, two positions of Na atoms, two S and four O (Okada and Osaka, 1980; Filatov et al., 2019)... The K (1) and K (2) cations are coordinated by twelve and ten oxygen atoms with average bond lengths of 3.06 Å and 2.87 Å, respectively. Na (1) is coordinated by six oxygen atoms to form an octahedron with bonds characteristic of Na–O (2.284–2.403 Å). Na (2) is coordinated by ten oxygen atoms with extremely elongated bonds (2.8 Å on average). The structure, as is typical for sulfates, is insular with isolated SO_4 tetrahedra.

HT Na_2SO_4 and K_2SO_4 polymorphs are isostructural, their crystal structures were determined more accurately in the hexagonal system, Sp. gr. $P6_3/mmc$ at elevated temperatures up to 420 and 640°C in (Naruse et al., 1987; Arnold et al., 1981), respectively. In the Na_2SO_4–K_2SO_4 system at high temperatures, there are a number of continuous solid solutions based on these hexagonal polymorphs, the temperature of the polymorphic transition for equimolar composition corresponds to approx. 470°C, the beginning of melting is about 880°C (Eysel et al., 1985; Kumari and Secco, 1983), the polymorphic transition of these solid solutions of the ordering - disordering type in this system is also discussed in (Kumari and Secco, 1983). Information on the thermal expansion of the low-temperature polymorph $KNaSO_4$ are given only in the range 300–500 K according to dilatometry data (Kassem et al., 2007).

The thermal behavior of a mineral of high-temperature genesis is of undoubted interest. In this work, we study the thermal behavior of natural and synthetic $KNaSO_4$ carried out *in situ* using methods of high-temperature X-ray diffraction of polycrystals and thermal analysis in atmospheric air.

EXPERIMENT

Thermal analysis (DSC and TG). The study of a natural sample of belomarinaite was carried out on a Netzsch STA 449-F3-Jupiter device in a ceramic crucible in air at an average heating rate of 10°C/min. Since the sample was in air for a long time, it was first heated in the temperature range 30–800°C, cooled and reheated in the range of 30–1000°C. The temperature of phase transformations was determined from the maximum of the peaks at the DSC curve (Fig. 1).

High-temperature X-ray diffraction. The studies were carried out using a Rigaku Ultima IV diffractometer ($CuK\alpha_{1+2}$, 40 kV, 30 mA, reflection geometry, high-speed energy-dispersive detector DTEX/ULTRA) with a high-temperature chamber “SHT-1500”. Diffraction angle range 2θ was 10–80 °. The sample was prepared on a substrate by deposition from a heptane suspension. Thermal expansion coefficients were determined using the Theta To Tensor software package (Bubnova et al., 2013).

Belomarinaite and its synthetic analogue were investigated by high-temperature X-ray diffraction. A synthetic analogue was obtained by heating a mechanical equimolar mixture of potassium and sodium sulfates to 800°C. At 700°C, the sample became a hexagonal homogeneous solid solution. This homogeneous solid solution was examined during cooling from 800°C to room temperature in 20°C steps. Since the synthetic sample was studied during cooling, natural belomarinaite was first heated to 800°C with a temperature step of 100°C, and only then was the study carried out during cooling with a smaller step of 10°C.

