MINERALOGICAL CRYSTALLOGRAPHY

Thermal Expansion of New Arsenate Minerals, Bradaczekite, $NaCu_4(AsO_4)_3$, and Urusovite, $Cu(AsAlO_5)$

S. K. Filatov[a], D. S. Rybin[a], S. V. Krivovichev[a], and L. P. Vergasova[b]

[a] Faculty of Geology, St. Petersburg State University, Universitetskaya nab. 7/9, St. Petersburg, 199034 Russia
[b] Institute of Volcanology, Far East Division, Russian Academy of Sciences, Boulevard Piipa, 9, Petropavlovsk-Kamchatsky, 683006 Russia
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Abstract—Thermal behavior of two new exhalation copper-bearing minerals, bradaczekite and urusovite, from the Great Tolbachik Fissure Eruption (1975–1976, Kamchatka Peninsula, Russia) has been studied by X-ray thermal analysis within the range 20–700°C in air. The following major values of the thermal expansion tensor have been calculated for urusovite: $\alpha_{11} = 10$, $\alpha_{22} = \alpha_b = 7$, $\alpha_{33} = 4$, $\alpha_V = 21 \times 10^{-6}°C^{-1}$, $\mu = c^\wedge \alpha_{33} = 49°$ and bradaczekite: $\alpha_{11aver} = 23$, $\alpha_{22} = 8$, $\alpha_{33aver} = 6 \times 10^{-6}°C^{-1}$, $\mu(c^\wedge\alpha_{33}) = 73°$. The sharp anisotropy of thermal deformations of these minerals, absences of phase transitions, and stability of the minerals in the selected temperature range corresponding to conditions of their formation and alteration during the posteruption period of the volcanic activity are established.

INTRODUCTION

The Great Tolbachik Fissure Eruption (GTFE 1975–1976, Kamchatka Peninsula, Russia) is among the six most famous fissure eruptions in human history. In addition, it is one of the most studied eruptions (The Great …, 1984). In the 30 years since the eruption, posteruption mineral formation has been regularly monitored at the newly formed Tolbachik volcanoes. For this time, 30 new minerals have been described, among which are a number of arsenates: lammerite, $Cu_3[(P,As)O_4]_2$; alarsite, $AlAsO_4$; coparsite, $Cu_4O_2[(As,V)O_4]Cl$, johillerite, $Na(Mg,Zn)_3Cu(AsO_4)_3$; urusovite, $Cu[AlAsO_5]$; bradaczekite, $NaCu_4(AsO_4)_3$; and filatovite, $K[(Al,Zn)_2(As,Si)_2O_8]$. Except for lammerite and johillerite, the listed mineral species are new.

Bradaczekite and urusovite examined in this study were found, among products of volcanic exhalations at the second cinder cone of the North break of the GTFE, to be intimately associated with hematite, tenorite, orthoclase, johillerite $Na(Mg,Zn)_3Cu(AsO_4)_3$, ponomarevite $K_4Cu_4OCl_{10}$, piypite $K_4Cu_4O_2(SO_4)_4MeCl$, sylvite, dolerophanite Cu_2OSO_4, and euchlorine $KNaCu_3O(SO_4)_3$.

Bradaczekite, $NaCu_4(AsO_4)_3$. The mineral is dark blue, with adamantine luster; streak ranges from pale sky blue to white; cleavage is not observed. Bradaczekite occurs as clusters of dark blue plates. The mineral is stable in air and almost insoluble in water and alcohol. The calculated density is 4.77(1) g/cm³. Luminescence was not displayed in short- or longwave UV light. Shortly after discovery of the mineral, it was established that there is a synthetic analogue, $NaCu_4(AsO_4)_3$, synthesized by Pertlik (1987) under hydrothermal conditions. The mineral was named in honor of Hans Bradazcek, a professor of Free Berlin University (Filatov et al., 2001).

Urusovite, $Cu(AlAsO_5)$. The mineral is light green, with adamantine luster; streak is white; cleavage is perfect parallel to (001). It occurs as clusters of plates extending parallel to [001] and intergrown along elongation. The temperature at the sampling locality was 400°C. The microhardness VHN is 378 kg/mm²; the Mohs hardness is 5. Urusovite is pleochroic in light green tints. It was named in honor of Academician V.S. Urusov (Vergasova et al., 2002).

The crystallochemical and mineralogical characteristics of bradaczekite and urusovite are given in the table.

