

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

*P. Tabero*<sup>\*</sup>

Technical University of Szczecin, Institute of Chemistry and Environment Protection, Al. Piastow 42, 71-065 Szczecin, Poland

### **Abstract**

Studies on thermal expansion of phases formed in the system  $\text{Nb}_2\text{O}_5\text{--MoO}_3$  ( $\text{WO}_3$ ) 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  $\text{ReO}_3$  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.

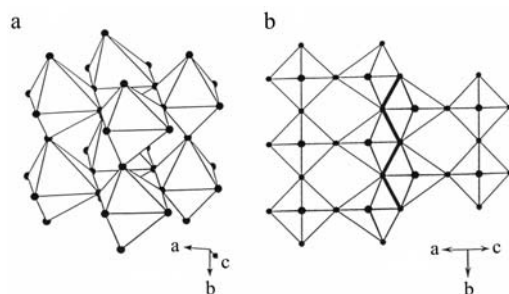
**Keywords:** shear structures, thermal expansion, XRD

### **Introduction**

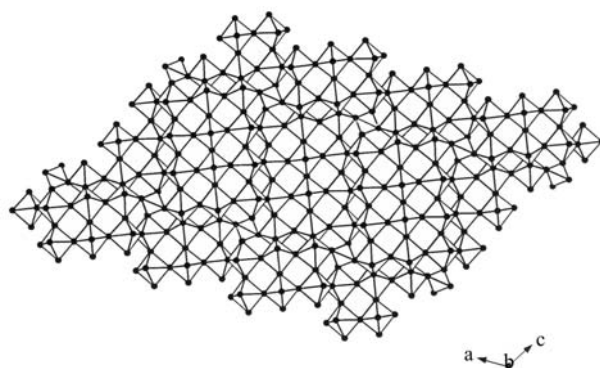
Literature review has shown that the phases  $\text{Nb}_{12}\text{MoO}_{33}$  and  $\text{Nb}_{14}\text{Mo}_3\text{O}_{44}$ , isostructural with  $\text{Nb}_{12}\text{WO}_{33}$  and  $\text{Nb}_{14}\text{W}_3\text{O}_{44}$  respectively [1, 2], as well as the phase  $\text{Nb}_2\text{Mo}_3\text{O}_{14}$  isostructural with  $\text{Mo}_5\text{O}_{14}$  [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  $\text{Mo}_5\text{O}_{14}$  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  $\text{ReO}_3$  type can be distinguished, built up from deformed  $\text{NbO}_6$  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  $\text{Mo}_5\text{O}_{14}$  resembles the structure of tetragonal tungsten bronzes (TTB) [6]. It is built up from  $\text{MO}_6$  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

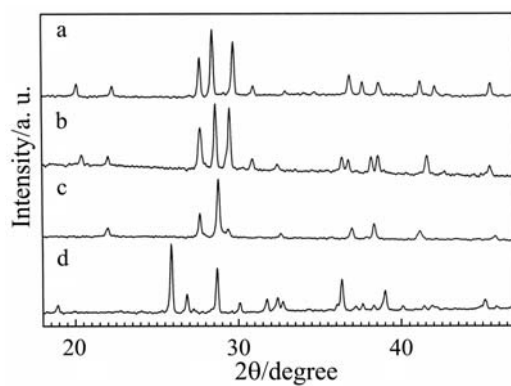
<sup>\*</sup> Author for correspondence: E-mail: ptab@ps.pl



**Fig. 1** Structural units of  $\text{Nb}_{12}\text{WO}_{33}$  phase [4]: a – deformed  $\text{NbO}_6$  octahedra sharing only corners and forming blocks of  $\text{ReO}_3$  type, b – edge-sharing blocks of  $\text{ReO}_3$  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

MO<sub>7</sub> bipyramids in the crystal lattice. In the structure of Nb<sub>2</sub>Mo<sub>3</sub>O<sub>14</sub> also infinitely long chains of corner sharing MO<sub>x</sub> polyhedra can be distinguished.

