

THERMAL EXPANSION OF PHASES FORMED IN THE SYSTEM $\text{Nb}_2\text{O}_5\text{--MoO}_3$

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Abstract

Studies on thermal expansion of phases formed in the system $\text{Nb}_2\text{O}_5\text{--MoO}_3$ (WO_3) have been carried out in the high-temperature X-ray diffraction attachment. In the case of $\text{Nb}_{14}\text{Mo}_3\text{O}_{44}$, $\text{Nb}_{12}\text{MoO}_{33}$ and $\text{Nb}_{12}\text{WO}_{33}$ the structure that consists of ReO_3 type blocks, the direction of minimal thermal expansion is consistent with direction in which the chains of corner-sharing polyhedra spread to infinity. On the contrary, for $\text{Nb}_2\text{Mo}_3\text{O}_{14}$, the structure of which resembles the structure of tetragonal tungsten bronzes, the maximal thermal expansion direction is consistent with above mentioned direction.

Keywords: shear structures, thermal expansion, XRD

Introduction

Literature review has shown that the phases $\text{Nb}_{12}\text{MoO}_{33}$ and $\text{Nb}_{14}\text{Mo}_3\text{O}_{44}$, isostructural with $\text{Nb}_{12}\text{WO}_{33}$ and $\text{Nb}_{14}\text{W}_3\text{O}_{44}$ respectively [1, 2], as well as the phase $\text{Nb}_2\text{Mo}_3\text{O}_{14}$ isostructural with Mo_5O_{14} [1] are formed in the system $\text{Nb}_2\text{O}_5\text{--MoO}_3$. The structure of phases $\text{Nb}_{12}\text{WO}_{33}$, $\text{Nb}_{14}\text{W}_3\text{O}_{44}$ and Mo_5O_{14} is known [3–5]. Thus in the structure of phases $\text{Nb}_{14}\text{Mo}_3\text{O}_{44}$ and $\text{Nb}_{12}\text{MoO}_{33}$ – by analogy – blocks of ReO_3 type can be distinguished, built up from deformed NbO_6 octahedra sharing only corners (Fig. 1a), with dimensions of $3 \times 4 \times \infty$ ($\text{Nb}_{12}\text{MoO}_{33}$) (Fig. 2) or $4 \times 4 \times \infty$ ($\text{Nb}_{14}\text{Mo}_3\text{O}_{44}$). Individual blocks share common edges (Fig. 1b). Two perpendicular to each other shear planes occur in such formed block structure (Fig. 2). The presence of two sets of shear planes causes a possibility of forming many intermediate phases, differing often only a little by their chemical composition, but distinguishable by XRD method (Fig. 3). In such formed three-dimensional lattices tetrahedral voids occur occupied in systematic way by molybdenum ions [3, 4].

The structure of the $\text{Nb}_2\text{Mo}_3\text{O}_{14}$ phase isostructural with Mo_5O_{14} resembles the structure of tetragonal tungsten bronzes (TTB) [6]. It is built up from MO_6 polyhedra linked only by their corners in such a way that 3, 4, 5 and 6-member rings are formed [5]. A part of pentagonal tunnels present in the structure is occupied in systematic way by oxygen and metal ions, which causes the additional presence of pentagonal

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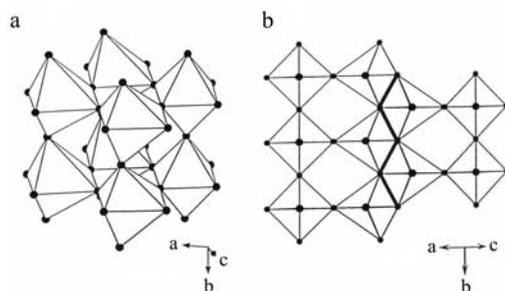


