

$\text{Li}_3\text{Ti}_{0.75}(\text{MoO}_4)_3$: A lyonsite-type oxide

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Abstract

Significant progress has been made in understanding the solid state crystal chemistry of the large lyonsite oxide family. Some of this progress is reviewed briefly, and the crystal structure of $\text{Li}_3\text{Ti}_{0.75}(\text{MoO}_4)_3$ is presented as further illustration of the adaptive nature of the lyonsite structure. $\text{Li}_3\text{Ti}_{0.75}(\text{MoO}_4)_3$ crystallizes in the orthorhombic space group $Pnma$ ($Z=4$) with cell parameters $a=5.047$ Å, $b=10.454$ Å, $c=17.538$ Å.

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1. Introduction

Solid state chemistry relies heavily on exploratory synthesis, and as is often the case, the complexity of possibilities can defy predictability when it comes to discovering new mixed metal oxides. In practice, solid state oxide chemistry is dominated by versatile structure types such as perovskite, apatite, hollandite, garnet, spinel, and fluorite. The structures of these important crystal frameworks allow for a wide range of elements, oxidation states, defects, and stoichiometries. Such adaptive crystal chemistry provides new and exciting avenues in the exploration of the intrinsic relationship between structure and composition.

An interesting ‘new’ family of oxides is lyonsite, which is shown in Fig. 1. Reviewed recently [1], the lyonsite family of oxides encompasses a large and growing number of vanadates, molybdates, and tungstates. The lyonsite crystal framework was first observed and described for $\text{NaCo}_{2.31}(\text{MoO}_4)_3$ by Ibers and Smith in 1964 [2], and a timeline of lyonsite oxides can be found in Table 1. The namesake mineral, $\alpha\text{-Cu}_3\text{Fe}_4(\text{VO}_4)_6$ [3], was not discovered until 1987, but no reference was made at that time to the relationship between this new

mineral and $\text{NaCo}_{2.31}(\text{MoO}_4)_3$. This is not surprising owing to their dissimilar chemical compositions. It is, indeed, quite remarkable that two phases which do not possess common elements, oxidation states, or stoichiometries can share a common crystal structure. This structural diversity is a defining characteristic of adaptive crystal frameworks, and no fewer than 23 different elements, in oxidation states from +1 to +6, have been observed in lyonsite compounds.

As an example of the lyonsite structure and the remarkable solid state crystal chemistry therein, the current work details the structure determination of $\text{Li}_3\text{Ti}_{0.75}(\text{MoO}_4)_3$ and the solid solution of $\square_{1-3x}\text{Li}_{2+4x}\text{Ti}_{1-x}\text{Mo}_3\text{O}_{12}$ ($0.23 \leq x \leq 0.26$, where \square represents a cation vacancy).

2. Experimental section

2.1. Crystal growth

Single crystals of $\text{Li}_3\text{Ti}_{0.75}(\text{MoO}_4)_3$ were grown from a mixture of 1.189 g Li_2CO_3 , 1.286 g TiO_2 , and 3.475 g MoO_3 . The mixture, corresponding to a 4:2:3 Li:Ti:Mo ratio, was ground in an agate mortar, packed into a platinum crucible, and heated at a rate of 600 °C h^{-1} to 700 °C. It was held at 700 °C for 1 h, cooled to 500 °C at a rate of 6 °C h^{-1} , and further cooled to room temperature at a rate of 600 °C h^{-1} . Transparent needle crystals were removed from the top of the solidified melt for

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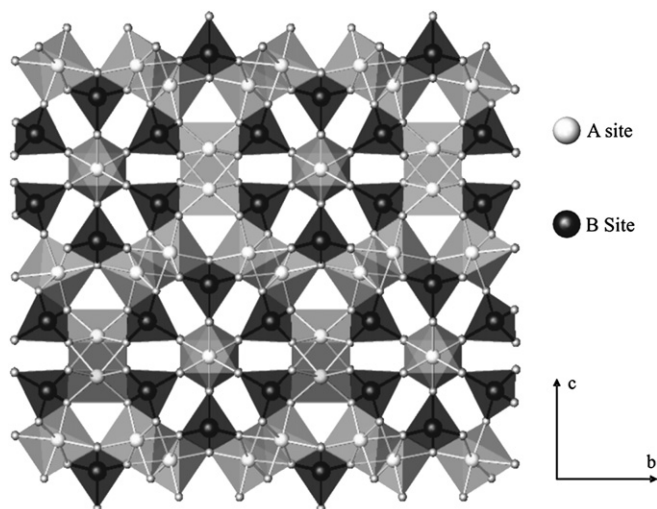


