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The nature of special points on unit cell parameters temperature dependences for crystal substances

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Abstract. Two factors complicating thermal expansion of crystals are given. (1) Heating of a metastable crystal phase at low temperatures represents usually thermal expansion only. At higher temperatures, above a glass transition temperature T_g, structural reconstruction to a stable phase is involved into the expansion. (2) The atomic vibration size in a direction of the longest vibration amplitudes can be sharply increased. In this case on heating above definite temperature, neighboring cations that were not in touch start to repel each other along this direction – an additional mechanism of thermal deformations switches on. The both these phenomena show as special points on temperature dependence for unit cell parameters.

Introduction

At first sight, thermal expansion of crystals looks like a simple process. On heating amplitude of atomic thermal vibrations increases and an anharmonicity of atomic thermal vibrations leads to a thermal expansion. High-temperature X-ray powder diffraction (HTXRPD) is traditionally applied for study of thermal expansion using unit cell temperature dependences. The character of these dependences increasing with temperature just slightly differs from a linear dependence and can be well described by polynomial approximation of the first, the second (rarely the third) order depending on the accuracy of the experiment.

In real situations, what is usually named thermal expansion hardly ever appears to be only an expansion process. Other processes caused by temperature changing make a contribution to a thermal expansion complicating its character. The processes might be connected with a structure reconstruction in the course of a polymorphic phase transition; (i) with polymorphic transitions of the first thermodynamic kind (with jump of volume and other parameters) and (ii) the second kind (with no jumps); (iii) with the change of intensity and of the type of particles thermal moving, for example when atoms and molecules start to rotate (rotary crystals) or (iv) jump (redistribution of atoms among the positions or "order-disorder" processes) at achievement of a sufficient energy; (v) with a loss of volatile components, oxidation, reduction or other changes of a chemical composition of a substance [1-3].

In addition to the factors listed above two more factors are described in the present work. The first factor is connected with the thermal behaviour of metastable crystal phases. On heating at low temperatures phases demonstrate usually thermal expansion only; at higher temperatures structural reconstruction into a stable crystalline state makes a contribution to the expansion. We have shown [4,5] that this is realized for crystals nearby a T_g glass transition temperature for glasses of the same composition. The second factor is of another nature. The atomic vibration size in a direction of the longest vibration amplitudes can be sharply increased. As a result, two neighboring cations, which were not in touch, start to repel each other along this direction above definite temperature − an additional mechanism of thermal deformations “switches on” [6]. Both phenomena manifest themselves as special (singular or flex) points on temperature unit cell parameters dependences. Examples are considered below.

Experimental data

Here we examine temperature dependences of unit cell parameters for α-KB_5O_8, α-RbB_5O_8, α-$Bi_2B_8O_{15}$, $Na_2B_4O_7$, CuO, and $BaBi_2B_4O_{10}$ taken from the authors’ HTXRPD studies, half of them being published for the first time. These compounds were studied in air using HTXRPD data collected by the DRON-3 X-ray diffractometer with a high-temperature camera in the range of 20-800 °C. Unit cell parameters were refined by the least-square methods. Main coefficients of the thermal expansion tensor and its orientation were determined using polynomial approximation of temperature unit-cell parameters dependences.

Similarity of thermal behaviour of crystals and glasses
α-KB_5O_8. Special points were observed on temperature unit cell parameters dependences (Figures 1a and b) [4] especially for *c* parameter for the samples of low- and high-temperature syntheses. Points temperatures (345 и 370 °C, accordingly) appeared to be near the T_g temperature of a melt of the same composition (380 °C). It is known, that on heating a glass "defreezes" within a T_g temperature range where glass viscosity decreases and ionic mobility increases. If metastable crystalline phases can be "defreezed" at this temperature minima in Figures 1a and b might be of the same nature. Hence, not only glasses, but metastable crystal phases also can sharply change the thermal expansion coefficients near T_g. At the same time stable β-KB_5O_8 phase has no flexes on temperature unit cell dependences [5].
α-RbB_5O_8. The HTXRPD study of isostructural metastable modification has revealed similar results: *α-RbB_5O_8* shows singular points at 310 °C (Figure 1c), T_g is 365 °C. The stable *β-RbB_5O_8* phase does not exhibit any flexes on the temperature parameters dependence [5].
α-$Bi_2B_8O_{15}$. Temperature dependences for *b* and *c* parameters of the monoclinic lattice exhibit pronounced kinks at ~ 300 °C (Figure 1d); T_g is about 400 °C [7].
$Na_2B_4O_7$. Temperature dependences for triclinic cell parameters (Figure 1e) show in the first approximation linear thermal expansion along *a*, *b* and *c* axes, and flexes for α, β and γ angles. Once more, these flexes appear to be near T_g = 465 °C [8]. It seems the angular parameters (angles between atomic rows) in ionic compounds are more sensitive to temperature changes, than the linear ones (interatomic distances).
Common features. Up to now we have found the special points on cell parameters temperature dependences around the T_g temperature for four metastable phases in viscous glassform-

