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Vacancy tuning in Li,V-substituted lyonsites

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The lyonsite structure, characterized by the formula $A_4M_3O_{12}$, is a relatively understudied tunneled crystal structure. This host structure is known to be compositionally flexible, able to incorporate a number of cations in various oxidation states into the A site. In the parent compound $\text{Co}_{3.75}\text{V}_{1.5}\text{Mo}_{1.5}\text{O}_{12}$, it is apparent that a stoichiometric vacancy of 0.25 is unavoidable as a result of Coulombic repulsion. This work focuses on the systematic elimination of vacancies by chemically introducing guest Li ions while maintaining host integrity. A full solid solution was found to exist with the formula $\square_{0.25-1/8}x\text{Li}_x\text{Co}_{3.75-7/8x}\text{V}_{1.5-3/4x}\text{Mo}_{1.5+3/4x}\text{O}_{12}$ ($0 \leq x \leq 2$), terminating at the known end member $\text{Li}_2\text{Co}_2\text{Mo}_3\text{O}_{12}$. Lattice refinements on PXRD data confirmed the isostructural nature of the whole series, and detailed structural analysis revealed that competition between Li and Co in the same crystallographic site is unequal, with Li exhibiting a stronger site preference for larger interstitial sites. Diffuse reflectance analysis revealed that the optical band gap is directly tunable with x , and supporting structure-property relationships were also explored via magnetometry and dielectric measurements.

Keywords: lyonsite; crystallography, magnetism, diffuse reflectance, dielectric

Introduction

Adaptable crystal structures with tunable physical properties have proven highly useful in a variety of applications, evident from ubiquitous families like the perovskites (1), spinels (2), pyrochlores (3-6), and alkali metal polyanionic frameworks. For example,

among the defect KB_2O_6 ($B = \text{Al, Ti, Ta}$) type pyrochlores, $KAl_{0.33}W_{1.67}O_6$ exhibits high ionic conductivity values due to polarization of the extended B_2X_6 network (7). Fast ion transport has also been demonstrated in Ag-exchanged $\alpha\text{-Zr}(\text{AgPO}_4)_2$, in which the greater polarizability of Ag^+ leads to higher conductivity than that of Na^+ and K^+ in their exchanged forms (8).

Among the polyanionic frameworks, one structure family clearly stands out in the field of ion conductors and ion exchange materials: Na super ionic conductors, or NASICONs. These structures, generalized as $A_xM_2(XO_4)_3$ ($A^+ = \text{Li, Na, M} = \text{Ti, Fe, V, and } X = \text{P, As, Mo, W, S}$), are exemplified in $\text{Na}_{1+x}\text{Zr}_2\text{P}_{3-x}\text{Si}_x\text{O}_{12}$ ($0 \leq x \leq 3$), which is a solid solution between $\text{NaZr}_2\text{P}_3\text{O}_{12}$ and $\text{Na}_4\text{Zr}_2\text{Si}_3\text{O}_{12}$ (Fig. 1 near here).

For decades, researchers like Clearfield have found great potential in these open framework structures (9). In particular, Clearfield's crystallography-heavy approach to materials discovery has laid the foundation for understanding the mechanisms by which ions diffuse through host structures. For example, in $\text{LiB}_2(\text{PO}_4)_3$ ($B = \text{Ti, Zr, Hf}$), crystallographic investigations determined that conductivity could be increased not only by changing the Li stoichiometry, but also by understanding and adjusting the cavity/bottleneck size to allow for free ion movement. This was demonstrated via substitutions on the Li site, e.g., $\text{Li}_{1+x}\text{Sc}_x\text{Ti}_{2-x}(\text{PO}_4)_3$ and $\text{Li}_{1+x}\text{In}_x\text{Hf}_{2-x}(\text{PO}_4)_3$ (10). Another example can be found in Sc-substituted NASICONs, in which the Sc for Zr substitution correlates with a corresponding Si for P adjustment to maintain the Na concentration. The host's flexibility allows for changes in symmetry as a function of Sc content or temperature while preserving, or even increasing, the conductivity (11). While NASICONs can be prepared by conventional solid state reaction methods, others, such as $\text{Na}_{2.88}(\text{Na}_{0.32}\text{Zr}_{1.68})\text{Si}_{1.84}\text{P}_{1.16}\text{O}_{11.54}$, can be prepared via sol-gel or hydrothermal synthesis with greater ease (12, 13). During these studies, it was noted that the

stoichiometry and subsequent conductivity are highly dependent on the chosen synthetic route (14).

In 2006, one of the lesser known framework families, the lyonsites, was given a thorough treatment in a seminal review (15), and what follows here is a brief recapitulation of that work. The lyonsite found its beginnings in the laboratory, being first synthesized in 1960 (16), and a general structure determination was carried out in 1964 (17). This compound, $\text{Na}_{2.31}(\text{MoO}_4)_3$ (*Pmcn*), was recognized as a new structure type. By 1970, two other compounds, $\text{Li}_3\text{Fe}(\text{MoO}_4)_3$ and $\text{Li}_2\text{Fe}_2(\text{MoO}_4)_3$ were discovered, and the structural similarity was noted, but no further elaboration was given (18). Contrary to the typical trend of mineralogy inspiring chemistry, a natural lyonsite was not discovered until 1987, in which the iron-copper vanadate $\alpha\text{-Cu}_3\text{Fe}_4(\text{VO}_4)_6$ (*Pmcn*) was a fumarolic sublimate at Izalco volcano in El Salvador; it was then named for mineralogist John B. Lyons (19).

Structural Description

The lyonsites can be described by a handful of general formulae, the most broad being $A_{16}M_{12}O_{48}$ (or $A_{16}(\text{MO}_4)_{12}$). The latter stoichiometry is shared in several other unrelated structures (e.g., fluorite derivatives (20) and cation-deficient perovskites (21,22)). In many cases, the stoichiometry is scaled down by a factor of 4 to yield $A_4M_3O_{12}$ (or $A_4(\text{MO}_4)_3$). Other common formula expressions also involve simple multipliers to clarify stoichiometric features or to facilitate ease of reading, e.g., scaling by 1.5 and introducing vacancies yields $\square_{1/6}A_{2.5}M_2O_8$.

This framework can be described by its structural motifs; a hexagonal tunnel comprised of zigzag sheets of edge-sharing AO_6 trigonal prisms and columns of edge-sharing AO_6 octahedra gives the overall appearance of a "bracelet", while the inner wall of this tunnel is lined with isolated MO_4 tetrahedra in a "pinwheel" fashion, and

passing through the center of the tunnel is an infinite chain of face-sharing AO_6 octahedra (Fig. 2 near here). Via symmetry, this tunnel can then be tessellated orthogonal to the primary viewing axis; in most cases, this is the a axis. While there are lyonsite-related minerals, these specific features are similar to only one other crystal system, even less studied than the lyonsite: the dumortierite structure (Fig. 3 near here) (23, 24).