Fig. 1. The lyonsite structure. AO_6 polyhedra are white and BO_4 tetrahedra are black.

analysis. In contrast, a nominal melt stoichiometry of ‘ $Li_2TiMo_3O_{12}$ ’ produced single crystals of $M-Li_2Mo_4O_{13}$ [4], whereas a nominal melt stoichiometry of ‘ $Li_2HfMo_3O_{12}$ ’ produced single crystals of $Li_{2.82}Hf_{0.795}Mo_3O_{12}$ [1], isostructural with $Li_3Ti_{0.75}(MoO_4)_3$.

Table 1
Lyonsite timeline^a

Reported crystal structure				Reported powder phase			
Year	Phase(s)	% A site vacant	Ref.	Year	Phase(s)	% A site vacant	Ref.
1964	$NaCo_{2.31}(MoO_4)_3$	17.25	[2]	1970	$Li_3Fe(MoO_4)_3$	0	[29]
1970	$Li_3Fe(MoO_4)_3$	0	[15]		$Li_3Al(MoO_4)_3$	0	[29]
1970	$Li_2Fe_2(MoO_4)_3$	0	[15]		$Li_3Sc(MoO_4)_3$	0	[29]
1971	$Cu_{3.85}Mo_3O_{12}$	3.75	[16]		$Li_3Ga(MoO_4)_3$	0	[29]
1977	$Li_2Ni_2(MoO_4)_3$	0	[17]		$Li_3In(MoO_4)_3$	0	[29]
1978	$Li_2Zr(MoO_4)_3$	25	[31]	1971	$Li_3Fe(MoO_4)_3$	0	[30]
1987	$Cu_3Fe_4(VO_4)_6$	12.5	[3]		$Li_3Al(MoO_4)_3$	0	[30]
1994	$Li_2Mg_2(WO_4)_3$	0	[18]		$Li_3Ga(MoO_4)_3$	0	[30]
1994	$Mg_{2.5}VMoO_8$	6.25	[7]		$Li_3Cr(MoO_4)_3$	0	[30]
1994	$Li_{1.6}Mn_{2.2}(MoO_4)_3$	5	[19]	1971	$Li_2Mg_2(MoO_4)_3$	0	[12]
1995	$Li_2Co_2(MoO_4)_3$	0	[20]		$Li_2Mg_2(WO_4)_3$	0	[12]
1996	$Mg_{2.54}V_{1.08}Mo_{0.92}O_8$	4.75	[8]		$Li_{10}Zr_2(MoO_4)_9$	0	[12]
1997	$Zn_{3.77}V_{1.54}Mo_{1.46}O_{12}$	5.75	[21]		$Li_{10}Hf_2(MoO_4)_9$	0	[12]
1998	$Mn_{2.47}V_{0.94}Mo_{1.06}O_8$	7.375	[22]	1972	$Li_2Zn_2(MoO_4)_3$	0	[32]
2000	$Co_4Fe_{3.33}(VO_4)_6$	8.375	[23]		$Li_2Cu_2(MoO_4)_3$	0	[32]
2001	$Cu_4Fe_{3.333}(VO_4)_6$	8.3375	[14]		$Na_2Zn_2(MoO_4)_3$	0	[32]
2001	$Cu_{4.05}Cr_{3.3}(VO_4)_6$	8.125	[14]		$Na_2Cu_2(MoO_4)_3$	0	[32]
2002	$Co_{3.6}Fe_{3.6}(VO_4)_6$	10	[24]	1973	$Li_2Zr(MoO_4)_3$	25	[11]
2003	$Co_5Cr_{2.667}(VO_4)_6$	4.1625	[25]		$Li_2Hf(MoO_4)_3$	25	[11]
2003	$Li_2Mg_2(MoO_4)_3$	0	[9]		$Li_2Ti(MoO_4)_3$	25	[11]
2003	$Li_3Sc(MoO_4)_3$	0	[26]	1976	$Li_2Mn_2(MoO_4)_3$	0	[33]
2003	$Co_{2.5}VMoO_8$	6.25	[27]		$Li_2Co_2(MoO_4)_3$	0	[33]
2006	$Mg_{2.56}V_{1.12}W_{0.88}O_8$	4	[28]		$Li_2Ni_2(MoO_4)_3$	0	[33]
2006	$Li_{2.82}Hf_{0.795}(MoO_4)_3$	9.625	[1]	1977	$Li_2Zn_2(MoO_4)_3$	0	[34]
2006	$Li_{3.35}Ta_{0.53}(MoO_4)_3$	3	[1]		$Li_2Mg_2(MoO_4)_3$	0	[34]
					$Li_2Co_2(MoO_4)_3$	0	[34]
					$Li_2Ni_2(MoO_4)_3$	0	[34]
					$Li_2Fe_2(MoO_4)_3$	0	[34]
				1992	$Li_3Co(MoO_4)_3$	0	[35]
				2006	$Li_{3.5-5x}Nb_{0.5+x}(MoO_4)_3$	Variable	[1]

