Journal of Solid State Chemistry 205 (2013) 149–153

Contents lists available at ScienceDirect

Journal of Solid State Chemistry

journal homepage: www.elsevier.com/locate/jssc

# New double molybdate $Na_9Fe(MoO_4)_6$: Synthesis, structure, properties

Aleksandra A. Savina [a,b,*], Sergey F. Solodovnikov [c,d], Olga M. Basovich [a], Zoya A. Solodovnikova [c], Dmitry A. Belov [e], Konstantin V. Pokholok [e], Irina A. Gudkova [c], Sergey Yu. Stefanovich [e], Bogdan I. Lazoryak [e], Elena G. Khaikina [a,b]

[a] *Baikal Institute of Nature Management, Siberian Branch, Russian Academy of Sciences, Sakh'yanova Street 6, Ulan-Ude 670047, Buryat Republic, Russia*
[b] *Buryat State University, Smolin Street 24a, Ulan-Ude 670000, Buryat Republic, Russia*
[c] *Nikolaev Institute of Inorganic Chemistry, Siberian Branch, Russian Academy of Sciences, Akademik Lavrentyev Avenue 3, Novosibirsk 630090, Russia*
[d] *Novosibirsk State University, Pirogov Street 2, Novosibirsk 630090, Russia*
[e] *Department of Chemistry, Moscow State University, Moscow 119899, Russia*

## ARTICLE INFO

*Article history:*
Received 15 May 2013
Received in revised form
5 July 2013
Accepted 8 July 2013
Available online 18 July 2013

*Keywords:*
Sodium–iron molybdate
Crystal structure
Solid-state electrolyte

## ABSTRACT

A new double molybdate $Na_9Fe(MoO_4)_6$ was synthesized using solid state reactions and studied with X-ray powder diffraction, second harmonic generation (SHG) technique, differential scanning calorimetry, X-ray fluorescence analysis, Mössbauer and dielectric impedance spectroscopy. Single crystals of $Na_9Fe(MoO_4)_6$ were obtained and its structure was solved (the space group $R\overline{3}$, $a = 14.8264(2)$, $c = 19.2402(3)$ Å, $V = 3662.79(9)$ Å$^3$, $Z = 6$, $R = 0.0132$). The structure is related to that of sodium ion conductor II-$Na_3Fe_2(AsO_4)_3$. The basic structure units are polyhedral clusters composed of central $FeO_6$ octahedron sharing edges with three $Na(1)O_6$ octahedra. The clusters share common vertices with bridging $MoO_4$ tetrahedra to form an open 3D framework where the cavities are occupied by Na(2) and Na(3) atoms. The compound melts incongruently at 904.7 ± 0.2 K. Arrhenius type temperature dependence of electric conductivity σ has been registered in solid state ($\sigma = 6.8 \times 10^{-2}$ S cm$^{-1}$ at 800 K), thus allowing considering $Na_9Fe(MoO_4)_6$ as a new sodium ion conductor.

## 1. Introduction

Double molybdates of iron (III) and alkali metals are of practical interest as prospective functional materials. For example, double molybdates $MFe(MoO_4)_2$ ($M$=Na, K, Rb) exhibit interesting multiferroic properties [1–7], and $Li_3Fe(MoO_4)_3$ is considered as a possible positive electrode in lithium cells [8,9]. Double molybdates $MFe(MoO_4)_2$ ($M$=Li–Cs), $M_3Fe(MoO_4)_3$ ($M$=Li, K), $M_5Fe(MoO_4)_4$ ($M$=K, Rb, Cs) were described in literature; their crystal structures belong to eight structure types [8,10–17].

Previously, in the system $Na_2MoO_4-Fe_2(MoO_4)_3$, the only compound of $NaFe(MoO_4)_2$ composition [18] was found, which is isostructural to $NaR(MoO_4)_2$ ($R$=Cr, Al) and the high-temperature modification of $NaSc(MoO_4)_2$ [10,11].