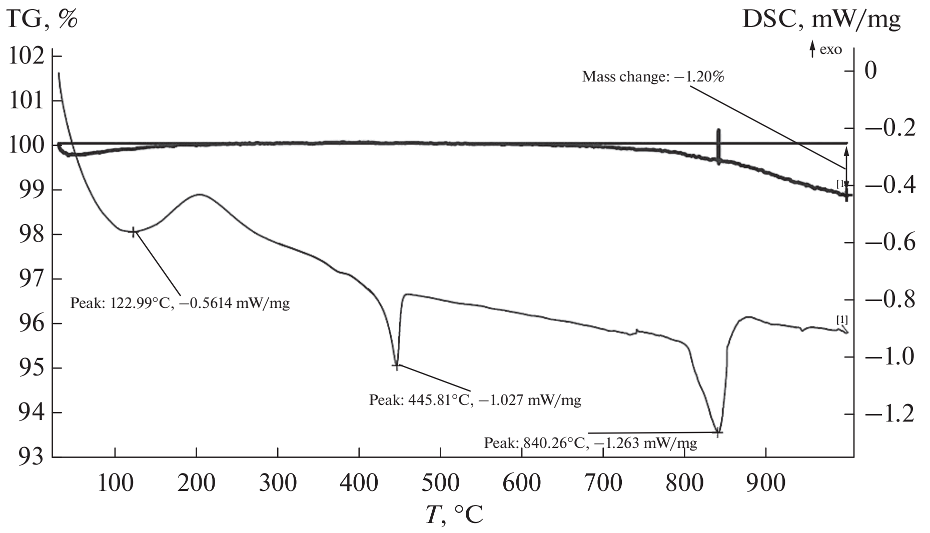

Fig. 1. DSC and TG curves for belomarinaite.

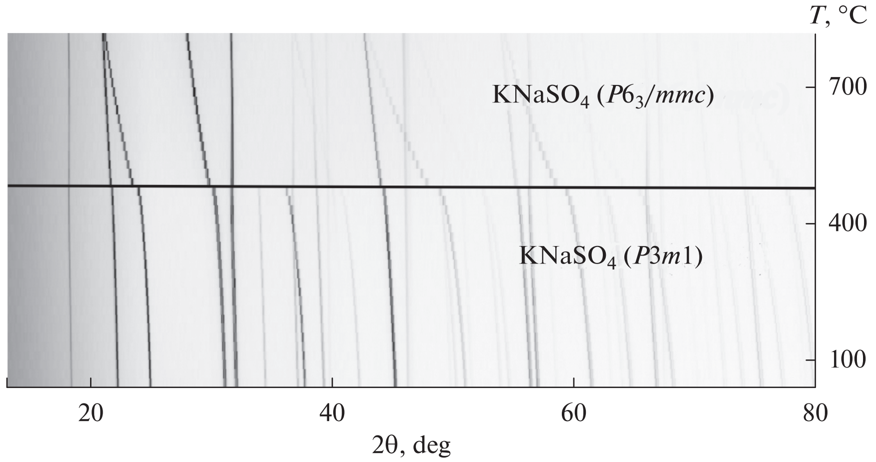

Fig. 2. Thermal phase transformation upon cooling in belomarinaite. The horizontal line indicates the phase transition temperature.

RESULTS

Thermal analysis data (DSC/TG). The TG curve shows an insignificant weight loss (1.2%) in the temperature range 700–1000°C. The DSC curve shows three effects (see Fig. 1), which agree with the literature data for a synthetic sample. In (Kassem et al., 1993), it was suggested that the first broad exothermic peak (123°C) corresponds to a second-order phase transition; our thermal X-ray data do not confirm this effect (Fig. 2). At a temperature of 446°C, a polymorphic transition from the LT phase to the high-temperature phase occurs, and at 840°C the high-temperature phase melts.

Polymorphic trigonal-hexagonal transition according to high-temperature X-ray diffraction data. High-temperature X-ray diffraction, as mentioned in the Experiment section, was carried out during cooling from 800°C. The results turned out to be similar for natural and synthetic samples. In the diffraction patterns of natural and synthetic samples, the peaks of the HT phase of $KNaSO_4$ when cooling down to 470 ± 5°C and 480 ± 10°C, respectively (see Fig. 2). With further cooling, a transition to LT-modification $KNaSO_4$ occurred through the two-phase region, with peaks of both phases being observed at 470°C, below the peaks of only trigonal belomarinaite were found: the transition is reversible as noted in (Eysel et al., 1985).