Typically, two cations occupy the A sites, the ionic radius range of which are empirically generalized to 0.46 to 1.02 Å (15). The oxidation states of these cations can range between +1 and +5 (15). The M site is limited to smaller, highly charged cations that prefer four-fold coordination (25, 26). To date, this only includes V^{5+} , Mo^{6+} , and W^{6+} (15). The A sites are further distinguished by their polyhedral sharing schemes: A1 (face-shared octahedra), A2 (edge-shared octahedra), and A3 (edge-shared trigonal prisms) (Fig. 2). The M sites are also crystallographically distinct: M1 and M2. Each oxygen is bonded to two A atoms and one M atom.

The majority of these oxides crystallize in the $Pnma$ space group; however, the structural flexibility has led to the observation of several lyonsites crystallizing in subgroups of $Pnma$. This structural flexibility is also reflected in the ability to incorporate vacancies, □; these vacancies tend to localize in the face-sharing octahedral chain. Consequently, the bonded oxygens will displace towards the higher oxidation state M cation. Substitutions can therefore be made into any site exclusively or across all sites with vacancy compensation.

The trigonal prism environment is an atypical one, even in this structure; in most of the molybdate lyonsites, the A3 site is fairly uniform; however, in Zn- and Cu-containing lyonsites, this site is highly distorted, with the cations pushed towards one of the square windows. They can be treated as distorted square pyramids ($Cu_{3.85}(MoO_4)_3$

(27), $(\text{Cu,Fe})_{3.63}(\text{MoO}_4)_3$ (28)) or square planes, in which one pair of $A\text{--O}$ bonds is significantly longer than the others, as in the case of $(\text{Cu,Mn})_{3.66}(\text{MoO}_4)_3$ (29), $(\text{Cu,Co})_{3.75}(\text{MoO}_4)_3$ (30), and $\text{Cu}_3\text{Fe}_4\text{V}_6\text{O}_{24}$ (19).

Molybdates

The molybdate members of this structure family exhibit the most diversity in A site substitutions (31). After the discovery of $\text{Li}_3\text{Fe}(\text{MoO}_4)_3$ and $\text{Li}_2\text{Fe}_2(\text{MoO}_4)_3$, structural similarities were noted in an increasing number of compounds over the 1971-1987 period (15). An empirical trend was observed: one A cation was an alkali metal ion (Li^+ , Na^+) and the other was of a flexible oxidation state. To maintain stoichiometry and charge neutrality, the possible A site combinations were found to be: $A^{+}_3A'^{3+}$ and $A^{+}_2A'^{2+}_2$. Some examples of such compounds include $\text{Li}_3(\text{Al,Sc})\text{Mo}_3\text{O}_{12}$ (32, 33), $\text{Li}_2(\text{Co,Cu,Ni,Zn})_2\text{Mo}_3\text{O}_{12}$ (34-38). Introducing higher oxidation state cations or breaking this pattern necessitated the creation of vacancies (e.g., 6.25% of the A site in $\text{Li}_3\text{Ti}_{0.75}\text{Mo}_3\text{O}_{12}$ (39) is vacant), and/or a change in oxidation states, as in $\text{Cu}_{3.85}\text{Mo}_3\text{O}_{12}$ (in which Cu^+ is present, and 3.75% of the A site is vacant) (27). One of the few lyonsites to exhibit cation and vacancy ordering in the $A1$ site is $\text{Li}_2\text{Zr}(\text{MoO}_4)_3$, in which the symmetry is reduced to $Pmn2_1$ (15).

Vanadates

The mineral $\alpha\text{-Cu}_3\text{Fe}_4(\text{VO}_4)_6$ (A site vacancy: 12.5 %) was the first discovered vanadate variety. Attempts to replicate this in a laboratory setting had been unsuccessful, and resulted in a $\beta\text{-Cu}_3\text{Fe}_4(\text{VO}_4)_6$ phase. It was surmised that synthesis of the α form was only possible at high pressures, mimicking that of the geological conditions for the mineral formation (40). However, the ability of the structure type to incorporate vacancies allowed for off-stoichiometries, resulting in compounds

like $(\text{Co,Cu})_4\text{Fe}_{3.33}(\text{VO}_4)_6$ (*A* site vacancy: 8.375%), $\text{Co}_{3.6}\text{Fe}_{3.6}(\text{VO}_4)_6$ (*A* site vacancy: 10 %), $\text{Cu}_{4.05}\text{Cr}_{3.3}(\text{VO}_4)_6$ (*A* site vacancy: 8.125 %), and $\text{Co}_5\text{Cr}_{2.667}(\text{VO}_4)_6$ (*A* site vacancy: 4.1625 %) (15). It was determined that all these samples fall on the $A_{3+1.5x}A'_{4-x}(\text{VO}_4)_6$ phase line. It is clear at this point that a fully occupied model for vanadates cannot be charge balanced, and must inherently have vacancies. For example, a more formal expression of $\alpha\text{-Cu}_3\text{Fe}_4(\text{VO}_4)_6$ would be $\square_2\text{Cu}_6\text{Fe}_8\text{V}_{12}\text{O}_{48}$.

Vanadomolybdates

The vanadomolybdates (in which past studies have often scaled down the stoichiometry by 1.5x for clarity (25, 41, 42)) are less studied than their molybdate and vanadate counterparts. One such example is $\text{Mg}_{2.5}\text{VMoO}_8$, which was found to be catalytically active for hydrocarbon oxidation. Like the vanadate varieties, these lyonsites contain unavoidable vacancies, e.g., $\text{Mg}_{2.5}\text{VMoO}_8$ is rewritten as $\text{Mg}_{15}\text{V}_6\text{Mo}_6\text{O}_{48}$. Of note are two particular compounds, $\text{Zn}_{2.5}\text{VMoO}_8$ (43), white in color, crystallizing as $P2_12_12_1$, and $\text{Co}_{2.5}\text{VMoO}_8$ (42), which appears almost black, crystallizing as $Pnma$. They are two of the few known lyonsites in which only one cation (and corresponding vacancies) occupy the *A* site (25, 26, 41, 43). Until recently, the site preference for Zn^{2+} in this structure was unknown. In addition, the other end member, $\text{Co}_{2.5}\text{VMoO}_8$, had been reported, but no physical properties had been explored (42). A recent investigation examined the structural and physical properties of a solid solution between these two species. Among the properties of the series was its color, exhibiting varying shades of green, tunable with *x* (44).

Following the conclusions of that work, with this behavior in mind, it was worth experimentation to coax and tune other colors from this system of compounds. Another investigation presented novel compositions and some physical properties of cationic

substitutions into the white Zn-rich end member, namely with Mn, Ni, and Cu ions (45). A structural treatment of the end member $\text{Mn}_{2.5}\text{VMoO}_8$ had been given in the literature (41), but no physical properties had been measured, so the possible color range was unknown. In addition, a fully substituted Ni lyonsite is not known to exist, and a fully substituted Cu lyonsite is demonstrated with Mo^{6+} as the only M cation (27). Substitutions with these two elements were therefore worthy of exploration, considering NiO/CuO are lower-cost precursors relative to CoO. In addition, Cu^{2+} is a Jahn-Teller active ion (46), which can create structural oddities (34, 47).