^a Adapted from Ref. [1].

2.2. Structure determination

A colorless crystal was mounted on a glass fiber for study by single crystal X-ray diffraction. Measurements were made on a Bruker Smart 1000 equipped with CCD detector and graphite monochromated Mo $K\alpha$ radiation, and integrated with the SAINT-Plus program [5]. The structure was solved by direct methods and refined by full matrix least squares against F^2 , and all calculations were performed with programs from the SHELXTL crystallographic software package [6]. Details of the structure determination are listed in Table 2, and the atomic positions and displacement parameters for $Li_3Ti_{0.75}(MoO_4)_3$ are listed in Table 3.

2.3. Polycrystalline powder synthesis

Polycrystalline samples were synthesized by grinding mixtures of Li_2CO_3 , TiO_2 , and MoO_3 in an agate mortar and packing the mixture into platinum crucibles. Initial stoichiometries corresponded to $x=0$ and $x=1/3$ in the solid solution $\square_{1-3x}Li_{2+4x}Ti_{1-x}Mo_3O_{12}$, and the range was narrowed subsequently until the solid solution was determined to be $0.23 \leq x \leq 0.26$. The mixtures were calcined at $550^\circ C$ for 24 h, and phase purity was confirmed by powder X-ray

Table 2
Crystallographic information for $\text{Li}_3\text{Ti}_{0.75}(\text{MoO}_4)_3$

Formula	$\text{Li}_3\text{Ti}_{0.75}(\text{MoO}_4)_3$
Crystal system	Orthorhombic
Space group	<i>Pnma</i>
<i>a</i> (Å)	5.0467(12)
<i>b</i> (Å)	10.454(3)
<i>c</i> (Å)	17.538(4)
<i>Z</i>	4
<i>V</i>	925.3(4)
<i>D</i> _{calc}	3.864
μ (Mo K α)	4.665
<i>R</i> ₁ [<i>I</i> > 2 σ (<i>I</i>)], <i>R</i> ₁ [all data]	0.0407, 0.0503
<i>wR</i> ₂ [<i>I</i> > 2 σ (<i>I</i>)], <i>wR</i> ₂ [all data]	0.0966, 0.1007

$$R_1 = \sum |F_o| - |F_c| / \sum |F_o|; wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}.$$

diffraction performed on a Rigaku diffractometer (Cu K α radiation, Ni filter, $2\theta = 10\text{--}70^\circ$, 0.05° step size, 1 s count time).

