Single crystal growth and characterization of $\text{Na}_x\text{Ln}_{1-x}\text{MoO}_4$, $\text{Ln} = \text{La}$, Ce , Pr , Nd , Sm , and Eu ($x = 0.397 - 0.499$)

*Anthony J. Cortese, Dileka Abeysinghe, Mark D. Smith, Hans-Conrad zur Loye**

Department of Chemistry and Biochemistry, University of South Carolina, Columbia, SC 29208

Corresponding Author: *Email: zurloye@mailbox.sc.edu

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Abstract

Single crystals of $\text{La}_{0.516(3)}\text{Na}_{0.484(3)}\text{MoO}_4$, $\text{Ce}_{0.512(2)}\text{Na}_{0.488(2)}\text{MoO}_4$, $\text{Pr}_{0.502(2)}\text{Na}_{0.498(2)}\text{MoO}_4$, $\text{Nd}_{0.501(2)}\text{Na}_{0.499(2)}\text{MoO}_4$, $\text{Sm}_{0.509(2)}\text{Na}_{0.491(2)}\text{MoO}_4$, and $\text{Eu}_{0.603(2)}\text{Na}_{0.397(2)}\text{MoO}_4$ were grown for the first time out of an alkali metal halide eutectic flux. All compounds crystallize in the tetragonal space group $I4_1/a$. UV/Vis measurements show the presence of an absorption edge for all compounds except $\text{Eu}_{0.603(2)}\text{Na}_{0.397(2)}\text{MoO}_4$. The temperature dependence of the magnetic susceptibility was measured for all compounds and found to be paramagnetic across the entire 2 – 300 K temperature range measured.

Keywords: molybdenum(V), metal reducing agent, *in situ* reduction, magnetism, crystal growth

1. Introduction

Crystal growth of compounds containing early transition metals in reduced oxidation states is an emerging area of materials chemistry that has historically been hampered due to the unique synthetic challenges involved in this type of crystal growth. It is, however, an interesting area of research for the creation of oxides containing unpaired electrons, in particular since early transition metals in reduced oxidation states can potentially lead to interesting electrical and magnetic properties. Historically, researchers have reported simple reduced early transition metal oxides such as VO_2 , V_2O_3 [1-3], TiO [4], and Ti_2O_3 [5], as well as some ternary and higher reduced oxides, including reduced perovskites and bronzes: $\text{SrTiO}_{2.5}$ [6], $\text{Ba}_6\text{Nb}_{14}\text{Si}_4\text{O}_{47}$ [7], $A_x\text{NbO}_3$ ($A=\text{Sr}, \text{Ba}$)[8,9], $\text{Ba}_3M_5\text{O}_{15}$ ($M=\text{Nb}, \text{Ta}$)[10,11] $A_{0.3}\text{MoO}_3$ ($A=\text{K}, \text{Rb}, \text{Tl}$)[12,13], $\text{Cs}_{0.33}\text{MoO}_3$ [14], $\text{K}_2\text{Mo}_4\text{Nb}_3\text{O}_{20}$ [15], and SrV_4O_9 [16] using crystal growth approaches that include fused salt electrolysis, chemical vapor transport, hydrothermal, and flux methods.

The limited number of known oxides containing reduced early transition metals has pushed us to pursue synthetic strategies to prepare such oxides and to explore their physical properties, including magnetism. One approach, a two step-hydrothermal method, has been very successful for preparing single crystals of hybrid materials containing V^{4+} and U^{4+} [17-23]. To explore the preparation of reduced oxides, we explored the use of flux crystal growth, a well-known, facile method for the crystal growth of a diverse oxides, including reduced ones[24]. In order to successfully grow reduced oxide crystals, we carefully selected alkali metal halides as redox neutral fluxes, which can be utilized as high temperature fluxes in sealed reaction vessels, making them excellent candidates for our work. Most compounds reported in the literature were prepared using niobium, tantalum or fused silica sealed tubes[10,25-30].

Our approach is based on the *in situ* reduction of early transition metal cations using a metal reductant, such as Mo, W, V, or Zn combined with eutectic alkali halide melts in an evacuated sealed fused silica tube. This method has been used by us very successfully for the preparation of reduced oxides containing Nb⁴⁺, Mo⁴⁺, Mo⁵⁺, V³⁺, V⁴⁺, and Eu²⁺[31-36].