The difference in the phase transition temperature according to the data of thermal analysis and high-temperature X-ray diffraction (~ 20°C) may be due to a non-standard combination of experimental modes:

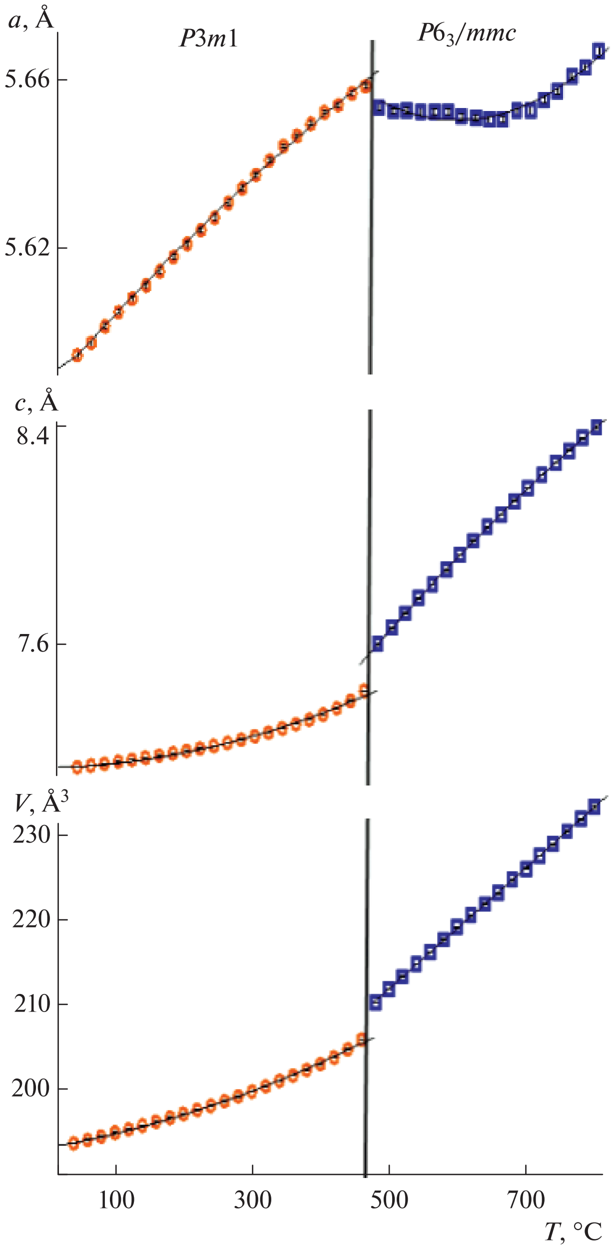

Fig. 3. Dependence of the parameters and volume of the unit cell on the temperature of belomarinaite. The vertical line shows the phase transition boundary.

rapid heating in thermal analysis and slow cooling during high-temperature X-ray diffraction measurements.

According to the study of the system (Eysel et al., 1985; Kumari and Secco, 1983), the HT modification of $KNaSO_4$ is a solid solution of sodium and potassium sulfates. The diffraction pattern of the HT $KNaSO_4$ modification corresponds to HT phases of Na_2SO_4 (Naruse et al., 1987) and of K_2SO_4 (Arnold et al., 1981) crystallizing in Sp.gr. $P6_3/mmc$...

Thermal expansion of polymorphic modifications. Changes in the parameters and volume of the unit cell of both polymorphic modifications as a function of temperature are plotted in Fig. 3. Since the process of thermal expansion is reversible and has no hysteresis, we can discuss the plots as measured during heating, although the survey was carried out with cooling from 800°C (see the Experiment section). In both phases, the parameters and unit cell volume increase with increasing temperature. The sharply anisotropic character of the LT phase is due to the tendency of the parameters of its cell to reach the values of the parameters of the HT phase. However, the polymorphic transition is completed without reaching the equality of parameters and volume (a_{LT} = 5.6568 (8) Å $\neq a_{HT}$ = 5.666 (2) Å, c_{LT} = 7.492 (1) Å $\neq c_{HT}$ 7.597 (1) Å and V_{LT} = 208.3 (3) Å$^3 \neq V_{HT}$ = 210.54 (6) Å^3 at 470 ± 5°C). That is, the parameters make insignificant jumps; therefore, this is a transition of the first thermodynamic order with an insignificant jump in volume (ΔV = 2.2 Å^3). Directionality of polymorphic trigonal—hexagonal transformation is consistent with the well-known tendency of increasing symmetry in a substance with increasing temperature. The nature of the thermal expansion of the LT phase is due to its tendency to turn into the HT-phase (Filatov, 1990). The uniqueness of this polymorphic transformation consists, first of all, in the fact that it reaches its virtually complete termination.