Tungstates/Vanadotungstates

Prior to 2006, only two compounds of this variety were known, $\text{Li}_2\text{Mg}_2(\text{WO}_4)_3$ and $\text{Mg}_{2.5}\text{VWO}_8$ (48, 49). Attempts to form $\text{Li}_2A'_2(\text{WO}_4)_3$ with anything other than Mg^{2+} have failed. Further investigation is therefore needed to understand the disparity in phase stability between Mo^{6+} - and W^{6+} - substituted lyonsites.

Physical Properties

Since their discovery, various lyonsite compounds have been proposed for direct functional applications, since recent studies have demonstrated that tunability was possible in the cation sites as well as vacancy concentrations (15). For example, the tungstate $\text{Li}_2\text{Mg}_2\text{W}_3\text{O}_{12}$ doped with Eu^{3+} was recently found to be a promising red phosphor for white light-emitting diodes (48). Other compounds, like the mentioned $\text{Li}_3\text{FeMo}_3\text{O}_{12}$, $\text{Li}_2\text{Mg}_2\text{Mo}_3\text{O}_{12}$, and $\text{Li}_2A'_2\text{Mo}_3\text{O}_{12}$ ($A' = \text{Zn}, \text{Ca}$), exhibit favorable microwave dielectric quality factors (50-52). Further still, compounds such as $\text{Zn}_{2.5}\text{VMoO}_8$ and $\text{Li}_3\text{FeMo}_3\text{O}_{12}$ are also noted for their photocatalytic activity (53, 54).

The location and variability in vacancies have also been used to explain ionic conduction in this family, though detailed mechanistic studies are still inconclusive.

$\text{Li}_2\text{Co}_2(\text{MoO}_4)_3$ can be considered to be a part of the NASICON (Na super ionic conductor) family, as it is constructed of a polyanionic framework with Li-occupied channels. This particular compound exhibits Li insertion/de-insertion at 4.9 V via oxidation of Co^{2+} to Co^{3+} , and at 1.5 V, de-insertion results in the reduction of Mo^{6+} to Mo^{5+} (55). Similarly, $\text{Li}_2\text{Ni}_2(\text{MoO}_4)_3$ exhibits a reversible discharge capacity of ≈ 115 mAh/g (56).

Other examples include $\text{Li}_{2-x}\text{Mg}_{2+x}(\text{MoO}_4)_3$ ($0 \leq x \leq 0.3$) and $\text{Li}_3A'^{3+}(\text{MoO}_4)_3$ ($A'^{3+} = \text{Cr, Fe}$) (31). While the framework is 3-dimensional, the conduction pathway is suggested to be along the trigonal prismatic A3 site, which is exclusively occupied by Li. It is possible that vacancies exist there in addition to the A1 site, though the A3 site would be preferable for ion migration due to the connectivity and window size ($\approx 3.95 \times 4.00 \text{ \AA}$). AC impedance spectroscopy indicates that the conduction is 1-dimensional, with σ_{300} values of $\sim 10^{-7} \text{ S/cm}$ for $\text{Li}_{2-x}\text{Mg}_{2+x}(\text{MoO}_4)_3$ and $\sim 10^{-6} \text{ S/cm}$ for $\text{Li}_3A'^{3+}(\text{MoO}_4)_3$. For the former series, the low conductivity (as x increases) was attributed to the presence of +2 cations in the A3 site, which impedes the Li-ion mobility. For the latter series, the observed conductivity is superior to that of other 1D ionic conductors like LiAlSiO_4 and LiSbO_3 (31). A similar example of this behavior exists in $\text{Li}_{3+x}\text{Fe}(\text{MoO}_4)_3$, in which electrochemical insertion and de-insertion of Li is reversible via the reduction of Fe^{3+} (57).

In one particular work, a complete solid solution was found between $\text{Li}_2\text{Mg}_2\text{Mo}_3\text{O}_{12}$ and the isostructural $\text{Mg}_{2.5}\text{VMoO}_8$, and was expressed as $\square_{0.25-1/6x}\text{Li}_{4/3x}\text{Mg}_{3.75-7/6x}\text{V}_{1.5-x}\text{Mo}_{1.5+x}\text{O}_{12}$ (in which the vacancy concentration varies as a function of charge neutrality, as well as stoichiometric preservation of each site) (58). This behaviour has also been demonstrated to be useful in catalysis and ionic conduction applications, e.g., the creation of cationic vacancies in the NASICON-like related

compound $(\text{Li,Na})_2\text{Fe}_2(\text{MoO}_4)_3$ facilitates Li-ion mobility (59). To further explore this flexibility and to examine the conclusions made in prior literature, a solid solution between the $\text{Li}_2\text{Co}_2(\text{MoO}_4)_3$ ($x = 0$) and $\text{Co}_{2.5}\text{VMoO}_8$ ($x_{0.25}\text{Co}_{3.75}\text{V}_{1.5}\text{Mo}_{1.5}\text{O}_{12}$) is detailed in this work; the Co-containing lyonsites were chosen as an extension of a previous study (44), but this substitution scheme could easily be adapted and attempted for other *A* cations.

Materials and Methods

Stoichiometric quantities of Li_2CO_3 (Sigma-Aldrich, 99.9%), CoCO_3 (Sigma-Aldrich, 46-48% as Co), V_2O_5 (Cerac, 99.9%), and MoO_3 (Sigma-Aldrich, 99.5%) were ground in an agate mortar, pressed into cylindrical pellets, and annealed between 600 and 975 °C in air.

X-ray diffraction data were collected using a benchtop Rigaku MiniFlex II diffractometer using $\text{Cu K}\alpha$ radiation and a graphite monochromator. Le Bail refinements were performed with KCl as an internal standard. Select ≈ 10 g samples were loaded in vanadium sample cans (15.6 mm diameter, 50 mm length), and room temperature neutron powder diffraction data were collected on the BT-1 beamline at the Center for Neutron Research at the National Institute of Standards and Technology. Measurement was conducted over a 2θ range of 3-167°, and a Cu (311) monochromator was employed, yielding an incident wavelength of 1.5403(2) Å (60). Collimation of 15' of arc was used before the monochromator, 20' before the sample, and 7' before the detectors. Small portions of each sample were also used to collect high-resolution synchrotron X-ray diffraction data on the 11-BM beamline at the Advanced Photon Source at Argonne National Laboratory. Samples were ground with amorphous silica gel to account for absorption. The resulting mixtures were packed into Kapton capillary tubes (0.8 mm diameter), mounted, and data were collected at room temperature

over a 2θ range of 34° , with data points collected every $0.001^\circ 2\theta$ and a scan speed of $0.01^\circ/\text{s}$ (61). Subsequent Rietveld analysis was performed via the General Structure Analysis System (GSAS) software equipped with EXPGUI (62, 63).