The presence in Nb<sub>12</sub>MoO<sub>33</sub> and Nb<sub>14</sub>Mo<sub>3</sub>O<sub>44</sub> 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<sub>x</sub> polyhedra as in the case of Nb<sub>2</sub>Mo<sub>3</sub>O<sub>14</sub>, 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 Nb<sub>2</sub>Mo<sub>3</sub>O<sub>14</sub>, Nb<sub>14</sub>Mo<sub>3</sub>O<sub>44</sub> and Nb<sub>12</sub>MoO<sub>33</sub> and to relate them with the structural features. For comparison the research was extended also on the phase Nb<sub>12</sub>WO<sub>33</sub> isostructural with Nb<sub>12</sub>MoO<sub>33</sub>. 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 MoO<sub>3</sub> (POCh Gliwice), WO<sub>3</sub> 99.9% (Fluka) and Nb<sub>2</sub>O<sub>5</sub> 99.9% (Aldrich). The Nb<sub>14</sub>Mo<sub>3</sub>O<sub>44</sub> and Nb<sub>2</sub>Mo<sub>3</sub>O<sub>14</sub> 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 Nb<sub>12</sub>MoO<sub>33</sub> phase the oxides were calcined under the following conditions: 2×873 K(24 h), +2×923 K(24 h)+1123 K(24 h). The Nb<sub>12</sub>WO<sub>33</sub> 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 $\theta$ . 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,  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> was applied as internal standard. The unit cell parameters and linear thermal expansion coefficients of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> 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-Nb<sub>2</sub>O<sub>5</sub> (curve a), Nb<sub>12</sub>MoO<sub>33</sub> (curve b), Nb<sub>14</sub>Mo<sub>3</sub>O<sub>44</sub> (curve c) and Nb<sub>2</sub>Mo<sub>3</sub>O<sub>14</sub> (curve d) recorded at 298 K. Analysis of the positions and intensities of the diffraction reflections as they

appear in the diffraction patterns of  $\text{H-Nb}_2\text{O}_5$ ,  $\text{Nb}_{12}\text{MoO}_{33}$  and  $\text{Nb}_{14}\text{Mo}_3\text{O}_{44}$  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  $\alpha/\text{K}^{-1}$  – linear thermal expansion coefficient of the parameter  $a$  (volumetric thermal expansion coefficient),  $a_1/\text{nm}$  ( $\text{nm}^3$ ) – value of unit cell parameter (unit cell volume) at the temperature  $T_1/\text{K}$ ,  $a_2/\text{nm}$  ( $\text{nm}^3$ ) – value of unit cell parameter (unit cell volume) at the temperature  $T_2/\text{K}$ . 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	$T/\text{K}$	$a/\text{nm}$	$b/\text{nm}$	$c/\text{nm}$	$\beta/^\circ$	$V/\text{nm}^3$
$\text{Nb}_2\text{Mo}_3\text{O}_{14}$	298	2.3180(2)	2.3180(2)	0.39998(8)		2.1491
$\text{Nb}_2\text{Mo}_3\text{O}_{14}$	873	2.3219(2)	2.3219(2)	0.4018(1)		2.1662
$\text{Nb}_{14}\text{Mo}_3\text{O}_{44}$	298	2.1043(2)	2.1043(2)	0.38157(7)		1.6896
$\text{Nb}_{14}\text{Mo}_3\text{O}_{44}$	873	2.1131(2)	2.1131(2)	0.38134(7)		1.7028
$\text{Nb}_{12}\text{MoO}_{33}$	298	2.2299(5)	0.3827(1)	1.7785(3)	123.42(4)	1.2668
$\text{Nb}_{12}\text{MoO}_{33}$	873	2.2372(5)	0.38231(9)	1.7859(4)	123.45(4)	1.2745
$\text{Nb}_{12}\text{WO}_{33}$	298	2.2340(3)	0.38228(8)	1.7765(3)	123.40(3)	1.2666
$\text{Nb}_{12}\text{WO}_{33}$	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	$\alpha_a/\text{K}^{-1}$	$\alpha_b/\text{K}^{-1}$	$\alpha_c/\text{K}^{-1}$	$\alpha_v/\text{K}^{-1}$
$\text{Nb}_2\text{Mo}_3\text{O}_{14}$	$2.93 \cdot 10^{-6}$	$2.93 \cdot 10^{-6}$	$7.91 \cdot 10^{-6}$	$1.38 \cdot 10^{-5}$
$\text{Nb}_{14}\text{Mo}_3\text{O}_{44}$	$7.27 \cdot 10^{-6}$	$7.27 \cdot 10^{-6}$	$-1.05 \cdot 10^{-6}$	$1.36 \cdot 10^{-5}$
$\text{Nb}_{12}\text{MoO}_{33}$	$5.69 \cdot 10^{-6}$	$-1.77 \cdot 10^{-6}$	$7.24 \cdot 10^{-6}$	$1.06 \cdot 10^{-5}$
$\text{Nb}_{12}\text{WO}_{33}$	$4.52 \cdot 10^{-6}$	$2.27 \cdot 10^{-7}$	$7.64 \cdot 10^{-6}$	$1.18 \cdot 10^{-5}$