ing borate systems. A metastable phase transforms always into a stable state and the transition rate increases with temperature. Rapid decreasing of glass viscosity owing to a jump of ionic mobility on heating up to the T_g temperature is well-known. Above T_g crystallization from glass starts. The crystalline metastable phase formed by atoms of the same chemical elements with the same chemical bonding exhibits a sharp increase of ionic mobility at T_g temperature on heating. And this, in its turn, should lead to "defreezing" of a metastable state. Unlike a stable condition, a metastable phase can have a number of slightly variable states and demonstrate differences in their thermal behaviour (Figure 1a and b).

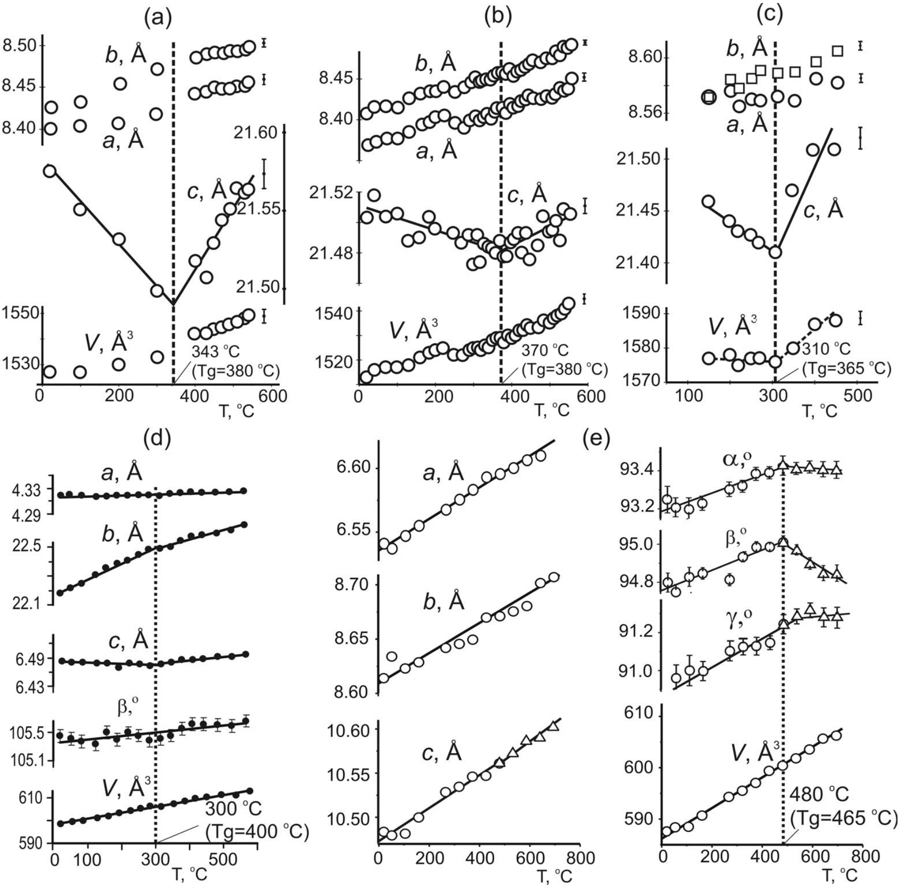


Figure 1. Special points on unit cell parameters temperature dependences: a – α-KB_5O_8 (420 ^{o}C / 22 h), b - α-KB_5O_8 (780 ^{o}C / 15 min), c - α-RbB_5O_8, d - α-$Bi_2B_8O_{15}$, e – $Na_2B_4O_7$.

“Switch” type of hinge thermal deformations

Hinge deformations "switch" is considered below using CuO and $BaBi_2B_4O_{10}$ thermal behaviour as an examples. In passing, conception of hinge deformations is developed.

Switch of a hinge mechanism by the CuO example. The term "hinge deformations" has been introduced by Sleight in 1998 [9]. Figure 2a shows a hinge mechanism: the hinge initial unit (black lines and dots) transforms into a reconstructed unit (grey lines and dots): the unit is compressed in a horizontal direction and extends in a vertical one; i. e. hinge deformations are of a sharp anisotropic nature. Long before the introduction of this term the hinge mechanism has been applied for an explanation of sharp anisotropic thermal deformations for CuO (tenorite) [6,2]. Temperature dependence for the monoclinic cell parameters of this compound unexpectedly appeared to be freakish (Figure 2c).

