New triple molybdate and tungstate
$\text{Na}_5\text{Rb}_7\text{Sc}_2(\text{XO}_4)_9$ ($X = \text{Mo}, W$)

Tatyana S. Spiridonova a,b, Aleksandra A. Savina a,b, Evgeniy V. Kvitunets a, Elena G. Khaikina a

a: Baikal Institute of Nature Management, Siberian Branch, Russian Academy of Sciences, 670047 Sakh’yanova st., 6, Ulan-Ude, Russia
b: Skolkovo Institute of Science and Technology, 121205 Bolshoy Blvd., 30, Moscow, Russia

* Corresponding author: spiridonova-25@mail.ru

This article belongs to the regular issue.

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Abstract

New compounds of the composition $\text{Na}_3\text{Rb}_2\text{Sc}_2(\text{XO}_4)_9$ ($X = \text{Mo}, W$) were established via the ceramic technology. The sequences of chemical transformations occurring during the formation of these compounds were established, and their primary characterization was performed. Both $\text{Na}_3\text{Rb}_2\text{Sc}_2(\text{XO}_4)_9$ ($X = \text{Mo}, W$) were found to melt incongruently at 857 K ($X = \text{Mo}$) and 889 K ($X = W$). They are isostructural to $\text{Ag}_3\text{Rb}_2\text{Sc}_2(\text{XO}_4)_9$ ($X = \text{Mo}, W$), $\text{Na}_3\text{Cs}_2\text{Ln}_2(\text{MoO}_4)_9$ ($\text{Ln} = \text{Tm}, \text{Yb}, \text{Lu}$) and crystallize in the trigonal crystal system (sp. gr. $R3\bar{2}$). The crystal structures were refined with the Rietveld method using the powder X-ray diffraction data. The thermal expansion of $\text{Na}_3\text{Rb}_2\text{Sc}_2(\text{WO}_4)_9$ was studied by high-temperature powder X-ray diffraction; it was shown that this triple tungstate belongs to high thermal expansion materials.

Keywords

sodium rubidium scandium triple molybdate triple tungstate synthesis crystal structure thermal expansion

Received: 03.12.2021
Revised: 10.12.2021
Accepted: 14.12.2021
Available online: 16.12.2021

1. Introduction

The search for new functional inorganic materials based on the development of ideas about the relationships between their structure and properties is one of the high-priority directions of modern solid state chemistry, crystal chemistry and materials science. The greatest attention is paid to the synthesis, study of the structure and properties of complex oxides, among which binary Mo (VI) and W (VI) compounds of various compositions occupy a significant place. In the last two decades, triple molybdates have been actively studied, and in recent years, triple tungstates have also attracted much attention as interesting research objects. Constant interest in such compounds is maintained due to their wide range of functional properties, such as catalytic, luminescent, laser, nonlinear optical, ferroelectric, ion-conducting, and others. Thus, numerous publications are devoted to triple molybdates and tungstates with the $\text{BaNd}_2(\text{MoO}_4)_4$-type structure, which are represented by two families of compounds: $\text{Li}_3\text{MR}_2(\text{MoO}_4)_4$ ($M = \text{K}, \text{Rb}, R = \text{Bi}, \text{Ln}$) and $\text{Li}_3\text{Ba}_2\text{Ln}_2(\text{XO}_4)_9$ ($X = \text{Mo}, W$). The prospects for possible application of these compounds as photo- and IR-phosphors, materials for UV radiation dosimeters, laser materials are shown in [1–10]. The latter is also facilitated by the fact that the maximum anisotropy of thermal expansion in several representatives of this family is lower than that in other successfully used laser crystals [11]. The molybdate phosphor $\text{NaCaLa}(\text{MoO}_4)_3$: $\text{ Tb}^{3+}/\text{Yb}^{3+}$ can be used as a spectral converter [12].