It can be seen (see Fig. 3) that for the LT polymorph parameter the dependence of a is a convex curve, while the curves for the parameter c and volume V are concave. For the LT phase, the dependence of the parameter c and volume V are convex, while for the parameter a a U-shaped relationship is observed with a minimum at 620°C. The parameters and volume of the LT-phase were approximated by polynomials of degree 2 in the temperature range 30–475°C:

$$a = 5.591 + 0.206 \times 10^{-3} t - 0.110 \times 10^{-6} t^2,$$

$$c = 7.17 - 0.013 \times 10^{-3} t + 1.288 \times 10^{-6} t^2,$$

$$V = 194.235 + 13.177 \times 10^{-3} t + 29.900 \times 10^{-6} t^2.$$

The parameters and volume of the HT-phase were also approximated by polynomials of the second degree in the range of 475–800°C:

$$a = 5.756 - 0.347 \times 10^{-3} t + 0.287 \times 10^{-6} t^2,$$

$$c = 6.064 + 3.720 \times 10^{-3} t - 0.966 \times 10^{-6} t^2,$$

$$V = 176.055 + 75.442 \times 10^{-3} t - 3.884 \times 10^{-6} t^2.$$

The principal values of the expansion tensor were calculated using the approximation coefficients (Bubnova et al., 2013). Table 2 lists the thermal expansion coefficients for natural and synthetic samples at several temperatures. It is seen that for the LT phase the expansion along the axis c increases from 15 to 157 × 10^{-6}°C^{-1}, while for the HT phase, the expansion along the axis c substantially decreases, from 370 to 270 ×

Table 2. Coefficients of thermal expansion of belomarinaite and its synthetic analogue at several temperatures

Phase	T, °C	Natural sample/synthetic sample		
		α_a (× $10^{6\circ}C^{-1}$)	α_c (× $10^{6\circ}C^{-1}$)	α_V (× $10^{6\circ}C^{-1}$)
$P3m1$	30	35(1)/33(1)	9(5)/15(5)	80(5)/83(5)
	100	33(1)/31(1)	34(2)/40(3)	100(2)/102(3)
	200	28(1)/29 (1)	69(2)/70 (1)	127(2)/128(1)
	300	24(1)/27 (1)	104(5)/100(2)	154(5)/153(2)
	400	21(1)/24(1)	138(4)/129(4)	180(4)/178(5)
	475	18(1)/22(1)	157(5)/151(5)	194(5)/196(5)
$P6_3/mmc$	475	−13(1)/−14(2)	370(2)/374(2)	342(3)/345(3)
	500	−10(1)/−12(2)	358(1)/365(2)	337(1)/340(3)
	600	0(1)/1(1)	322(1)/325(2)	321(1)/326(2)
	700	10(1)/13(1)	289(2)/287(1)	308(2)/314(2)
	800	16(1)/26(2)	270(2)/256(2)	302(2)/305(3)

$10^{-6\circ}C^{-1}$. The volumetric coefficients of thermal expansion for the modifications vary in the intervals for which they were studied, for the LT-phase from 80 to 200 ($\times 10^{-6\circ}C^{-1}$) and for the HT phase from 350 to 300 (× $10^{-6\circ}C^{-1}$). The thermal expansion in both modifications is sharply anisotropic; during the polymorphic transition, the volume expansion doubles; on the whole, the expansion of the HT modification increases by factors of 2–3 relative to the expansion of the LT phase.

The crystal structure of belomarinaite can be described in terms of pseudo-dense cation packings (O'Keeffe and Hyde, 1985; Krivovichev and Filatov, 1999; Vegas, 2000). Potassium and sodium cations form a pseudo-dense cation packing with hexagonal layers parallel to the (001) plane. The thermal expansion of such structures is similar to the classical thermal expansion of layered compounds, which explains the maximum thermal expansion of belomarinaite along the axis *c*, that is, perpendicular to the layers of the most dense hexagonal packing (Fig. 4). Most likely, the sharp increase in the thermal expansion of the crystal structure of the high-temperature modification along the *c*-axis is due to oscillations and afterwards with rotation of SO_4 tetrahedra. This is confirmed by the interpretation of the crystal structures of K_2SO_4 and Na_2SO_4 – $P6_3/mmc$ at high temperatures according to monocrystal data (Arnold et al., 1981; Naruse et al., 1987).

