THERMAL EXPANSION OF MNbO$_4$ PHASES WHERE *M*=Al, Cr, Fe, Ga

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Studies on thermal expansion of the MNbO$_4$ type phases where *M*=Al, Cr, Fe, Ga have been carried out in the high-temperature X-ray diffraction attachment. In the case of isotypic AlNbO$_4$ and GaNbO$_4$ compounds the structure of which consists of the ReO$_3$ type blocks, the direction of minimal thermal expansion is consistent with the direction in which these blocks spread to infinity. In the case of CrNbO$_4$, the maximal thermal expansion direction is consistent with the [001] direction parallel to which the edge shared octahedra building its structure form infinite chains. FeNbO$_4$ has the highest coefficients of thermal expansion in this group of compounds.

Keywords: MNbO$_4$ type phases, shear structures , thermal expansion, XRD

Introduction

The survey of publications has shown that components of the M$_2$O$_3$–Nb$_2$O$_5$ systems where *M*=Al, Cr, Fe and Ga, react in the solid state to form compounds of the MNbO$_4$ type formula [1–7]. AlNbO$_4$ and GaNbO$_4$ are isostructural and crystallize in a monoclinic system, space group C2/m [1, 2]. In the crystal structure of AlNbO$_4$ the blocks of ReO$_3$ type can be distinguished, built from distorted MO$_6$ octahedra sharing only corners (Fig. 1), with dimensions of 2×2×∞ (Fig. 2). Individual blocks share common edges. Two perpendicular to each other shear planes occur in such a formed block structure. In the structure of AlNbO$_4$ also infinitely long chains of corner sharing MO$_6$ octahedra, speading to infinity along *Y* axis can be distinguished as well (Fig. 1). On the other hand, CrNbO$_4$ crystallizes in a tetragonal system, space group P4$_2$/mm, adopting the rutile type structure in which the edge shared (Cr,Nb)O$_6$ octahedra form straight chains along the *c* directions [3]. The adjacent chains are corner sharing (Fig. 3). The literature survey has shown that the polymorphism of FeNbO$_4$ is very complex [4–7]. Below 1358 K FeNbO$_4$ crystallizes with the monoclinic wolframite type structure (space group P2/c) built of the edge-shared octahedra, forming zig-zag chains. Each chain contains either iron or niobium ions (Fig. 4). Between 1358 and 1653 K an orthorhombic α-PbO$_2$ type phase is formed, in which the separate chains of NbO$_6$ and FeO$_6$ octahedra in the wolframite structure become identical (Fe,Nb)O$_6$. At 1653 K a further transition to the tetragonal rutile structure occurs in which the (Fe,Nb)O$_6$ octahedra change from
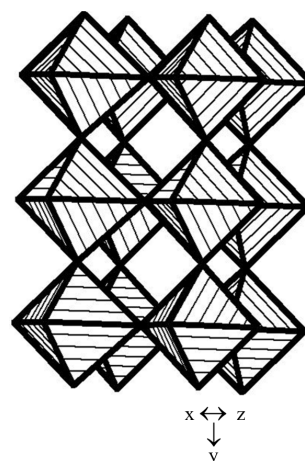

Fig. 1 The ReO$_3$ type blocks building the AlNbO$_4$ structure [1]
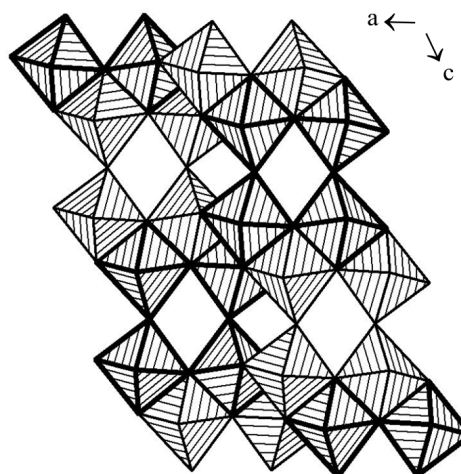

