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Natromolybdite, $Na_2MoO_4 \cdot 2H_2O$, a new mineral from fumarole deposits of the Tolbachik volcano, Kamchatka, Russia

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Running title: Natromolybdite, a new mineral

Abstract

The new mineral natromolybdite, ideally $Na_2MoO_4 \cdot 2H_2O$, was found in the Arsenatnaya fumarole, Second scoria cone of the Northern Breakthrough of the Great Tolbachik Fissure Eruption, Tolbachik volcano, Kamchatka, Russia. The associated minerals are halite, sylvite, aphthitalite, belomarinaite, powellite, hematite, sanidine, tilasite, johillerite, bradaczekite, badalovite, arsmirandite, wrightite, arsenatrotitanite, dmisokolovite, litidionite, rutile, and cristobalite. Natromolybdite occurs as rectangular, octagonal or rhomb-like lamellar to thin-tabular crystals up to 40 μm across and up to 3 μm thick, in near-parallel, pile-like or rose-like aggregates and crystal crusts up to 0.2 mm across. It is transparent and colourless, with vitreous lustre. D_{calc} is 2.573 g/cm^3. Synthetic analogue of natromolybdite is optically biaxial (+), α = 1.575(2), β = 1.576(2), γ = 1.598(3) and $2V_{meas}$ = 20(10)°. The chemical composition (wt.%, electron microprobe, H_2O is calculated by stoichiometry) is: Na_2O 25.51, K_2O 0.66, SO_3 1.04, MoO_3 58.21, H_2O_{calc} 15.05, total 100.47. The empirical formula, calculated based on O = 6 *apfu*, is $(Na_{1.971}K_{0.034})_{\Sigma 2.005}(Mo_{0.968}S_{0.031})_{\Sigma 0.999}O_4 \cdot 2H_2O$. Natromolybdite is orthorhombic, space group *Pbca*, *a* = 8.483(1), *b* = 10.577(2), *c* = 13.842(2) Å, *V* = 1242.0(2) Å^3 and *Z* = 8. The nine strongest reflections of the powder XRD pattern [*d*,Å(*I*)(*hkl*)] are: 6.92(100)(002), 4.243(20)(200), 4.206(32)(022), 3.618(31)(202), 3.310(31)(220), 3.169(49)(131), 3.067(21)(114), 2.987(30)(222)

and 2.681(15)(204, 311). Natromolybdite (IMA-accepted symbol Nmyb) is named for the chemical composition. It is a natural analogue of a well-studied synthetic sodium molybdate dihydrate.

Keywords: natromolybdite; new mineral; sodium molybdate dihydrate; fumarole sublimate; Tolbachik volcano.

Introduction

Molybdenum mineralization is not generally common in volcanic environments, however, in the fumaroles of some volcanoes, Mo minerals have been reported (Zelenski *et al*., 2012 and references therein). Very rich molybdenum mineralization of fumarolic origin occurs in deposits of the active, high-temperature reducing-type fumaroles at the Kudriavy volcano (Iturup, Kurily Islands, Russia) in which molybdenite, typically Re-enriched, is abundant. In the upper zones of the fumarole systems at Kudriavy, in contact with atmospheric air, oxides and oxysalts of Mo^{4+} and Mo^{6+} form, namely tugarinovite MoO_2, molybdite MoO_3, ilsemannite $(Mo^{6+},Mo^{4+})_3O_8 \cdot nH_2O$, powellite $CaMoO_4$ and Mo-enriched scheelite $Ca(W,Mo)O_4$ (Bykova *et al*., 1995; Chaplygin, 2009). Similar, though not so abundant, molybdenum mineralization was described from fumaroles of the Iwodake volcano (Satsuma-Iwojima, Kyushu, Japan): molybdenite, tugarinovite, molybdite and so-called "molybdenum blue" (ilsemannite?) occur there (Nitta *et al*., 2006). Diverse molybdenum mineralization was discovered in exhalations of active oxidizing-type fumaroles at the Tolbachik volcano (Kamchatka peninsula, Russia). Only oxysalt minerals with Mo^{6+} occur there. The minerals with species-defining Mo are represented by members of the vergasovaite $Cu_3O(MoO_4)(SO_4)$ – cupromolybdite $Cu_3O(MoO_4)_2$ isomorphous series (Bykova *et al*., 1998; Zelenski *et al*., 2012), rhabdoborite-(Mo) $Mg_{12}Mo^{6+}_{1.33}O_6(BO_3)_6F_2$ (Pekov *et al*., 2020b), powellite, wulfenite $PbMoO_4$ and the new mineral species natromolybdite $Na_2MoO_4 \cdot 2H_2O$ described in the present paper. In addition, Mo^{6+} substitutes for V^{5+} or W^{6+} in some sublimate Cu vanadates (pseudolyonsite, lyonsite, starovaite, yaroshevskite and dokuchaevite contain up to several wt.% MoO_3), in rhabdoborite-(V) $Mg_{12}(V^{5+},W^{6+},Mo^{6+})_{1.33}O_6\{(BO_3)_{6-x}(PO_4)_xF_{2-x}\}$, rhabdoborite-(W) $Mg_{12}(W^{6+},Mo^{6+})_{1.33}O_6(BO_3)_6F_2$ (Pekov *et al*., 2018b, 2020b, c), and in scheelite formed in Tolbachik fumaroles.

