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# **Structure, characterization, and properties of BaMoO<sub>4</sub> and BaKYb(MoO<sub>4</sub>)<sub>3</sub> flux-grown single-crystals**

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## Abstract

Crystals of the barium molybdates  $\text{BaKYb}(\text{MoO}_4)_3$  and  $\text{BaMoO}_4$  were obtained by spontaneous nucleation from high-temperature flux experiments. The compounds were characterized by energy-dispersive spectrometry (EDS) and Raman spectroscopy, and their structure was solved from single-crystal X-ray diffraction data at room temperature.  $\text{BaMoO}_4$  crystallizes in the tetragonal  $I4_1/a$  symmetry with  $a = b = 5.5723(4)$  and  $c = 12.7954(9)$  Å. With the scheelite-type structure,  $\text{BaMoO}_4$  displays sharp and intense lines in its FT-Raman spectrum registered at room temperature. The new triple molybdate  $\text{BaKYb}(\text{MoO}_4)_3$  is described in a monoclinic lattice  $C2/c$  of parameters  $a = 17.3517(5)$ ,  $b = 12.1477(4)$ ,  $c = 5.2481(2)$  Å,  $\beta = 105.344(2)^\circ$ . The  $\text{Yb}^{3+}$  ions are surrounded by oxygen leading to  $\text{YbO}_8$  coordination polyhedra while atomic disorder is observed for the cations  $\text{Ba}^{2+}$  and  $\text{K}^+$ , statistically sharing their positions inside 8-vertex coordination polyhedra. The Raman spectrum confirms the presence of distorted  $\text{MoO}_4$  tetrahedra for the  $\text{BaKYb}(\text{MoO}_4)_3$  molybdate. Investigation of its magnetic properties was undertaken in order to check whether a magnetic ordering occurs at low temperature.

**Keywords:** Molybdate, Crystal structure, Raman investigation; Magnetic susceptibility

## 1. Introduction

Simple molybdates with the general formula  $MeMoO_4$  ( $Me^{2+} = Ba, Sr, Ca, Pb$ ) and the scheelite-like structure are potential stimulated Raman scattering (SRS) materials and promising hosts for the incorporation of optically active ions [1-3]. On the other hand, double molybdates of general formula  $ALnMoO_4$  ( $A^+ =$  alkaline metals, Cu or Tl) have received considerable attention due to their amazing properties and their thermal and chemical stability [4-10]. They have a high potential application in various fields, such as lanthanide ( $Ln$ ) luminescence [5-6], Li-ion or Na-ion batteries [7, 8], and laser hosts activated by  $Ln^{3+}$  ions [9, 10].  $Yb^{3+}$ -doped solid state lasers with large ground state  $^2F_{7/2}$  splitting through strong crystal field effects (CF) are interesting alternatives to those based on  $Nd^{3+}$  as large homogeneous spectral broadening and larger laser gain bandwidths could be reached [11]. Since CF effects are dependent on the structural characteristics of the lanthanide site in the crystal network, the search for new materials with a multisite  $Yb^{3+}$  occupation and highly distorted coordination polyhedra around  $Yb^{3+}$  has generated a lot of interest. The results presented in the current paper have been obtained in the course of a more general study aimed at the synthesis and structural evaluation of Yb-based magnetically-concentrated double molybdates more recently described [12, 13].  $KYb(MoO_4)_2$  crystallizes in the orthorhombic symmetry, space group  $Pbcn$  (No. 60), with a complete ordering of the  $Yb^{3+}$  and  $Mo^{6+}$  cations [12]. The  $Yb^{3+}$  ions are located in distorted  $YbO_8$  antiprisms which form chains, by sharing edges, aligned along the  $c$ -axis.  $LiYbMo_2O_8$  displays the tetragonal symmetry and is described in the noncentrosymmetric  $I\bar{4}$  space group (No. 82) [13] with an atomic local disorder as  $Li^+$  and  $Yb^{3+}$  cations share their sites inside regular  $MO_8$  dodecahedra ( $M = Li/Yb$ ).

The high-temperature synthesis of  $BaMoO_4$  and  $BaKYb(MoO_4)_3$ , grown from the solution as millimeter-sized single crystals, is described. Besides, the monoclinic structure of the new molybdate  $BaKYb(MoO_4)_3$  is provided with also a structural determination from crystal

diffraction of the tetragonal  $\text{BaMoO}_4$  scheelite-like structure. The room temperature structural study is completed by vibrational characterizations via Raman spectroscopy. The magnetic properties of the ternary molybdate are presented with both the temperature-dependent susceptibility and the field-dependent magnetization recorded from 1.8 to 300 K.

## 2. Experimental

### 2.1. Materials preparation

The flux growth was carried out by the slow-cooling method with spontaneous nucleation.  $\text{Ba}_3\text{Yb}_4\text{O}_9$  was chosen as the solute as we already synthesized this pure phase for previous works, and  $\text{K}_2\text{CO}_3$  (or  $\text{Rb}_2\text{CO}_3$ )- $3\text{MoO}_3$  mixtures as the fluxes (solvents). All the starting reagents are high purity Alfa Aesar commercial products,  $\text{MoO}_3$  (99.95%),  $\text{Yb}_2\text{O}_3$  (99.9%),  $\text{BaCO}_3$  (99%),  $\text{K}_2\text{CO}_3$  (99%),  $\text{Rb}_2\text{CO}_3$  (99%), and were used as received.  $\text{Ba}_3\text{Yb}_4\text{O}_9$  was synthesized via a solid-state reaction from  $3\text{BaCO}_3$  and  $2\text{Yb}_2\text{O}_3$  heated at  $1400^\circ\text{C}$  during 12 hours in the air (see Supplementary Materials S.1). The  $\text{K}_2\text{CO}_3$ - $3\text{MoO}_3$  mixture (or  $\text{Rb}_2\text{CO}_3$ - $3\text{MoO}_3$ ) was heated in air at  $520^\circ\text{C}$  for at least 8 days. This step allowed to get high quantities of  $\text{K}_2\text{Mo}_3\text{O}_{10}$  or  $\text{Rb}_2\text{Mo}_3\text{O}_{10}$  compounds in the powder form. We did not tried to use the self-flux method consisting to directly prepare the compound by heating a stoichiometric mixture of all the required oxides, as for example  $\text{K}_2\text{O}$ - $\text{BaO}$ - $\text{Yb}_2\text{O}_3$  and  $\text{MoO}_3$ .