Triple molybdates $\text{Na}_3\text{Cs}_2\text{R}_2(\text{MoO}_4)_3$ ($R = \text{In}, \text{Sc}$ or $\text{Fe}$) [13, 14] and $\text{Na}_3\text{Cs}_4\text{Co}_5(\text{MoO}_4)_3$ [15], built on the basis of alluaudite $(\text{Na},\text{Ca})\text{Mn}((\text{Fe},\text{Mg})_2(\text{PO}_4)_3$, $\text{M}_4\text{S}_4\text{R}_6(\text{MoO}_4)_3$ [16, 17] with the NASICON-type structure, $\text{K}_3\text{Sc}(\text{MoO}_4)_3$ [18] with the $\text{K}_3\text{InHf}((\text{MoO}_4)_3$-type structure, and $\text{AgRbIn}(\text{MoO}_4)_3$ [19], $\text{AgRbSc}(\text{WO}_4)_9$ [20], $\text{AgRb}_2\text{Sc}_2(\text{XO}_4)_9$ ($X = \text{Mo}, W$) [21] that formed their own structural types are considered to be promising solid state electrolytes.

In this work, the family of triple molybdates and tungstates represented by formula $\text{M}_5\text{R}_2(\text{XO}_4)_3$ [21, 22] is extended by two new compounds, $\text{Na}_3\text{Rb}_2\text{Sc}_2(\text{XO}_4)_9$ ($X = \text{Mo}, W$). The primary characterization of these phases was carried out. Their crystal structure was refined by the Rietveld method from powder X-ray diffraction data. In addition, the thermal expansion of $\text{Na}_3\text{Rb}_2\text{Sc}_2(\text{WO}_4)_9$ was studied.
2. Experimental

2.1. Preparation of materials

Commercially available chemically pure MoO$_3$, WO$_3$ (ReaKhim, Ltd, Russia), AgNO$_3$ (KhimKo, Ltd, Russia) and high purity Sc$_2$O$_3$ (SibMetalTorg, Ltd, Russia), Rb$_2$CO$_3$ (Sigma-Aldrich, China) were used as starting materials for preparing molybdates and tungstates. Rb$_2$XO$_3$ ($X = \text{Mo, W}$) was prepared by high temperature annealing of a stoichiometric mixture of Rb$_2$CO$_3$ and XO$_3$ (723–823 K, 80 h). Sc$_2$(XO$_4$)$_3$ ($X = \text{Mo, W}$) was obtained from Sc$_2$O$_3$ and XO$_3$ ($X = \text{Mo}$, 773–1023 K, 80 h; $X = \text{W}$, 773–1123 K, 80 h). Anhydrous Na$_2$XO$_4$ ($X = \text{Mo, W}$) used in this work were obtained by calcining the corresponding crystalline hydrates at 823–873 K.

The phase purity of the prepared samples was confirmed by powder X-ray diffraction (PXRD). The PXRD patterns of Na$_2$XO$_4$, Rb$_2$XO$_4$, Sc$_2$(XO$_4$)$_3$ ($X = \text{Mo, W}$) were in good agreement with the literature data [23].

2.2. Instrumental characterization methods

The processes that occur during the solid-state syntheses were monitored with PXRD using a D8 ADVANCE Bruker diffractometer (VANTEC detector, Cu Kα radiation, $\lambda = 1.5418$ Å, reflection geometry, secondary monochromator). High temperature X-ray measurements of Na$_3$Rb$_5$Sc$_2$(WO$_4$)$_9$ were performed with the same instrument using an Anton Paar HTK 16 high temperature chamber in the temperature range of 303–823 K. The heating rate was 20 K min$^{-1}$. Prior to measurements, the sample was kept at a specified temperature for 25 min.

The unit cell parameters of Na$_3$Rb$_5$Sc$_2$(XO$_4$)$_9$ ($X = \text{Mo, W}$) were refined by the least-squares method using ICDD program package for preparing experimental standards. The Smith–Snyder F30 criterion was used as a validation criterion for X-ray patterns indexing [24]. The crystal structures refinement of Na$_3$Rb$_5$Sc$_2$(XO$_4$)$_9$ ($X = \text{Mo, W}$) at room temperature and the unit cell parameters determination in high-temperature studies were carried out by the Rietveld method [25] using the TOPAS 4.2 software [26].