Natromolybdite (Cyrillic: натромолибдит) is named for the chemical composition. Both the new mineral and its name have been approved by the IMA Commission on New Minerals, Nomenclature and Classification (IMA CNMNC), IMA2022–130. The IMA-accepted symbol is Nmyb. A fragment of the holotype specimen is deposited in the systematic collection of the Fersman Mineralogical Museum, Moscow with the catalogue number 98146.

Occurrence and general appearance

Natromolybdite occurs at the active Arsenatnaya fumarole located at the summit of the Second scoria cone of the Northern Breakthrough of the Great Tolbachik Fissure Eruption (NB GTFE) at the Tolbachik volcano. This scoria cone is a monogenetic volcano formed in 1975. Many fumaroles belonging to the oxidizing type, including several richly mineralised ones, are still active here (Vergasova and Filatov, 2016; Pekov *et al.*, 2020a and references therein). Arsenatnaya is the largest fumarole at the Second scoria cone of the NB GTFE. It is an outstanding mineralogical occurrence because of its great mineral mineral diversity and uniqueness: more than 200 mineral species have been reliably identified here, including 72 new minerals. Detailed mineralogical descriptions of the Arsenatnaya fumarole were reported by Pekov *et al*. (2018a) and Shchipalkina *et al*. (2020).

Natromolybdite was found very sparingly in specimens collected by us in July 2022 from a pocket located about 0.7 m below the day surface. The temperature measured when collected in this pocket using a chromel-alumel thermocouple was about 100°C. The minerals intimately associated with natromolybdite are halite, sylvite, aphthitalite (including its Cr^{6+}-bearing variety), belomarinaite, powellite, and an insufficiently studied potassium molybdate; earlier sublimate minerals in this assemblage are hematite, sanidine, tilasite, johillerite, bradaczekite, badalovite, arsmirandite, wrightite, arsenatrotitanite, dmisokolovite, litidionite, rutile, and cristobalite.

Natromolybdite occurs as rectangular, octagonal or rhomb-like lamellar to thin-tabular (flattened probably on [001]) crystals up to 40 μm across and up to 3 μm thick. By analogy with synthetic $Na_2MoO_4 \cdot 2H_2O$ (see below), we assume that the major crystal form is the pinacoid {001}; lateral faces were not indexed. Natromolybdite crystals are usually crude, split and form near-parallel, sometimes pile-like or rose-like, aggregates (Figs 1a-c). Some small (up to 15 μm across) crystals are well-shaped (Fig. 1d). Natromolybdite crystal crusts (Figs 1c, d) up to 0.2 mm across overgrow aggregates of aphthitalite, belomarinaite, halite or sylvite.

We suggest that natromolybdite was deposited directly from the gas phase as a volcanic sublimate in the temperature range of 100–200ºC. As our previous data show, the minerals containing OH groups or/and H_2O molecules form in Tolbachik fumaroles at temperatures not higher than 200ºC whereas from hotter gas only H-free minerals crystallize (Pekov *et al*., 2018b).

Physical properties and optical data

Natromolybdite is transparent, colourless, with white streak and vitreous lustre. It is brittle. Cleavage or parting could not be observed because natromolybdite crystals are so thin that the examination of these properties, even under the scanning electron microscope, is difficult; however, the synthetic analogue of natromolybdite demonstrates perfect (001) cleavage, so we assume that the mineral also can have (001) cleavage (in more detail see Discussion). The fracture across a crystal is uneven (observed under the scanning electron microscope). The density calculated using the empirical formula and unit-cell volume found from the powder X-ray diffraction (XRD) data is 2.573 g/cm^3.

Due to tiny size of perfect crystals of natromolybdite (Fig. 1d) and split character of larger crystals (Figs 1a-c), the optical data were obtained for its synthetic analogue (see below). Synthetic $Na_2MoO_4 \cdot 2H_2O$ is optically biaxial (+), α = 1.575(2), β = 1.576(2), γ = 1.598(3) (589 nm); 2*V* (meas.) = 20(10)º (visually estimated by the curvature of isogyre), 2*V* (calc.) = 24º. Dispersion of optical axes is very strong, $r < v$. Orientation: $Z = c$. In transmitted plane-polarized light, the synthetic analogue of natromolybdite is colourless and non-pleochroic.