The solute/flux powders,  $\text{Ba}_3\text{Yb}_4\text{O}_9$  and  $\text{K}_2\text{CO}_3$ - $3\text{MoO}_3$  (or  $\text{Rb}_2\text{CO}_3$ - $3\text{MoO}_3$ ) were mixed in 10/90 weight proportions and an amount of 20 g of powder was loaded into a Pt crucible covered with a lid. This solute + flux mixture was heated in a resistance-heated furnace at  $970^\circ\text{C}$  for 3 hours in the air to ensure a good dissolution of the solute. The complete dissolution of the solute in the flux has not been specially monitored or measured. After that, the sample was cooled by decreasing first the temperature to  $600^\circ\text{C}$  at the rate of  $0.9^\circ/\text{h}$ , and next to room temperature at  $200^\circ/\text{h}$ .

## 2.2. *Materials characterization*

The materials obtained as individualized colorless crystals were characterized by classical analyses such as EDX, Raman spectroscopy, and X-ray diffraction. Their chemical composition was obtained by Energy Dispersive X-ray spectroscopy on a Quanta 200 FEG (FEI) scanning electron microscope equipped with an SDD diode detector (Oxford INCA). The spectra were recorded under a primary vacuum (around  $10^{-5}$  Torr) at a voltage of 15 kV. To control the quality/homogeneity of the crystals, at least three zones were probed for each sample.

## 2.3. *X-ray diffraction*

A stereo microscope equipped with a polarizing filter was used to select single colorless and faceted crystals suitable for X-ray diffraction data collection (Mo  $K\alpha$  radiation, room temperature) either using an Xcalibur CCD (Oxford diffraction) or a Bruker D8 Venture diffractometer. The appropriate software suites CrysAlis [14] or Apex [15] were used for the treatment of data, the Lorentz-polarization, and absorption corrections. The structures were solved and refined using the SHELX programs [16, 17] and anisotropic displacement parameters were considered for all atoms in full-matrix least-squares refinements on  $F^2$ . The entire filling of the sites was checked by the free refinement of site occupation factors. Structural representations have been drawn using the program Diamond [18].

## 2.4. *Raman measurements*

Unpolarized Raman spectra were recorded at room temperature on a LabRam Aramis spectrometer (Horiba Jobin-Yvon) at the He-Ne wavelength ( $\lambda = 632.8$  nm). This device is equipped with a CCD detector cooled by the Peltier effect and a motorized stage. According to

the instrumental error of  $1\text{ cm}^{-1}$  on the measurement, the frequencies of Raman vibration modes in wavenumber, are given to within one unit.

### 2.5. *Magnetic measurements*

Magnetic measurements were carried out using a commercial Superconducting Quantum Interference Device (SQUID) MPMS-7XL magnetometer in DC mode, allowing to explore the temperature range of 1.8 - 300 K with H external magnetic fields ranging from 0 to 5 Tesla with a sensitivity of the order of  $10^{-8}$  emu. A powdered sample of  $\text{BaKYb}(\text{MoO}_4)_3$  of 63.6 mg was weighed and placed in a capsule introduced in a plastic straw. The negligible diamagnetic contribution of the straw has not been subtracted from our data.

## 3. Results and discussion

### 3.1. *Growth of crystals*

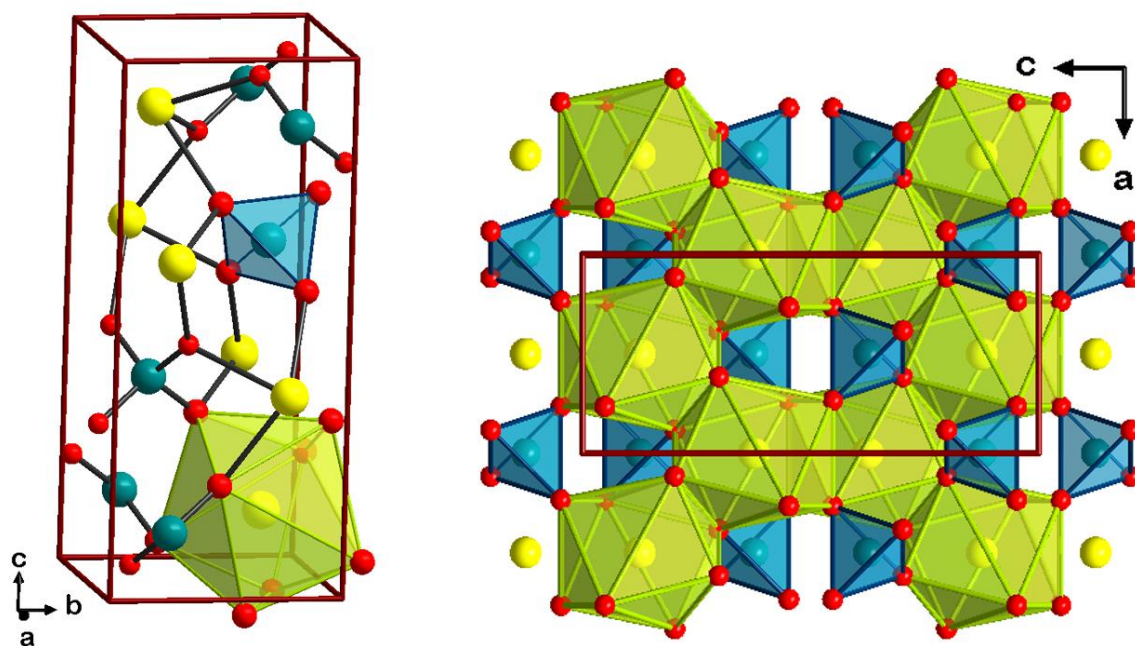
At the end of each high temperature flux growth experiment, the solidified mixture was dissolved in water, and numerous colorless and transparent crystals spontaneously grown (0.2-2 mm in size) were isolated. No post-growth annealing was applied.