3. Results and discussion

3.1. The lyonsite structure

The general formula for lyonsite-type oxides can be written as $\text{A}_{16}\text{B}_{12}\text{O}_{48}$ ($\text{A}_{16}(\text{BO}_4)_{12}$) and the structure is depicted in Fig. 1. Hexagonal tunnel is created by zigzag sheets of edge sharing A centered trigonal prisms that are joined with columns of edge sharing A centered octahedra, shown in Fig. 2. Isolated BO_4 tetrahedra line the inner wall of the tunnel, and infinite chains of face shared AO_6 octahedra pass through the center of these tunnels. The face sharing octahedra, a key feature of the lyonsite crystal framework, allow a significant and variable concentration of cation vacancies to occur, that in turn provides the required charge compensation when the identity of the A site element is varied.

3.2. The importance of cation vacancies in lyonsite

The ability of perovskites, apatites, fluorites, etc. to adopt non-stoichiometric compositions is well documented, as variable cation or anion compositions are often required to

accommodate a range of cations with different oxidation states. Likewise, the large and growing family of lyonsite phases occur with variable compositions owing to different levels of cation vacancies.

Three compounds will be used here to demonstrate the remarkable effect that cation vacancies can have: $\alpha\text{-Cu}_3\text{Fe}_4(\text{VO}_4)_6$ [3], $\text{Mg}_{2.5}\text{VMoO}_8$ [7,8], and $\text{Li}_2\text{Mg}_2(\text{MoO}_4)_3$ [9]. The relationship between the three stoichiometries is detailed in Table 4. The mineral $\alpha\text{-Cu}_3\text{Fe}_4(\text{VO}_4)_6$, with $Z = 2$, can be written as $(\text{Cu}_6\text{Fe}_8)\text{V}_{12}\text{O}_{48}$ ($\text{A}_{14}\text{B}_{12}\text{O}_{48}$). In contrast, the general lyonsite formula is $\text{A}_{16}\text{B}_{12}\text{O}_{48}$. Therefore, the mineral formula can be written as $\square_2\text{A}_{14}\text{B}_{12}\text{O}_{48}$, and 1/7th of the Cu/Fe positions are vacant. Similarly, $\text{Mg}_{2.5}\text{VMoO}_8$, with $Z = 6$, can be written as $\text{Mg}_{15}(\text{V}_6\text{Mo}_6)\text{O}_{48}$ ($\square\text{A}_{15}\text{B}_{12}\text{O}_{48}$), where 1/16th of the Mg sites are unoccupied. Finally, $\text{Li}_2\text{Mg}_2(\text{MoO}_4)_3$, with $Z = 4$, can be written as $(\text{Li}_8\text{Mg}_8)\text{Mo}_{12}\text{O}_{48}$ ($\text{A}_{16}\text{B}_{12}\text{O}_{48}$) where there are no cation vacancies. Furthermore, the level of cation vacancies can be adjusted in the complete solid solution $\square_{1/4-x/6}\text{Li}_{4x/3}\text{Mg}_{15/4-7x/6}\text{V}_{3/2-x}\text{Mo}_{3/2+x}\text{O}_{12}$ ($0 \leq x \leq 1.5$) [10], where the two end members are $\text{Mg}_{2.5}\text{VMoO}_8$ ($x = 0$) and $\text{Li}_2\text{Mg}_2(\text{MoO}_4)_3$ ($x = 1.5$). As shown in Table 1, the variable A site composition gives rise to many different stoichiometries and solid solutions.

These cation vacancies, when present, are generally localized on the face shared octahedral site, in order to alleviate the coulombic repulsions that arise from placing cations in close proximity. In $\alpha\text{-Cu}_3\text{Fe}_4(\text{VO}_4)_6$, half of the copper positions are vacant along the infinite chain of face sharing octahedra, and the copper atoms likely alternate with cation vacancies along the chain. In $\text{Mg}_{2.5}\text{VMoO}_8$, one quarter of the magnesium sites are vacant along the infinite chain, and the cation vacancies likely alternate with magnesium trimers. These examples illustrate how cation vacancies contribute to the chemical diversity that is possible with lyonsite.