Infrared spectroscopy

Due to the scarcity of available natural material, the infrared (IR) spectrum was obtained from the synthetic analogue of natromolybdite. The sample of synthetic $Na_2MoO_4 \cdot 2H_2O$ was powdered, mixed with anhydrous KBr, pelletized, and analyzed using an ALPHA FTIR spectrometer (Bruker Optics) at a resolution of 4 cm^{-1}. A total of 16 scans were collected. The IR spectrum of similar pellet of pure KBr was used as a reference.

The IR spectrum of synthetic $Na_2MoO_4 \cdot 2H_2O$ (Fig. 2) contains strong bands in the ranges of O–H stretching vibrations (3000-4000 cm^{-1}), H–O–H bending vibrations of H_2O molecules (at 1677 and 1698 cm^{-1}), stretching (800-900 cm^{-1}) and bending (500-700 cm^{-1}) modes of the $(MoO_4)^{2-}$ group. Weak absorption in the range 1300-1500 cm^{-1} may correspond to numerous overlapping bands of combination (Mo–O stretching and O–Mo–O bending) modes. Two bands of nondegenerate H–O–H bending modes correspond to two nonequivalent H_2O molecules, in accordance with the structural data for synthetic orthorhombic $Na_2MoO_4 \cdot 2H_2O$ (Matsumoto *et al.*, 1975; Capitelli *et al.*, 2006).

The correlation between O–H stretching frequencies in IR spectra of minerals and O···O distances (in Å) for hydrogen bonds obtained from structural data is expressed by the equation (Libowitzky, 1999): $\nu\ (\mathrm{cm}^{-1}) = 3592 - 304 \cdot 10^9 \cdot \exp[-d(\mathrm{O} \cdots \mathrm{O})/0.1321]$. Thus, the bands at 3440 and 3301 cm^{-1} correspond to the O···O distances of 2.83 and 2.74 Å. These values are close to the O···O distances of 2.828, 2.827 and 2.790 Å obtained from the crystal structure refinement (Capitelli *et al.*, 2006).

The shoulder at 3270 cm^{-1} may be a result of Fourier resonance with the overtone of H–O–H bending vibrations.

Chemical data

The chemical composition of natromolybdite was studied by electron microprobe using a Jeol JSM-6480LV scanning electron microscope (SEM) equipped with an INCA-Wave 500 wavelength-dispersive spectrometer (WDS) and a Jeol IT-500 SEM equipped with an X-Max-50 energy-dispersive spectrometer (EDS), both in the Laboratory of Analytical Techniques of High Spatial Resolution, Dept. of Petrology, Lomonosov Moscow State University. The operating conditions (WDS / EDS) were: an acceleration voltage 20 / 20 kV, a beam current 10 / 1 nA, and the electron beam diameter 3 / 1 µm. The obtained results are very similar. Special attention was paid to possible overlap of analytical lines of Mo ($L\alpha$) and S ($K\alpha$) in ED spectrum. Chemical data (in wt.%, averaged for 5 spot analyses) are given in Table 1. The contents of other elements with atomic numbers higher than C are below detection limits. H_2O was not analysed because of paucity of material. The IR spectrum of synthetic analogue of natromolybdite (Fig. 2) shows the presence of H_2O.

The empirical formula of natromolybdite, calculated on the basis of 6 oxygen atoms per formula unit, including 2 oxygen atoms belonging to H_2O molecules, is $(Na_{1.971}K_{0.034})_{\Sigma 2.005}(Mo_{0.968}S_{0.031})_{\Sigma 0.999}O_4{\cdot}2H_2O$. The idealised formula is $Na_2MoO_4{\cdot}2H_2O$ which requires Na_2O 25.62, MoO_3 59.48, H_2O 14.90, total 100.00 wt.%.

The Gladstone-Dale compatibility index (Mandarino, 1981) based on the optical data of the synthetic analogue of natromolybdite is 0.054 (good).

Natromolybdite should readily dissolve in water at room temperature, as tested on its synthetic analogue.

X-ray crystallography

Attempts to obtain single-crystal XRD data for natromolybdite were unsuccessful due to small size and low quality of crystals. However, the powder XRD data undoubtedly show that the mineral is a natural analogue of the well-known synthetic sodium molybdate dihydrate, $Na_2MoO_4{\cdot}2H_2O$, whose crystal structure has been reported in several publications (Atovmyan and D'yachenko, 1969; Mitra and Verma, 1969; Matsumoto *et al*., 1975; Capitelli *et al*., 2006; Dominic Fortes, 2015). In all cited works, the orthorhombic space group *Pbca* (in the standard setting with $c > b > a$) and very similar unit-cell parameters were obtained for this compound.