Fig. 2 The crystal structure of AlNbO$_4$ [1]
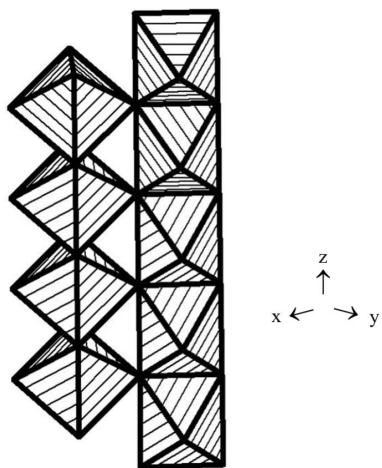
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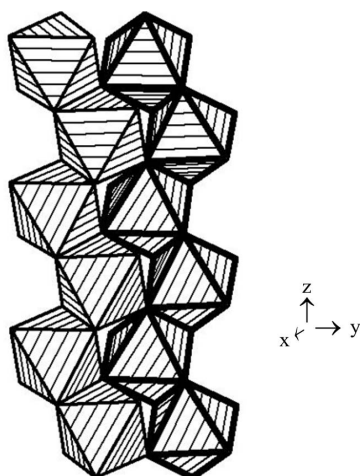**Fig. 3** The straight chains of corner-shared octahedra in the rutile type CrNbO$_4$ structure [3]

Fig. 4 The zig-zag chains of corner-shared octahedra in the wolframite type FeNbO$_4$ structure [6]

the zig-zag configuration in the α-PbO$_2$ structure to straight chains characteristic of the rutile structure. Solid state synthesis at 1673 K yields another modification of FeNbO$_4$ with the monoclinic AlNbO$_4$ type structure.

It is noteworthy that the structure of CrNbO$_4$ and FeNbO$_4$ is based upon an ABAB stacking sequence of closest packing of oxygen atoms where 1/4 of octahedral voids is occupied by metal ions. The difference in ion distribution in cationic sublattice leads, however to straight edge-shared chains of octahedra in the case of CrNbO$_4$ and zig-zag chains for FeNbO$_4$. On the other hand, the crystal structure of isotypical AlNbO$_4$ and GaNbO$_4$ compounds is based on the ReO$_3$ type structure with an ABCABC stacking sequence of closest packing of oxygen atoms, where 3/4 of accessible for oxygen sites are occupied by these anions in an ordered

way i.e. every other layer is half-occupied by oxygen ions [8].

The presence of AlNbO$_4$ and GaNbO$_4$ the $2\times2\times\infty$-type blocks in the crystal lattice, distinctly delimited in two dimensions (2×2) and spreading infinitely in the third dimension, or infinitely long chains of the edge-sharing MO$_6$ octahedra as in the case of CrNbO$_4$ and FeNbO$_4$, may cause a marked anisotropy of physical properties of these compounds. The studies conducted [9] revealed that in the case of the shear type Nb$_{14}$Mo$_3$O$_{44}$, Nb$_{12}$MoO$_{33}$ and Nb$_{12}$WO$_{33}$ phases, the structure of which consists of the ReO$_3$ type blocks, the direction of minimal thermal expansion is consistent with the direction in which these blocks spread to infinity. Moreover, in the case of the Nb$_{14}$Mo$_3$O$_{44}$ and Nb$_{12}$MoO$_{33}$ phases, the thermal expansion coefficients connected with this direction have negative values. The occurrence of this relatively seldom phenomenon makes the investigations of phases of this type structure particularly interesting. It seemed, therefore interesting to determine the mean values of linear thermal expansion coefficients of the MNbO$_4$ type phases and to relate them with the structural features.

The studies of thermal expansion were carried out using high-temperature X-ray attachment. It is noteworthy, that an undoubted advantage of this measurement technique in comparison to conventional dilatometry is a possibility of simultaneous monitoring the thermal expansion in several strictly defined crystallographic directions and unambiguous identification of the investigated object during the measurements [10–14].

Experimental

The following reagents: Fe$_2$O$_3$ a.p. (POCh Gliwice), Cr$_2$O$_3$ 98% (Sigma-Aldrich) Al$_2$O$_3$ p. (POCh Gliwice), Ga$_2$O$_3$ specpure (Johnson Mathey Chemicals Ltd.) and Nb$_2$O$_5$ 99.9% (Sigma-Aldrich) were used for research. The MNbO$_4$ type phases were prepared by heating oxides weighed in appropriate proportions at 1273 and 1373 K in 12 h cycles and additionally at 1473 and 1573 K for 4 h. Each heating cycle was followed by the XRD (DRON-3 diffractometer, Bourevestnik, Sankt Petersburg, Russia, radiation CoK$_\alpha$/Fe) examination of the samples. X-ray phase analysis of the preparations after the last heating cycle shows that they are monophase and contained AlNbO$_4$ and GaNbO$_4$ of the AlNbO$_4$ type structure, CrNbO$_4$ of the rutile type structure and FeNbO$_4$ of the wolframite type structure.