3.3. The structure of $\text{Li}_3\text{Ti}_{0.75}\text{Mo}_3\text{O}_{12}$

The general structure of $\text{Li}_3\text{Ti}_{0.75}\text{Mo}_3\text{O}_{12}$ is identical to that of other lyonsite-type oxides and is depicted in Fig. 3. The

Table 3
Atomic positions for $\text{Li}_3\text{Ti}_{0.75}(\text{MoO}_4)_3$

Atom	Wyckoff Position	<i>x</i>	<i>y</i>	<i>z</i>	Occ.	<i>U</i> _{eq}
Mo(1)	4c	0.22039(12)	0.25	0.44220(4)	1	0.00744(19)
Mo(2)	8d	0.72419(9)	−0.02668(5)	0.34353(3)	1	0.00901(18)
Ti(1)	4c	0.3884(8)	0.25	0.24990(16)	0.50	0.0232(11)
Li(1)	4c	0.3884(8)	0.25	0.24990(16)	0.25	0.0232(11)
Ti(2)	8d	0.7561(8)	0.0741(5)	0.5268(2)	0.125	0.0086(14)
Li(2)	8d	0.7561(8)	0.0741(5)	0.5268(2)	0.875	0.0086(14)
Li(3)	4c	0.7444(3)	0.25	0.6963(8)	1	0.021(3)
O(1)	4c	0.1326(12)	0.25	0.3422(3)	1	0.0155(12)
O(2)	4c	−0.0511(11)	0.25	0.5060(3)	1	0.0139(11)
O(3)	8d	0.4204(7)	0.1170(4)	0.4617(2)	1	0.0139(8)
O(4)	8d	0.4449(7)	−0.1141(3)	0.3740(2)	1	0.0131(8)
O(5)	8d	0.9249(7)	−0.1214(4)	0.2866(2)	1	0.0170(9)
O(6)	8d	0.6381(8)	0.1204(3)	0.2934(2)	1	0.0131(8)
O(7)	8d	0.9201(8)	0.0119(4)	0.4239(2)	1	0.0148(8)

$$U_{eq} = (U_{11} + U_{22} + U_{33})/3.$$

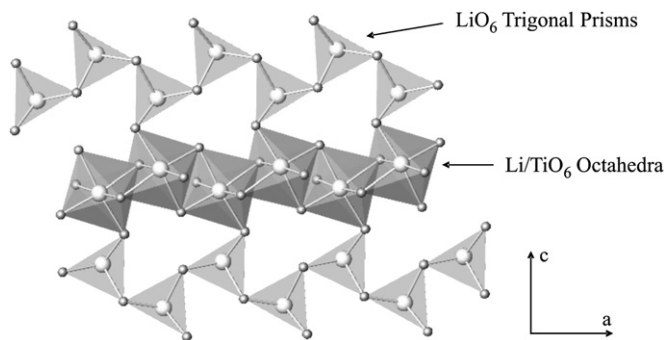


Fig. 2. The hexagonal tunnels created by AO_6 octahedra and trigonal prisms.

face sharing octahedral site consists of about 50% Ti/25% Li/25% \square , the other octahedral site consists of about 12.5% Ti and 87.5% Li, and the trigonal prism site consists of 100% Li. Chains of edge sharing LiO_6 trigonal prisms are linked with chains of edge sharing $(\text{Li/Ti})\text{O}_6$ octahedra to form the pseudo-hexagonal tunnels along the a axis (see Fig. 2), and isolated MoO_4 tetrahedra line the tunnel wall. The cation vacancies were placed on the face shared octahedral site, consistent with other reported lyonsite structures. However, we recognize the insensitivity of X-rays to lithium and acknowledge that the vacancies could, in principle, be distributed on any of the three positions. With cation vacancies on the face sharing octahedra, one out of every four positions along the infinite chain is vacant and is similar to what is observed in $\text{Mg}_{2.5}\text{VMoO}_8$. This arrangement allows for the formation of Ti/Li trimers bordered by vacancies. All oxygen atoms are 3 coordinate (not counting cation vacancies), each bonded to one molybdenum and two titanium and/or lithium atoms.