Recently we reported the synthesis and characterization of several potassium doped europium molybdates containing Mo^{5+/6+} and Eu^{2+/3+}[32]. In order to fully explore the phase space of these structures we attempted to prepare sodium doped molybdates using analogous reaction conditions, which has resulted in the six title compounds: La_{0.516(3)}Na_{0.484(3)}MoO₄, Ce_{0.512(2)}Na_{0.488(2)}MoO₄, Pr_{0.502(2)}Na_{0.498(2)}MoO₄, Nd_{0.50}Na_{0.50}MoO₄, Sm_{0.509(2)}Na_{0.491(2)}MoO₄, and Eu_{0.603(2)}Na_{0.397(2)}MoO₄. All six compositions crystallize in the scheelite structure (CaWO₄/ABO₄), which consists of corner sharing 8-coordinate *A* and 4-coordinate *B* sites. To the best of our knowledge there do not appear to be any other systems that contain a MoO₄ unit with mixed valance Mo. Mixed valance molybdates such as molybdenum bronzes, however, are widely studied due to their interesting structural and physical properties: superconductivity, metal-semiconductor transition driven by charge density wave state, and quasi-one/two-dimensional metallic systems [13,37,38].

To characterize the structure and the oxidation states of the metals within the flux grown single crystals, a combination of single crystal X-ray diffraction, bond valence sum calculations and magnetic susceptibility measurements were employed. Herein, we report the synthesis, crystal structure and physical property characterization La_{0.516(3)}Na_{0.484(3)}MoO₄, Ce_{0.512(2)}Na_{0.488(2)}MoO₄, Pr_{0.502(2)}Na_{0.498(2)}MoO₄, Nd_{0.501(2)}Na_{0.499(2)}MoO₄, Sm_{0.509(2)}Na_{0.491(2)}MoO₄, and Eu_{0.603(2)}Na_{0.397(2)}MoO₄.

2. Experimental details

2.1 Reagents

MoO₃ (99.95%, Alfa Aesar), Mo metal (99.9%, ~250 mesh, Alfa Aesar) and CeO₂ (99.99%, Alfa Aesar) were used as received. NaCl (ACS grade, Fisher) and CsCl (99.9%, Alfa Aesar) were dried prior to synthesis for 24 hours at 260 °C in an oven. La₂O₃ (99.99%, Alfa Aesar), Nd₂O₃ (99.99%, Alfa Aesar), Sm₂O₃ (99.99%, Alfa Aesar), and Eu₂O₃ (99.99%, Alfa Aesar) were activated at 1000 °C for 12 hours in a furnace before use. Pr₆O₁₁ (Alfa Aesar, 99.9%) was reduced to Pr₂O₃ under 4% H₂/96% N₂ at 800 °C for 12 hours before use.

2.2 Synthesis

Single crystals of the title compounds were grown in vacuum sealed fused silica tubes out of a NaCl/CsCl eutectic melt. As detailed in Table 1, the respective amounts of reagents were placed in a fused silica tube, evacuated to a pressure of $\sim 10^{-4}$ torr, and flame sealed. The title compounds were obtained by heating the mixture at a rate of 10 °C/min to a temperature of 825 °C, dwelling for 24 hours and cooling the mixture to 450 °C at a rate of 6 °C/hr. Single crystals were isolated via vacuum filtration by dissolving the remaining flux in water aided by gentle sonication. As shown in Figure S1, the powder X-ray diffraction patterns (PXRD) of the ground crystals match the patterns calculated using the single crystal structural data.

2.3 Energy-dispersive spectroscopy (EDS)

Elemental analysis was performed on all reported single crystals using a TESCAN Vega-3 SBU scanning electron microscope (SEM) with EDS capabilities. The crystals were mounted on carbon tape and analyzed using a 20 kV accelerating voltage and an accumulation time of 1 minute. As a qualitative measure, EDS confirmed the presence of each reported element in the title compounds.

2.4 Single crystal X-ray diffraction (SXRD)

X-ray intensity data from crystals of title compounds were collected at 296(2) K using a Bruker SMART APEX diffractometer (Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$)[39]. The data collection covered 100% of reciprocal space to $2\theta_{\max}$ $65.1 - 75.6^\circ$, with an average reflection redundancy of $5.6 - 13.4$ and $R_{\text{int}} = 0.0179 - 0.0377$ after absorption correction. The raw area detector data frames were reduced and corrected for absorption effects with the SAINT+ and SADABS programs[39]. Final unit cell parameters were determined by least-squares refinement of $298 - 444$ independent reflections from the data sets. Atomic coordinates of the common CaWO_4 structure type were used as an initial structural model. Subsequent difference Fourier calculations and full-matrix least-squares refinement against F^2 were performed with SHELXL-2013/4[40] using the ShelXle interface[41].