In case of use of the K-based flux, two kinds of single-crystals were obtained with a growth yield of about 20%. Plate-like as-grown crystals with the  $\text{KYb}(\text{MoO}_4)_2$  composition [12], and bulky and well-faceted crystals with no inclusion visible to the eyes (Supporting information Figure S2). The EDX analyses have confirmed the formula  $\text{BaKYb}(\text{MoO}_4)_3$  giving an atomic ratio Ba:K:Yb:Mo:O of 1.1(1):1.1(1):0.9(1):3:12(1) with no significant variation in chemical composition when scanning across the raw surface of the crystal. When using the Rb-based flux for the growth experiment, only one kind of single-crystals with under-millimeter size was obtained with a yield of about 5 %. The EDX analysis indicated that neither Rb nor Yb entered into the compound composition, leading to the barium molybdate  $\text{BaMoO}_4$ .

### 3.2. Single-crystal structure of $\text{BaMoO}_4$

The single-crystal structure of  $\text{BaMoO}_4$  refined in the tetragonal space group  $I4_1/a$  to a final agreement factor  $R_1$  of 1.28% is in very good agreement with the previous works mentioned in the Pearson Crystal structure database [19] among which, only one, with  $R_1 = 14\%$ , refers to a single-crystal refinement [20]. It also closely matches the most recent and accurate structural determination undertaken on a nanosized polycrystalline sample using synchrotron data [21].

The structural model includes Mo at  $4a$ , Ba at  $4b$  and O at  $16f$  positions. Regular  $\text{MoO}_4$  tetrahedra ( $\bar{4}$  symmetry) are characterized by  $4 \times$  Mo-O distances of  $1.761(1) \text{ \AA}$  with  $4 \times 108.2(1)$  and  $2 \times 112.1(1)^\circ$  O-Mo-O angles that are close to those reported for a  $\text{BaMoO}_4$  ceramic prepared by conventional solid-sintering method [22]. Eight oxygen atoms, 4 at  $2.741(1)$  and 4 at  $2.777(1) \text{ \AA}$  from Ba, are arranged at the vertices of  $\text{BaO}_8$  coordination polyhedra with  $\bar{4}$  symmetry (Figure 1). The full CIF file is freely available with the CSD number 2112357 at the Cambridge Crystallographic Data Center [23].





**Figure 1.** Representations of the scheelite-like BaMoO<sub>4</sub> structure with blue MoO<sub>4</sub> tetrahedra and green BaO<sub>8</sub> coordination polyhedra. The unit cell is drawn as brown lines. Yellow balls for Ba, red for O, and blue for Mo.

### 3.3. Single-crystal structure of BaKYb(MoO<sub>4</sub>)<sub>3</sub>

The main structural parameters and the X-ray data collection parameters are reported in Table 1 for the two barium molybdates.

**Table 1.** Crystal data, structure refinement, and data collection details

Formula	BaMoO <sub>4</sub>	BaKYb(MoO <sub>4</sub> ) <sub>3</sub>
<i>Lattice and symmetry</i>		
Symmetry	tetragonal	monoclinic
Space group	<i>I</i> 4 <sub>1</sub> /a (88)	<i>C</i> 2/ <i>c</i> (15)
Lattice dimensions (Å, °)	<i>a</i> = <i>b</i> = 5.5723(4) <i>c</i> = 12.7954(9)	<i>a</i> = 17.3517(5) <i>b</i> = 12.1477(4) <i>c</i> = 5.2481(2) <i>β</i> = 105.344(2)
Lattice volume (Å <sup>3</sup> )	397.30(6)	1066.78(6)
Z	4	4
Calculated density	6.307	5.164
<i>Data collection at 298 K</i>		
Radiation, wavelength (Å)	Mo Kα, 0.71073	Mo Kα, 0.71073
θ range (°)	3.9–28.8	3.3–37.8
Absorption coefficient (mm <sup>−1</sup> )	13.03	16.19
<i>Full-matrix least-squares refinement on F<sup>2</sup></i>		
Independent reflections	253 [R <sub>int</sub> = 0.025]	2596 [R <sub>int</sub> = 0.029]
Final indices [ <i>I</i> > 2σ( <i>I</i> )] <i>R</i> 1, <i>wR</i> 2	0.0128, 0.0361	0.0152, 0.0333
<i>R</i> 1, <i>wR</i> 2 (all data)	0.0137, 0.0364	0.0154, 0.0334
Density residuals (e.Å <sup>−3</sup> )	0.60/−0.39	0.25/−1.15

The reflections initially collected for a crystal selected as a single crystal indicated the *I*-centering for a monoclinic cell with  $a = 5.2$ ,  $b = 12.1$ ,  $c = 16.4$  Å,  $\beta = 92^\circ$  but slight dispersion was noted in the diffraction images suggests twinning. Since the monoclinic angle does not deviate too much from  $90^\circ$ , a two-fold rotation around any of the axes would lead to an almost perfect lattice overlay. Yet, a reasonable structural solution could be found after transformation into a monoclinic *C*-cell with  $a = 17.4$ ,  $b = 12.1$ ,  $c = 5.2$  Å,  $\beta = 105^\circ$  by applying the transformation matrix  $[\bar{1}0\bar{1}010100]$  to the data. The structure was finally confirmed by the full structural refinement to  $R1 = 1.52\%$  using a new set of reflections collected later for a suitable single crystal,  $C2/c$ ,  $a = 17.3517(5)$ ,  $b = 12.1477(4)$ ,  $c = 5.2481(2)$  Å,  $\beta = 105.344(2)^\circ$ .