The thermal measurements were carried out using an STA 449 F1 Jupiter NETZSCH thermoanlyser (Pt crucible, heating rate of 10 K min$^{-1}$ in a flow of argon).

3. Results and discussion

3.1. Synthesis and characterization of Na$_3$Rb$_5$Sc$_2$(XO$_4$)$_9$ ($X = \text{Mo, W}$)

Polycrystalline Na$_3$Rb$_5$Sc$_2$(XO$_4$)$_9$ ($X = \text{Mo, W}$) were synthesized by annealing the stoichiometric mixtures of Na$_2$XO$_4$, Rb$_2$XO$_4$ and Sc$_2$(XO$_4$)$_3$ at 773–823 K for 80 h ($X = \text{Mo}$), 100 h ($X = \text{W}$).

The final powder products are of white color, insoluble in water and common organic solvents, soluble in HCl (Na$_3$Rb$_5$Sc$_2$(MoO$_4$)$_9$ at room temperature, Na$_3$Rb$_5$Sc$_2$(WO$_4$)$_9$ – at heating).

According to the results of PXRD data, the sequence of chemical transformations in the course of Na$_3$Rb$_5$Sc$_2$(WO$_4$)$_9$ formation from a stoichiometric mixture of simple tungstates can be illustrated by the following scheme:

\[
\begin{array}{c}
\text{Na}_3\text{WO}_4 \\
\text{Rb}_2\text{WO}_4 \\
\text{Sc}_2\text{(WO}_4)_3
\end{array} \quad \begin{array}{c}
573–623 \text{K, 100 h} \\
673 \text{K, 100 h} \\
723–823 \text{K, 100 h}
\end{array} \quad \begin{array}{c}
\text{Na}_3\text{WO}_4 \\
\text{Rb}_2\text{WO}_4 \\
\text{Sc}_2\text{(WO}_4)_3 \\
\text{Na}_3\text{Rb}_5\text{Sc}_2\text{(WO}_4)_9
\end{array}
\]

Scheme 1: The sequence of chemical transformations in the course of Na$_3$Rb$_5$Sc$_2$(WO$_4$)$_9$ formation

In the Mo-containing system the formation of Na$_3$Rb$_5$Sc$_2$(MoO$_4$)$_9$ started at the stage when NaRb$_2$(MoO$_4$)$_2$ and RbSc(MoO$_4$)$_2$ appeared. The corresponding scheme differs from that for ternary tungstate only in shorter synthesis times.

Both Mo- and W-based Na$_3$Rb$_5$Sc$_2$(XO$_4$)$_9$ melt incongruently at 857 K ($X = \text{Mo}$) and 889 K ($X = \text{W}$) (Fig. 1). Reflections of both NaSc(MoO$_4$)$_2$ and a phase with an alluoudite-type structure together with the initial phase were found in the PXRD pattern of the cooled Na$_3$Rb$_5$Sc$_2$(MoO$_4$)$_9$ melt. The cooled melt of Na$_3$Rb$_5$Sc$_2$(WO$_4$)$_9$ contains the double tungstates RbSc(WO$_4$)$_2$ and NaSc(WO$_4$)$_2$ and an alluoudite-like phase. The amount of the latter phase was dominant.

![Fig. 1 The DSC curves for polycrystalline Na$_3$Rb$_5$Sc$_2$(XO$_4$)$_9$ ($X = \text{W, Mo}$) (2 of 8)](image-url)
The PXRD patterns of prepared single-phase compounds Na$_3$Rb$_3$Sc$_3$(XO$_4$)$_9$ ($X = \text{Mo, W}$) are similar and show that these complex oxides are isosstructural to trigonal Na$_3$Co$_3$Yb$_2$(MoO$_4$)$_9$, Ag$_3$Rb$_3$Sc$_3$(XO$_4$)$_9$ ($X = \text{Mo, W}$) (sp. gr. $R32$, $Z = 3$) [21, 22]. This allows satisfactorily indexing the PXRD patterns of Na$_3$Rb$_3$Sc$_3$(XO$_4$)$_9$ ($X = \text{Mo, W}$) (in the case of molybdate $F(30) = 141.6$ (0.0056; 38), for tungstate $F(30) = 287.2$ (0.0028; 37)). The obtained crystallographic characteristics are shown in Table 1, the results of indexing of Na$_3$Rb$_3$Sc$_3$(WO$_4$)$_9$ are shown in Table 2 as an example.