Zero-field-cooled (ZFC) DC magnetization experiments were performed using a Quantum Design PPMS, from 5-300 K. Oxidation states were confirmed by fitting the inverse magnetic susceptibility curves to the reciprocal of the Curie-Weiss Law ($1/\chi_{\text{mol}} = (T-\theta)/C$) and extracting effective magnetic moments (in Bohr magnetons, μ_B) via $\mu_{\text{eff}} = 2.84C^{1/2}$. Diamagnetic corrections were applied during calculations of experimental μ_B . Vis-NIR diffuse reflectance data were obtained (out to 2500 nm) using a Jasco V-670 spectrophotometer fitted with an integrating sphere. The data were then converted to pseudo-absorbance units via the Kubelka-Munk relationship, $F(R) = (1-R)^2/(2R)$ (64), to generate corresponding Tauc plots.

Dielectric constant measurements were performed on an in-house parallel plate capacitor setup. Sintered pastilles of 75% density or greater were painted with Ag paint, cured at $\approx 120^\circ\text{C}$ for 2 h, placed between Pt electrodes, and a differential voltage was applied. Capacitance data were then collected as a function of temperature and frequency on an HP 4284 LCR meter at fixed frequencies of 1, 10, 100, 500, and 1000 kHz over a temperature range of 30-200 $^\circ\text{C}$.

Results and Discussion

Crystal Structure

A full solid solution was found to exist in the $0 \leq x \leq 2$ range (Fig. 4 near here). The similarity in Shannon ionic radii between Li^+ (0.74 Å) and Co^{2+} (0.745 Å) should result in little (if any) change in cell parameters (65). The difference between V^{5+} (0.355

Å) and Mo^{6+} (0.41 Å), though, is significant, and causes a unit cell expansion (Fig. 5 near here) commensurate with Vegard's law.

A related molybdate, $\text{Li}_{2-2x}\text{Zn}_{2+x}(\text{MoO}_4)_3$, which also exhibits vacancy flexibility, follows a similar substitution scheme to this work: $2 \text{Li}^+ \rightarrow \text{Zn}^{2+} + \square$ (66). As Zn content increased, the vacancy concentration increased in the A1 site, alleviating the electrostatic repulsion between the ions in that face-sharing site. The anisotropic atomic displacement parameters (ADPs) also reflected that scenario, as the thermal ellipsoids elongate along the axis of the AO_6 chain. The overall result is an expansion in the (100) and contraction along the [100] due to vacancy-induced steric strain relief. This behavior is also observed in this work, but the contraction along [100] is obfuscated by the difference in the *M* site radii.

A combined refinement obtained from constant-wavelength (CW) neutron diffraction and synchrotron X-ray diffraction was performed for a member of this series ($x = 1.25$). The pattern indexes well to *Pnma*, and lattice constants were consistent with that obtained from a benchtop diffractometer (Fig. 6 near here). The initial refinement strategy involved an equal distribution of atoms across their respective sites (Li, Co across the *A* sites, and V, Mo across the *M* sites). The vacancy concentration was localized to the A1 site, as per precedent. Chemical constraints were added for the A2, A3, M1, and M2 sites to a total occupancy of 1 for each site. Furthermore, chemical restraints were added to incorporate charge neutrality into the model, e.g., all Li occupancies adding up to the expected stoichiometry. All O sites were determined to be fully occupied, and were fixed at a value of 1. Anisotropic ADP values for all sites were reasonable and did not significantly affect the reliability statistics; this parameter was therefore refined under the assumption of isotropic displacement.

Overall, the most significant finding from this combined refinement is the site preference of Li over Co in the A3 (trigonal prismatic) site, compared to the A1 (face-sharing octahedra) and A2 (edge-sharing octahedra) (Table 1 near here). Against a nominal formula of $\square_{0.09}\text{Li}_{1.25}\text{Co}_{2.66}\text{V}_{0.56}\text{Mo}_{2.4}\text{O}_{12}$, the refined formula agrees well: $\square_{0.04}\text{Li}_{1.56}\text{Co}_{2.4}\text{V}_{0.6}\text{Mo}_{2.4}\text{O}_{12}$.

Magnetic Properties

Magnetic susceptibility measurements indicate that all samples are largely paramagnetic, and exhibit Curie-Weiss behavior in the high temperature region (≈ 150 -300 K) (Fig. 7 near here). However, the Weiss constants θ_w are negative enough (Table 2 near here) to warrant closer inspection of the susceptibility plots for signs of ordering. Evidence of antiferromagnetic (AFM) exchange between the Co^{2+} magnetic moments can be found in $d\chi/dT$ curves, in which the peaks below 15 K are indicators of the ordering temperature T_N (Fig. 8 near here).

In most 3d transition metal ions, the total magnetic moment is derived solely from the spin moment (e.g., the spin-only effective moment (μ_s) for a high-spin d^7 ion ($S = 3/2$) is $3.87 \mu_B$). Clearly, the observed values do not correlate well to the spin-only moment. In such cases, the net contribution from the orbital angular moment is nonzero, leading to a higher effective moment. The magnetic moment is therefore expressed as a function of both S and L , i.e., μ_{S+L} . For Co^{2+} , this corresponds to an expected moment of $5.21 \mu_B$ via $\mu_{S+L} = [(4S(S+1) + L(L+1))]^{1/2} \mu_B$ (67, 68). In short, these results can only occur if the only magnetically active ion is Co in the +2 oxidation state; this also implies that there are no O vacancies, and that V and Mo are in their highest oxidation states to preserve charge neutrality.

Optical Properties

The vacancy-rich end member was reported to be very dark green in color (44), while the Li-rich end member is blue (Fig. 9 near here). Visually, the transition from dark green to blue is difficult to grasp, with the first hint of blue occurring at the $x = 1.5$ member. The diffuse reflectance spectra also show a dramatic drop in absorbance in the 500-650 nm range between $x = 2$ and $x = 1.5$, after which point, changes are not as marked (Fig. 10 near here). These set of peaks correspond to the spin-allowed $d-d$ excitations from the Co^{2+} environments, but curiously, the absorbance drops as Co^{2+} content increases, which could signify a change in local geometry as the preferential occupation of Li^+ in the trigonal prismatic site becomes a less significant factor.

The higher energy peak is attributed to a ligand-to-metal charge transfer band (LMCT) from the O $2p$ to M cation's empty d orbitals. In addition, these LMCT bands in the 350-500 nm range shift gradually with x toward lower energies, corresponding with the increase in V^{5+} content and decreasing Mo^{6+} content. The non-absorbing trough region corresponds to the observed green color. The complexity of the cation distributions over the various structurally similar coordination environments renders specific transition assignments impractical. The NIR reflectance of the solid solution resembles that of other common Co^{2+} compounds, such as CoAl_2O_4 spinel (69), with moderately high reflectance, but with a dip around 1500 nm (Fig. 11 near here).

While direct assignment of electronic transitions is impractical in this series, it is possible to glean some information about the optical band gap E_g . While it is common to extrapolate a band gap from a direct Kubelka-Munk pseudo-absorbance conversion, the graphical representations of the plots during fitting may skew the results. This is often the case, as particle size and/or synthetic conditions directly influence the absorbance data (70). Without corrective measures, the dispersion of extrapolated

band gap values can be significant, e.g., the band gaps given for the standard Degussa P25 TiO₂ have been shown to vary even up to 0.24 eV (71).