Among the ten independent positions, a general site  $8f$  and a special site  $4e$  were attributed to the most electropositive elements, a site  $8f$  and a site  $4e$  to molybdenum atoms, and the six remaining  $8f$  sites to oxygen atoms. As the same contents are expected for K, Ba, and Yb, an atomic mixing must be considered on the two sites assigned to electropositive elements, Table 2.

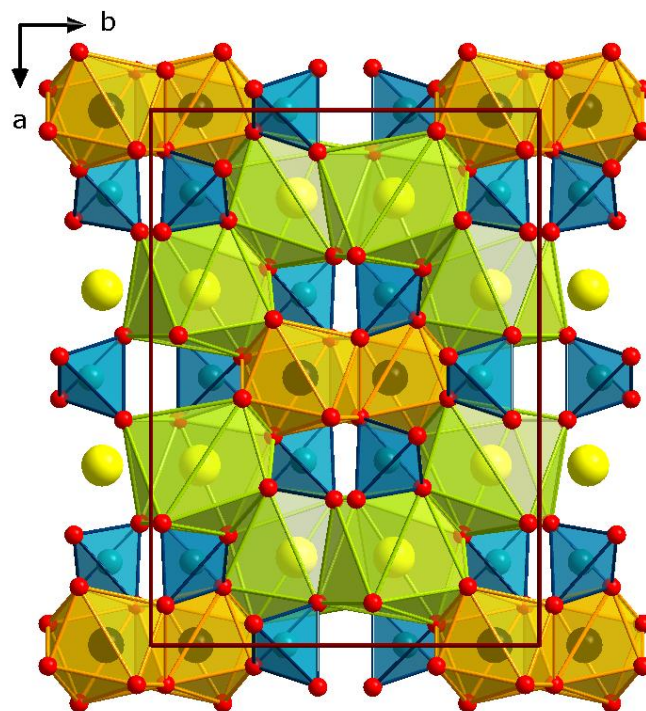
**Table 2.** Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ )

Atom	site	x	y	z	U <sub>eq</sub>
Yb	4e	0	6154(1)	2500	7(1)
Mo1	4e	0	1551(1)	2500	9(1)
Mo2	8f	1552(1)	3928(1)	3976(1)	8(1)
Ba/K	8f	3359(1)	3747(1)	752(1)	13(1)
O1	8f	394(1)	2350(1)	266(2)	14(1)
O2	8f	742(1)	4629(1)	1435(2)	11(1)
O3	8f	2059(1)	3019(1)	2461(2)	15(1)
O4	8f	786(1)	707(1)	4203(2)	19(1)
O5	8f	2723(1)	285(1)	3807(2)	16(1)

O6	8f	3912(1)	1850(1)	3965(2)	13(1)
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With a higher symmetric environment and slightly shorter distances to surrounding oxygen atoms, the 4*e* site was found filled by ytterbium. Potassium and barium larger cations, with ionic radii of 1.42 and 1.51 Å, compared to 1.14 for Yb cation, are statistically mixed at the 8*f* position. Their fraction at this site freely refines, within the standard deviation limits, to equivalent amounts leading to the formula Ba<sub>3.98</sub>K<sub>4.02</sub>Yb<sub>3.97</sub>(MoO<sub>4</sub>)<sub>12</sub> in which the charge balance is almost perfectly fulfilled without any constrain to the final formula is BaKYb(MoO<sub>4</sub>)<sub>3</sub>. A bond valence sum analysis was performed using the most recently established parameters [24], available from IUCR resources [25]. This is an empirical way to estimate the oxidation state of a metal ion from its distances to surrounding ligands. It leads to valence numbers close to 6 for Mo and 3 for Yb and adds further weight to the complete ordering of the Yb atoms on the 4*e* site. The Mo-O distances are in range 1.732-1.866 Å and more precisely the tetrahedra with symmetry 2 are built around Mo atom at 4*e* site with 2 × 1.751(1) and 2 × 1.792(1) Å distances while a greater distortion is found at the tetrahedra formed around Mo at the 8*f* site (symmetry 1, distances 1.732(1), 1.754(1), 1.780(1) and 1.866(1) Å). The Yb atoms are surrounded by eight oxygen at 2.313(1)-2.405(1) Å within YbO<sub>8</sub> units while the Ba/K atoms have eight oxygen neighbors located at longer distances from 2.702(1) to 2.866(1) Å. The full CIF file with the CSD number 2112359 can be freely obtained from the Cambridge Crystallographic Data Center [23].

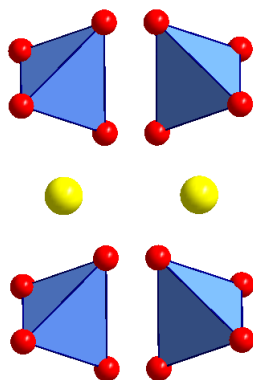


**Figure 2.** Representation of the structure of  $\text{BaKYb}(\text{MoO}_4)_3$  with blue  $\text{MoO}_4$  tetrahedra. The unit cell is drawn as brown lines, the 8-vertex coordination polyhedra around Ba/K in green, and around Yb in orange. Yellow balls for Ba/K, red for O, blue for Mo, and brown for Yb.