(1) The main feature of a hinge deformation is a synchronous change of two linear unit cell parameters in opposite directions in parallel to the intermediate behaviour of the other linear parameters and the unit cell volume. In case of CuO *a* parameter increases, *b* decreases.

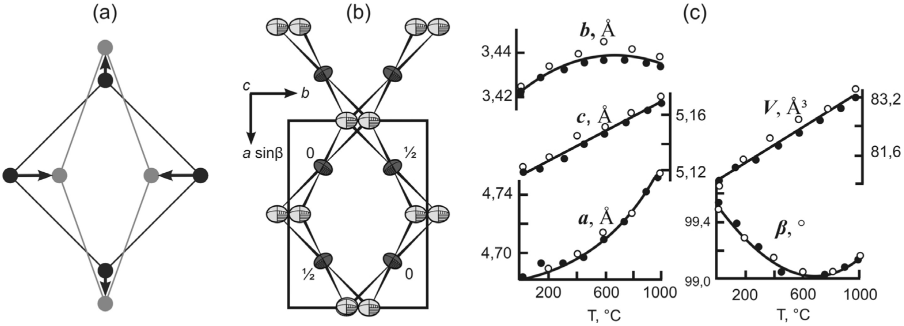


Figure 2. Hinge deformations: (a) a scheme of the hinge; (b) hinge cell in the CuO crystal structure; (c) temperature dependences of the monoclinic cell parameters for CuO, two experiments.

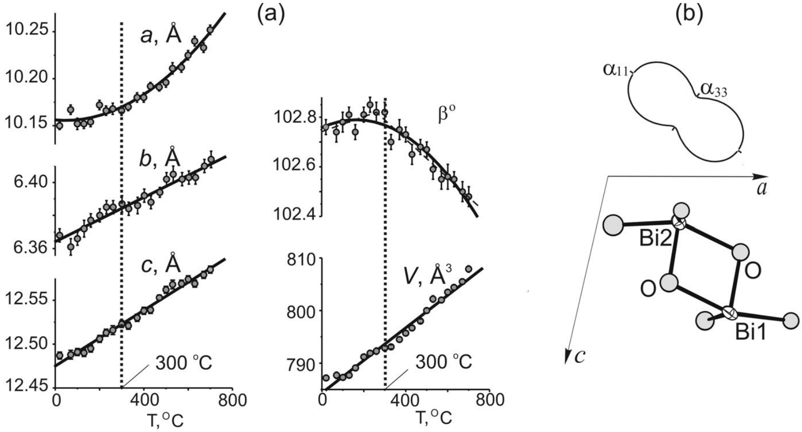
(2) Hinge cell. Copper atoms (Figure 2b) are in CuO_4 "squares" characteristic for Cu^{2+}. The squares are interconnected by edges in (110) and (1-10) planes. If a rhombus (hinge cell) formed by four CuO_4 squares is forcibly stretched along *a* axis, it has to contract along *b* axis like it is actually observed at high temperatures (Figure 2c).

(3) Motivation for hinge mechanism. Now we have to find out the motivation for this synchronous change in opposite directions of parameters (*a* and *b* in CuO), i.e. to answer the following question. Why do they change in such a way? (For CuO *a* increases, *b* decreases). The amplitude of Cu thermal vibrations transversely to a plane of CuO_4 square is approximately twice larger comparing to the amplitude along the plane. For Cu atoms located at one height (Figure 2b, z = 0 or 1/2) the maximal axes of the vibrations ellipsoids are directed differently. Atoms of each pair are located 2.9 Å apart from each other at room temperature, this value slightly exceeding the sum of two covalent radii for Cu atom 2R = 2.70 Å [10]. Heating is accompanied by thermal vibrations amplitude increasing, i.e. by increase in the vibrating size of atoms, and the atoms start to repel each other. The ellipsoids of the Cu atoms pair (for example z = 0) are equal in size and parallel, thus, the most simple way for

them to move apart is by displacement at which the longest ellipsoid axes of two atoms move apart. When they move the *a* parameter increases, *b* decreases.

(4) "A switch" of hinge deformations. For a given crystal structure the presence of a hinge cell is insufficient to exhibit the hinge mechanism. It is necessary "to switch" hinge mechanism. For example, the CuO structure was potentially a hinge at room temperature; however starting heating did not reveal any hinge deformations (see Figure 2c). They appeared at definite temperatures. Interatomic Cu-Cu distance has played a specific role of "switch" for the hinge in CuO crystal structure. If this distance is less than the sum of two covalent radii (2R(Cu) = 2.70 Å), like it is for CuO at low temperatures, Cu atoms do not disturb and not repel each other, and the observed thermal expansion is rather isotropic. If atoms start to repel each other on heating (while vibrations amplitudes increase), anisotropic hinge mechanism of thermal deformations "switches" at average temperatures in the case of CuO.