### Table 2 The PXRD data for Na$_3$Rb$_3$Sc$_3$(WO$_4$)$_9$

| $h$ | $k$ | $l$ | $2\theta_{exp}$, $^\circ$ | $d_{exp}$, Å | $\Delta = 2\theta_{exp} - 2\theta_{calc}$, $^\circ$ |
|----|----|----|----------------|-------------|----------------|
| 1 0 1 | 10.322 | 1 | 8.563 | -0.003 |
| 0 1 2 | 11.183 | 2 | 7.906 | -0.002 |
| 1 0 4 | 14.117 | 1L | 6.268 | +0.003 |
| 0 0 6 | 14.911 | 1L | 5.936 | +0.004 |
| 0 1 5 | 15.974 | 1L | 5.544 | +0.004 |
| 1 1 0 | 17.390 | 20 | 5.095 | +0.001 |
| 1 1 3 | 18.938 | 42 | 4.682 | +0.000 |
| 1 0 7 | 20.131 | 1 | 4.407 | +0.000 |
| 0 2 1 | 20.264 | 1 | 4.379 | -0.001 |
| 2 0 2 | 20.724 | 2 | 4.283 | -0.001 |
| 0 0 9 | 22.454 | 13 | 3.956 | -0.002 |
| 1 1 6 | 22.987 | 100 | 3.865 | +0.000 |
| 2 0 5 | 23.694 | 1 | 3.752 | +0.007 |
| 0 2 7 | 26.722 | 2 | 3.333 | +0.001 |
| 2 1 1 | 26.824 | 15 | 3.209 | +0.000 |
| 1 0 10 | 26.973 | 1L | 3.029 | +0.005 |
| 1 2 2 | 27.178 | 3 | 3.278 | +0.000 |
| 1 1 9 | 28.541 | 59 | 3.124 | -0.001 |
| 0 1 11 | 29.345 | 2 | 3.041 | +0.018 |
| 1 2 5 | 29.546 | 5 | 3.020 | +0.002 |
| 0 0 12 | 30.094 | 1 | 2.967 | -0.004 |
| 0 3 0 | 30.362 | 54 | 2.941 | -0.001 |
| 3 0 3 | 31.304 | 1 | 2.855 | -0.001 |
| 2 1 7 | 32.067 | 2 | 2.788 | -0.006 |
| 1 2 8 | 33.548 | 3 | 2.669 | -0.002 |
| 3 0 6 | 33.989 | 5 | 2.635 | -0.002 |
| 2 0 11 | 34.335 | 1L | 2.609 | -0.006 |
| 1 1 12 | 34.964 | 15 | 2.541 | -0.002 |
| 2 2 0 | 35.200 | 5 | 2.547 | +0.000 |
| 2 2 3 | 36.031 | 1 | 2.490 | -0.002 |
| 0 0 14 | 36.738 | 1L | 2.444 | +0.004 |
| 1 3 1 | 36.779 | 2 | 2.441 | -0.002 |
| 2 1 10 | 36.898 | 1L | 2.434 | -0.004 |
| 3 1 2 | 37.057 | 1L | 2.424 | -0.012 |
| 3 0 9 | 38.091 | 6 | 2.365 | -0.002 |
| 2 2 6 | 38.423 | 8 | 2.340 | -0.001 |
| 3 1 5 | 38.875 | 2 | 2.317 | +0.001 |
| 1 3 7 | 40.884 | 1 | 2.205 | -0.001 |
| 4 0 1 | 40.950 | 1 | 2.202 | +0.002 |
| 0 4 2 | 41.201 | 1 | 2.189 | -0.004 |
| 1 0 16 | 41.799 | 1L | 2.159 | +0.025 |
| 1 1 15 | 41.952 | 9 | 2.151 | +0.002 |
| 2 2 9 | 42.156 | 19 | 2.148 | -0.002 |