Fig. 1 Structural units of $\text{Nb}_{12}\text{WO}_{33}$ phase [4]: a – deformed NbO_6 octahedra sharing only corners and forming blocks of ReO_3 type, b – edge-sharing blocks of ReO_3 type neighbouring with one another (common edges are bold lines). Filled circles denote oxygen ions

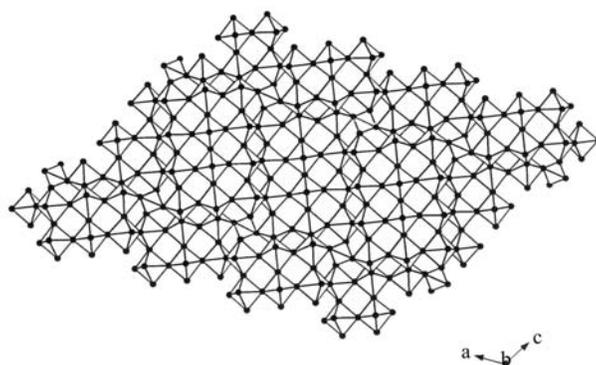


Fig. 2 Projection of $\text{Nb}_{12}\text{WO}_{33}$ structure [4] onto XZ plane. Filled circles denote oxygen ions

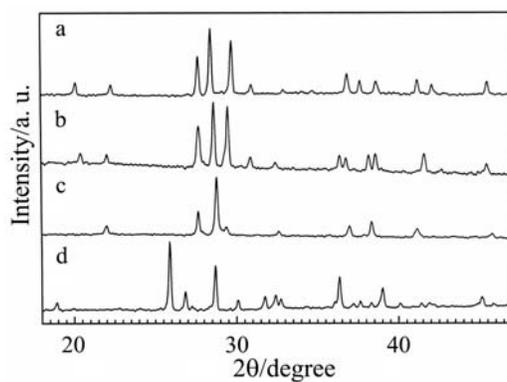


Fig. 3 X-ray powder diffraction patterns of a – $\text{H-Nb}_2\text{O}_3$, b – $\text{Nb}_{12}\text{MoO}_{33}$, c – $\text{Nb}_{14}\text{Mo}_3\text{O}_{44}$ and d – $\text{Nb}_2\text{Mo}_3\text{O}_{14}$ recorded at 298 K

MO₇ bipyramids in the crystal lattice. In the structure of Nb₂Mo₃O₁₄ also infinitely long chains of corner sharing MO_x polyhedra can be distinguished.

The presence in Nb₁₂MoO₃₃ and Nb₁₄Mo₃O₄₄ crystal lattice of $n \times m \times \infty$ -type blocks, distinctly delimited in two dimensions ($n \times m$) and spreading infinitely in the third dimension, or of infinitely long chains of corner-sharing MO_x polyhedra as in the case of Nb₂Mo₃O₁₄, may cause a marked anisotropy of physical properties of these compounds. It seemed therefore interesting to determine mean values of linear thermal expansion coefficients of the phases Nb₂Mo₃O₁₄, Nb₁₄Mo₃O₄₄ and Nb₁₂MoO₃₃ and to relate them with the structural features. For comparison the research was extended also on the phase Nb₁₂WO₃₃ isostructural with Nb₁₂MoO₃₃. The investigations of thermal expansion were carried out using high-temperature X-ray attachment. 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 [7–16].

Experimental

The reagents used for research were pure MoO₃ (POCh Gliwice), WO₃ 99.9% (Fluka) and Nb₂O₅ 99.9% (Aldrich). The Nb₁₄Mo₃O₄₄ and Nb₂Mo₃O₁₄ phases were obtained by sintering suitable oxides weighed in appropriate portions for the following cycles: 4×873 K(24 h)+4×923 K(24 h)+973 K(8 h). In the case of Nb₁₂MoO₃₃ phase the oxides were calcined under the following conditions: 2×873 K(24 h), +2×923 K(24 h)+1123 K(24 h). The Nb₁₂WO₃₃ phase was obtained also from oxides in the following cycles: 1273 K(24 h)+1373 K(24 h)+1473 K(24 h). The obtained phases were identified by means of XRD method (Fig. 3).