CONCLUSIONS

For a new mineral type of volcanic exhalations of belomarinaite $KNaSO_4$ (sp. gr. $P3m1$), which is a product of degassing of an active trachyandesite lava flow, the thermal behavior was studied in the range of 30–800°C in air.

A high-temperature modification of this mineral is shown to exist above 470°C. This allows one to expect that under favorable conditions (the presence of impurities), a high-temperature polymorphic modification can be found in nature under atmospheric conditions. This was the case, for example, for thenardite Na_2SO_4 (sp. gr. *Fddd*), for which the scientific group of prof. I.V. Pekov discovered a high-temperature modification called metatenardite Na_2SO_4 (sp. gr. $P6_3/mmc$) among the products of exhalations of Tolbachik Volcano (Pekov et al., 2020b). The discovery of such a high-temperature modification was predicted for the first time in (Lacroix, 1910).

The causes of a sharp anisotropy of thermal expansion in both modifications have been identified. Volumetric expansion α_V varies for the low-temperature phase in the range 80–200 × $10^{-6\circ}C^{-1}$, and for high-temperature phase in the range 350–300 × $10^{-6\circ}C^{-1}$ for the temperatures at which they were studied, i.e., the expansion of the HT phase exceeds the expansion of the LT phase by an average of 2–2.5 times. The direction of the polymorphic trigonal–hexagonal transformation is consistent with the well-known tendency to increase the symmetry of a substance upon heating. The sharply anisotropic character of the LT phase is due to the tendency of its unit cell parameters to converge to the parameters of the HT phase. However, completing the polymorphic transition and not reaching equality, the crystal structure makes an insignificant jump $\Delta V = 2.2$ Å^3, i.e., this polymorphic transition is a first-order phase transition.

The studies were carried out using the equipment of the resource center of St. Petersburg State University "X-ray Diffraction Research Methods". Thy high-temperature X-ray diffraction photography was carried out at the resource center "X-ray Diffraction Research Methods" of the scientific park of St. Peters-