It is therefore more accurate, however marginal, to use the Tauc method (72). A McLean analysis is first applied to the pseudo-absorbance data to determine whether the optical band gap is direct or indirect, and whether the transitions are allowed or forbidden (71). Not performing this analysis may give a larger spread of values for the estimated band gaps. As mentioned, the Kubelka-Munk relation is given by

$$F(R) = \frac{\alpha}{s} = \frac{(1-R)^2}{2R} \quad (1)$$

in which α is the absorption coefficient, R is the reflectance, and s is the scattering factor. It is clear from this relationship that s is wavelength-independent, and thus $F(R)$ is directly proportional to α . The McLean analysis incorporates this as

$$\alpha h\nu = k(h\nu - E_g)^{1/n} \quad (2)$$

in which h is the Planck constant, ν is the frequency, k is a proportional constant, E_g is the optical band gap, and n signifies the type of transition. A plot of $(F(R)h\nu)^n$ vs. $h\nu$ can reveal the transition type (Table 3 goes here):

Direct transitions do not involve the absorption nor emission of a phonon, while indirect transitions do; any and all of these transitions can occur in a semiconducting material. The plot that exhibits the most linear drop-off at the absorption edge corresponds to the transition type, and is therefore the most appropriate model to use in E_g calculations. From Fig. 12, it is apparent that the $n = 2$ model satisfies this condition, and is a direct allowed band-to-band transition.

The substitution of n yields $F(R)h\nu = k(h\nu - E_g)^{1/2}$, and a Tauc plot of $(F(R)h\nu)^2$ vs. $h\nu$ can be generated. Subsequent determination of the inflection point at the

absorbance onset is done via the first derivative of the Tauc plots. A tangent line can then be plotted and extrapolated to the x -axis (Fig. 13 near here). The x -intercepts are then taken to be the estimated optical band gaps (Table 4 near here).

It is apparent that E_g is tunable, and increases with x , which corresponds to: decreasing concentrations, increasing Li^+ content, decreasing Co^{2+} content, decreasing V^{5+} content, and increasing Mo^{6+} content. The M site is likely the primary cause of this trend, as the energies at the absorption edges align with that of the O-to- M charge transfer excitations.

Dielectric Properties

Dielectric constants were measured for the $x = 0$ and $x = 2$ members, as they have not been reported. The relative permittivity for the $x = 0$ compound exhibits both temperature and frequency dependence, increasing with both parameters as expected (Fig. 14 near here). This compound is also very lossy, with high loss tangent values. At room temperature, κ is frequency-independent, and the experimental data correlate well to the polarizability values obtained from the Clausius-Mossotti relation (73, 74), with $\kappa_{\text{th}} = 9.47$ at 1 MHz, and $\kappa_{\text{exp}} = 10.04$. It must be noted that there is no established literature value for the atomic polarizability of Mo, and as such, it had to be approximated as 4.00, neighboring the Nb value of 3.97. The $x = 2$ compound exhibited little temperature and frequency dependence, and displayed high loss values, which hints at a conduction mechanism (Fig. 15 near here). This sample also corresponds to a Li-rich compound, and the high loss could be due to ionic conduction along the A3 site as mentioned (31, 55-57). However, the lack of vacancies would prevent this pathway; it is more likely that the conduction pathway is three-dimensional, reversibly changing the entire host structure as the Li ions move through interstitial spaces. The room

temperature experimental permittivity (6.24 at 1 MHz) also agrees well with the polarizability obtained from the Clausius-Mossotti relation (9.25 at 1 MHz).

Conclusions

The vacancy concentrations of $\square_{0.25-1/8-x}\text{Li}_x\text{Co}_{3.75-7/8x}\text{V}_{1.5-3/4x}\text{Mo}_{1.5+3/4x}\text{O}_{12}$ were systematically varied as a function of Li content, and all cation sites were adjusted to preserve charge neutrality. A full solid solution was found to exist, a testament to the host structural integrity in light of the high variation in composition. Lattice refinements correlate well to the expected trends based on ionic radii, and detailed structural refinements revealed a strong site preference of Li for the trigonal prismatic site. All samples exhibit Curie-Weiss behavior in the high temperature region, and the peaks below 15 K in the $d\chi/dT$ plots indicate AFM ordering, correlating well to the implications of the Weiss constants. All members exhibited varying shades of green/blue colors, which are tied to the coexistence of LMCT bands and $d-d$ transitions in the optical spectra. The tunable optical band gap (leaning towards the lower wavelength visible region) is notable, and is correlated to the complex substitution scheme. The dielectric constants are low, and the measured compounds exhibit high loss. The temperature and frequency dependence are composition-dependent, and the high loss in the $x = 2$ end member is possibly due to thermally activated three-dimensional conduction.

This study focused on the structure-property relationships of these compounds under non-wetted conditions. The demonstrated structural and compositional flexibility opens questions about the ability of this family to act as cation-exchanging resins in aqueous environments. At the structural level, the dielectric and optical properties of these compounds have implications on the selectivity and strength of the interfacial van der Waals interactions in a three-body system (adsorbent, intervening medium, and

adsorbate), expressed as an effective Hamaker constant within the Lifshitz theory. In extension, the interplay between atomic structure and macroscopic powder processing can influence the performance of the resin due to changes in microstructure, porosity, and surface area. Future work should therefore seek to explore and benchmark the ion exchanging properties of this family of materials with respect to inorganic ions, and possibly organics and biomolecules.

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References:

- (1) S. Vasala, M. Karppinen, $A_2B'B''O_6$ perovskites : A review, *Prog. Solid State Chem.* 43 (2015) 1–36. [doi:10.1016/j.progsolidstchem.2014.08.001](https://doi.org/10.1016/j.progsolidstchem.2014.08.001).
- (2) A. P. Ramirez, Colossal magnetoresistance, *J. Phys. Condens. Matter* 9 (1997) 8171– 8199. [doi:10.1088/0953-8984/9/39/005](https://doi.org/10.1088/0953-8984/9/39/005).
- (3) M. A. Subramanian, G. Aravamudan, G. V. Subba Rao, Oxide pyrochlores A review, *Prog. Solid State Chem.* 15 (1983) 55–143. [doi:10.1016/0079-6786\(83\)90001-8](https://doi.org/10.1016/0079-6786(83)90001-8).
- (4) F. Jona, G. Shirane, R. Pepinsky, Dielectric, X-ray, and optical study of ferroelectric $Cd_2Nb_2O_7$ and related compounds, *Phys. Rev.* 98 (1955) 903–909. [doi:10.1103/ PhysRev.98.903](https://doi.org/10.1103/PhysRev.98.903).
- (5) R. Jin, J. He, S. McCall, C. S. Alexander, F. Drymiotis, D. Mandrus, Superconductivity in the correlated pyrochlore $Cd_2Re_2O_7$, *Phys. Rev. B* 64 (2001) 180503(R). [doi:10.1103/PhysRevB.64.180503](https://doi.org/10.1103/PhysRevB.64.180503).
- (6) A. W. Sleight, New ternary oxides of mercury with the pyrochlore structure, *Inorg. Chem.* 7 (1968) 1704–1708. [doi:10.1021/ic50067a003](https://doi.org/10.1021/ic50067a003).
- (7) M. Subramanian, R. Subramanian, A. Clearfield, Fast ion conduction in the defect pyrochlore system $KB_xW_{2-x}O_6$ ($B = Al, Ti$ and Ta), *Solid State Ionics* 15 (1) (1985) 15–19. [doi:10.1016/0167-2738\(85\)90101-8](https://doi.org/10.1016/0167-2738(85)90101-8).
- (8) M. Subramanian, A. Clearfield, Ionic conductivity of Ag^+ exchanged α -zirconium phosphate, *Mater. Res. Bull.* 19 (9) (1984) 1135 – 1140. [doi:10.1016/ 0025-5408\(84\)90063-1](https://doi.org/10.1016/0025-5408(84)90063-1).
- (9) A. Clearfield, *Inorganic Ion Exchange Materials*, CRC Press, 1982.
- (10) M. Subramanian, R. Subramanian, A. Clearfield, Lithium ion conductors in the system $AB(IV)_2(PO_4)_3$ ($B = Ti, Zr$ and Hf), *Solid State Ionics* 18-19 (1986) 562 – 569. [doi:10.1016/0167-2738\(86\)90179-7](https://doi.org/10.1016/0167-2738(86)90179-7).
- (11) M. Subramanian, P. Rudolf, A. Clearfield, The preparation, structure, and conductivity of scandium-substituted NASICONs, *J. Solid State Chem.* 60 (2) (1985) 172–181. [doi:10.1016/0022-4596\(85\)90109-4](https://doi.org/10.1016/0022-4596(85)90109-4).
- (12) A. Clearfield, M. Subramanian, W. Wang, P. Jerus, The use of hydrothermal procedures to synthesize NASICON and some comments on the stoichiometry of NASICON phases, *Solid State Ionics* 9-10 (1983) 895 – 902. [doi:10.1016/ 0167-2738\(83\)90108-X](https://doi.org/10.1016/0167-2738(83)90108-X).
- (13) P. Rudolf, M. Subramanian, A. Clearfield, J. Jorgensen, The crystal structure of a nonstoichiometric NASICON, *Mater. Res. Bull.* 20 (6) (1985) 643 – 651. [doi: 10.1016/0025-5408\(85\)90142-4](https://doi.org/10.1016/0025-5408(85)90142-4).

- (14) A. Clearfield, M. Subramanian, P. Rudolf, A. Moini, Stoichiometry, structure and conductivity of nasicon, *Solid State Ionics* 18-19 (1986) 13 – 20. [doi:10.1016/0167-2738\(86\)90085-8](https://doi.org/10.1016/0167-2738(86)90085-8).
- (15) J. P. Smit, P. C. Stair, K. R. Poeppelmeier, The adaptable lyonsite structure, *Chem. Eur. J.* 12 (2006) 5944–5953. [doi:10.1002/chem.200600294](https://doi.org/10.1002/chem.200600294).
- (16) G. W. Smith, Crystal structure of orthorhombic cobalt molybdate, *Nat.* 188 (1960) 306–308. [doi:10.1038/188306b0](https://doi.org/10.1038/188306b0).
- (17) J. A. Ibers, G. W. Smith, Crystal structure of a sodium cobalt molybdate, *Act. Crystallogr.* 17 (1964) 190–197. [doi:10.1107/S0365110X64000482](https://doi.org/10.1107/S0365110X64000482).
- (18) R. F. Klevtsova, S. A. Magarill, Crystal structure of lithium-ferriferrous molybdates $\text{Li}_3\text{Fe}(\text{MoO}_4)_3$ and $\text{Li}_2\text{Fe}_2(\text{MoO}_4)_3$, *Kristallografiya* 15 (1970) 710–715.
- (19) J. M. Hughes, S. J. Starkey, M. L. Malinconico, L. L. Malinconico, Lyonsite, $\text{Cu}^{2+}_3\text{Fe}^{3+}_4(\text{VO}_4)^{3-}_6$, a new fumarolic sublimate from Izalco Volcano, El Salvador; descriptive mineralogy and crystal structure, *Am. Mineral.* 72 (1987) 1000-1005.
- (20) C. R. Stanek, C. Jiang, B. P. Uberuaga, K. E. Sickafus, A. R. Cleave, R. W. Grimes, Predicted structure and stability of $\text{A}_4\text{B}_3\text{O}_{12}$ δ -phase compositions, *Phys. Rev. B* 80 (2009) 174101. [doi:10.1103/PhysRevB.80.174101](https://doi.org/10.1103/PhysRevB.80.174101).
- (21) L. Fang, H. Zhang, Q. Yu, H. Su, B. Wu, X. Cui, $\text{Sr}_3\text{LaNb}_3\text{O}_{12}$: A new low loss and temperature stable $\text{A}_4\text{B}_3\text{O}_{12}$ -type microwave dielectric ceramic, *J. Am. Ceram. Soc.* 92.
- (22) L. Fang, S.-S. Meng, H. Zhang, Z.-Q. Liu, $\text{Ba}_2\text{La}_2\text{TiNb}_2\text{O}_{12}$: A new microwave dielectric of $\text{A}_4\text{B}_3\text{O}_{12}$ -type cation-deficient perovskites, *Mater. Lett.* 60 (9) (2006) 1147 – 1150. [doi:10.1016/j.matlet.2005.10.097](https://doi.org/10.1016/j.matlet.2005.10.097).
- (23) R. J. Evans, L. A. Groat, Structure and topology of dumortierite and dumortierite-like materials, *Can. Mineral.* 50 (5) (2012) 1197–1231. [doi:10.3749/canmin.50.5.1197](https://doi.org/10.3749/canmin.50.5.1197).
- (24) A. Pieczka, R. Evans, E. Grew, L. Groat, C. Ma, G. Rossman, The dumortierite supergroup. I. A new nomenclature for the dumortierite and holtite groups, *Mineral. Mag.* 77 (2013) 2825–2839. [doi:10.1180/minmag.2013.077.6.09](https://doi.org/10.1180/minmag.2013.077.6.09).
- (25) X. Wang, J. D. Pless, D. A. Vander Griend, P. C. Stair, K. R. Poeppelmeier, Z. Hu, J. D. Jorgensen, Vanadium and molybdenum disorder in $\text{M}_{2.5}\text{VMoO}_8$ (M = Mg, Mn, and Zn) determined with neutron powder diffraction and phase formation studies of $\text{Mg}_{2.5+x}\text{V}_{1+2x}\text{Mo}_{1-2x}\text{O}_8$, *J. Alloys Compd.* 379 (2004) 87–94. [doi:10.1016/j.jallcom.2004.02.015](https://doi.org/10.1016/j.jallcom.2004.02.015).
- (26) J. P. Smit, H. Kim, I. Saratovsky, K. B. Stark, G. Fitzgerald, G. W. Zajac, J. Gaillard, K. R. Poeppelmeier, P. C. Stair, A spectroscopic and computational investigation of the vanadomolybdate local structure in the lyonsite phase $\text{Mg}_{2.5}\text{VMoO}_8$, *Inorg. Chem.* 46 (2007) 6556–6564. [doi:10.1021/ic7006815](https://doi.org/10.1021/ic7006815).
- (27) L. Katz, A. Kasenally, L. Kihlberg, The crystal structure of the reduced copper molybdate $\text{Cu}_{4-x}\text{Mo}_3\text{O}_{12}$ (x approx.= 0.15), *Acta Crystallogr., Sect. B: Struct. Sci* 27 (1971) 2071–2077. [doi:10.1107/S0567740871005387](https://doi.org/10.1107/S0567740871005387).
- (28) O. Sedello, H. Müller-Buschbaum, Synthese und kristallstruktur von $(\text{Cu,Fe})_{3.63}\text{Mo}_3\text{O}_{12}$: Ein oxometallat mit eindimensional flächenverknüpften oktaederketten / Synthesis and crystal structure of $(\text{Cu,Fe})_{3.63}\text{Mo}_3\text{O}_{12}$: An oxometallate showing one-dimensional chains of face sharing octahedra, *Z. Naturforsch., B: Chem. Sci.* 51 (1996) 90–94. [doi:10.1515/znB-1996-0117](https://doi.org/10.1515/znB-1996-0117).
- (29) O. Sedello, H. Müller-Buschbaum, Zur kristallstruktur von $(\text{Cu,Mn})_{3.66}\text{Mo}_3\text{O}_{12}$ / On the crystal structure of $(\text{Cu,Mn})_{3.66}\text{Mo}_3\text{O}_{12}$, *Z. Naturforsch., B: Chem. Sci.* 51 (1996) 447–449. [doi:10.1515/znB-1996-0325](https://doi.org/10.1515/znB-1996-0325).