It can be concluded that bradaczekite and urusovite as exhalative minerals are formed at high temperatures and occur at high temperatures and atmospheric pressures on cooling volcanoes for a certain time after formation. Therefore, the aim of this article is to study the thermal behavior of these minerals by X-ray thermal analysis under conditions close to natural. The occurrence of such toxic elements as arsenic in the studied minerals attaches special importance to this work. The probable release of As from the crystal structure of these minerals and its migration in the biosphere is a subject of doubtless concern. Rybin et al. (2007) and Filatov et al. (2007) reported the preliminary results of this study.

Corresponding author: S.K. Filatov. E-mail: filatov@crystalspb.com

Crystallochemical and mineralogical characteristics of bradacze-kite and urusovite

Parameter	Bradaczekite	Urusovite
Chemical formula	$NaCu_4(AsO_4)_3$	$Cu(AsAlO_5)$
Symmetry, space group	Monoclinic, $C2/c$	Monoclinic, $P2_1/c$
a (Å)	12.053(2)	7.314(2)
b (Å)	12.432(2)	10.223(3)
c (Å)	7.2529(13)	5.576(2)
β (deg)	117.793	99.79
V (Å³)	961.5(3)	410.9(2)
Calculated density, D_x, g/cm³	4.77	3.93
Mohs hardness	–	5
Color	Dark blue	Light green
Origin	Volcanic exhalation	Volcanic exhalation

EXPERIMENTAL

The X-ray diffraction patterns of polycrystals were obtained in air using a DRON-3 diffractometer equipped with a KRV-1100 high-temperature device, using Cuk_α radiation, Ni β-filter, and tape recording of reflections. The temperature range is 20–700°C; temperature step is 40°C.

The dimensions of monoclinic unit cell were determined by the least squares procedure using the Unit Cell program and approximated by equations not higher than of the second order. The thermal expansion coefficients were calculated with the DTC program; patterns were drawn according to the DTP program (Belousov and Filatov, 2007).

RESULTS AND DISCUSSION

No phase transitions were detected for either mineral in the temperature range of 20 to 700°C. The selected range covers typical temperatures of formation and transformation of exhalative minerals at volcanoes. Heating simulation is appropriate to the results of 30-year-regime observations, when local temperature oscillations of cooling at the cones of the GTFE reached 400°C (Vergasova et al., 2007). The results of study of thermal expansion of the minerals are given below.

Bradaczekite. The temperature-dependent variations of monoclinic unit-cell dimensions (Fig. 1a) were fitted by polynomials not higher than the second order: $a = 12.049 + 0.104 \times 10^{-3} \times T + 0.139 \times 10^{-6} \times T^2$, $b = 12.418 + 0.129 \times 10^{-3} \times T$, $c = 7.251 + 0.099 \times 10^{-3} \times T + 0.075 \times 10^{-6} \times T^2$ (Å), $\beta = 117.82 + 0.83 \times 10^{-3} \times T$(deg), $V = 959.5 + 24.2 \times 10^{-3} \times T + 21.1 \times 10^{-6} \times T^2$ (Å³). The coefficients of thermal expansion along the crystal axes calculated on the basis of these data are as follows: $\alpha_a = 8.4 \times 10^{-6} + 16.4 \times 10^{-9} \times T$ (average value in the range 20–700°C; $\alpha_{a\,average} = 14.0$), $\alpha_b = 8.0 \times 10^{-6}$, $\alpha_c = 13.9 \times 10^{-6} + 21.6 \times 10^{-9} \times T$ ($\alpha_{c\,aver} = 21.2$), $\alpha_\beta = 6.8 \times 10^{-6}°C^{-1}$.

Comparison of the thermal expansion of bradaczekite along atomic rows make it possible to distinguish axis c as the direction of the greatest expansion (average value $\alpha_c = 21.5 \times 10^{-6}°C^{-1}$), whereas the expansion along axes a and b is 1.5 and 2.5 times less, respectively.

The major values of the thermal expansion tensor of the mineral reveal a much greater anisotropy of deformations: $\alpha_{11} = 16 + 0.02 \times T$ (average value $\alpha_{11\,average} = 23$), $\alpha_{22} = 8$, $\alpha_{33} = -1 + 0.02 \times T$ ($\alpha_{33\,average} = 6$) ($10^{-6}°C^{-1}$), $\mu(c\,^\wedge\alpha_{33}) = 73°$.