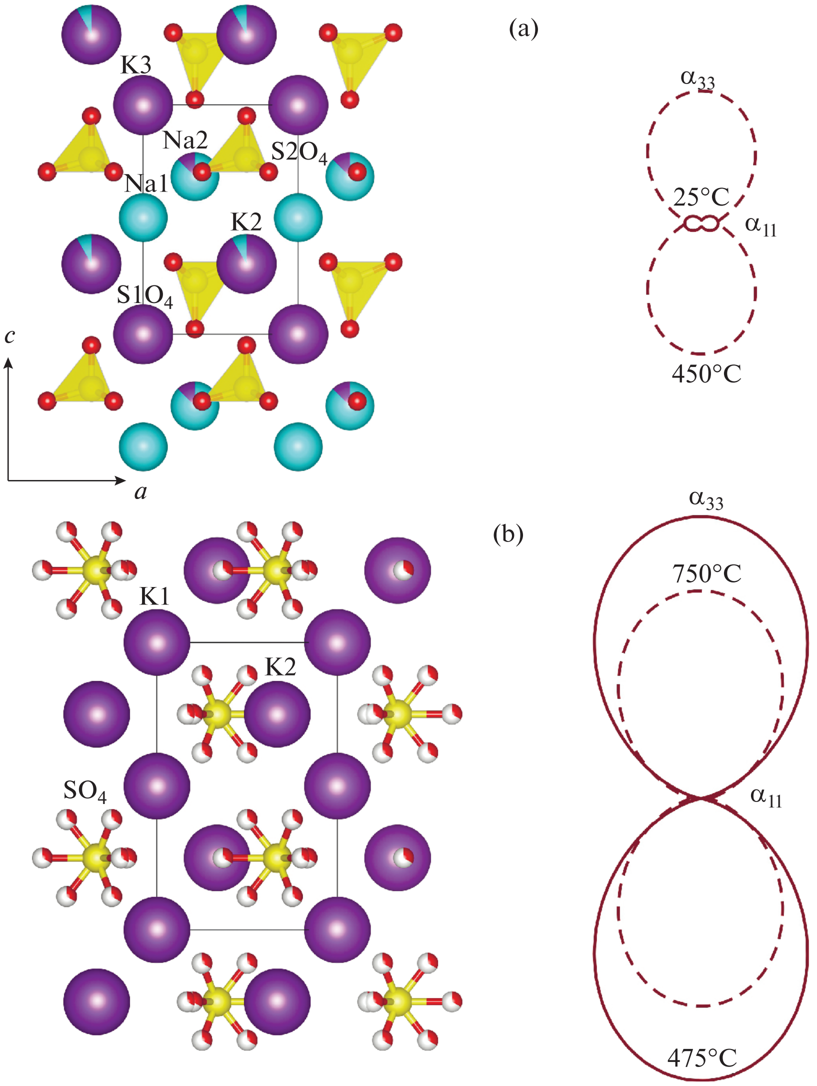

Fig. 4. Comparison of the cross sections of the thermal expansion tensor with the crystal structures of belomarinaite (a) (Filatov et al., 2019) and α-K_2SO_4 (740°C) (b) (Arnold et al., 1981).

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REFERENCES

Arnold, H., Kurtz, W., Richter-Zinnius, A., et al., The phase transition of K_2SO_4 at about 850 K, *Acta Crystallographica,* 1981, vol. B37, pp. 1643–1651.

Belousov, A., Belousova, M., Edwards, B., Volynets, A., and Melnikov, D., Overview of the precursors and dynamics of the 2012-2013 basaltic fissure eruption of Tolbachik Volcano, Kamchatka, Russia, *Journal of Volcanology and Geothermal Research,* 2015, vol. 307, pp. 22–37.

Bol'shoe treshchinnoe Tolbachinskoe izverzhenie, 1975-1976 gg., Kamchatka (The Great Tolbachik Fissure Eruption, 1975–1976, Kamchatka), Fedotov, S.A., Ed., Moscow: Nauka, 1984.

Bubnova, R.S., Firsova, V.A., and Filatov, S.K., A program for determining the tensor of thermal expansion and for visualizing its characteristic surface (Theta To Tensor, TTT), *Fizika i Khimiya Stekla,* 2013, vol. 39, pp. 505–509.

Chukanov, N.V., Aksenov, S.M., Rastsvetaeva, R.K., et al., Möhnite, $(NH_4)K_2Na(SO_4)_2$, a new guano mineral from Pabellón de Pica, Chile, *Mineralogy and Petrology,* 2015, vol. 109, pp. 643–648.

Eysel, W., Hoefer, H.H., Keester, K.L., et al., Crystal chemistry and structure of Na_2SO_4 (I) and its solid solutions, *Acta Crystallographica,* 1985, vol. B41, pp. 5–11.

Filatov, S.K., *Vysokotemperaturnaya kristallokhimiya* (High Temperature Crystal Chemistry), Leningrad: Nedra, 1990.

1 Filatov, S.K., Karpov, G.A., Shablinskii, A.P., et al., Ivsite, $Na_3H(SO_4)_2$ – a new mineral of volcanic exhalations from fumaroles of the Tolbachik Fissure Eruption, *Dokl. Akad. Nauk,* 2016, vol. 468, pp. 690–693.

Filatov, S.K., Shablinskii, A.P., Vergasova, L.P., et al., Belomarinaite $KNaSO_4$: A new sulphate from 2012-2013 Tolbachik Fissure eruption, Kamchatka Peninsula, Russia, *Mineralogical Magazine,* 2019, vol. 83, pp. 569–575.

Filatov, S.K., Shablinskii, A.P., Krivovichev, S.V., et al., Petrovite, $Na_{10}CaCu_2(SO_4)_8$, a new fumarolic sulfate from the Great Tolbachik fissure eruption, Kamchatka Peninsula, Russia, *Mineralogical Magazine,* 2020. https://doi.org/10.1180/mgm.2020.53

Gorelova, L.A., Vergasova, L.P., Krivovichev, S.V., et al., Bubnovaite, $K_2Na_8Ca(SO_4)_6$, a new mineral species with modular structure from the Tolbachik Volcano, Kamchatka peninsula, Russia, *European Journal of Mineralogy,* 2016, vol. 28, pp. 677–686.