3.4. Crystal chemistry of $\square_{1-3x}\text{Li}_{2+4x}\text{Ti}_{1-x}\text{Mo}_3\text{O}_{12}$; $0 \leq x \leq 1/3$

The solid state crystal chemistry of $\text{Li}_3\text{Ti}_{0.75}\text{Mo}_3\text{O}_{12}$ demonstrates the unique role of cation vacancies. As mentioned, $\text{Li}_3\text{Ti}_{0.75}\text{Mo}_3\text{O}_{12}$ is A site deficient and the formula can be written as $\square_{0.25}\text{Li}_3\text{Ti}_{0.75}\text{Mo}_3\text{O}_{12}$, where \square represents a cation vacancy. While it may not be obvious, or perhaps counterintuitive, $\square_{0.25}\text{Li}_3\text{Ti}_{0.75}\text{Mo}_3\text{O}_{12}$ contains excess titanium, which creates the cation vacancies. For example, a fully occupied and charge balanced (assuming Ti^{4+} and Mo^{6+}) stoichiometry would correspond to ' $\text{Li}_{3.33}\text{Ti}_{0.67}\text{Mo}_3\text{O}_{12}$ ' ($x = 1/3$). However, when this composition was calcined for 24 h at 550 °C, an excess of Li_2MoO_4 was observed, and therefore the true formula will contain additional titanium. Each additional titanium ($x < 1/3$) leads to three corresponding cation vacancies to maintain charge neutrality, and the single phase region will occur somewhere along the line $\square_{1-3x}\text{Li}_{2+4x}\text{Ti}_{1-x}\text{Mo}_3\text{O}_{12}$.

Table 4
Cation vacancy comparisons

Formulation	Z	Total	Vacant
$\text{Cu}_3\text{Fe}_4(\text{VO}_4)_6$	2	$\square_2\text{Cu}_6\text{Fe}_8\text{V}_{12}\text{O}_{48}$	1/7
$\text{Mg}_{2.5}\text{VMoO}_8$	6	$\square\text{Mg}_{15}\text{V}_6\text{Mo}_6\text{O}_{48}$	1/16
$\text{Li}_2\text{Mg}_2(\text{MoO}_4)_3$	4	$\text{Li}_8\text{Mg}_8\text{Mo}_{12}\text{O}_{48}$	0

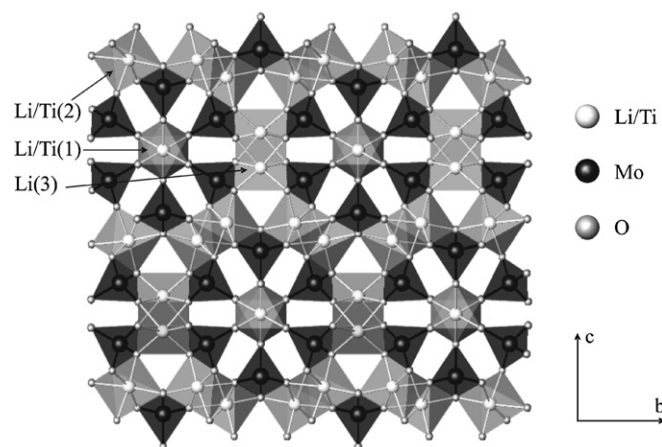


Fig. 3. The lyonsite structure of $\text{Li}_3\text{Ti}_{0.75}(\text{MoO}_4)_3$.

Furthermore, when a nominal stoichiometry of ' $\square\text{Li}_2\text{TiMo}_3\text{O}_{12}$ ' ($x = 0$) was calcined, an excess of TiO_2 and MoO_3 was observed, and ultimately the $\square_{1-3x}\text{Li}_{2+4x}\text{Ti}_{1-x}\text{Mo}_3\text{O}_{12}$ solid solution was observed for $0.23 \leq x \leq 0.26$. This range is similar to the solid solution that was observed for $\square_{1-3x}\text{Li}_{2+4x}\text{Hf}_{1-x}\text{Mo}_3\text{O}_{12}$ ($0.19 \leq x \leq 0.22$) [1]. Although the compounds $\text{Li}_2\text{Ti}(\text{MoO}_4)_3$ [11] and $\text{Li}_{3.33}\text{Ti}_{0.67}(\text{MoO}_4)_3$ [12] have been reported, under the conditions reported here, we saw no evidence of these phases.