Cu Kα, radiation ($\lambda = 1.54056$ Å)

| $X$ | $a$, Å | $c$, Å | $V$, Å³ |
|-----|-------|-------|--------|
| Mo | 10.126(1) | 35.6570(7) | 3172.80 |
| W | 10.189(2) | 35.6096(9) | 3202.12 |
3.2. Rietveld refinement of Na$_2$Rb$_7$Sc$_6$(XO$_4$)$_9$ (X = Mo, W) structure

The positional atomic parameters for the Ag$_3$Rb$_3$Sc$_2$(MoO$_4$)$_9$ structure [21] were taken as a starting model for the refinement of the Na$_2$Rb$_7$Sc$_6$(XO$_4$)$_9$ (X = Mo, W) structures by the Rietveld method. The refinement was carried out by gradually adding the refined parameters with the simultaneous graphical simulation of the background. The Pearson VII Function was used to describe the shape of peaks. Isotropic displacement parameters (Biso) for all atoms in Na$_2$Rb$_7$Sc$_6$(MoO$_4$)$_9$ were refined separately, while for the O atoms in Na$_2$Rb$_7$Sc$_6$(WO$_4$)$_9$ they were taken as equal. The refinement procedure included corrections for the sample preferred orientation and broadening of peaks due to anisotropy within the model of spherical harmonics [27]. The Rietveld refinement results for Na$_2$Rb$_7$Sc$_6$(XO$_4$)$_9$ (X = Mo, W) are shown in Table 3. Experimental, theoretical and difference PXRD patterns for Na$_2$Rb$_7$Sc$_6$(XO$_4$)$_9$ (X = Mo, W) are shown in Fig. 2 and 3. The fractional atomic coordinates, isotropic atomic displacement parameters, cation occupancies and main selected interatomic distances are presented in Tables 4–7.

The crystal structures of Na$_2$Rb$_7$Sc$_6$(MoO$_4$)$_9$ and Na$_2$Rb$_7$Sc$_6$(WO$_4$)$_9$ were deposited in the Cambridge Crystallographic Data Centre with Cambridge Structural Database (CSD) No 2124713 and No 2124691, respectively [28].

Table 3 Main structure parameters for Na$_2$Rb$_7$Sc$_6$(XO$_4$)$_9$ (X = Mo, W) after the Rietveld refinement

| Compound | Na$_2$Rb$_7$Sc$_6$(MoO$_4$)$_9$ | Na$_2$Rb$_7$Sc$_6$(WO$_4$)$_9$ |
|----------|-----------------------------|-----------------------------|
| Sp. gr.  | R32                         | R32                         |
| a, Å     | 10.13752(9)                 | 10.19247(9)                 |
| c, Å     | 35.6615(4)                  | 35.6191(4)                  |
| V, Å$^3$ | 3173.91(7)                  | 3204.59(7)                  |
| Z        | 3                           | 3                           |
| 2θ-interval, ° | 8–100                     | 8–100                       |
| R$_{exp}$, % | 4.15                      | 4.56                        |
| R$_{ref}$, % | 3.20                      | 3.42                        |
| R$_{app}$, % | 2.04                      | 1.81                        |
| X        | 2.04                        | 2.51                        |
| R$_{o}$, % | 1.64                       | 2.11                        |

In the structures of Na$_2$Rb$_7$Sc$_6$(XO$_4$)$_9$ (X = Mo, W), Na1 and Na2 atoms are located in threefold special positions with the point symmetry 32; Sc, Rb1, and Rb2 sit at threefold axes; Rb3, Mo2 (W2), and Na3 are settled at twofold axes, and Mo1 (W1) and oxygen atoms are in general positions. Both Mo and W atoms have tetrahedral coordination, while Sc, Na1 and Na3 possess octahedral coordination. It is worth noting that, unlike the octahedron surrounding Na1, the octahedron around Na3 is distorted. The half-occupied Na2 site has a trigonal-prismatic environment. Rb1 and Rb2 atoms have 9-fold environments, while Rb3 exhibits CN = 8. The general view of the structure is illustrated in Fig. 4a.