Looking at the arrangement of polyhedra, the structure of  $\text{BaKYb}(\text{MoO}_4)_3$  represented in Figure 2 bears a strong resemblance with that of  $\text{BaMoO}_4$ , which can be otherwise formulated  $\text{Ba}_3(\text{MoO}_4)_3$ , given in Figure 1. They both contain discrete  $\text{MoO}_4$  tetrahedra having no common O, but sharing their four O vertices with the neighboring  $\text{XO}_8$  units ( $X = \text{Ba}, \text{K}, \text{or Yb}$ ). Instead, the  $\text{XO}_8$  units are involved in chains of polyhedra (Figures 1 and 2) by sharing edges with neighboring analogs.

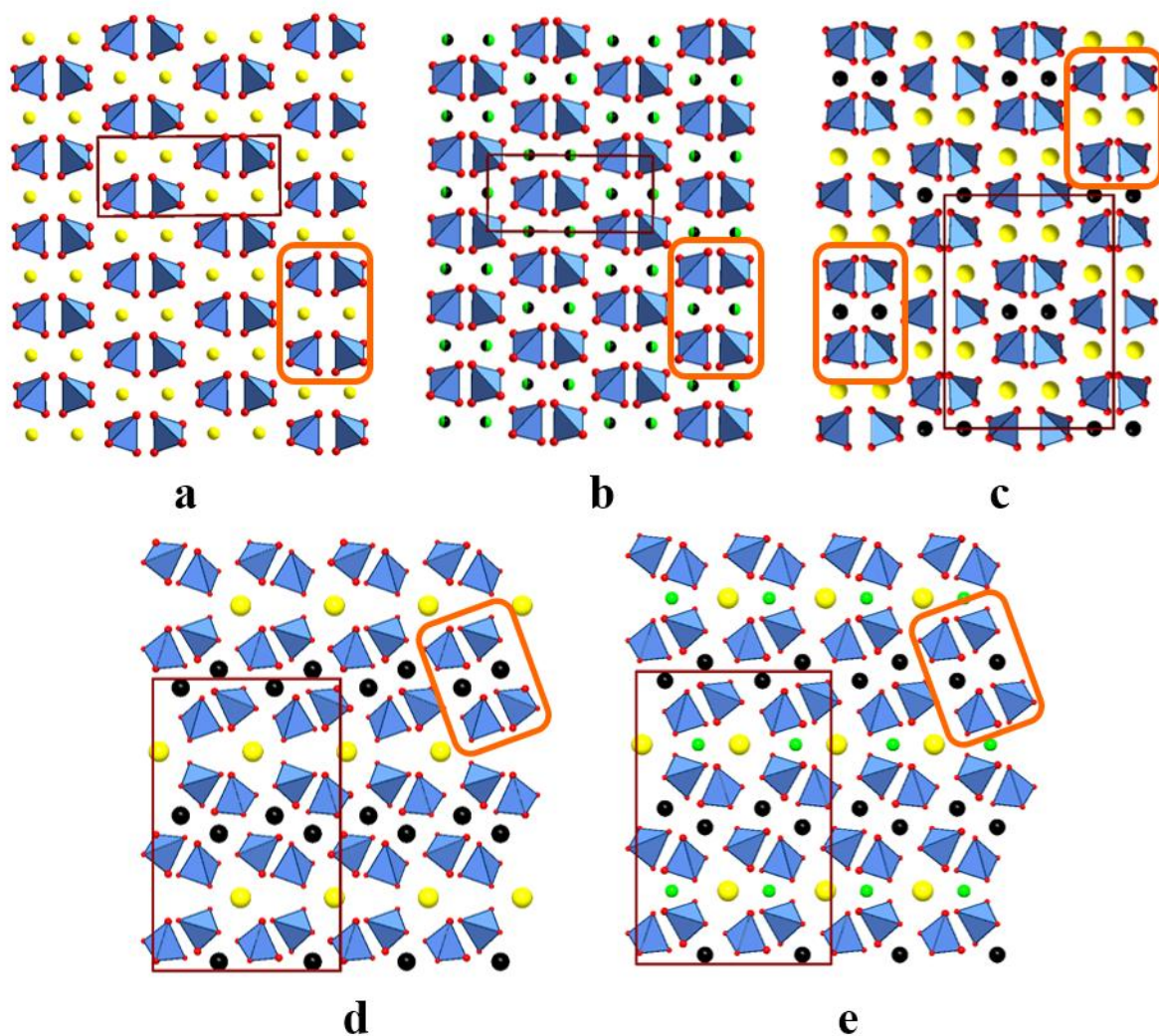
### 3.4 Common building blocks

$\text{BaMoO}_4$  and  $\text{BaKYb}(\text{MoO}_4)_3$  structures are composed with the same building blocks represented in Figure 3 involving four  $\text{MoO}_4$  tetrahedra around two cationic positions (separated by 4.24 Å in  $\text{BaMoO}_4$ ).



**Figure 3.** The common building blocks in the  $\text{Ba}_3(\text{MoO}_4)_3$  and  $\text{BaKYb}(\text{MoO}_4)_3$  structures. Blue  $\text{MoO}_4$  tetrahedra and yellow balls for Ba/K, red for O.