All title compounds crystallize in the tetragonal system. The space group $I4_1/a$ (No. 88, origin choice 2) was determined uniquely by the pattern of systematic absences in the intensity data. The compound adopts the scheelite (CaWO_4) structure type. The asymmetric unit consists of three atomic positions: one mixed Ln/Na position (site $4b$, $-4..$ site symmetry), one Mo atom (site $4a$, $-4..$ site symmetry) and one oxygen atom (general position, site $16f$). The $4b$ site is occupied by a mixture of Ln and Na based on trial refinements. The total site occupancy of the mixed Ln/Na site was constrained to sum to unity. The atomic ratio refined to $\text{Ln}/\text{Na} = 0.516(3)/0.484(3)$ for La, $0.512(2)/0.488(2)$ for Ce, $0.502(2)/0.498(2)$ for Pr, $0.501(2)/0.499(2)$ for Nd, $0.509(2)/0.491(2)$ for Sm, and $0.603(2)/0.397(2)$, for Eu. All atoms were refined with anisotropic displacement parameters. No significant deviation from unity occupancy was observed for the Mo or O atoms. Final atomic coordinates were standardized with Structure

Tidy[42-44]. Crystallographic data, atomic coordinates and isotropic displacement parameters, and selected interatomic distances are listed in Tables 2 – 4.

2.5 *Powder X-ray diffraction (PXRD)*

Powder X-ray diffraction data were collected on either a Rigaku D/Max-2100 or an Ultima(IV) powder X-ray diffractometer using Cu K α radiation. The step-scan covered the angular range 5 – 65° 2 θ in steps of 0.04°. The calculated and experimental PXRD patterns are in excellent agreement (see Supporting information, Figure S2).

2.6 *UV-vis diffuse reflectance spectroscopy (UV/Vis)*

UV–vis diffuse reflectance spectroscopy data of the powder samples of the reported materials were obtained using a Perkin-Elmer Lambda 35 UV–vis scanning spectrophotometer equipped with an integrating sphere in the range of 200 – 900 nm.

2.8 *Magnetic susceptibility*

The magnetic susceptibility of the reported materials was measured using a Quantum Design MPMS SQUID magnetometer. The zero-field cooled magnetic susceptibility was measured as a function of temperature between 2 and 300 K in an applied field of 1000 Oe. The measured magnetic moment was corrected for shape and radial offset effects using the methods reported by Morrison et al.[45], which determines the correction factors by comparing the moments observed from DC and VSM scans at a single temperature, 30 K.

3. **Results and discussion**

3.1 *Synthesis*

The flux technique was employed to synthesize the bipyramidal single crystals of the title compounds. Although the flux technique is widely utilized for crystal growth, not all fluxes are

appropriate for the synthesis of reduced oxides because many of them do not facilitate the necessary redox neutral environment required at elevated reaction temperatures where crystal growth takes place. Alkali metal chlorides, which are redox neutral and known to dissolve a wide variety of elements, can be used for this purpose. A NaCl/CsCl eutectic flux was used to ensure a long liquid range, lower the melting point of the flux, and functions as a source of sodium ions during the crystallization process. By selecting CsCl, we could reasonably expect to exclude the exceptionally large cesium cations from being incorporated into the product crystals while still lowering the melting point of the flux. Reactions using a NaCl/KCl eutectic resulted in multiple unidentified phases being present in the product. Mo powder was used as the reducing agent in an attempt to reduce Mo(VI) to Mo(V) *in situ*. This approach worked well for $\text{Eu}_{0.603(2)}\text{Na}_{0.397(2)}\text{MoO}_4$, but was less effective for the remaining title compounds. However, in the case of $\text{Ce}_{0.512(2)}\text{Na}_{0.488(2)}\text{MoO}_4$, the Mo powder did prove to be an effective reducing agent for the reduction of Ce(IV) in CeO_2 to Ce(III) in the product crystal. Interestingly, in the case of $\text{Eu}_{0.603(2)}\text{Na}_{0.397(2)}\text{MoO}_4$, the Mo powder did not reduce Eu(III) from Eu_2O_3 to Eu(II) in the product crystal. All products formed in yields approximately between 65% - and 80% based on Ln_2O_3 or CeO_2 .

3.2 Structure

The title compounds crystallize in the tetragonal space group $I4_1/a$ adopting the scheelite (CaWO_4) structure and they exhibit a three dimensional structure consisting of MoO_4 tetrahedra and Na/LnO_8 polyhedra. A representation of the three-dimensional structure along the a - axis is shown in Figure 1. Each Na/LnO_8 polyhedron corner shares with eight adjacent MoO_4 polyhedra. Mo atoms are located in regular tetrahedra with Mo(1) – O bond distances ranging from 1.7709 Å – 1.7746 Å. The eight coordinate Na/Ln cations form a distorted eight coordinate polyhedron