Investigations of thermal expansion in the temperature range 298–873 K were conducted in a high-temperature X-ray diffractometric attachment UVD-2000 (Bourestnik, Sankt Petersburg, Russia) coupled with an X-ray diffractometer HZG4. 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°2 θ . The source of radiation was a copper tube equipped with a nickel filter. Two series of independent measurements were performed in each case. In order to determine the exact positions of diffraction reflections, α -Al₂O₃ was applied as internal standard. The unit cell parameters and linear thermal expansion coefficients of α -Al₂O₃ determined in previous research were in agreement with the data presented in the work [17].

Results and discussion

The measurements in high-temperature X-ray attachment were carried out at 298 and 873 K. Figure 3 presents powder diffraction patterns of H-Nb₂O₅ (curve a), Nb₁₂MoO₃₃ (curve b), Nb₁₄Mo₃O₄₄ (curve c) and Nb₂Mo₃O₁₄ (curve d) recorded at 298 K. Analysis of the positions and intensities of the diffraction reflections as they

appear in the diffraction patterns of H-Nb₂O₅, Nb₁₂MoO₃₃ and Nb₁₄Mo₃O₄₄ indicates a close similarity occurring among these phases. This is undoubtedly related with their close structural relationship, they all being built up from blocks of $n \times m \times \infty$ type differing in size however. The powder diffraction patterns of the investigated phases recorded at various 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 873 K. Table 2 in turn presents mean values of linear thermal expansion coefficients and volumetric thermal expansion coefficients in the temperature range 298–873 K that were calculated on the base of the equation [18]:

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

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.

Table 1 Unit cell parameters and unit cell volumes at 298 and 873 K

Formula	T/K	a/nm	b/nm	c/nm	$\beta/^\circ$	V/nm^3
Nb ₂ Mo ₃ O ₁₄	298	2.3180(2)	2.3180(2)	0.39998(8)		2.1491
Nb ₂ Mo ₃ O ₁₄	873	2.3219(2)	2.3219(2)	0.4018(1)		2.1662
Nb ₁₄ Mo ₃ O ₄₄	298	2.1043(2)	2.1043(2)	0.38157(7)		1.6896
Nb ₁₄ Mo ₃ O ₄₄	873	2.1131(2)	2.1131(2)	0.38134(7)		1.7028
Nb ₁₂ MoO ₃₃	298	2.2299(5)	0.3827(1)	1.7785(3)	123.42(4)	1.2668
Nb ₁₂ MoO ₃₃	873	2.2372(5)	0.38231(9)	1.7859(4)	123.45(4)	1.2745
Nb ₁₂ WO ₃₃	298	2.2340(3)	0.38228(8)	1.7765(3)	123.40(3)	1.2666
Nb ₁₂ WO ₃₃	873	2.2398(3)	0.38233(7)	1.7843(3)	123.43(3)	1.2752

Table 2 Mean values of linear thermal expansion coefficients and volumetric thermal expansion coefficients in temperature range 298–873 K

Formula	α_a/K^{-1}	α_b/K^{-1}	α_c/K^{-1}	α_v/K^{-1}
Nb ₂ Mo ₃ O ₁₄	$2.93 \cdot 10^{-6}$	$2.93 \cdot 10^{-6}$	$7.91 \cdot 10^{-6}$	$1.38 \cdot 10^{-5}$
Nb ₁₄ Mo ₃ O ₄₄	$7.27 \cdot 10^{-6}$	$7.27 \cdot 10^{-6}$	$-1.05 \cdot 10^{-6}$	$1.36 \cdot 10^{-5}$
Nb ₁₂ MoO ₃₃	$5.69 \cdot 10^{-6}$	$-1.77 \cdot 10^{-6}$	$7.24 \cdot 10^{-6}$	$1.06 \cdot 10^{-5}$
Nb ₁₂ WO ₃₃	$4.52 \cdot 10^{-6}$	$2.27 \cdot 10^{-7}$	$7.64 \cdot 10^{-6}$	$1.18 \cdot 10^{-5}$