The characteristic details of the title compounds are so-called 'lanterns' [Sc$_2$(XO$_4$)$_9$] (X = Mo, W) composed by two ScOs tetrahedral sharing corners with six terminal and three bridging XOs tetrahedra (Fig. 4b). Together with the Rb1, Rb2 and Na3 cations they form two-tiered hexagonal layers parallel to (001) plane, which resemble the motif of the K$_3$Na(SO$_4$)$_2$ glaserite structure [29]. The layers are folded with a displacement along the b axis and are connected by Na3, Na1 and Rb3 cations (Fig. 4c).

Similar "lanterns" [M$_4$(TO$_4$)$_5$] (M is an octahedrally coordinated cation, TO$_4$ is a tetrahedral oxoanion), and hexagonal layers formed by them also characterize the structures of previously studied Ag$_3$Rb$_3$Sc$_2$(MoO$_4$)$_9$, Ag$_3$Rb$_3$Sc$_2$(WO$_4$)$_9$ and Na$_3$Cs$_7$Yb$_3$(MoO$_4$)$_9$ [21]. The relationship between structure of the considered family M$_3$M$_7$R$_6$(XO$_4$)$_9$ (X = Mo, W) and many rhombohedral triple molybdates and tungstates with a = 9–10 Å and large c-periods (more than 20 Å) was discussed in [21].

3.3. Thermal expansion of Na$_2$Rb$_7$Sc$_6$(WO$_4$)$_9$

The thermal expansion of Na$_2$Rb$_7$Sc$_6$(WO$_4$)$_9$ was studied by high-temperature X-ray diffraction. The thermal expansion of this compound, which crystallizes in a trigonal symmetry, is defined by two linear thermal expansion coefficients (LTECs) measured along ($a_2$) and across ($a_3$) the threefold axis. The average LTEC can be calculated as follows: $\alpha_{av} = \alpha_2/3 = (2\alpha_2 + \alpha_3)/3$. Thermal expansion anisotropy is quantitatively defined as $|\alpha_2 - \alpha_3|$. 

![Fig. 2 Observed, calculated and difference diffractograms of Na$_2$Rb$_7$Sc$_6$(MoO$_4$)$_9$](image1)

![Fig. 3 Observed, calculated and difference diffractograms of Na$_2$Rb$_7$Sc$_6$(WO$_4$)$_9$](image2)

![Fig. 4a General view of the structure](image3)
Fig. 4 The crystal structure of Na₅Rb₇Sc₂(ХO₄)₉ (Х = Mo, W): a general view (a); [Sc₂(ХO₄)₉] cluster (b); layers of [Sc₂(ХO₄)₉] clusters (c).

Table 4 Fractional atomic coordinates and isotropic displacement parameters (Å²) for Na₅Rb₇Sc₂(MoO₄)₉

| Atom | x    | y    | z    | Biso | Occ. |
|------|------|------|------|------|------|
| Rb1  | 0    | 0    | 0.2332(1) | 1.9(1) | 1   |
| Rb2  | 0    | 0    | 0.1074(1) | 2.0(1) | 1   |
| Rb3  | 0    | 0.3687(3) | 0    | 4.6(2) | 1   |
| Na1  | 0    | 0    | 0    | 1.9(6) | 1   |
| Na2  | 0    | 0    | 0.3376(8) | 2.1(3) | 0.5 |
| Na3  | 0.4030(9) | 0.4030(9) | 0.5 | 2.1(3) | 1   |
| Sc2  | 0    | 0    | 0.4253(3) | 2.1(2) | 1   |
| Mo1  | 0.3429(2) | 0.3265(3) | 0.39176(4) | 1.30(9) | 1   |
| Mo2  | 0.7331(2) | 0.7331(2) | 0.5 | 0.9(1) | 1   |
| O1   | 0.458(1) | 0.269(1) | 0.3746(4) | 3.2(4) | 1   |
| O2   | 0.362(1) | 0.480(1) | 0.3662(3) | 1.4(4) | 1   |
| O3   | 0.406(1) | 0.394(1) | 0.4344(3) | 0.4(3) | 1   |
| O4   | 0.147(1) | 0.180(1) | 0.3938(3) | 1.8(2) | 1   |
| O5   | 0.566(1) | 0.719(1) | 0.4937(4) | 1.6(4) | 1   |
| O6   | 0.822(1) | 0.839(2) | 0.5391(3) | 1.8(2) | 1   |