with Na/Ln – O bond distances ranging from 2.466 Å – 2.561 Å. Bond valance sum [46,47] (BVS) calculations, assuming Mo(VI), for Mo in each compound were found to be 5.77 for $\text{La}_{0.516(3)}\text{Na}_{0.484(3)}\text{MoO}_4$, 5.74 for $\text{Ce}_{0.512(2)}\text{Na}_{0.488(2)}\text{MoO}_4$, 5.76 for $\text{Pr}_{0.502(2)}\text{Na}_{0.498(2)}\text{MoO}_4$, 5.72 for $\text{Nd}_{0.501(2)}\text{Na}_{0.499(2)}\text{MoO}_4$, 5.73 for $\text{Sm}_{0.509(2)}\text{Na}_{0.491(2)}\text{MoO}_4$, and 5.78 for $\text{Eu}_{0.603(2)}\text{Na}_{0.397(2)}\text{MoO}_4$. These sums are consistent with the reported compositions.

3.3 *UV-vis diffuse reflectance spectroscopy (UV/Vis)*

The UV-vis diffuse reflectance data were collected on ground crystals of the title compounds and were converted to absorbance via the Kubelka-Munk function and are shown in Figure 2. The data for $\text{La}_{0.516(3)}\text{Na}_{0.484(3)}\text{MoO}_4$, $\text{Ce}_{0.512(2)}\text{Na}_{0.488(2)}\text{MoO}_4$, $\text{Pr}_{0.502(2)}\text{Na}_{0.498(2)}\text{MoO}_4$, $\text{Nd}_{0.501(2)}\text{Na}_{0.499(2)}\text{MoO}_4$, and $\text{Sm}_{0.509(2)}\text{Na}_{0.491(2)}\text{MoO}_4$, show strong absorption edges clustered approximately around 3.5 eV, indicating insulating behavior, which is expected since the concentration of Mo(V) cations is dilute. For $\text{Nd}_{0.501(2)}\text{Na}_{0.499(2)}\text{MoO}_4$ characteristic *f-f* transitions are observed between 550 – 900 nm.

3.4 *Magnetic susceptibility*

Unpaired *d* electrons from MoO_4 units and unpaired *f* electrons from the lanthanide cations are expected to contribute to the magnetic moment of the compounds and can be observed in magnetic susceptibility measurements. The temperature dependence of the magnetic susceptibilities of $\text{La}_{0.516(3)}\text{Na}_{0.484(3)}\text{MoO}_4$, $\text{Ce}_{0.512(2)}\text{Na}_{0.488(2)}\text{MoO}_4$, $\text{Pr}_{0.502(2)}\text{Na}_{0.498(2)}\text{MoO}_4$, $\text{Nd}_{0.501(2)}\text{Na}_{0.499(2)}\text{MoO}_4$, $\text{Sm}_{0.509(2)}\text{Na}_{0.491(2)}\text{MoO}_4$, and $\text{Eu}_{0.603(2)}\text{Na}_{0.397(2)}\text{MoO}_4$ were measured in an applied field of 1000 Oe and are shown in Figure 3. As the amount of Mo^{5+} is very small for all compounds, no magnetic coupling is expected or observed for molybdenum. The ratios of Mo^{5+} to Mo^{6+} are listed in Table 5. As the lanthanide sites are spatially far apart, no magnetic

coupling is expected or observed. Down to 2K, for each compound, the data do not reveal any long range magnetic order. Above 150 K the data for $\text{La}_{0.516(3)}\text{Na}_{0.484(3)}\text{MoO}_4$, $\text{Ce}_{0.512(2)}\text{Na}_{0.488(2)}\text{MoO}_4$, $\text{Pr}_{0.502(2)}\text{Na}_{0.498(2)}\text{MoO}_4$, and $\text{Nd}_{0.501(2)}\text{Na}_{0.499(2)}\text{MoO}_4$ follow the Currie–Weiss (C-W) law and experimental magnetic moments can be determined. The theoretical and experimental magnetic moments for $\text{La}_{0.516(3)}\text{Na}_{0.484(3)}\text{MoO}_4$, $\text{Ce}_{0.512(2)}\text{Na}_{0.488(2)}\text{MoO}_4$, $\text{Pr}_{0.502(2)}\text{Na}_{0.498(2)}\text{MoO}_4$, and $\text{Nd}_{0.501(2)}\text{Na}_{0.499(2)}\text{MoO}_4$ are collected in Table 5 and are in good agreement. It is well known that samples containing Sm^{3+} and Eu^{3+} do not follow the C-W law[48], and hence, to determine the experimental magnetic moment of $\text{Sm}_{0.509(2)}\text{Na}_{0.491(2)}\text{MoO}_4$ and $\text{Eu}_{0.603(2)}\text{Na}_{0.397(2)}\text{MoO}_4$, χT vs T plots were prepared and are shown in Figure 3. The magnetic moments of $\text{Sm}_{0.509(2)}\text{Na}_{0.491(2)}\text{MoO}_4$ and $\text{Eu}_{0.603(2)}\text{Na}_{0.397(2)}\text{MoO}_4$ at 300 K are in good agreement with the theoretical 300 K values and are listed in Table 5.