The volume expansion of the structure $\alpha_V = 23 + 0.038 \times T$ ($\alpha_{V\,average} = 36 \times 10^{-6}°C^{-1}$) is estimated as that expected for arsenate compounds.

The cause of the anisotropic thermal expansion of bradaczekite can be established from comparison of the α values with the crystal structure of the mineral. Bradaczekite belongs to the alluaudite, $Na[MnFe_2(PO_4)_3]$, structural type. In the structure, there are three independent Cu^{2+} atoms. The Cu(1) atom is square-coordinated with a mean bond length of $Cu^{2+}–O = 1.91$ Å. Cu(2) and Cu(3) atoms (Fig. 2) exhibit distorted tetrahedral coordination due to the Jahn–Teller effect. Two symmetrically independent As atoms are tetrahedrally coordinated with average As–O bond lengths of 1.69 Å and 1.70 Å for As(1) and As(2), respectively. The structure is based on a sheet of octahedrons $[Cu(2)O_6]$ and $[Cu(3)O_6]$ combined with tetrahedrons $[As(2)O_4]$ (Fig. 2a). Edge-sharing octahedrons make up zigzag chains, which form a sheet via $[As(2)O_4]$ Tetrahedrons. The sheets are linked to a framework via $[As(1)O_4]$ tetrahedrons and $[Cu(1)O_4]$ squares. Na^+ cations occupy cages in the framework (Krivovichev et al., 2001).

In Fig. 2b, the pattern of coefficients of the thermal expansion of bradaczekite is comparable with the crystal structure of this mineral. Four short equatorial bonds $\langle Cu^{2+}–O_{eq}\rangle = 1.98$ (solid lines) and two long apical bonds $\langle Cu^{2+}–O_{ap}\rangle = 2.49$ Å (dashed lines) are distinguished for each Cu(2) and Cu(3) octahedrons. It is seen that the longest (and weakest) Cu–O bonds (dashed lines in Fig. 2b) are close in orientation to axis α_{11} of the maximal thermal expansion of the structure.

Thus, the anisotropy of thermal deformations of the bradaczekite structure is caused by nonequivalent lengths of chemical bonds in octahedrons $Cu(2)O_6$ and $Cu(3)O_6$ distorted due to the Jahn-Teller effect.