"Switching" of hinge mechanism for the case of $BaBi_2B_4O_{10}$. Thermal expansion is nearly isotropic up to about 300 °C (Figure 3). On further heating changes in the temperature dependence of *a* and *β* parameters occur. This allows to assume that the compound exhibits hinge deformation, and the temperature ~ 300 °C corresponds to the hinge "switching" [11].



Fiure 3. "Switch hinge" in $BaBi_2B_4O_{10}$ [11]: (a) temperature dependence of unit cell parameters; (b) "switch hinge" in comparison with figure of thermal expansion coefficients (600 °C).

Hinge deformations are usually revealed by a strong structure fragment. It can be true for a flat rigid construction of Bi2-O-Bi1-O that form a rhomb in *ac* monoclinic plane (Figure 3b) where Bi atoms are 3.56 Å apart from each other. The value exceeds a sum of two Bi^{3+} covalent radii (3.20 Å) [10]. Therefore, these Bi atoms are not in touch. On heating atomic vibration amplitudes increase, and thermal ellipsoids of Bi1 and Bi2 atoms are strongly stretched (Figure 3b), the longest axes of the ellipsoids being directed against each other. Thus, the atoms come in contact soon enough, they start to repel each other, and the structure has to expand along the Bi1-Bi2 direction. The expansion can be viewed as a deformation of the *ac* monoclinic plane due to the change in the *β* angle (Figure 3b). If the *β* angle decreases the structure expands intensely along the short diagonal of the *ac* parallelogram and synchronically contracts along the long diagonal. This takes place above ~ 300 °C, β angle decreasing and *a* parameter elongation occur (Figure 3a). The temperature (~ 300 °C) at which Bi atoms come in contact and start to move apart is the temperature of hinge "switching".

Concluding remarks

The present paper draws your attention to the fact, that thermal expansion of crystal substances is quite often complicated by other thermal structural changes. In addition to the complications already known [2] two new types of these deformations are described herein. The first type of structural changes is connected with the reconstruction of metastable phases into a stable state. It has been shown that an ionic mobility necessary for this reconstruction is reached at T_g glass transition temperature. Just around the T_g sharp or smooth flexes are observed on unit cell parameters temperature dependences. Another type of thermal expansion complications is characteristic for hinge structures when hinge deformations are revealed within the part of the studied temperatures range only. In particular, if the two neighboring cations are not in contact they will likely exhibit the maximal thermal vibrations in a direction towards each other. At definite temperature the vibrations of these atoms can increase to such an extent, that atoms will start to disturb and repel each other, i.e. the hinge mechanism of deformation "switches" producing special points.

References

1. Krishnan, R.S., Srinivasan, R. & Devanarayanan, S., 1979, *Thermal Expansion of Crystals* (Oxford e.a.: Pergamon Press).
2. Filatov S.K., 1990, *High temperature crystal chemistry (Vysokotemperaturnaia kristallokhimia)* (Leningrad: Nedra, in Russian, ISBN 5-247-01334-4).
3. High-temperature and high-pressure crystal chemistry. Eds Hazen, R.M. & Downs, R.T. Reviews in Mineralogy and Geochemistry, **41** (2000).
4. Bubnova, R.S., Polyakova, I.G., Anderson, Yu.E., Filatov S.K., 1999, *Glass Phys. & Chem*. **25,** 183-194.
5. Filatov, S.K., Bubnova, R.S., 2000, *Phys. Chem. Glass.* **41,** 216-224.
6. Domnina, M.I., Filatov, S.K., Zyuzyukina, I.I., Vergasova, L.P., 1986, *Inorg. Mater.* **22,** 1992-1999.
7. Bubnova, R.S., Aleksandrova, Yu.V., Filatov, S.K., Egorysheva, A.V., Kargin, Y.F. (private communication).
8. Sennova, N.A., Bubnova, R.S., Filatov, S.K., Polyakova, I.G., 2007, *Glass Phys. & Chem.* **33**, 217-225.
9. Sleight A.W., 1998, *Inorg. Chem.* **37,** 2854-2860.
10. Slater J.C., 1965, *Quantum theory of molecules and solids. Symmetry and energy bonds in crystals. Vol. 2* (London: McGraw-Hill Book Co).
11. Bubnova, R.S., Krivovichev, S.V., Filatov, S.K., Egorysheva, A.V., Kargin, Y.F., 2007, *JSSC*, **180** 596-603.

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