4. Conclusion

We successfully synthesized $\text{La}_{0.516(3)}\text{Na}_{0.484(3)}\text{MoO}_4$, $\text{Ce}_{0.512(2)}\text{Na}_{0.488(2)}\text{MoO}_4$, $\text{Pr}_{0.502(2)}\text{Na}_{0.498(2)}\text{MoO}_4$, $\text{Nd}_{0.501(2)}\text{Na}_{0.499(2)}\text{MoO}_4$, $\text{Sm}_{0.509(2)}\text{Na}_{0.491(2)}\text{MoO}_4$, and $\text{Eu}_{0.603(2)}\text{Na}_{0.397(2)}\text{MoO}_4$. Mo powder was found to be an effective reducing agent in the case of $\text{Ce}_{0.512(2)}\text{Na}_{0.488(2)}\text{MoO}_4$, reducing Ce(IV) to Ce(III) and in the case of $\text{Eu}_{0.603(2)}\text{Na}_{0.397(2)}\text{MoO}_4$, reducing Mo(VI) to Mo(V). As a result of the diluteness of the Mo^{5+} in the title compounds, only simple paramagnetic behavior is observed. The agreement of the experimental and theoretical magnetic moments confirms the stoichiometric ratio of Na/ Ln in the title compounds.

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Table 1. Respective amounts of reagents and flux used in each reaction and their respective products obtained with crystal morphologies.

Reagents (mmol)	Reducing agent (mmol)	Flux (g)	Product	Crystal Color and Morphology
MoO ₃ :La ₂ O ₃	Mo	CsCl:NaCl	La _{0.516(3)} Na _{0.484(3)} MoO ₄	black tetragonal bipyramids
2:1	0.5	2.25:0.5		
MoO ₃ :CeO ₂	Mo	CsCl:NaCl	Ce _{0.512(2)} Na _{0.488(2)} MoO ₄	black tetragonal bipyramids
2:1	0.5	2.25:0.5		
MoO ₃ :Pr ₂ O ₃	Mo	CsCl:NaCl	Pr _{0.502(2)} Na _{0.498(2)} MoO ₄	transparent grey tetragonal bipyramids
2:1	0.5	2.25:0.5		
MoO ₃ :Nd ₂ O ₃	Mo	CsCl:NaCl	Nd _{0.501(2)} Na _{0.499(2)} MoO ₄	transparent purple tetragonal bipyramids
2:1	0.5	2.25:0.5		
MoO ₃ :Sm ₂ O ₃	Mo	CsCl:NaCl	Sm _{0.509(2)} Na _{0.491(2)} MoO ₄	black tetragonal bipyramids
2:1	0.5	2.25:0.5		
MoO ₃ :Eu ₂ O ₃	Mo	CsCl:NaCl	Eu _{0.603(2)} Na _{0.397(2)} MoO ₄	black tetragonal bipyramids
2:1	0.5	2.25:0.5		

Table 2. Crystallographic data for La_{0.516(3)}Na_{0.484(3)}MoO₄, Ce_{0.512(2)}Na_{0.488(2)}MoO₄, Pr_{0.502(2)}Na_{0.498(2)}MoO₄, Nd_{0.501(2)}Na_{0.499(2)}MoO₄, Sm_{0.509(2)}Na_{0.491(2)}MoO₄, and Eu_{0.603(2)}Na_{0.397(2)}MoO₄. Temperature: 296(2) K, crystal system: tetragonal, space group *I*4₁/*a*, and *Z* = 4.

Formula	La _{0.516(3)} Na _{0.484(3)} MoO ₄	Ce _{0.512(2)} Na _{0.488(2)} MoO ₄	Pr _{0.502(2)} Na _{0.498(2)} MoO ₄
Formula weight	242.74	242.90	242.07
<i>a</i> (Å)	5.3414(2)	5.3173(2)	5.30090(15)
<i>c</i> (Å)	11.7393(6)	11.6652(6)	11.6089(7)
Volume (Å ³)	334.93(3)	329.82(3)	326.20(3)
Density (g/cm ³)	4.814	4.892	4.929
Abs. coeff. (mm ⁻¹)	10.214	10.757	11.227
Crystal size (mm ³)	0.10 x 0.08 x 0.05	0.08 x 0.06 x 0.05	0.07 x 0.05 x 0.04
θ ° range	4.192 – 32.565	4.212 – 37.802	4.226 – 35.015
Reflections collected	4161	5910	2053
Completeness to $\theta_{\max}$	100.0	100.0	100.0
<i>R</i> _(int)	0.0179	0.0377	0.0253
GOF (<i>F</i> ²)	1.396	1.224	1.042
<i>R</i> (<i>F</i>) ^a	0.0271	0.0222	0.0195
<i>R</i> _w (<i>F</i> _o ²) ^b	0.0434	0.0439	0.0491
^a <i>R</i> (<i>F</i>) = $\Sigma F_o - F_c /\Sigma F_o $			
^b <i>R</i> _w (<i>F</i> _o ²) = $[\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$			