The solid solution range for $\square_{1-3x}\text{Li}_{2+4x}\text{Ti}_{1-x}\text{Mo}_3\text{O}_{12}$ is very small and $\square_{0.25}\text{Li}_3\text{Ti}_{0.75}\text{Mo}_3\text{O}_{12}$ is nearly a line phase. Remarkably, lyonsite oxides occur with both near line phase compositions such as $\square_{0.25}\text{Li}_3\text{Ti}_{0.75}\text{Mo}_3\text{O}_{12}$, in addition to solid solutions such as $\square_{1/4-x/6}\text{Li}_{4/3}\text{Mg}_{15/4-7/6}\text{V}_{3/2-x}\text{Mo}_{3/2+x}\text{O}_{12}$ ($0 \leq x \leq 1.5$) [10].

While cation vacancies allow the amazing diversity of elements that are possible, the number of cation vacancies tolerated depends upon the chosen elements. For example, all of the known vanadates exhibit some amount of A site vacancies (see Table 1). When stoichiometries along the $\text{Cu}_{3+1.5x}\text{Fe}_{4-x}(\text{VO}_4)_6$ compositional phase line were further investigated, the lyonsite phase could be synthesized at ambient pressure for the compositional range $0.667 \leq x \leq 0.778$ [13]. Attempts to synthesize $\alpha\text{-Cu}_3\text{Fe}_4(\text{VO}_4)_6$ ($x = 0$) at ambient pressure resulted in a lower density phase, $\beta\text{-Cu}_3\text{Fe}_4(\text{VO}_4)_6$, indicating that the mineral may be a high pressure phase [14]. In contrast, the molybdates can have full occupancy of the A site if the cations have oxidation states +1 to +3. However, increasing the oxidation state of the cations to +4 or +5 seems to create necessary cation vacancies.

4. Conclusion and future areas of research

The structure of $\text{Li}_3\text{Ti}_{0.75}(\text{MoO}_4)_3$ has been determined and found to crystallize in the lyonsite structure type. The solid solution $\square_{1-3x}\text{Li}_{2+4x}\text{Ti}_{1-x}\text{Mo}_3\text{O}_{12}$ was determined to be $0.23 \leq x \leq 0.26$. Its structure and solid solution behavior are representative of the large lyonsite family of oxides. While this particular cation combination ($x = 0.25$) is essentially

stoichiometric and shows little variation, other phases in the lyonsite family can show considerable variation. Although the lyonsite family of oxides is large, thus far it has been limited to vanadates, molybdates, and tungstates. Further investigations of this diverse group of oxides, including main group phosphates, arsenates, etc. would appear to be promising.