However, the heterovalent substitution of two Ba in the  $\text{Ba}_3(\text{MoO}_4)_3$  formula by one K and one Yb changes the symmetry so that a lower-symmetry and larger monoclinic unit cell is needed to describe the compound  $\text{BaKYb}(\text{MoO}_4)_3$ . Also, the cationic sites that were all equivalent in  $\text{BaMoO}_4$ , Figure 4a, are now divided into two categories, those filled with a Ba/K mixture and those filled with Yb, each of which being involved in a building block, Figure 4c. Depending on the nature of the cation, this causes local distortions of the building blocks that can be visualized with the greater spaces between the tetrahedra placed in the same layers as Yb at  $a = 0, \frac{1}{2}$  (see also in Figure 2) than the separation between tetrahedra placed in the same layers as Ba/K cations. The interatomic distances inside the Ba/K and Yb cationic pairs are measured respectively at 4.020(1) and 3.839(1) Å. Interestingly, the same building blocks are found in the structure of  $\text{LiYb}(\text{MoO}_4)_2$  (Figure 4b) where the statistical Li/Yb atom distribution on the cationic sites allows the tetragonal symmetry to be maintained (with only a shift in the origin of the cell) [13]. Note that the distance between the cationic sites is here shortened to 3.77 Å.



**Figure 4.** Respective arrangement of the  $4 \times \text{MoO}_4$  tetrahedra building blocks (highlighted with orange shapes) in some barium molybdates. Brown lines represent the unit cell limits. The representations were drawn from the structure data available in the literature. a-  $\text{Ba}(\text{MoO}_4)$  [this work], b-  $\text{LiYb}(\text{MoO}_4)_2$  [13], c-  $\text{BaKYb}(\text{MoO}_4)_3$  [this work], d-  $\text{BaYb}_2(\text{MoO}_4)_4$  [26], and e-  $\text{BaLi}_{1.5}\text{Gd}_{1.4}\text{Yb}_{0.1}(\text{MoO}_4)_4$  [27]. Yellow balls for Ba/K, green for Li, black for Yb and red for O.

Going further in the structural comparison reveals some similarities with the arrangement of polyhedra in the two barium molybdates  $\text{BaYb}_2(\text{MoO}_4)_4$  and  $\text{BaLi}_{1.5}\text{Gd}_{1.4}\text{Yb}_{0.1}(\text{MoO}_4)_4$  reported in the Pearson Crystal database [19]. These two monoclinic isostructural compounds are also formed with similar building blocks around the Yb cations, alternately tilted on the left or tilted on the right in the successive layers (Figure 4d and 4e).

The barium ytterbium molybdate  $\text{BaYb}_2(\text{MoO}_4)_4$  can be viewed as deriving from  $\text{BaMoO}_4$  (or  $\text{Ba}_4(\text{MoO}_4)_4$ ) by changing three Ba for two Yb and one vacancy and would be then formulated  $\text{Ba}\square\text{Yb}_2(\text{MoO}_4)_4$ . From there, the substitution of Yb for Li and Gd is almost entirely achieved in the molybdate  $\text{BaLi}_{1.5}\text{Gd}_{1.4}\text{Yb}_{0.1}(\text{MoO}_4)_4$  with additional Li found on an "insertion" position. As the Li, Gd, and Yb atoms are statistically distributed in proportions 25:70:5 at two sites, this molybdate could be formulated  $\text{BaLi}(\text{Li/Gd/Yb})_2(\text{MoO}_4)_4$ . The Yb to Yb distances within the Yb cationic pairs is 3.87 Å in these barium molybdates and the Li to Ba separation in the latter compound is 3.75 Å.

Figure 4 illustrates the role played by the nature, size, and distribution of the cations between the  $\text{MoO}_4$  tetrahedra in the whole structure packing. Starting with  $\text{BaYb}_2(\text{MoO}_4)_4$  and replacing the Yb atoms with Gd and Li atoms provides an isostructural arrangement where Gd is in place of Yb. For the heavy atoms Yb and Gd, there is little change in the covalent radii (1.94 and 1.79 Å) or even in the more appropriate Shannon effective ionic radii (0.868 and 0.938 Å), and the smaller ionic radii of  $\text{Li}^+$  (0.76 Å) allows lithium to take place at insertion positions [28]. On the contrary, the path from  $\text{BaYb}_2(\text{MoO}_4)_4$  to  $\text{BaKYb}(\text{MoO}_4)_3$  needs to change Yb atoms for larger Ba or K elements, whether one considers their covalent (2.17 and 2.27 Å) or ionic (1.37 and 1.35 Å) radii, and this cannot be achieved without a structural reorganization.

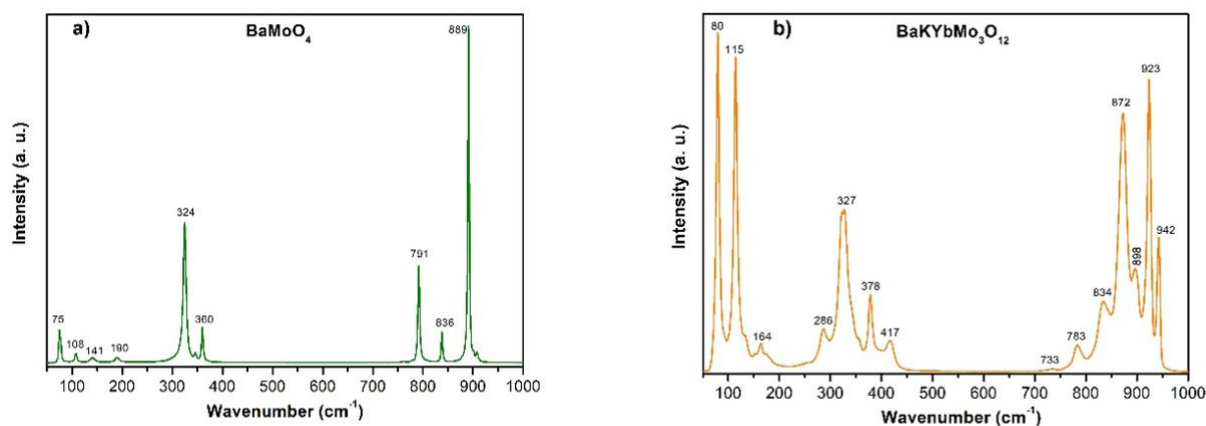
### 3.5. *Vibrational properties*

The unpolarized Raman scattering spectra were recorded at room temperature on the as-grown crystalline samples, Figure 5. It should be mentioned that no Raman band is observed in the frequency range beyond  $1000\text{ cm}^{-1}$ .