Table 2 (cont.). Crystallographic data for $\text{La}_{0.516(3)}\text{Na}_{0.484(3)}\text{MoO}_4$, $\text{Ce}_{0.512(2)}\text{Na}_{0.488(2)}\text{MoO}_4$, $\text{Pr}_{0.502(2)}\text{Na}_{0.498(2)}\text{MoO}_4$, $\text{Nd}_{0.501(2)}\text{Na}_{0.499(2)}\text{MoO}_4$, $\text{Sm}_{0.509(2)}\text{Na}_{0.491(2)}\text{MoO}_4$, and $\text{Eu}_{0.603(2)}\text{Na}_{0.397(2)}\text{MoO}_4$. Temperature: 296(2) K, crystal system: tetragonal, space group $I4_1/a$, and $Z = 4$.

Formula	$\text{Nd}_{0.501(2)}\text{Na}_{0.499(2)}\text{MoO}_4$	$\text{Sm}_{0.509(2)}\text{Na}_{0.491(2)}\text{MoO}_4$	$\text{Eu}_{0.603(2)}\text{Na}_{0.397(2)}\text{MoO}_4$
Formula weight	243.68	247.79	260.67
a (Å)	5.2854(2)	5.2560(2)	5.2797(2)
c (Å)	11.5675(6)	11.4921(6)	11.5869(7)
Volume (Å ³)	323.14(3)	317.48(3)	322.99(3)
Density (g/cm ³)	5.009	5.184	5.361
Abs. coeff. (mm ⁻¹)	11.822	13.255	15.429
Crystal size (mm ³)	0.10 x 0.08 x 0.05	0.10 x 0.08 x 0.07	0.08 x 0.06 x 0.06
θ ° range	4.239 – 35.040	4.264 – 35.106	4.242 – 32.604
Reflections collected	4184	4133	3773
Completeness to $\theta_{\max}$	100.0	100.0	100.0
$R_{\text{(int)}}$	0.0260	0.0247	0.0200
GOF (F^2)	1.118	1.212	1.158
$R(F)^a$	0.0185	0.0252	0.0161
$R_w(F_o^2)^b$	0.0474	0.0664	0.0334
^a $R(F) = \Sigma F_o - F_c /\Sigma F_o $			
^b $R_w(F_o^2) = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$			

Table 3. Selected interatomic distances (Å) for $\text{La}_{0.516(3)}\text{Na}_{0.484(3)}\text{MoO}_4$, $\text{Ce}_{0.512(2)}\text{Na}_{0.488(2)}\text{MoO}_4$, $\text{Pr}_{0.502(2)}\text{Na}_{0.498(2)}\text{MoO}_4$, $\text{Nd}_{0.501(2)}\text{Na}_{0.499(2)}\text{MoO}_4$, $\text{Sm}_{0.509(2)}\text{Na}_{0.491(2)}\text{MoO}_4$, and $\text{Eu}_{0.603(2)}\text{Na}_{0.397(2)}\text{MoO}_4$.

$\text{La}_{0.516(3)}\text{Na}_{0.484(3)}\text{MoO}_4$					
La(1) – O(1) x 4	2.525(2)	La(1) – O(1) x 4	2.561(2)	Mo(1) – O(1) x 4	1.771(2)
$\text{Ce}_{0.512(2)}\text{Na}_{0.488(2)}\text{MoO}_4$					
Ce(1) – O(1) x 4	2.5058(14)	Ce(1) – O(1) x 4	2.5419(14)	Mo(1) – O(1) x 4	1.7729(14)
$\text{Pr}_{0.502(2)}\text{Na}_{0.498(2)}\text{MoO}_4$					
Pr(1) – O(1) x 4	2.4943(15)	Pr(1) – O(1) x 4	2.5288(15)	Mo(1) – O(1) x 4	1.7722(15)
$\text{Nd}_{0.501(2)}\text{Na}_{0.499(2)}\text{MoO}_4$					
Nd(1) – O(1) x 4	2.4842(13)	Nd(1) – O(1) x 4	2.5146(13)	Mo(1) – O(1) x 4	1.7746(13)
$\text{Sm}_{0.509(2)}\text{Na}_{0.491(2)}\text{MoO}_4$					
Sm(1) – O(1) x 4	2.4664(15)	Sm(1) – O(1) x 4	2.4909(15)	Mo(1) – O(1) x 4	1.7742(14)
$\text{Eu}_{0.603(2)}\text{Na}_{0.397(2)}\text{MoO}_4$					
Eu(1) – O(1) x 4	2.4905(17)	Eu(1) – O(1) x 4	2.5108(16)	Mo(1) – O(1) x 4	1.7709(16)