Kassem, M.E., Abboudy, S., Hamed, A.E., et al., Stoichiometric ratio and doping effects on the thermal properties of sodium potassium sulphate crystals, *Journal of Thermal Analysis,* 1993, vol. 39, pp. 301–308.

Kato, K. and Saalfield, H., The crystal structure of hanksite, $KNa_{22}(Cl(CO_3)_2(SO_4)_9)$ and its relation to the K_2SO_4 I structure type, *Acta Crystallographica,* 1972, vol. B28, pp. 3614–3617.

Krivovichev, S.V. and Filatov, S.K., Metal arrays in structural units based on anion-centered metal tetrahedral, *Acta Crystallographica,* 1999, vol. B55, pp. 664–676.

Lacroix, A., *Mineralogie de la France* (in four volumes), Paris, France: Librairie Polytechnique, 1910.

Nazarchuk, E.V., Siidra, O.I., Agakhanov, A.A., et al., Itelmenite, $Na_2CuMg_2(SO_4)_4$, a new anhydrous sulphate mineral from the Tolbachik volcano, *Mineralogical Magazine,* 2018, vol. 82, pp. 1233–1241.

Okada, K. and Osaka, J., Structures of potassium sodium sulphate, *Acta Crystallographica,* 1980, vol. 36, pp. 919–921.

O'Keeffe, M. and Hyde, B.G., An alternative approach to crystal structures with emphasis on the arrangements of cations, *Structure and Bonding,* 1985, vol. 61, pp. 77–144.

Pekov, I.V., Zubkova, N.V., Agakhanov, A.A., et al., Dravertite, $CuMg(SO_4)_2$, a new mineral species from the Tolbachik volcano, Kamchatka, Russia, *European Journal of Mineralogy,* 2017, vol. 29, pp. 323–330.

Pekov, I.V., Agakhanov, A.A., Zubkova, N.V., et al., Fumarolic oxidizing systems on Tolbachik Volcano—a mineralogical and geochemical miracle, *Geol. Geofiz.,* 2020a, vol. 61, pp. 826–843.

Pekov, I.V., Shchipalkina, N.V., Zubkova, N.V., et al., Alkali sulfates with aphthitalite-like structures from fumaroles of the Tolbachik volcano, Kamchatka, Russia. I. Metathénardite, a natural high-temperature modification of Na_2SO_4, *Canadian Mineralogist,* 2020b, vol. 57(6), pp. 885–901.

Shablinskii, A.P., Filatov, S.K., Vergasova, L.P., et al., Dobrovolskyite, IMA 2019-106. CNMNC Newsletter 54, *European Journal of Mineralogy,* 2020, vol. 32, pp. 275–283.

Siidra, O.I., Nazarchuk, E.V., Zaitsev, A.N., et al., Copper oxosulphates from fumaroles of Tolbachik volcano: puninite, $Na_2Cu_3O(SO_4)_3$ – a new mineral species and structure refinements of kamchatkite and alumoklyuchevskite, *European Journal of Mineralogy,* 2017, vol. 29(3), pp. 499–510.

Siidra, O.I., Nazarchuk, E.V., Lukina, E.A., et al., Saranchinaite, $Na_2Cu(SO_4)_2$, A New Exhalative Mineral from Tolbachik Volcano, Kamchatka, Russia, and a product of the Reversible Dehydration of Kröhnkite, $Na_2Cu(SO_4)_2(H_2O)_2$, *Mineralogical Magazine,* 2018, vol. 82, pp. 257–274.

Siidra, O.I., Nazarchuk, E.V., Zaitsev, A.N., et al., Koryakite, $NaKMg_2Al_2(SO_4)_6$, a new NASICON-related anhydrous sulfate mineral from Tolbachik volcano, Kamchatka, Russia, *Mineralogical Magazine,* 2020, vol. 83(2), pp. 283–287.

Vegas, A., Cations in inorganic solids, *Crystallography Rev.,* 2000, vol. 7, pp. 189–283.

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