Compared to the  $T_d$  symmetry of an isolated  $\text{MoO}_4$  tetrahedron, the symmetry of  $[\text{MoO}_4]^{2-}$  units with strong covalent bonds Mo-O is reduced to  $S_4$  (or  $\bar{4}$ ) point symmetry in the scheelite-type  $\text{BaMoO}_4$  with tetragonal symmetry  $C_{4h}^6$ . This leads to a splitting of the degenerate vibrations due to the Crystal Field (CF) effect and Davydov Splitting (DS) [9]. The  $\text{MoO}_4$  internal modes are



then identified as  $\nu_1$  ( $A_g$ ),  $\nu_3$  ( $B_g$  and  $E_g$ ) (stretching modes),  $\nu_2$  ( $A_g$  and  $B_g$ ), and  $\nu_4$  ( $B_g$  and  $E_g$ ) (bending modes) which are Raman-active vibration modes [1, 29]. The range of stretched vibrations of  $\text{MoO}_4$  polyhedral is  $700\text{--}1000\text{ cm}^{-1}$ . The narrowest and intensive line at  $895\text{ cm}^{-1}$  is associated with antisymmetric Mo–O stretching vibrations into the  $\text{MoO}_4$  tetrahedra, and attributed to the bond vibration line  $\nu_1$  ( $A_g$ ) of  $\text{BaMoO}_4$  crystal [1, 29]. The bands at  $791$  and  $836\text{ cm}^{-1}$  are assigned to the  $\nu_3$  modes, and the frequencies of internal bending vibrations of  $\text{MoO}_4$  tetrahedra are in the  $300\text{--}400\text{ cm}^{-1}$  range as already reported [1, 29]. The external modes, called lattice phonon modes, correspond to the motion of the deltahedral  $[\text{BaO}_8]$  clusters and the rigid molecular unit and are present under  $150\text{ cm}^{-1}$  [1, 29].



**Figure 5.** The Raman spectra in  $50\text{--}1000\text{ cm}^{-1}$  range measured on the as-grown crystals of a)  $\text{BaMoO}_4$  and b)  $\text{BaKYb(MoO}_4)_3$ .

The Raman spectrum for the  $\text{BaKYb(MoO}_4)_3$  material presents three main segment bands between  $50$  and  $200\text{ cm}^{-1}$ ,  $250\text{--}450\text{ cm}^{-1}$ , and  $700\text{--}1000\text{ cm}^{-1}$ , Figure 5b. The maximum phonon frequency is  $942\text{ cm}^{-1}$ . Compared to  $\text{BaMoO}_4$ , Figure 5a, the Raman spectrum of the ternary molybdate is composed of bands with larger width at half maximum in agreement with the existence of two independent crystallographic sites for Mo atoms in its disordered structure. It is interesting to remark the strong resemblance of the Raman spectrum recorded in the current



study for BaKYb(MoO<sub>4</sub>)<sub>3</sub> with that reported for the yttrium homolog [30]. This was expected given the presumed isotypy of their structures (same lattice and symmetry), despite some differences in the atomic coordinates reported for BaKY(MoO<sub>4</sub>)<sub>3</sub> [31]. However, no complete cif-file is available precluding further comparison with the Yb-based triple molybdate under study. We think that a transcription error in the atomic positions is at the origin of an erroneous description of this structure with two types of polyhedra, MoO<sub>4</sub> and MoO<sub>6</sub>. Our diagnosis is confirmed in the recent paper giving both the Raman spectra and the structure of the yttrium molybdate described with only oxygen tetrahedra around Mo atoms [32].

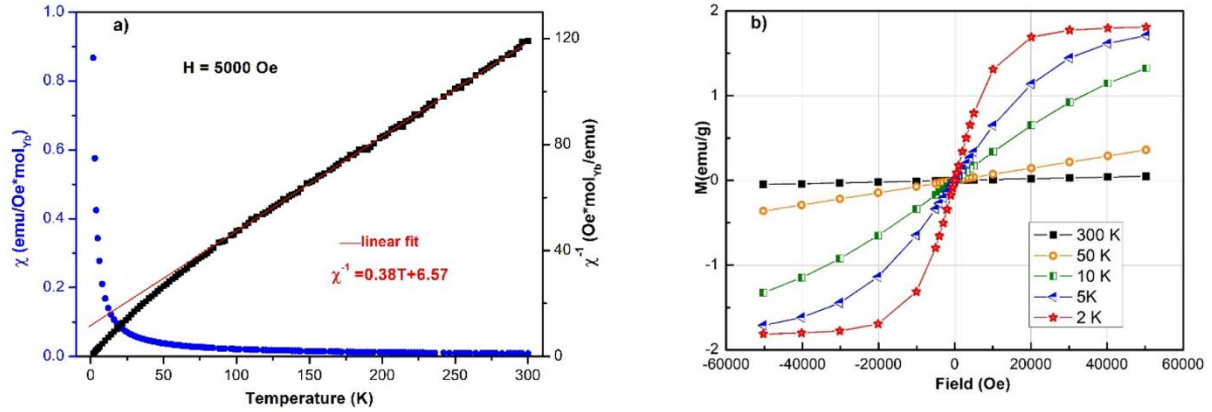
In the monoclinic structure of BaKYb(MoO<sub>4</sub>)<sub>3</sub>, the Mo<sup>6+</sup> ions coordinate with oxygen in isolated tetrahedral (MoO<sub>4</sub>)<sup>2-</sup> polyhedra, which means that no Mo-O-Mo bridge is present in the structure. The complexity of the spectrum is well explained by the degeneracy removal of the stretching modes due to the symmetry lowering ( $T_d \rightarrow C_1$ ) of the distorted MoO<sub>4</sub> tetrahedra since four lines can be present in the symmetric stretching domain and up to 12 in the asymmetric range [33]. The bands in the range 250 - 450 cm<sup>-1</sup> are assigned to the internal asymmetric and symmetric bending vibration  $\delta(\text{O-Mo-O})$  of the MoO<sub>4</sub> tetrahedra [12, 13, 33]. Below 200 cm<sup>-1</sup>, the bands are due to external vibrations that involve the rotational and translational modes of the (MoO<sub>4</sub>)<sup>2-</sup> anions and the translational modes of the cations [12, 13, 33].