Table 4. Atomic coordinates and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $\text{La}_{0.516(3)}\text{Na}_{0.484(3)}\text{MoO}_4$, $\text{Ce}_{0.512(2)}\text{Na}_{0.488(2)}\text{MoO}_4$, $\text{Pr}_{0.502(2)}\text{Na}_{0.498(2)}\text{MoO}_4$, $\text{Nd}_{0.501(2)}\text{Na}_{0.499(2)}\text{MoO}_4$, $\text{Sm}_{0.509(2)}\text{Na}_{0.491(2)}\text{MoO}_4$, and $\text{Eu}_{0.603(2)}\text{Na}_{0.397(2)}\text{MoO}_4$.

$\text{La}_{0.516(3)}\text{Na}_{0.484(3)}\text{MoO}_4$	Occupancy	x	y	z	$U_{\text{(eq)}}$
La(1)	0.516(3)	0	$\frac{1}{4}$	0.6250	12(1)
Na(1)	0.484(3)	0	$\frac{1}{4}$	0.6250	12(1)
Mo(1)	1	0	$\frac{1}{4}$	0.6250	10(1)
O(1)	1	0.2388(4)	0.1087(4)	0.0424(2)	15(1)

$\text{Ce}_{0.512(2)}\text{Na}_{0.488(2)}\text{MoO}_4$	Occupancy	x	y	z	$U_{\text{(eq)}}$
Ce(1)	0.512(2)	0	$\frac{1}{4}$	0.6250	10(1)
Na(1)	0.488(2)	0	$\frac{1}{4}$	0.6250	10(1)
Mo(1)	1	0	$\frac{1}{4}$	0.6250	9(1)
O(1)	1	0.1427(2)	0.0101(3)	0.2081(1)	15(1)

$\text{Pr}_{0.502(2)}\text{Na}_{0.498(2)}\text{MoO}_4$	Occupancy	x	y	z	$U_{\text{(eq)}}$
Pr(1)	0.502(2)	0	$\frac{1}{4}$	0.6250	12(1)
Na(1)	0.498(2)	0	$\frac{1}{4}$	0.6250	12(1)
Mo(1)	1	0	$\frac{1}{4}$	0.6250	12(1)
O(1)	1	0.1440(3)	0.0098(3)	0.2084(1)	18(1)

$\text{Nd}_{0.501(2)}\text{Na}_{0.499(2)}\text{MoO}_4$	Occupancy	x	y	z	$U_{\text{(eq)}}$
Nd(1)	0.501(2)	0	$\frac{1}{4}$	0.6250	11(1)
Na(1)	0.499(2)	0	$\frac{1}{4}$	0.6250	11(1)
Mo(1)	1	0	$\frac{1}{4}$	0.1250	11(1)
O(1)	1	0.2407(2)	0.1043(2)	0.413(1)	18(1)

$\text{Sm}_{0.509(2)}\text{Na}_{0.491(2)}\text{MoO}_4$	Occupancy	x	y	z	$U_{\text{(eq)}}$
Sm(1)	0.509(2)	0	$\frac{1}{4}$	0.6250	12(1)
Na(1)	0.491(2)	0	$\frac{1}{4}$	0.6250	12(1)
Mo(1)	1	0	$\frac{1}{4}$	0.1250	12(1)
O(1)	1	0.2418(3)	0.1025(3)	0.0410(1)	19(1)

$\text{Eu}_{0.603(2)}\text{Na}_{0.397(2)}\text{MoO}_4$	Occupancy	x	y	z	$U_{\text{(eq)}}$
Eu(1)	0.603(2)	0	$\frac{1}{4}$	0.6250	12(1)
Na(1)	0.397(2)	0	$\frac{1}{4}$	0.6250	12(1)
Mo(1)	1	0	$\frac{1}{4}$	0.1250	13(1)
O(1)	1	0.1458(2)	0.0095(3)	0.2082(2)	19(1)

Table 5. Magnetic data for $\text{La}_{0.516(3)}\text{Na}_{0.484(3)}\text{MoO}_4$, $\text{Ce}_{0.512(2)}\text{Na}_{0.488(2)}\text{MoO}_4$, $\text{Pr}_{0.502(2)}\text{Na}_{0.498(2)}\text{MoO}_4$, $\text{Nd}_{0.501(2)}\text{Na}_{0.499(2)}\text{MoO}_4$, $\text{Sm}_{0.509(2)}\text{Na}_{0.491(2)}\text{MoO}_4$, and $\text{Eu}_{0.603(2)}\text{Na}_{0.397(2)}\text{MoO}_4$. For Sm and Eu the calculated moment was taken from a plot of χT as the compound does not obey the C-W law. The ratios of Mo^{5+} to Mo^{6+} are also tabulated.