Table 5 Fractional atomic coordinates and isotropic displacement parameters (Å²) for Na₅Rb₇Sc₂(WO₄)₉

| Atom | x    | y    | z    | Biso | Occ. |
|------|------|------|------|------|------|
| Rb1  | 0    | 0    | 0.2331(2) | 1.1(2) | 1   |
| Rb2  | 0    | 0    | 0.1083(2) | 1.7(2) | 1   |
| Rb3  | 0    | 0.3671(5) | 0    | 3.1(2) | 1   |
| Na1  | 0    | 0    | 0    | 2.1(1) | 1   |
| Na2  | 0    | 0    | 0.329(2) | 3(1) | 0.5 |
| Na3  | 0.418(1) | 0.418(1) | 0.5 | 4.3(6) | 1   |
| Sc2  | 0    | 0    | 0.4241(3) | 0.5(3) | 1   |
| W1   | 0.3410(1) | 0.3251(1) | 0.39174(3) | 0.8(1) | 1   |
| W2   | 0.7329 (1) | 0.7329(1) | 0.5 | 0.9(1) | 1   |
| O1   | 0.4660(7) | 0.2580(8) | 0.3785(3) | 1.0(2) | 1   |
| O2   | 0.376(1) | 0.4839(7) | 0.3633(2) | 1.0(2) | 1   |
| O3   | 0.4104(8) | 0.3974(9) | 0.4371(2) | 1.0(2) | 1   |
| O4   | 0.1487(9) | 0.1756(9) | 0.3976(4) | 1.0(2) | 1   |
| O5   | 0.5570(8) | 0.7196(7) | 0.4896(2) | 1.0(2) | 1   |
| O6   | 0.823(1) | 0.840(1) | 0.5412(2) | 1.0(2) | 1   |
Table 6 Main bond lengths (Å) in Na,Rb,Sc₃(MoO₄)₉

|                  | M₀₁-tetrahedron | M₀₂-tetrahedron | Sc-octahedron |
|------------------|-----------------|-----------------|---------------|
| M₀₁-O₁           | 1.660(9)        | 1.641(× 2)      | 2.021(× 3)    |
| -O₂              | 1.731(1)        | 1.711(× 2)      | -06           |
| -O₃              | 1.661(1)        | <M₀₂-O>         | -06           |
| -O₄              | 1.791(1)        | 1.67            | 2.08          |
| <M₀₁-O>          | 1.71            |                 |               |

Table 7 Main bond lengths (Å) of Na,Rb,Sc₃(WO₄)₉

|                  | W₁-tetrahedron | W₂-tetrahedron | Sc-octahedron |
|------------------|----------------|----------------|---------------|
| W₁-O₁            | 1.785(5)       | 1.786(6)       | 1.921(× 3)    |
| -O₂              | 1.788(7)       | -06            | 2.121(× 3)    |
| -O₃              | 1.771(8)       | <W₂-O>         | 2.02          |
| -O₄              | 1.792(7)       | 1.784          |               |

The reflections in the X-ray diffraction patterns of Na₂Rb₃Sc₉(WO₄)₉ regularly shift with increasing temperature (Fig. 5) due to an increase in the unit cell parameters (Fig. 6).