Urusovite. In urusovite, the monoclinic unit-cell dimensions linearly vary with temperature to a first approximation (Fig. 1b): $a = 7.304 + 38 \times 10^{-6} \times T$ (Å); $b = 10.169 + 69 \times 10^{-6} \times T$ (Å); $c = 5.575 + 37 \times 10^{-6} \times T$ (Å); $\beta = 99.82 - 0.32 \times 10^{-3} \times T$ (deg); $V = 408.1 + 8.0 \times 10^{-3} \times T$ (Å³). The coefficients of thermal expansion are as follows: $\alpha_a = 5.5$, $\alpha_b = 6.9$, $\alpha_c = 7.2$, $\alpha_\beta = -3.0 \times 10^{-6}°C^{-1}$; the major values of tensor of thermal expansions are α_{11}
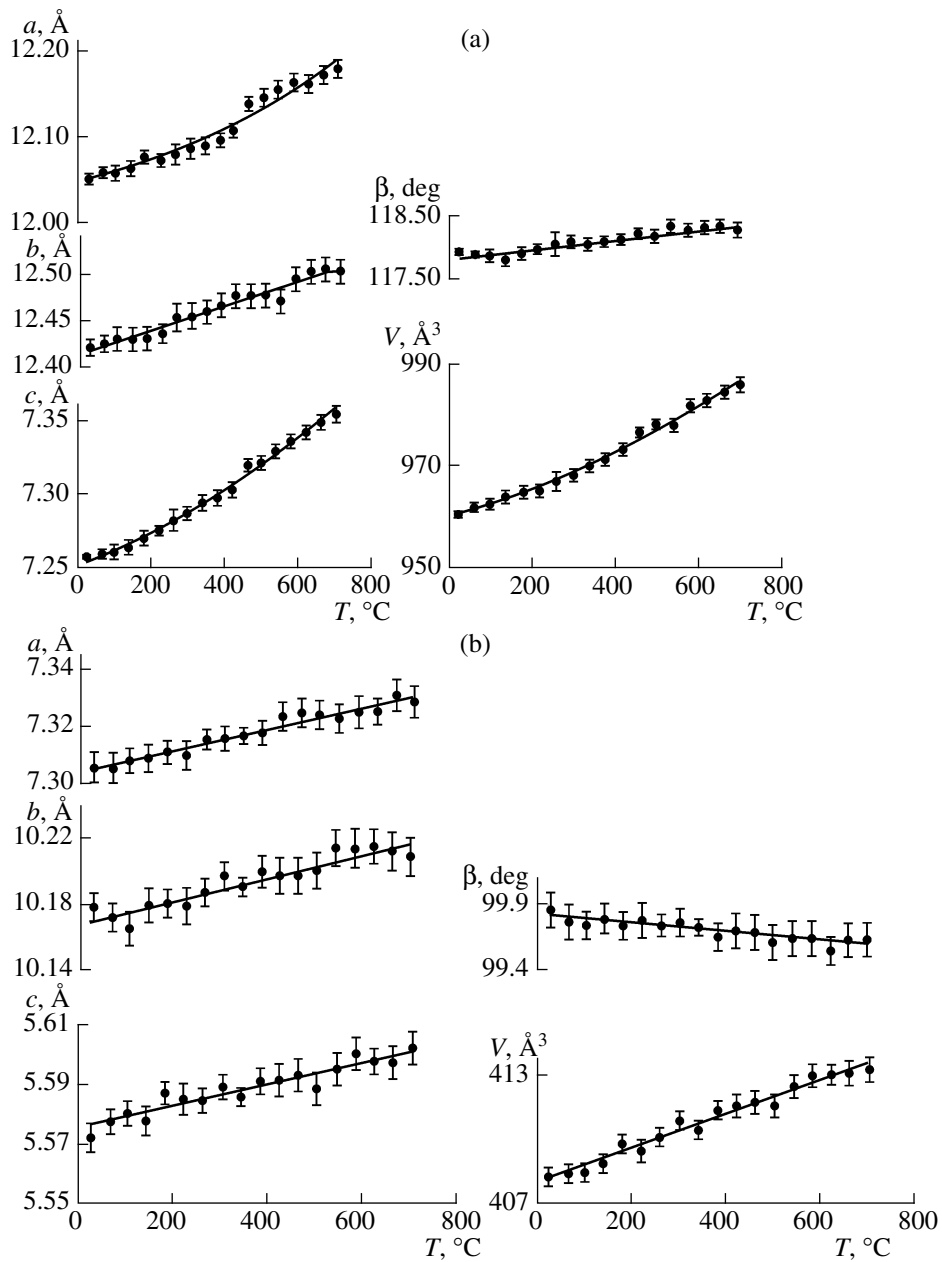
Fig. 1. Unit-cell dimensions of (a) bradaczekite and (b) urusovite versus temperature.

$= 10$, $\alpha_{22} = \alpha_b = 7$, $\alpha_{33} = 4$, $\alpha_V = 21 \times 10^{-6}$ °C^{-1}, $\mu = c^\wedge\alpha_{33} = 49°$.

Thus, urusovite exhibits a moderate thermal volume expansion ($\alpha_V = 21 \times 10^{-6}$°C^{-1}) characteristic of silicates, aluminosilicates, and their aluminate and arsenate analogues.

To account for the anisotropic character of thermal deformations of the mineral, consider its crystal structure. According to the determination of the structure (Krivovichev et al., 2000), the mineral is layered. The radical of the AlAsO$_5$ sheet is similar to that of tetrahedral net Si$_2$O$_5$ differing in that two tetravalent Si^{4+}

atoms are substituted for Al^{3+} and As^{5+} (the total number of valences is also 8).