This work describes a new double molybdate $Na_9Fe(MoO_4)_6$ and contains data of its crystal structure and physicochemical properties.

## 2. Experimental

Commercially available chemically pure $Fe(NO_3)_3 \cdot 9H_2O$, $MoO_3$ and high-purity $Na_2MoO_4 \cdot 2H_2O$ were used as starting materials for the synthesis of molybdates. Iron molybdate $Fe_2(MoO_4)_3$ was synthesized in air by annealing stoichiometric mixtures $Fe(NO_3)_3 \cdot 9H_2O$ and $MoO_3$ in two stages (573–723 K for 25–40 h and 873 K for 60 h). Anhydrous $Na_2MoO_4$ was obtained by calcination of the corresponding crystalline hydrate at 823–873 K. Monophasity of the prepared substances was confirmed by powder X-ray diffraction (XRD) and thermal analysis. Thermal and XRD characteristics of the obtained substances were in accord with the published data.

Single crystals for structural investigations were obtained by spontaneous crystallization. Heating of ground mixtures, their isothermal holding and slow cooling of the melts were controlled and kept automatically with an accuracy of ±0.5°.

Products of solid-state synthesis and crystallization were studied with powder XRD on a D8 ADVANCE Bruker diffractometer (Cu$K\alpha$ radiation, secondary monochromator, maximal $2\theta = 100°$, scan step 0.02076°). The unit cell parameters were refined by the least-squares method using ICDD program package for preparing experimental standards.

Single crystal X-ray diffraction data for structure determination were collected at room temperature on a Bruker–Nonius X8 Apex

---

* Corresponding author at: Baikal Institute of Nature Management, Siberian Branch, Russian Academy of Sciences, Sakh'yanova Street 6, Ulan-Ude 670047, Buryat Republic, Russia. Fax: +7 301 2434753.
*E-mail address:* alex551112@mail.ru (A.A. Savina).

0022-4596/$ - see front matter © 2013 Elsevier Inc. All rights reserved.
http://dx.doi.org/10.1016/j.jssc.2013.07.007

CCD area-detector diffractometer (Mo$K\alpha$ radiation, graphite monochromator, $\varphi$ scans with $\Delta\varphi=0.5^\circ$). The structure was solved and refined by using SHELX97 package [19].

Differential scanning calorimetric (DSC) measurements were performed on a NETZSCH STA 409 thermoanalyzer in the temperature range from 373 to 973 K with heating/cooling rates of 10 K min$^{-1}$.

Determination of chemical composition was carried out by X-ray fluorescence analysis (XRF) on a PANanalytical Axios Advanced spectrometer. Characteristic X-rays were excited using a 4 kW Rh-anode X-ray tube. The excited radiation was recorded by a scanning channel with five exchangeable wave crystals and a detector. Measurements were made in transmission geometry in vacuum. Specimens were prepared as pellets with a binder ($C_8H_9$) in proportion 5:1.

Mössbauer spectroscopy experiments were performed in transmission geometry using a constant acceleration Mössbauer spectrometer coupled with a 1024 multichannel analyzer. A $^{57}$Co/Rh $\gamma$-ray source was used. The velocity scale was calibrated relative to $\alpha$-Fe. All isomer shift values ($\delta$) given hereafter are referred to $\alpha$-Fe.

The second harmonic generation (SHG) response of powder samples was measured with a Q-switched YAG:Nd laser at $\lambda_\omega=1064$ nm, in the reflection mode. The intensities of the SHG signal ($I_{2\omega}$) from the sample and that from the reference sample (polycrystalline $\alpha$-$SiO_2$) were registered.

Blocking ionic transport electrodes were put by firing of Pt paste (ChemPur, Germany) on both large surfaces of the pellets at 823 K for 2 h. Electric conductivity of the samples was determined by impedance spectroscopy in the temperature range 343–803 K at heating and cooling rates of 2 K min$^{-1}$ using two-probe measurements in NorECs ProboStat cell. The signal was monitored with a Novocontrol Beta-N impedance analyzer at applied voltage of 0.5 V in frequency range from 0.3 Hz to 1 MHz.