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  $\text{NbO}_6$  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  $\text{NbO}_6$  polyhedra spread to infinity. An analogous phenomenon was observed also in the case of the  $\text{M}_3\text{O}_5$  phases of a pseudobrookite-type structure containing similar, infinitely long chains of  $\text{MO}_6$  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  $\text{ReO}_3$ -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  $\text{NbO}_6$  octahedra. The interconnection of two neighbouring octahedra by a common edge causes bringing nearer to each other of central ions with high charge ( $\text{Nb}^{5+}$ ), 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  $\text{NbO}_6$  polyhedra and limiting the thermal expansion in the direction of spreading infinitely long chains of corner-sharing  $\text{NbO}_6$  polyhedra. At the same time, lengthening selected distances within the edge-sharing  $\text{NbO}_6$  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  $\text{MO}_6$  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  $\text{MO}_x$  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  $\text{MO}_x$  polyhedra spread to infinity.

## References

- 1 T. Ekstrom, Acta. Chem. Scand., 25 (1971) 2591.
- 2 S. Andersson, Z. Anorg. Allg. Chem., 366 (1969) 96.

- 3 R. S. Roth and A. D. Wadsley, *Acta Cryst.*, 19 (1965) 38.
- 4 R. S. Roth and A. D. Wadsley, *Acta Cryst.*, 19 (1965) 32.
- 5 L. Kihlborg, *Ark. Kemi.*, 21 (1963) 427.
- 6 F. Krumeich, C. Bartsch and R. Gruehn, *J. Solid State Chem.*, 120 (1995) 268.
- 7 P. Tabero, M. Bosacka and M. Kurzawa, *J. Therm. Anal. Cal.*, 65 (2001) 865.
- 8 V. I. Pet'kov, A. I. Orlova, G. N. Kazantsev, S. G. Samoilov and M. L. Spiridanova, *J. Therm. Anal. Cal.*, 66 (2001) 623.
- 9 L. D. Brown, A. S. Ray, P. S. Thomas and J. P. Guerbois, *J. Therm. Anal. Cal.*, 68 (2002) 31.
- 10 K. Tozaki, R. Masuda, S. Matsuda, C. Tokitomo, H. Hayashi, H. Inaba, Y. Yoshimura and T. Kimura, *J. Therm. Anal. Cal.*, 64 (2001) 331.
- 11 M. Iijima, T. Hatakeyama, M. Takahashi and H. Hatakeyama, *J. Therm. Anal. Cal.*, 64 (2001) 617.
- 12 H. Yoshida, Y. Houshito, K. Mashiko, K. Masaka and S. Nakamura, *J. Therm. Anal. Cal.*, 64 (2001) 453.
- 13 D. M. Price, *J. Therm. Anal. Cal.*, 64 (2001) 323.
- 14 P. Myslinski, P. Kamasa and A. Wasik, *J. Therm. Anal. Cal.*, 64 (2001) 1201.
- 15 P. V. Morra, A. J. Bottger and E. J. Mittemijer, *J. Therm. Anal. Cal.*, 64 (2001) 905.
- 16 G. Bayer, *J. Less-Comm. Met.*, 24 (1971) 129.
- 17 W. J. Campbell and C. Grain, *Advan. X-ray Anal.*, 5 (1962) 244.
- 18 *International Tables for X-ray Crystallography*, Vol. III, Eds K. Lonsale, C. H. Macgorillany and G. G. Rieckj, The Kynoch Press, Birmingham 1968.