Analogy of the urusovite sheet AlAsO$_4$ with net Si$_2$O$_5$ suggests that the structure is layered. The sheets in the layered silicates are usually linked by residual bonds, i.e., atoms of alkaline metals (M$^+$) or water molecules. Therefore, the maximal thermal expansion perpendicular to the sheet is characteristic of them. In urusovite, the sheets are linked by bivalent copper (Fig. 3). The single independent site of Cu atoms is coordinated by five O atoms forming a tetragonal pyramid. Four oxygen atoms are arranged at the bottom of this pyramid at distances of 1.960–1.975 Å from the
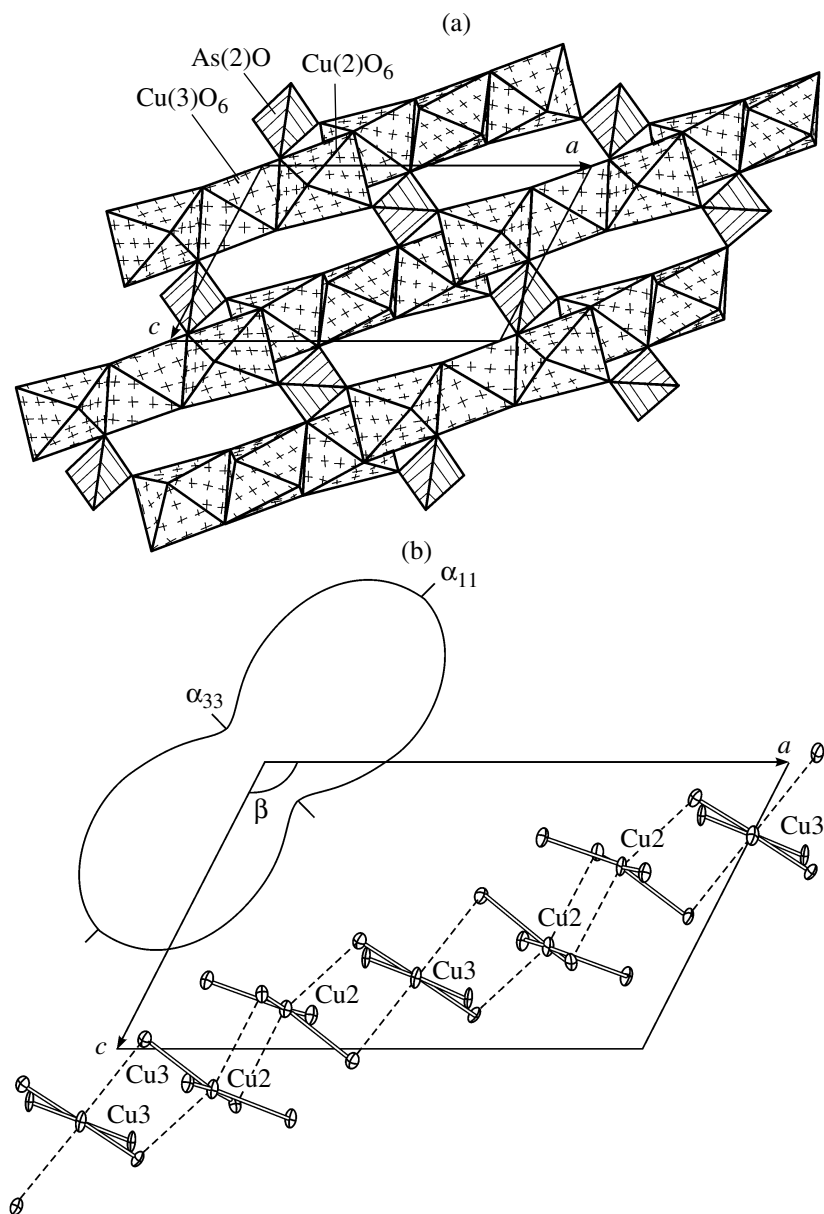
FILATOV et al.

Fig. 2. (a) Sheet *ac* and (b) chain of octahedrons [Cu(2)O$_6$] and [Cu(3)O$_6$] in the structure of bradaczekite. Long bonds (Jahn–Teller effect) in octahedrons (CuO$_6$) are shown by dashed lines.

Cu atom, whereas the O atom at the apex of the pyramid is at a distance of 2.370 Å from the Cu atom (Filatov et al., 2001).

In this case, all five Cu–O bonds participate in interlayer interaction, including the four shortest, substantially covalent bonds in square CuO$_4$. Apparently, just these covalent bonds between aluminoarsenate sheets of the urusovite structure prevent maximal thermal expansion of the mineral perpendicularly to the sheet, as is characteristic of other micaceous minerals.

At the same time, Fig. 1b demonstrates that the β value of the mineral unit cell decreases from 99.8° to 99.6° in the temperature range of 20 to 700°C. This suggests that the anisotropy of thermal deformations is

of a shear nature (Filatov, 1990). In this case, decrease in abut angle β with increasing temperature should cause expansion of the structure near its bisector and compression in the perpendicular direction (Fig. 3). The general thermal expansion superimposed on these deformations will result in enhanced expansion and weakened or neutralized compression. Indeed, the real pattern of the thermal expansion coefficients of urusovite is distinguished by such character and orientation (Fig. 3).