- (30) H. Szillat, H. Müller-Buschbaum, Zur kenntnis des oxocuprats $(\text{Cu},\text{Co})_{3.75}\text{Mo}_3\text{O}_{12}$ / On the oxocuprate $(\text{Cu},\text{Co})_{3.75}\text{Mo}_3\text{O}_{12}$, Z. Naturforsch., B: Chem. Sci. 50 (1995) 707–711. [doi:10.1515/znB-1995-0503](https://doi.org/10.1515/znB-1995-0503).
- (31) L. Sebastian, Y. Piffard, a. K. Shukla, F. Taulelle, J. Gopalakrishnan, Synthesis, structure and lithium-ion conductivity of $\text{Li}_{2-2x}\text{Mg}_{2+x}(\text{MoO}_4)_3$ and $\text{Li}_3\text{M}(\text{MoO}_4)_3$ ($\text{M}^{\text{III}} = \text{Cr}, \text{Fe}$), J. Mater. Chem. 13 (2003) 1797. [doi:10.1039/b301189e](https://doi.org/10.1039/b301189e).
- (32) D. E. Bugaris, H.-C. zur Loye, $\text{Li}_3\text{Al}(\text{MoO}_4)_3$, a lyonsite molybdate., Acta Crystallogr., Sect. C: Cryst. Struct. Commun. 68. [doi:10.1107/S0108270112020513](https://doi.org/10.1107/S0108270112020513).
- (33) U. Kolitsch, E. Tillmanns, $\text{Li}_3\text{Sc}(\text{MoO}_4)_3$: substitutional disorder on three (Li,Sc) sites, Acta Crystallogr., Sect. E: Struct. Rep. Online 59 (2003) i55–i58. [doi:10.1107/S1600536803004872](https://doi.org/10.1107/S1600536803004872).
- (34) M. Wiesmann, M. Geselle, H. Weitzel, H. Fueß, Crystal structure of lithium copper molybdate, $\text{Li}_2\text{Cu}_2(\text{MoO}_4)_3$, Z. Kristallogr. 209 (1994) 615. [doi:10.1524/zkri.1994.209.7.615](https://doi.org/10.1524/zkri.1994.209.7.615).
- (35) M. Wiesmann, I. Svoboda, H. Weitzel, H. Fuess, Crystal structure of lithium cobalt molybdate, $\text{Li}_2\text{Co}_2(\text{MoO}_4)_3$, Z. Kristallogr. 210 (1995) 1995. [doi:10.1524/zkri.1995.210.7.525](https://doi.org/10.1524/zkri.1995.210.7.525).
- (36) L. Xue, Y. Wang, P. Lv, D. Chen, Z. Lin, J. Liang, F. Huang, Z. Xie, Growth, structures, and properties of $\text{Li}_2\text{Zn}_2(\text{MoO}_4)_3$ and Co-doped $\text{Li}_2\text{Zn}_2(\text{MoO}_4)_3$, Cryst. Growth Des. 9 (2009) 914–920. [doi:10.1021/cg800700h](https://doi.org/10.1021/cg800700h).
- (37) M. Ozima, S. Sato, T. Zoltai, The crystal structure of a lithiumnickel molybdate, $\text{Li}_2\text{Ni}_2\text{Mo}_3\text{O}_{12}$, and the systematics of the structure type, Acta Crystallogr., Sect. B: Struct. Sci 33 (1977) 2175–2181. [doi:10.1107/S0567740877007973](https://doi.org/10.1107/S0567740877007973).
- (38) B. M. Wanklyn, F. R. Wondre, W. Davison, Flux growth of crystals of some magnetic oxide materials: $\text{Mn}_7\text{SiO}_{12}$, CuO , MCr_2O_4 , MTiO_3 , Ni_2NbBO_6 , MMoO_4 and $\text{Li}_2\text{M}_2(\text{MoO}_4)_3$, ($\text{M} = \text{Mn}, \text{Co}, \text{Ni}$), J. Mater. Sci. 11 (1976) 1607–1614. [doi:10.1007/BF00737516](https://doi.org/10.1007/BF00737516).
- (39) J. P. Smit, T. M. McDonald, K. R. Poeppelmeier, $\text{Li}_3\text{Ti}_{0.75}(\text{MoO}_4)_3$: A lyonsite-type oxide, Solid State Sci. 10 (2008) 396–400.
- (40) M. Lafontaine, J. Grenéche, Y. Lalignant, G. Férey, $\beta\text{-Cu}_3\text{Fe}_4(\text{VO}_4)_6$: Structural study and relationships; physical properties, J. Solid State Chem. 1–10 [doi:10.1006/jssc.1994.1001](https://doi.org/10.1006/jssc.1994.1001).
- (41) X. Wang, K. R. Heier, C. L. Stern, K. R. Poeppelmeier, Crystal growth and structure of $\text{Mn}_{2.47}\text{V}_{0.94}\text{Mo}_{1.06}\text{O}_8$, J. Alloys Compd. 267 (1998) 79–85. [doi:10.1016/S0925-8388\(97\)00574-4](https://doi.org/10.1016/S0925-8388(97)00574-4).
- (42) M. Kurzawa, M. Bosacka, P. Jakubus, The structure and selected properties of $\text{Co}_{2.5}\text{VMoO}_8$, J. Mater. Sci. 38 (2003) 3137–3142. [doi:10.1023/A:1024785415727](https://doi.org/10.1023/A:1024785415727).
- (43) X. Wang, K. R. Heier, C. L. Stern, K. R. Poeppelmeier, Crystal structure of $\text{Zn}_{3.77}\text{V}_{1.54}\text{Mo}_{1.46}\text{O}_{12}$ containing ZnO_6 trigonal prisms, J. Alloys Compd. 255 (1997) 190–194. [doi:10.1016/S0925-8388\(96\)02812-5](https://doi.org/10.1016/S0925-8388(96)02812-5).
- (44) J. N. Tang, J. Li, M. A. Subramanian, Structural investigation and selected properties of $\text{Zn}_{2.5-x}\text{Co}_x\text{VMoO}_8$ lyonsites, J. Solid State Chem. 266 (2018) 155–160. [doi:10.1016/j.jssc.2018.07.007](https://doi.org/10.1016/j.jssc.2018.07.007).
- (45) J. N. Tang, M. A. Subramanian, Novel compositions and physical property comparisons for $(\text{A},\text{A}')_{2.5}\text{VMoO}_8$ lyonsites ($\text{A} = \text{Zn}, \text{A}' = \text{Mn}, \text{Ni}, \text{Cu}$), J. Solid State Chem. 271 (2019) 154–161. [doi:10.1016/j.jssc.2018.12.045](https://doi.org/10.1016/j.jssc.2018.12.045).
- (46) H. A. Jahn, E. Teller, Stability of polyatomic molecules in degenerate