Compound	μ_B theoretical	μ_B experimental	Mo(V):Mo(VI)
$\text{La}_{0.516(3)}\text{Na}_{0.484(3)}\text{MoO}_4$	0.31	0.28	0.032 : 0.968
$\text{Ce}_{0.512(2)}\text{Na}_{0.488(2)}\text{MoO}_4$	1.84	1.88	0.024 : 0.976
$\text{Pr}_{0.502(2)}\text{Na}_{0.498(2)}\text{MoO}_4$	2.54	2.59	0.004 : 0.996
$\text{Nd}_{0.501(2)}\text{Na}_{0.499(2)}\text{MoO}_4$	2.56	2.53	0.002 : 0.998
$\text{Sm}_{0.509(2)}\text{Na}_{0.491(2)}\text{MoO}_4$	1.26	1.31	0.018 : 0.982
$\text{Eu}_{0.603(2)}\text{Na}_{0.397(2)}\text{MoO}_4$	2.75	2.79	0.206 : 0.794

Figure 1. The 3D structure along the a axis. The MoO_4 polyhedra, Ln/Na positions, and O spheres are shown in cyan, orange, and red, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Figure 2. UV-vis diffuse reflectance spectroscopy data for $\text{La}_{0.516(3)}\text{Na}_{0.484(3)}\text{MoO}_4$ (cyan), $\text{Ce}_{0.512(2)}\text{Na}_{0.488(2)}\text{MoO}_4$ (red), $\text{Pr}_{0.502(2)}\text{Na}_{0.498(2)}\text{MoO}_4$ (pink), $\text{Nd}_{0.501(2)}\text{Na}_{0.499(2)}\text{MoO}_4$ (black), $\text{Sm}_{0.509(2)}\text{Na}_{0.491(2)}\text{MoO}_4$ (blue), and $\text{Eu}_{0.603(2)}\text{Na}_{0.397(2)}\text{MoO}_4$ (green).

Figure 3. Magnetic susceptibility plots for $\text{La}_{0.516(3)}\text{Na}_{0.484(3)}\text{MoO}_4$, $\text{Ce}_{0.512(2)}\text{Na}_{0.488(2)}\text{MoO}_4$, $\text{Pr}_{0.502(2)}\text{Na}_{0.498(2)}\text{MoO}_4$, $\text{Nd}_{0.501(2)}\text{Na}_{0.499(2)}\text{MoO}_4$, $\text{Sm}_{0.509(2)}\text{Na}_{0.491(2)}\text{MoO}_4$, and $\text{Eu}_{0.603(2)}\text{Na}_{0.397(2)}\text{MoO}_4$. χ and $1/\chi$ are shown in red and blue, respectively. For $\text{Sm}_{0.509(2)}\text{Na}_{0.491(2)}\text{MoO}_4$ and $\text{Eu}_{0.603(2)}\text{Na}_{0.397(2)}\text{MoO}_4$ a χT plot is shown, as they do not obey the C-W law.

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Graphical Abstract

Single crystals of $\text{La}_{0.516(3)}\text{Na}_{0.484(3)}\text{MoO}_4$, $\text{Ce}_{0.512(2)}\text{Na}_{0.488(2)}\text{MoO}_4$, $\text{Pr}_{0.502(2)}\text{Na}_{0.498(2)}\text{MoO}_4$, $\text{Nd}_{0.501(2)}\text{Na}_{0.499(2)}\text{MoO}_4$, $\text{Sm}_{0.509(2)}\text{Na}_{0.491(2)}\text{MoO}_4$, and $\text{Eu}_{0.603(2)}\text{Na}_{0.397(2)}\text{MoO}_4$ were grown for the first time out of an alkali metal halide eutectic flux. All compounds crystallize in the tetragonal space group $I4_1/a$. $\text{Eu}_{0.603(2)}\text{Na}_{0.397(2)}\text{MoO}_4$ was found to possess the highest Mo^{5+} content at 20.6%. UV/Vis, magnetic susceptibility, and a bond valence sum analysis were performed on all samples.