Investigations of thermal expansion in the temperature range 298–1073 K were conducted in a high-temperature X-ray diffractometric attachment UVD-2000 (Bourevestnik, Sankt Petersburg, Russia)

Table 1 Unit cell parameters and unit cell volumes at 298 and 1073 K

Formula	T/K	a/nm	b/nm	c/nm	β/degree	V/nm³
CrNbO₄	298	0.46482(8)	0.46482(8)	0.30163(5)		0.0652
	1073	0.46662(8)	0.46662(8)	0.30350(7)		0.0661
FeNbO₄	298	0.4644(1)	0.5622(2)	0.4993(2)	89.90(3)	0.1304
	1073	0.4694(2)	0.5649(2)	0.5035(2)	90.19(4)	0.1335
AlNbO₄	298	1.2166(1)	0.37388(5)	0.64944(6)	107.65(1)	0.2815
	1073	1.2232(2)	0.37467(7)	0.65417(9)	107.70(2)	0.2856
GaNbO₄	298	1.2479(1)	0.37886(5)	0.6620(1)	107.85(2)	0.2979
	1073	1.2558(2)	0.37886(7)	0.6664(1)	107.87(2)	0.3018

Table 2 Mean values of linear and volumetric thermal expansion coefficients in temperature range 298–1073 K of the MNbO$_4$ phases and Nb$_{12}$MoO$_{33}$ phase in the 298–873 K range [9]

Formula	α_a/K^{-1}	α_b/K^{-1}	α_c/K^{-1}	α_v/K^{-1}
CrNbO₄	5.00·10⁻⁶	5.00·10⁻⁶	8.00·10⁻⁶	1.78·10⁻⁵
FeNbO₄	1.39·10⁻⁵	6.20·10⁻⁶	1.09·10⁻⁵	3.07·10⁻⁵
AlNbO₄	7.00·10⁻⁶	2.73·10⁻⁶	9.40·10⁻⁶	1.88·10⁻⁵
GaNbO₄	8.17·10⁻⁶	0	8.58·10⁻⁶	1.69·10⁻⁵
Nb₁₂MoO₃₃	5.69·10⁻⁶	−1.77·10⁻⁶	7.24·10⁻⁶	1.06·10⁻⁵

coupled with an X-ray diffractometer HZG-4 (Freiberger Prazisions-Mechanic, Germany, radiation CuK$_\alpha$/Ni). After attaining a temperature that was set for given measurement the samples were kept at constant temperature for 30 min. Next applying a step scanning technique (step=0.02°, t=1 s) the diffraction patterns were recorded in the angular range 10–70° 2θ. In order to determine the exact positions of diffraction reflections, α-Al$_2$O$_3$ was applied as internal standard. The unit cell parameters and linear thermal expansion coefficients of α-Al$_2$O$_3$ determined in this research were in agreement with the data presented in the work [15]. The measurements in high-temperature X-ray attachment were conducted at 298 and 1073 K. The powder diffraction patterns of the investigated phases recorded at given temperatures were indexed by using the program Refinement. Table 1 lists the unit cell parameters and unit cell volumes of the investigated phases at temperatures of 298 and 1073 K. On the other hand, Table 2 presents mean values of linear thermal expansion coefficients and volumetric thermal expansion coefficients in the temperature range 298–1073 K calculated on the base of the equation [16]:

$$\alpha = (a_2 - a_1)/a_1(T_2 - T_1)$$

where α/K^{-1} – linear thermal expansion coefficient of the parameter a (volumetric thermal expansion coefficient), a_1/nm (nm³) – value of unit cell parameter (unit cell volume) at the temperature T_1/K, a_2/nm (nm³) – value of unit cell parameter (unit cell

volume) at the temperature T_2/K. This method of calculation of thermal expansion coefficient is based on the assumption that the thermal expansion coefficient is a constant independent on temperature.