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References

- [1] J.P. Smit, P.C. Stair, K.R. Poeppelmeier, *Chem.—Eur. J.* 12 (2006) 5944–5953.
- [2] J.A. Ibers, G.W. Smith, *Acta Crystallogr.* 17 (1964) 190–197.
- [3] J.M. Hughes, S.J. Starkey, M.L. Malinconico, L.L. Malinconico, *Am. Mineral.* 72 (1987) 1000–1005.
- [4] J.P. Smit, P.C. Stair, K.R. Poeppelmeier, *Cryst. Growth Des.* 7 (2007) 521–525.
- [5] SAINT-Plus, Version 6.02A, Bruker Analytical X-ray Instruments, Inc., Madison, WI, 2000.
- [6] G.M. Sheldrick, *SHELXTL*, Version 6.14, Bruker Analytical X-ray Instruments, Inc., Madison, WI, 2003.
- [7] V.G. Zubkov, I.A. Leonidov, K.R. Poeppelmeier, V.L. Kozhevnikov, *J. Solid State Chem.* 111 (1994) 197–201.
- [8] X. Wang, C.L. Stern, K.R. Poeppelmeier, *J. Alloys Compd.* 243 (1996) 51–58.
- [9] L. Sebastian, Y. Piffard, A.K. Shukla, F. Taulelle, J. Gopalakrishnan, *J. Mater. Chem.* 13 (2003) 1797–1802.
- [10] J.P. Smit, H.-S. Kim, J.D. Pless, P.C. Stair, K.R. Poeppelmeier, *Inorg. Chem.* 45 (2006) 521–528.
- [11] P.V. Klevtsov, E.S. Zolotova, *Izv. Akad. Nauk SSSR, Neorg. Mater.* 9 (1973) 79–82.
- [12] V.K. Trunov, *Zh. Neorg. Khim.* 16 (1971) 553–554.
- [13] A.A. Belik, A.P. Malakho, K.V. Pokholok, B.I. Lazoryak, *J. Solid State Chem.* 156 (2001) 339–348.
- [14] M.A. Lafontaine, J.M. Greneche, Y. Laligant, G. Ferey, *J. Solid State Chem.* 108 (1994) 1–10.
- [15] R.F. Klevtsova, S.A. Magarill, *Kristallografiya* 15 (1970) 710–715.
- [16] L. Katz, A. Kasenally, L. Kihlberg, *Acta Crystallogr., Sect. B* 27 (1971) 2071–2077.
- [17] M. Ozima, S. Sato, T. Zoltai, *Acta Crystallogr., Sect. B* B33 (1977) 2175–2181.
- [18] Z. Fu, W. Li, *Powder Diffr.* 9 (1994) 158–160.
- [19] S.F. Solodovnikov, Z.A. Solodovnikova, R.F. Klevtsova, L.A. Glinskaya, P.V. Klevtsov, E.S. Zolotova, *Zh. Strukt. Khim.* 35 (1994) 136–144.
- [20] M. Wiesmann, I. Svoboda, H. Weitzel, H. Fuess, *Z. Kristallogr.* 210 (1995) 525.
- [21] X. Wang, K.R. Heier, C.L. Stern, K.R. Poeppelmeier, *J. Alloys Compd.* 255 (1997) 190–194.
- [22] X. Wang, K.R. Heier, C.L. Stern, K.R. Poeppelmeier, *J. Alloys Compd.* 267 (1998) 79–85.
- [23] X. Wang, D.A. Vander Griend, C.L. Stern, K.R. Poeppelmeier, *Inorg. Chem.* 39 (2000) 136–140.
- [24] A.A. Belik, F. Izumi, T. Ikeda, A. Nisawa, T. Kamiyama, K. Oikawa, *Solid State Sci.* 4 (2002) 515–522.
- [25] A.P. Malakho, A.A. Belik, B.I. Lazoryak, *Zh. Neorg. Khim.* 48 (2003) 709–714.
- [26] U. Kolitsch, E. Tillmanns, *Acta Crystallogr., Sect. E: Struct. Rep. Online* E59 (2003) i55–i58.
- [27] M. Kurzawa, M. Bosacka, P. Jakubus, *J. Mater. Sci.* 38 (2003) 3137–3142.
- [28] J.D. Pless, H.-S. Kim, J.P. Smit, X. Wang, P.C. Stair, K.R. Poeppelmeier, *Inorg. Chem.* 45 (2006) 514–520.
- [29] P.V. Klevtsov, *Kristallografiya* 15 (1970) 797–802.
- [30] V.K. Trunov, V.A. Efremov, *Zh. Neorg. Khim.* 16 (1971) 2026–2027.
- [31] R.F. Klevtsova, A.A. Antonova, L.A. Glinskaya, *Kristallografiya* 24 (1979) 1043–1047.
- [32] V.A. Efremov, V.K. Trunov, *Zh. Neorg. Khim.* 17 (1972) 2034–2039.
- [33] B.M. Wanklyn, F.R. Wondre, W. Davison, *J. Mater. Sci.* 11 (1976) 1607–1614.
- [34] V.G. Penkova, P.V. Klevtsov, *Zh. Neorg. Khim.* 22 (1977) 1713–1715.
- [35] M.A. Juri, M. Viola, G. Narda, J.C. Pedregosa, *Acta Cient. Venez.* 43 (1992) 14–18.