The parameter \( a \) changes with temperature almost linearly; the temperature variation of the parameter \( c \) is described by a polynomial of the second degree (Table 8). Table 8 also presents the coefficients of thermal linear expansion and thermal expansion anisotropy. The obtained results allowed classifying Na₂Rb₃Sc₉(WO₄)₉ as belonging to high thermal expansion materials.

### 4. Conclusions

Two new compounds Na₆Rb₃Sc₉(AD₉)₉ (\( X = \text{Mo, W} \)) were obtained by a solid-phase synthesis, supplementing the previously discovered family of isostructural triple molybdates and tungstates of the composition \( M'_1M'_2R_6(XO₄)_₉ \). The thermal stability of obtained compounds was studied and the thermal expansion of Na₆Rb₃Sc₉(WO₄)₉ was examined by the high-temperature XRD diffraction method; it was shown that this compound belongs to highly expanding substances. The crystal structure of Na₆Rb₃Sc₉(AD₉)₉ (\( X = \text{Mo, W} \)) was refined by the Rietveld method using the PXRD data.

![Fig. 5](https://example.com/fig5.png)
The obtained compounds crystallize in the chiral sp. gr. R32 and together with their formula and structural analogues \( \text{Ag}_5\text{Rb}_3\text{Sc}_6(\text{XO}_4)_9 \) (X = Mo, W), \( \text{Na}_2\text{Cs}_3\text{Ln}_2(\text{MoO}_4)_9 \) (Ln = Tm, Yb, Lu) belong to the series of rhombohedral triple molybdates and tungstates with \( a = 9–10 \text{ Å} \) and long \( c \)-parameter, more than 20 Å; many of those have noticeable ionic conductivity at elevated temperatures [19–21]. For two representatives of the \( M'_4M'_5R_6(\text{XO}_4)_9 \) family, namely, \( \text{Ag}_5\text{Rb}_3\text{Sc}_6(\text{XO}_4)_9 \) (X = Mo, W) and \( \text{Na}_2\text{Cs}_3\text{Ln}_2(\text{MoO}_4)_9 \) (Ln = Tm, Yb, Lu), we confirmed this experimentally earlier [21]. This stimulates our research to find new representatives of this group of phases, as well as to continue the study of the ion-conducting properties of already obtained compounds – (Na,Rb,Rb,Sc,(XO)9 (X = Mo, W) and Na2Cs3Ln2(MoO4)9 (Ln = Tm, Yb, Lu). In addition, it seems expedient to carry out a further study of thermophysical properties for representatives of the considered structural type to reveal the influence of the nature of one-, three- and hexavalent elements on the value of thermal expansion coefficients and anisotropy in these phases.

Acknowledgments

This work was financially supported by the Russian Foundation for Basic Research, project № 20-03-00533 (synthesis and research of \( \text{Na}_2\text{Rb}_3\text{Sc}_6(\text{W}_3\text{O})_9 \)) and by the Ministry of Science and Higher Education of the Russian Federation, Basic Project of BINM SB RAS Nº 0273-2021-0008 (synthesis and research of \( \text{Na}_2\text{Rb}_3\text{Sc}_6(\text{MoO}_4)_9 \)). X-ray powder diffraction and thermal analysis results were obtained using the equipment of the Collective Use Center BINM SB RAS.

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**Table 8** Fitting polynomials for temperature dependent LTECs and average LTECs for \( \text{Na}_2\text{Rb}_3\text{Sc}_6(\text{WO}_4)_9 \) in the temperature range 303–823 K

| Composition          | Polynomials for \( a(T) \) and \( c(T) \) Å | \( \alpha_a \) | \( \alpha_c \) | \( \alpha_{av} \) | \( |\alpha_a - \alpha_c| \) |
|----------------------|---------------------------------------------|----------------|----------------|----------------|-----------------|
| \( \text{Na}_2\text{Rb}_3\text{Sc}_6(\text{WO}_4)_9 \) | \( a = 0.00037T + 10.18 \) \( c = 1 \times 10^{-6}T^2 + 0.0002T + 35.612 \) | 27.8(3) | 22.9(2) | 26.2(3) | 4.9 |
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