Results and discussion

The obtained values of mean linear thermal expansion coefficients of the AlNbO$_4$, GaNbO$_4$, FeNbO$_4$ and CrNbO$_4$ phases (Table 2), indicate a marked anisotropy of their thermal expansion. The highest values of the thermal expansion coefficients were calculated in the case of FeNbO$_4$ and the least in the case of GaNbO$_4$. It is worth noticing that despite the substantial differences in values of the linear thermal expansion coefficients, the volumetric expansion coefficients of AlNbO$_4$, GaNbO$_4$ and CrNbO$_4$ get close values. An analysis of the data presented in Table 2 evidences a close similarity of thermal expansion of the isostructural AlNbO$_4$ and GaNbO$_4$ phases. The least values of thermal expansion coefficients, including also the 0 value in the case of GaNbO$_4$, characteristic of these compounds are connected with the shortest unit cell parameters b. Their size close to 0.38 nm corresponds to the height of distorted MO$_6$ octahedra that build the structure of these phases. The direction of minimal thermal expansion is also consistent with the direction in which the chains of corner-sharing MO$_6$ octahedra spread to infinity (Fig. 1). An analogous phenomenon was observed also in the case of the Nb$_{14}$Mo$_3$O$_{44}$, Nb$_{12}$MoO$_{33}$ and Nb$_{12}$WO$_{33}$ block-type phases the structure of which contains similar, infinitely spreading blocks of corner-shared MO$_6$ octahedra [9].

In the investigated AlNbO$_4$ and GaNbO$_4$ phases much greater values of thermal expansion coefficients were registered along the directions determining the XZ plane in which the shear planes divide the basic ReO$_3$-type structure into blocks of the 2×2 dimensions (Fig. 2). The presence of shear planes is due to the edge-sharing MO$_6$ octahedra occurring in the structure. The literature survey has shown that the

crystal structure of isotypical $AlNbO_4$ and $GaNbO_4$ compounds is built of two types of highly distorted corner and edge shared octahedra [1, 2]. The first is preferentially occupied by aluminum (gallium), the other one by niobium. The M–O bond lengths are confined in the boundary of 0.173 to 0.229 nm. The main axes of octahedra measured in the [010] direction consistent with the direction of the shortest unit cell parameter b, are the shortest and equal to 0.374 nm ($AlNbO_4$). Thus the interconnection of two adjacent octahedra by a common edge causes bringing nearer to each other the central ions with high charge (Nb^{5+}, Ga^{3+}, Al^{3+}) and relatively small radii, which results in an increase of their mutual repulsion. A consequence of this is shortening of the edge shared by both polyhedra and a concomitant lengthening of some M–O and O–O bonds (Fig. 2). This effect will contribute to flattening the MO_6 polyhedra as well as limiting the thermal expansion in the direction of spreading infinitely long chains of corner-sharing MO_6 octahedra. The octahedra building the $AlNbO_4$ and $GaNbO_4$ structure are situated in the crystal lattice in such a way that the longest M–O bonds are almost parallel to the X and Z axes. Thus lengthening the selected distances within the edge-sharing MO_6 polyhedra facilitates also an increase of thermal expansion along the X and Z directions (Table 2).

An analysis of the data presented in Table 2 indicates that although both structures of $CrNbO_4$ and $FeNbO_4$ are based upon an ABAB stacking sequence of closest packing of oxygen atoms, the difference in distribution of metal ions in cationic sublattice leads to a different behaviour of the phases during heating. It is noteworthy, that the crystal structure of $CrNbO_4$ is built up from the least distorted octahedra in the whole group of phases under study (M–O bond lengths confined in the boundary of 0.1986 to 0.1992 nm) and the anisotrophy of thermal expansion in this case is the least marked (Table 2) [3, 8]. In the case of this phase adopting the rutile type structure the greatest value of thermal expansion coefficient is associated with the direction [001] (unit cell parameter c) in which the edge shared $(Cr,Nb)O_6$ octahedra form straight chains (Fig. 3). This may be due to the fact that connection of adjacent octahedra by common edges results in the shortening of the common edge and lengthening the O–O edges parallel to the direction of the chain (axis Z). On the other hand, in the

case of the $FeNbO_4$, the structure of which is built up from highly distorted octahedra (M–O bond lengths confined in the boundary of 0.1859 to 0.2163 nm) such a phenomenon does not occur. However, the values of thermal expansion coefficient characteristic of $FeNbO_4$ are the highest in the whole group of phases under study. It is noteworthy that the second in respect of order of magnitude value of thermal expansion coefficient of $FeNbO_4$, associated with the direction [001] (unit cell parameter c), in which the zig-zag chains of edge-shared octahedra spread to infinity, is substantially higher than this of $CrNbO_4$ (unit cell parameter c, Table 2). The explanation of this problem requires, however a more exact analysis involving a much greater number of investigated objects.

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