Powder XRD data for natromolybdite (Table 2) were collected in Debye-Scherrer geometry by means of a Rigaku RAXIS Rapid II diffractometer equipped with curved (semi-cylindrical) imaging plate detector (r = 127.4 mm), using Co$K\alpha$ radiation (λ = 1.79021 Å) generated by a rotating anode (40 kV, 15 µA) with microfocus optics; exposure time was 15 min. The imaging plate was calibrated against a NIST Si standard. The image-to-profile data processing was performed using osc2xrd software (Britvin *et al*., 2017). Parameters of the orthorhombic unit cell of natromolybdite calculated based on the data for synthetic $Na_2MoO_4 \cdot 2H_2O$ (Table 2) are: a = 8.483(1), b = 10.577(2), c = 13.842(2) Å, V = 1242.0(2) Å^3 and Z = 8. The space group *Pbca* (#61) is accepted by analogy with synthetic $Na_2MoO_4 \cdot 2H_2O$. Systematic absences in the powder XRD pattern of natromolybdite agree with this space group.

Discussion

Natromolybdite is the first natural sodium molybdate without other species-defining cations and the first mineral of the $Na_2MoO_4 \cdot 2H_2O$ structure type.

In spite of the absence of single-crystal XRD data and directly measured H_2O content in natromolybdite, there are no doubts that this mineral is a natural analogue of synthetic sodium molybdate dihydrate, $Na_2MoO_4 \cdot 2H_2O$, a compound well-known and studied in detail due to wide use in agriculture, pigment industry, metallurgy, and medicine (Capitelli *et al*., 2006). The only slight chemical difference between natural and synthetic samples is in the presence of minor K and S admixtures in natromolybdite (Table 1), *i.e*., synthetic $Na_2MoO_4 \cdot 2H_2O$ is a full analogue of the end-member natromolybdite. Measured and calculated powder XRD patterns of synthetic $Na_2MoO_4 \cdot 2H_2O$ (see, *e.g*., JCPDS-ICDD, #34-0076) are very close to the powder XRD pattern of natromolybdite (Table 2).

The crystal structure of $Na_2MoO_4 \cdot 2H_2O$ has quasi-layered character (Atovmyan and D'yachenko, 1969; Matsumoto *et al*., 1975; Capitelli *et al*., 2006). It can be described as built of (001) layers of slightly elongate tetrahedral $(MoO_4)^{2-}$ groups and Na^+ cations. These layers are connected *via* (001) layers of H_2O molecules (Fig. 3a). Two crystallographically non-equivalent Na cations have different coordination: the Na1 site is octahedrally coordinated by four O atoms participating in MoO_4 tetrahedra and two O atoms of H_2O molecules (Fig. 3b) whereas Na2 has square-pyramidal coordination by three oxygen atoms of Mo-centered tetrahedra and two O atoms of water molecules (Fig. 3c).

We checked by electron microprobe and powder XRD the reagent-grade chemical labeled as sodium molybdate dihydrate, commercially available from the Sigma-Aldrich company, and found it to be identical to both the structurally studied $Na_2MoO_4 \cdot 2H_2O$ and natromolybdite (Table 2). This synthetic $Na_2MoO_4 \cdot 2H_2O$ was used for our spectroscopic and optical studies. The transparent colourless crystals (up to 3 mm in size) of the studied synthetic $Na_2MoO_4 \cdot 2H_2O$ are tabular and some of them are very similar in shape to natromolybdite crystals shown in Fig. 1a. Synthetic crystals have perfect cleavage parallel to the plane in which the crystal is flattened. Taking into account the quasi-layered character of the structure, with layers of H_2O molecules between the Na–

MoO_4 layers which alternate along the *c* axis (see the text above and Fig. 3), we suspected that the cleavage plane is (001), and the pinacoid {001} is the major form of flattened crystals of synthetic $Na_2MoO_4 \cdot 2H_2O$. This assumption was confirmed by the direct determination of crystal orientation using a Rigaku-Oxford diffraction XtaLAB Synergy-S single-crystal diffractometer. Based on the morphological similarity of synthetic and natural crystals, we believe that natromolybdite crystals (Fig. 1) are also flattened on [001] and thus the pinacoid {001} is the major form.

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Table 1. Chemical composition of natromolybdite.