A nonfixed symmetry angle of monoclinic unit cell tending to right angle indicates a tendency of increasing symmetry of crystals with temperature. About 2/3 of
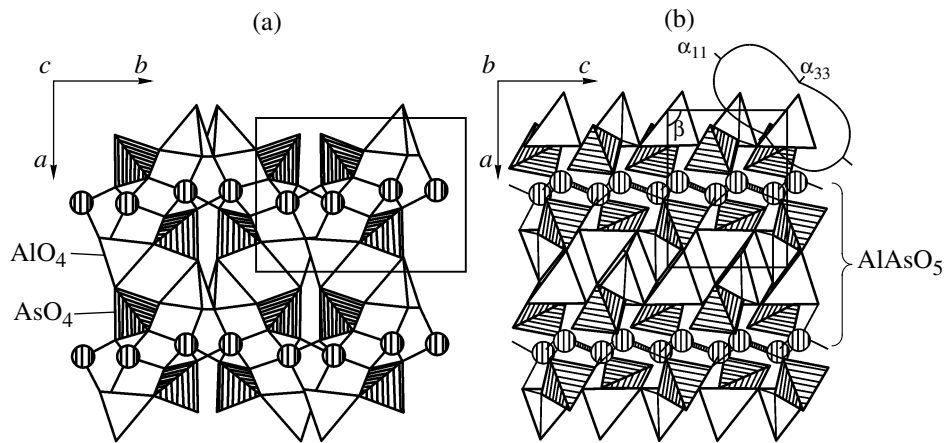
Fig. 3. Structure of urusovite projected on (a) (001) and (b) (010) and pattern of coefficients of thermal expansion.

monoclinic crystals behave in such a manner (Filatov et al., 1990).

CONCLUSIONS

The phase transitions, which can occur in exhalative minerals at variable temperature during the postmagmatic period of volcanic activity, were modeled by X-ray thermal analysis. It was revealed that both of the studied arsenate minerals, bradaczekite $NaCu_4(AsO_4)_3$ and urusovite $Cu(AsAlO_5)$, are stable throughout the temperature range of 20 to 700°C.

The absence of phase transitions is a dull result in terms of crystal chemistry and physical chemistry, but is undoubtedly important in terms of ecology and environmental protection. Indeed, in the whole real temperature range of the formation and transformation of exhalative minerals at volcanoes, arsenic incorporated into bradaczekite and urusovite is firmly retained in the crystal structure of the minerals and remains nonhazardous in such a state to people (primarily for the volcanologists working close to the localities of arsenate findings) and the environment.

Thermal deformations of these minerals are substantially anisotropic; anisotropy is significantly controlled by the strength of chemical bonds. In the structure of bradaczekite, the Jahn–Teller distortion of the octahedral site of copper atoms was the controlling factor that determined anisotropic thermal deformations of the crystal structure.

In contrast, in the case of urusovite, anisotropy of thermal expansion of the structure expected due to the layered character of T_2O_5 (T = Al, As) and perfect cleavage parallel to (100) of the mineral was not displayed because of linkage of layers by covalent Cu–O bonds. In this situation, the crystal structure of urusovite more likely may be considered a framework composed of apex-sharing running tetrahedrons $[AlO_4]$ and $[AsO_4]$ and strong fivefold polyhedrons $[CuO_5]$. The Mohs hardness of 5 typical of urusovite is consistent with such a framework. Under those conditions, the low thermal expansion of urusovite looks appropriate.

The coefficients of thermal expansion of $\alpha_V = 36 \times 10^{-6}°C^{-1}$ and $21 \times 10^{-6}°C^{-1}$ of bradaczekite and urusovite, respectively, allow us to verify the aforementioned assumption. The measured α values are typical of arsenates and aluminoarsenates. They may be used as the thermodynamic characteristics of these minerals. The elevated expansion of bradaczekite in comparison with urusovite is explained by univalent Na^+ in the structure of bradaczekite, which attenuates chemical bonds in the compound and results in elevated thermal expansion. The expansion of urusovite is lower in comparison with silicates (average $\alpha_V \sim 30 \times 10^{-6}°C^{-1}$).

The strength properties of urusovite (high hardness and low thermal expansion) along with copper as its constituent are attractive for utilization of this mineral. It is also important that this aluminoarsenate has only centrosymmetrical modification in the temperature range of 20 to 700°C.

ACKNOWLEDGMENTS

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