## 3. Results and discussion

### 3.1. Synthesis and characterization of $Na_9Fe(MoO_4)_6$

$Na_9Fe(MoO_4)_6$ ceramics was synthesized in air by annealing stoichiometric mixtures of $Na_2MoO_4$ and $Fe_2(MoO_4)_3$ at 823–853 K for 140 h. Intermittent grindings were performed every 15 h for better sample homogenization. $Na_9Fe(MoO_4)_6$ was found to melt at $904.7\pm0.2$ K. In the solidified melt, $Na_2MoO_4$, $Na_2Mo_2O_7$ and $Fe_2O_3$ along with the parent phase $Na_9Fe(MoO_4)_6$ were found.

Turquoise single crystals for structure determination were obtained in air by spontaneous crystallization of melting stoichiometric composition, which was heated to 913 K, held for 30 min, cooled down at the rate of 4 h$^{-1}$ to 473 K and then left in a switched-off furnace.

The determination of chemical composition of a polycrystalline sample of $Na_9Fe(MoO_4)_6$ by XRF showed: Na—16.8 ± 0.2%, Fe—4.5 ± 0.2%, Mo—47.1 ± 0.2%, O—31.3 ± 0.2%. Calculated: Na—16.93%, Fe—4.57%, Mo—47.09%, O—31.41%.

### 3.2. Crystal structure of $Na_9Fe(MoO_4)_6$

The structure of $Na_9Fe(MoO_4)_6$ was solved in the space group $R\overline{3}$ taking into account merohedral twinning with lattices of twin domains superimposed by rotation around the [110] direction. The minor twin component contribution was found to be 0.4486(5) at final $R=0.0132$. The correctness of choosing the centrosymmetrical group was confirmed by absence of SHG effect from the compound in both powder and ceramic forms under laser illumination. Crystal and X-ray analysis data for $Na_9Fe(MoO_4)_6$ are summarized in Table 1, and atomic coordinates, equivalent isotropic displacement parameters and selected interatomic distances are listed in Tables 2 and 3. The atomic coordinates, anisotropic atomic displacement parameters, and further details of the crystal structure investigation can be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany, (fax: +497247-808-666; e-mail: crysdata@fiz.karlsruhe.de, ⟨http://www.fiz-karlsruhe.de/request⟩) on quoting the depository number CSD 426076 for $Na_9Fe(MoO_4)_6$.

The crystal structure of $Na_9Fe(MoO_4)_6$ is completely ordered, its asymmetric unit is shown in Fig. 1. The Fe atom is located in the special position at the three-fold axis, while 2Mo, 3Na and six basic oxygen atoms are in general positions. Both sorts of the molybdenum atoms have the usual tetrahedral coordination with distances Mo–O 1.737(2)–1.806(1) Å, the $Fe^{3+}$ cations are octahedrally coordinated with bond lengths Fe–O 1.994(1)–2.008(1) Å. The Na(1) and Na(2) atoms possess a distorted octahedral coordination (CN 4+2) with distances Na(1)–O 2.342(2)–2.448(2)+2.635(2)–2.744(2) Å; Na(2)–O 2.324(2)–2.441(2)+2.627(2)–2.776(2) Å; the Na(3) forms a trigonal bipyramidal oxygen environment with Na(3)–O 2.312(2)–2.528(2) Å.

The basic structure units are polyhedral clusters composed of the central $FeO_6$-octahedron sharing edges with three Na(1)$O_6$ octahedra. The clusters are connected by sharing vertices with bridging $MoO_4$ tetrahedra to form an open 3D framework (Fig. 2). The Na(2) and Na(3) atoms are in the framework cavities.