Constituent	wt.%	Range	Standard deviation	Reference material
Na_2O	25.51	23.95 – 26.01	0.94	jadeite
K_2O	0.66	0.37 – 1.13	0.29	microcline
SO_3	1.04	0.00 – 2.43	0.90	ZnS
MoO_3	58.21	56.42 – 60.05	1.43	$CaMoO_4$
H_2O (calc.)*	15.05			
Total	100.47			

*The content of H_2O is calculated by stoichiometry, for two H_2O molecules per formula unit, by analogy with synthetic $Na_2MoO_4·2H_2O$.

Table 2. Powder X-ray diffraction data (*d* in Å, *I* in %) and unit-cell parameters of natromolybdite and its synthetic analogue $Na_2MoO_4·2H_2O$.

Natromolybdite			**Synthetic $Na_2MoO_4·2H_2O$**				*hkl*
			Our data: sample used for IR spectroscopic and optical studies		JCPDS-ICDD #70-1710, calculated from single-crystal structure data by Matsumoto *et al*. (1975)		
I_{obs}	d_{obs}	d_{calc}	I_{obs}	d_{obs}	I_{calc}*	d_{calc}	
100	**6.92**	6.921	**100**	**6.94**	**100**	**6.914**	002
12	5.97	5.970	8	5.99	10	5.958	111
13	5.29	5.289	6	5.30	9	5.276	020
9	4.784	4.783	6	4.792	7	4.775	112
20	**4.243**	4.241	**10**	**4.250**	**14**	**4.232**	200
32	**4.206**	4.202	**14**	**4.207**	**26**	**4.194**	022
9	3.785	3.787, 3.785	7	3.789	6, 6	3.779, 3.779	211, 113
31	**3.618**	3.616	**24**	**3.622**	**30**	**3.609**	202
6	3.462	3.461	6	3.464	3	3.457	004
5	3.426	3.422	4	3.426	4	3.414	212
31	**3.310**	3.309	**20**	**3.313**	**27**	**3.301**	220
11	3.218	3.218, 3.217	8	3.222	7, 7	3.211, 3.211	221, 123
49	**3.169**	3.169	**25**	**3.172**	**42**	**3.162**	131
21	**3.067**	3.067	**20**	**3.070**	**18**	**3.062**	114
30	**2.987**	2.985	**22**	**2.988**	**26**	**2.979**	222
12	2.895	2.896	9	2.898	10	2.892	024
7	2.741	2.740	4	2.742	3	2.736	124
15	**2.681**	2.681, 2.680	**13**	**2.684**	**12, 12**	**2.677, 2.677**	204, 311
12	2.663	2.661, 2.660	7	2.661	8, 8	2.655, 2.655	231, 133
5	2.600	2.599, 2.597	5	2.602	4, 4	2.595, 2.595	214, 041
4	2.454	2.454, 2.453	3	2.454	2, 2	2.449, 2.449	321, 025
3	2.393	2.392	2	2.393	2	2.387	224
6	2.353	3.356, 2.351	4	2.354	3, 3	2.353, 2.346	125, 313
2	2.307	2.307	2	2.308	1	2.305	006
2	2.295	2.294			1	2.290	043

1	2.266	2.265	1	2.266	0.5	2.261	215
2	2.215	2.215, 2.215	1	2.215	1, 1	2.210, 2.210	241, 143
11	2.179	2.178, 2.178	**11**	**2.179**	8, 8	2.176, 2.176	331, 116
4	2.144	2.144	2	2.146	2	2.140	314
5	2.120	2.121	3	2.123	4	2.116	400
13	2.031	2.030, 2.028	8	2.030	10, 10	2.026, 2.026	151, 402
4	1.970	1.968, 1.968	2	1.970	2, 2	1.964, 1.964	420, 152
8	1.894	1.893, 1.893	7	1.894	7, 7	1.889, 1.889	422, 250
7	1.878	1.876, 1.875	3	1.876	5, 5	1.871, 1.871	251, 153
2	1.818	1.817	1	1.818	0.5	1.813	430
3	1.810	1.811, 1.808	3	1.809	2, 2	1.805, 1.805	423, 404
4	1.763	1.763, 1.763	4	1.763	4, 4	1.760, 1.760	060, 316
4	1.744	1.743	3	1.743	4	1.740	245
3	1.726	1.725	3	1.725	3	1.722	335
3	1.711	1.713, 1.711	3	1.711	2, 2	1.707, 1.707	161, 424
4	1.697	1.697, 1.695	3	1.695	2, 2	1.695, 1.695	227, 108
9	1.681	1.681	7	1.681	9	1.677	351
5	1.649	1.649, 1.648	4	1.648	4, 4	1.646, 1.646	155, 502
2	1.615	1.617, 1.614			1, 1	1.613, 1.613	163, 128
2	1.561	1.563, 1.561	2	1.561	1.5, 1.5	1.559, 1.559	255, 406
2	1.535	1.535, 1.533	2	1.534	1.5, 1.5	1.532, 1.532	263, 228
2	1.521	1.520, 1.519	3	1.520	2, 2	1.516, 1.516	531, 435
4	1.481	1.484	2	1.483	3	1.481	247
		1.481	2	1.479	1.5	1.478	346
2	1.463	1.462, 1.462	2	1.462	2, 2	1.460, 1.460	318, 362
2	1.422	1.420, 1.420	1	1.421	1, 1	1.417, 1.417	445, 541
4	1.414	1.416, 1.416	2	1.415	2, 2	1.413, 1.413	173, 271
2	1.396	1.395, 1.395	2	1.395	1.5, 1.5	1.393, 1.393	427, 525
1	1.375	1.373, 1.373	1	1.374	0.5, 0.5	1.370, 1.370	612, 364
1	1.366	1.366, 1.365			0.5, 0.5	1.363, 1.363	620, 356
3	1.356	1.356, 1.355	4	1.355	3, 3	1.353, 1.353	516, 1.1.10
1	1.340	1.338, 1.338	1	1.338	1, 1	1.336, 1.336	437, 535
2	1.330	1.330, 1.330	2	1.329	1.5	1.328	462
Parameters of orthorhombic unit cell							
8.483(1)			8.487(2)		8.463(3)		*a* (Å)
10.577(2)			10.572(3)		10.552(3)		*b* (Å)
13.842(2)			13.835(4)		13.827(6)		*c* (Å)
1242.0(2)			1241.4(10)		1234.8		*V* (Å^3)