The obtained values of mean linear thermal expansion coefficients of the phases $\text{Nb}_2\text{Mo}_3\text{O}_{14}$, $\text{Nb}_{14}\text{Mo}_3\text{O}_{44}$, $\text{Nb}_{12}\text{MoO}_{33}$ and $\text{Nb}_{12}\text{WO}_{33}$ (Table 2) indicate a marked anisotropy of their thermal expansion. It is worthy to notice that the volumetric expansion coefficients get close values. In the case of the $\text{Nb}_{14}\text{Mo}_3\text{O}_{44}$ and $\text{Nb}_{12}\text{MoO}_{33}$ phases, the thermal expansion coefficients have got negative values. This relatively seldom-occurring phenomenon was observed among others in the case of pseudobrookite-type phases [16] or $\text{A}_{5-4x}\text{Zr}(\text{PO}_4)_3$ type phases, where $A=\text{Na}, \text{K}$ [8]. Analysis of the data presented in Table 2 evidences a close similarity of thermal expansion of the phases $\text{Nb}_{14}\text{Mo}_3\text{O}_{44}$, $\text{Nb}_{12}\text{MoO}_{33}$ and $\text{Nb}_{12}\text{WO}_{33}$. The least values of thermal expansion coefficients, including also the negative ones, characteristic of these compounds are related with the shortest identity periods. Their size close to 0.4 nm corresponds to the height of deformed NbO_6 polyhedra that are basic units building the structure of these phases. The direction of minimal thermal expansion is also consistent with the direction in which the chains of corner-sharing NbO_6 polyhedra spread to infinity. An analogous phenomenon was observed also in the case of the M_3O_5 phases of a pseudobrookite-type structure containing similar, infinitely long chains of MO_6 octahedra [8].

In the investigated phases $\text{Nb}_{14}\text{Mo}_3\text{O}_{44}$, $\text{Nb}_{12}\text{MoO}_{33}$ and $\text{Nb}_{12}\text{WO}_{33}$, much greater values of thermal expansion coefficients were registered along the directions determining a plane in which the shear planes divide the basic ReO_3 -type structure into blocks of the $n \times m$ dimensions. The presence of shear planes is due to occurring in the structure of edge-sharing NbO_6 octahedra. The interconnection of two neighbouring octahedra by a common edge causes bringing nearer to each other of central ions with high charge (Nb^{5+}), which results in an increase of their mutual repulsion. A consequence of this is shortening the edge shared by both polyhedra and a concomitant lengthening of some Nb-O and O-O distances (Fig. 2). This effect will contribute on the one hand to flattening the NbO_6 polyhedra and limiting the thermal expansion in the direction of spreading infinitely long chains of corner-sharing NbO_6 polyhedra. At the same time, lengthening selected distances within the edge-sharing NbO_6 polyhedra facilitates an increase of thermal expansion along the direction that is determined by the lengthened bonds. It seems that each correlation of this type is associated with the size of the $n \times m \times \infty$ blocks and thus with the number of edge-sharing MO_6 polyhedra. This problem requires however a more exact analysis involving a much greater number of investigated objects. Analysis of the data presented in Table 2 indicates a different behaviour of the $\text{Nb}_2\text{Mo}_3\text{O}_{14}$ phase during its heating. In this case the least value of identity period is associated with the greatest value of thermal expansion coefficient. This may be due to the fact that common edges shared by the polyhedra MO_x are symmetrically distributed in the plane XY and because of this they do not cause a significant limitation of thermal expansion in the direction along which the chains of corner-sharing MO_x polyhedra spread to infinity.

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