The structural organization of $Na_9Fe(MoO_4)_6$ is close to that of rhombohedral triple molybdates $K_{3+x}Li_{1-x}M_4(MoO_4)_6$ ($M$=Co, Mn, Mg; $0\le x\le 0.3$) [20] and $K_3NaM_4(MoO_4)_6$ ($M$=Co, Ni, Mg) [21] obtained

**Table 1**
Crystal data and structure refinement details for $Na_9Fe(MoO_4)_6$.

| | |
|---|---|
| Formula | $Na_9Fe(MoO_4)_6$ |
| Formula weight | 1222.40 |
| Temperature (K) | 296(2) |
| Crystal system, space group | Trigonal, $R\overline{3}$ |
| Unit cell dimensions (Å) | $a=14.8264(2)$<br>$c=19.2402(3)$ |
| $V$ (Å$^3$)/$Z$ | 3662.79(9)/6 |
| Calculated density (g cm$^{-3}$) | 3.325 |
| Crystal size (mm) | 0.006 × 0.05 × 0.04 |
| $\mu$(Mo$K\alpha$) (mm$^{-1}$) | 3.819 |
| $\theta$ Range (deg) for data collection | 1.91–33.19 |
| Miller index ranges | $-22\le h\le 18$, $-22\le k\le 21$, $-21\le l\le 29$ |
| Reflections collected/unique | 10,997/3112 [$R$(int)=0.0147] |
| No. of variables | 213 |
| Goodness-of-fit on $F^2$ (GOF) | 1.137 |
| Final $R$ indices [$I>2\sigma(I)$] | $R(F)=0.0132$,<br>$wR(F^2)=0.0328$ |
| $R$ indices (all data) | $R(F)=0.0144$,<br>$wR(F^2)=0.0334$ |
| Extinction coefficient | 0.000070(11) |
| Largest difference peak/hole (e Å$^{-3}$) | 0.449/−0.462 |

**Table 2**
Atomic coordinates and equivalent isotropic displacement parameters for $Na_9Fe(MoO_4)_6$.

| Atom | $x/a$ | $y/b$ | $z/c$ | $U_{eq}$ (Å$^2$)[a] |
|---|---|---|---|---|
| Mo (1) | 0.52525 (1) | 0.85747 (1) | 0.02687 (1) | 0.01421 (4) |
| Mo (2) | 0.51496 (1) | 0.65014 (1) | 0.52272 (1) | 0.01605 (4) |
| Fe | 0 | 0 | 0.25343 (2) | 0.01161 (7) |
| Na (1) | 0.00986 (9) | 0.22836 (7) | 0.25067 (5) | 0.0317 (2) |
| Na (2) | 0.01280 (8) | 0.23039 (8) | 0.05091 (4) | 0.0303 (2) |
| Na (3) | 0.01831 (8) | 0.24046 (7) | 0.45009 (4) | 0.0295 (2) |
| O (1) | 0.58345 (13) | 0.78097 (13) | 0.03101 (8) | 0.0285 (3) |
| O (2) | 0.49785 (14) | 0.88323 (16) | 0.11054 (7) | 0.0331 (4) |
| O (3) | 0.61159 (12) | 0.97809 (12) | −0.01123 (8) | 0.0288 (3) |
| O (4) | 0.40498 (11) | 0.79566 (11) | −0.02115 (7) | 0.0209 (3) |
| O (5) | 0.58126 (14) | 0.78553 (13) | 0.52312 (8) | 0.0326 (4) |
| O (6) | 0.47783 (14) | 0.60405 (14) | 0.60754 (7) | 0.0342 (4) |
| O (7) | 0.60287 (12) | 0.61246 (13) | 0.49161 (8) | 0.0276 (3) |
| O (8) | 0.40053 (12) | 0.60264 (12) | 0.46865 (7) | 0.0209 (3) |

[a] $U_{eq}=(U_{11}+U_{22}\sin^2\beta+U_{33}+2U_{13}\cos\beta)/3\sin^2\beta$.