* For the calculated pattern, only reflections with intensities ≥ 0.5 are given; the strongest reflections are marked in boldtype.

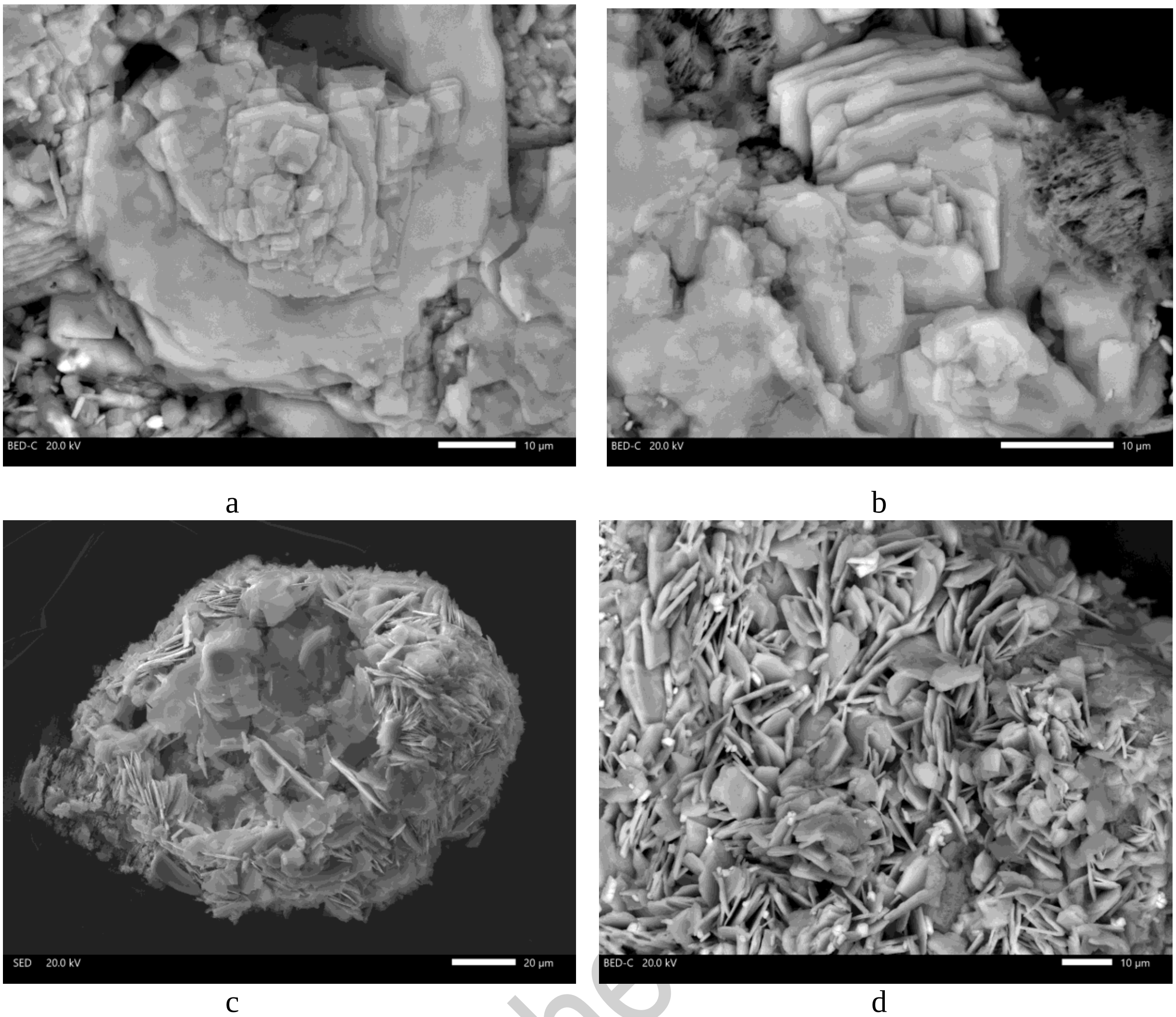


Figure 1. Morphology of natromolybdite crystals and aggregates: a – aggregate of split rhomb-like thin-tabular crystals on crust of tiny cubic halite crystals; b – near-parallel and rose-like aggregates of thin-tabular crystals on cellular aphthitalite crust; c – crust of lamellar crystals which almost completely covers crude hexagonal thick-tabular aphthitalite crystal; d – crust of well-shaped lamellar crystals on halite. SEM images (a, b, d – BSE mode, c – SE mode). Field-of-view widths are (µm): (a) 76, (b) 49, (c) 178, (d) 114.