### 3.6. *Magnetic properties*

The magnetization of the triple molybdate BaKYb(MoO<sub>4</sub>)<sub>3</sub> was measured for a powdered sample placed in a constant magnetic field  $H$  of 0.5 T at temperatures ranging from 1.8 to 300 K. The magnetic susceptibility  $\chi$  is defined as  $M/H$ . The electronic configuration of the paramagnetic Yb<sup>3+</sup> isolated ion is  $[Xe] 4f^{13}$  and the effective magnetic moment  $\mu_{\text{eff}}$  of Yb<sup>3+</sup> is equal to 4.54  $\mu_B$ .

The normalized Yb molar dc magnetic susceptibility is temperature-dependent, as shown in Figure 6.

No anomaly is visible on the  $\chi$  curve in the entire temperature range studied.



**Figure 6.** (a) Magnetic and inverse susceptibility  $\chi$  of crushed BaKYb(MoO<sub>4</sub>)<sub>3</sub> crystals in a constant  $H$  field as a function of the temperature, with a Curie-Weiss fit (red line) of the high-temperature data, (b)  $M$ - $H$  curves recorded at different temperatures normalized by the mass.

From 300 K down to 75 K, the inverse magnetic susceptibility  $\chi^{-1}$  is linear that characterizes a localized paramagnetic behavior, Figure 6a. The data obey a Curie-Weiss law  $\chi_{mol} = C/(T - \theta_p)$  with the least-squares parameters  $C = 2.63(1)$  emu.mol $^{-1}$  (Curie constant) and  $\theta_p = -33.8$  K (paramagnetic Curie-Weiss temperature). The deviation from the Curie-Weiss law appears at  $72 \pm 2$  K. The experimental effective magnetic moment  $\mu_{eff}$  of  $4.59(1)$   $\mu_{B/Yb}$ , calculated for BaKYb(MoO<sub>4</sub>)<sub>3</sub> from the Curie constant  $C$  and the equation  $\mu_{eff} = (8 \times C)^{1/2}$ , is in good agreement with the value expected for  $\mu_{eff}$  of the Yb<sup>3+</sup> free-cation ( $4f^{13}$ ,  $J = 7/2$ ). The large negative value of  $\theta_p$  ( $-33.8$  K) suggests an antiferromagnetic exchange interaction between the Yb<sup>3+</sup> magnetic moments in the low temperature range.

In the 1.8-75 K temperature range and for  $H = 5000$  Oe, the inverse susceptibility data no longer follow a strict linear behavior with temperature. Such a deviation of the data from the expected

Curie-Weiss behavior for free ions would be rather assigned to the splitting of the J-multiplet ground state of the  $\text{Yb}^{3+}$  Kramers ion under the influence of the CF effect than to a magnetic order (no Néel temperature).

Figure 6b shows the field-dependent M-H curves registered for  $\text{BaKYb}(\text{MoO}_4)_3$  for temperatures ranging from 2 K up to 300 K. The temperature variation was found to significantly impact the shape of the curves. As already observed for Yb-based molybdates, different magnetic regimes are observed [12, 13]. At  $T = 300$  K, the normalized magnetization  $M$  is a linear function of the external alternating magnetic field  $H$  in good accordance with a paramagnetic behavior. At  $T = 2$  K, the magnetization displays a large field dependence with a saturation zone starting from  $H = 20$  kOe up to the highest applied magnetic field  $H = 50$  kOe. The  $H$  strength is sufficient to magnetize the sample to saturation. This M-H curve shape could be attributed to an antiferromagnetic behavior between the  $\text{Yb}^{3+}$  magnetic moments.

#### 4. Conclusion

The new  $\text{BaKYb}(\text{MoO}_4)_3$  triple molybdate was obtained as transparent and colorless single crystals, using a high-temperature solution technique. The flux-grown material crystallizes in the monoclinic symmetry with the  $\text{Mo}^{\text{VI}}$  valence state and displays an ordered distribution of the  $\text{Yb}^{3+}$  cations on a  $C_2$  symmetry position while the  $\text{K}^+$  and  $\text{Ba}^{2+}$  are mixed at a general position. The Raman analysis confirms that the symmetry lowering around the  $\text{Mo}^{6+}$  position from  $\text{BaMoO}_4$  to  $\text{BaKYb}(\text{MoO}_4)_3$  leads to a degeneracy rise and thus to an increase of the number of bands assigned to the internal Mo-O vibrations of  $\text{MoO}_4$  tetrahedra. Magnetic properties of  $\text{BaKYb}(\text{MoO}_4)_3$  have been investigated from 1.8 to 300 K. The temperature-dependent magnetic susceptibility follows a Curie-Weiss law from 75 to 300 K, with a large negative paramagnetic constant  $\theta_p$  of -33.8 K which may indicate an antiferromagnetic behavior between the  $\text{Yb}^{3+}$  ions

in the low temperature range. Therefore, an investigation of the magnetic interactions, and the magnetic unit cell, is needed to elucidate all interactions present.

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