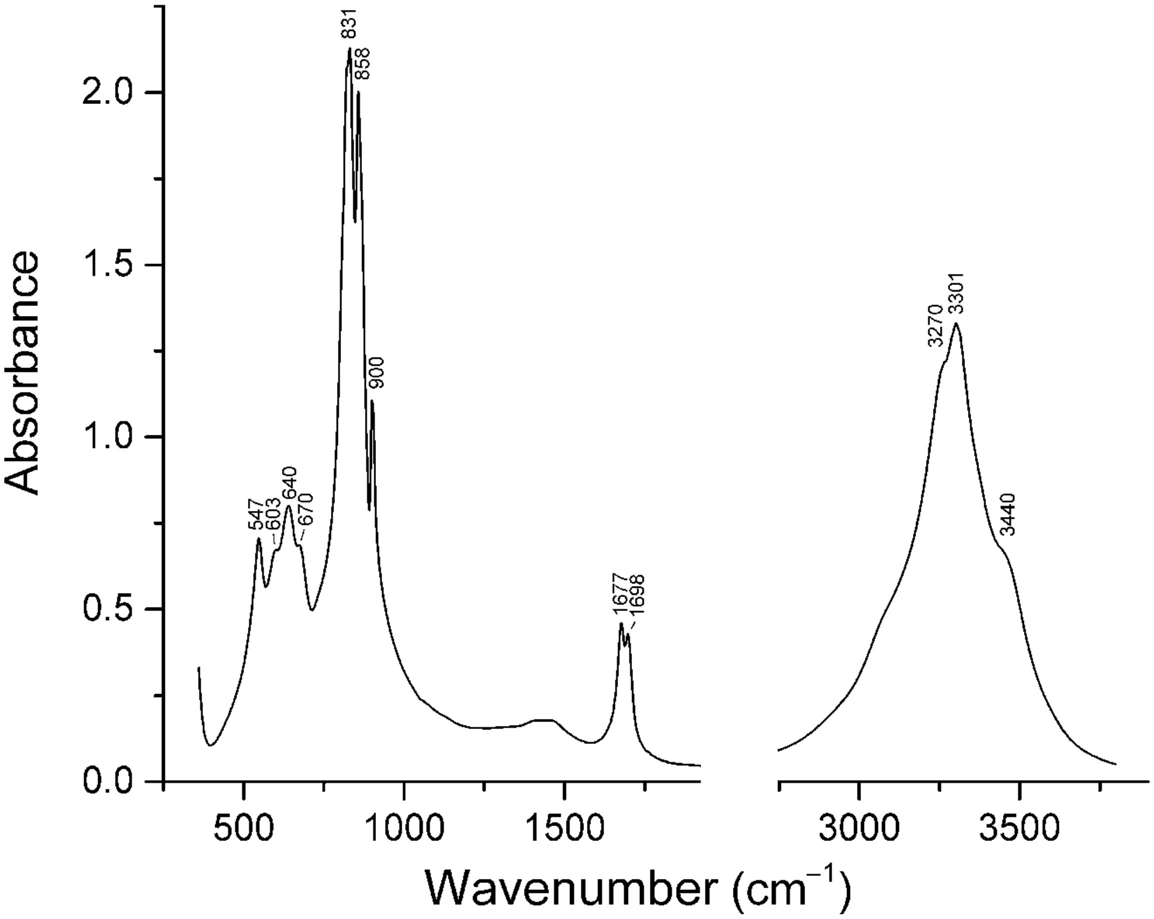
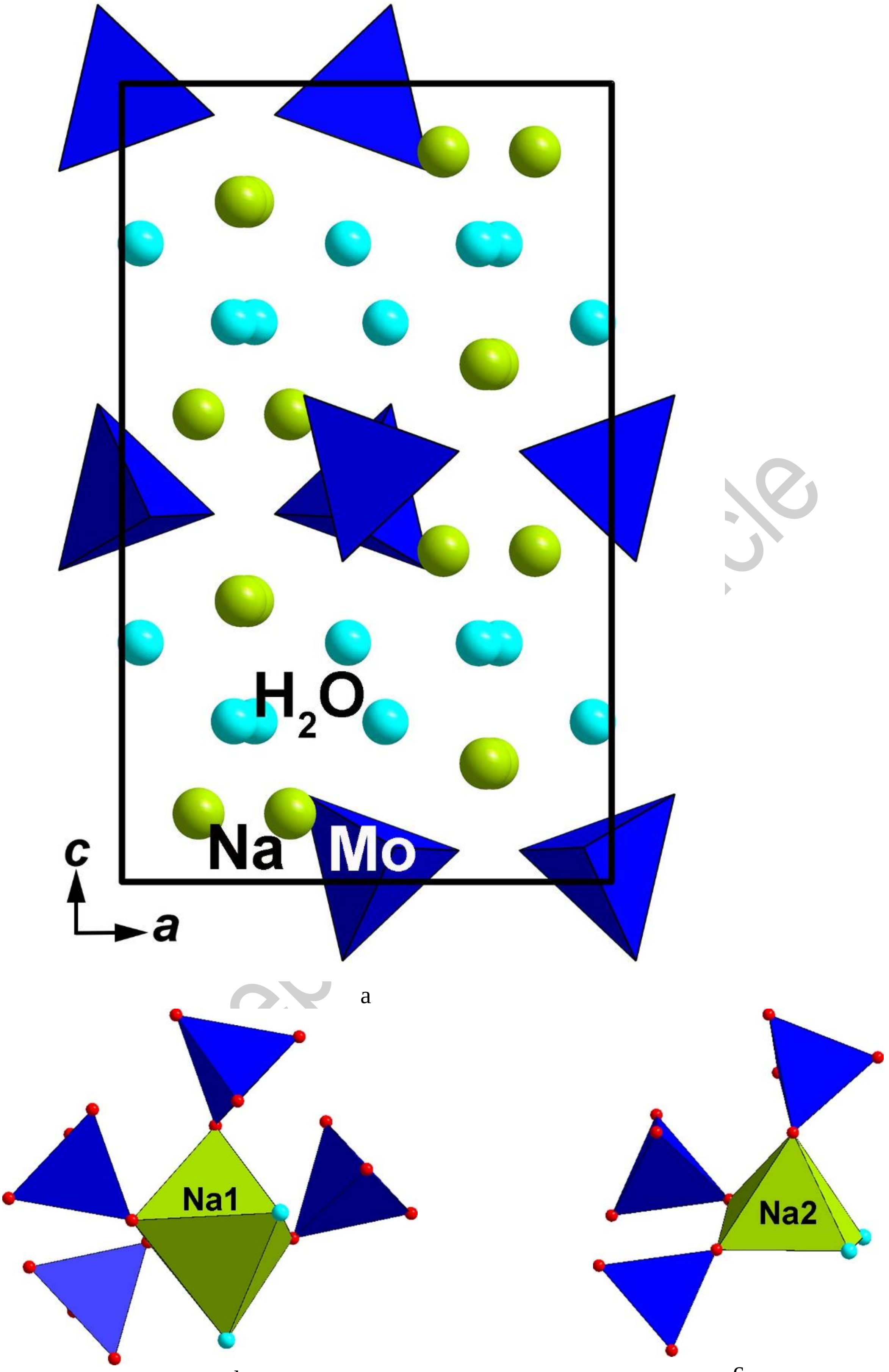


Figure 2. The IR spectrum of synthetic analogue of natromolybdite, $Na_2MoO_4 \cdot 2H_2O$.



a

b

c

Figure 3. The crystal structure of synthetic $Na_2MoO_4 \cdot 2H_2O$ with MoO_4 groups shown as blue tetrahedra (a) and Na-centered polyhedra linked with MoO_4 tetrahedra in it (b, c): drawn based on the data by Matsumoto *et al*. (1975). Light blue balls in (b) and (c) are O atoms belonging to H_2O molecules. The unit cell is outlined in (a).