- electronic states: I-orbital degeneracy, Proc. R. Soc. London A 161 (1937) 220–235. [doi: 10.1098/rspa.1937.0142](https://doi.org/10.1098/rspa.1937.0142).
- (47) A. A. Belik, A. P. Malakho, K. V. Pokholok, B. I. Lazoryak, Phase formation in $\text{Cu}_{3+1.5x}\text{R}_{4-x}(\text{VO}_4)_6$ ($\text{R} = \text{Fe}$ and Cr) systems: crystal structure of $\text{Cu}_{2.5}\text{Fe}_{4.333}(\text{VO}_4)_6$, $\text{Cu}_4\text{Fe}_{3.333}(\text{VO}_4)_6$, and $\text{Cu}_{4.05}\text{Cr}_{3.3}(\text{VO}_4)_6$, J. Solid State Chem. 156 (2001) 339–348. [doi:10.1006/jssc.2000.9004](https://doi.org/10.1006/jssc.2000.9004).
- (48) Z. Mu, E. Song, D. Zhu, J. Feng, Y. Yang, Red phosphor $\text{Li}_2\text{Mg}_2(\text{WO}_4)_3\text{:Eu}^{3+}$ with lyonsite structure for near ultraviolet light-emitting diodes, Displays 43 (2016) 18–22. [doi:10.1016/j.displa.2016.04.001](https://doi.org/10.1016/j.displa.2016.04.001).
- (49) J. D. Pless, H.-S. Kim, J. P. Smit, X. Wang, P. C. Stair, K. R. Poeppelmeier, Structure of $\text{Mg}_{2.56}\text{V}_{1.12}\text{W}_{0.88}\text{O}_8$ and vibrational raman spectra of $\text{Mg}_{2.5}\text{VWO}_8$ and $\text{Mg}_{2.5}\text{VMoO}_8$, Inorg. Chem. 45 (2006) 514–520. [doi:10.1021/ic051740h](https://doi.org/10.1021/ic051740h).
- (50) Q. Liao, Y. Wang, F. Jiang, D. Guo, Ultra-low fire glass-free $\text{Li}_3\text{FeMo}_3\text{O}_{12}$ microwave dielectric ceramics, J. Am. Ceram. Soc. 97 (2014) 2394–2396. [doi:10.1111/jace.13073](https://doi.org/10.1111/jace.13073).
- (51) D. Zhou, C. A. Randall, L. Pang, H. Wang, X. Wu, J. Guo, G. Zhang, L. Shui, X. Yao, Microwave dielectric properties of $\text{Li}_2(\text{M}^{2+})_2\text{Mo}_3\text{O}_{12}$ and $\text{Li}_3(\text{M}^{3+})\text{Mo}_3\text{O}_{12}$ ($\text{M} = \text{Zn}, \text{Ca}, \text{Al}$, and In) lyonsite-related-type ceramics with ultra-low sintering temperatures, J. Am. Ceram. Soc. 94 (2011) 802–805. [doi:10.1111/j.1551-2916.2010.04148.x](https://doi.org/10.1111/j.1551-2916.2010.04148.x).
- (52) J. Zhang, R. Zuo, Synthesis and microwave dielectric properties of $\text{Li}_2\text{Mg}_2(\text{WO}_4)_3$ ceramics, Mater. Lett. 158 (2015) 92–94. [doi:10.1016/j.matchemphys.2009.08.037](https://doi.org/10.1016/j.matchemphys.2009.08.037).
- (53) D. Wang, Z. Zou, J. Ye, A novel series of photocatalysts $\text{M}_{2.5}\text{VMoO}_8$ ($\text{M} = \text{Mg}, \text{Zn}$) for O_2 evolution under visible light irradiation, Catal. Today 93–95 (2004) 891–894. [doi:10.1016/j.cattod.2004.06.090](https://doi.org/10.1016/j.cattod.2004.06.090).
- (54) K. Gourai, A. El Bouari, B. Belhorma, L. Bih, Adsorption of methylene blue on the $\text{Li}_3\text{Fe}_{1-x}\text{Cr}_x(\text{MoO}_4)_3$ ($x=0,0.5,1$) lyonsite phases, Am. J. Chem. 6 (2016) 47–54. [doi:10.5923/j.chemistry.20160602.04](https://doi.org/10.5923/j.chemistry.20160602.04).
- (55) S. Prabakaran, S. Ramesh, M. Michael, K. Begam, Characterization of soft-combustion-derived NASICON-type $\text{Li}_2\text{Co}_2(\text{MoO}_4)_3$ for lithium batteries, Mater. Chem. Phys. 87 (2–3) (2004) 318–326. [doi:10.1016/j.matchemphys.2004.05.041](https://doi.org/10.1016/j.matchemphys.2004.05.041).
- (56) S. Prabakaran, A. Fauzi, M. Michael, K. Begam, New NASICON-type $\text{Li}_2\text{Ni}_2(\text{MoO}_4)_3$ as a positive electrode material for rechargeable lithium batteries, Solid State Ionics 171 (3–4) (2004) 157–165. [doi:10.1016/j.ssi.2004.05.001](https://doi.org/10.1016/j.ssi.2004.05.001).
- (57) M. Alvarez-Vega, U. Amador, M. E. Arroyo-de Dompablo, Electrochemical study of $\text{Li}_3\text{Fe}(\text{MoO}_4)_3$ as positive electrode in lithium cells, J. Electrochem. Soc. 152 (2005) A1306–A1311. [doi:10.1149/1.1925069](https://doi.org/10.1149/1.1925069).
- (58) J. P. Smit, H.-S. Kim, J. D. Pless, P. C. Stair, K. R. Poeppelmeier, Probing the vanadyl and molybdenyl bonds in complex vanadomolybdate structures., Inorg. Chem. 45 (2) (2006) 521–8. [doi:10.1021/ic051741+](https://doi.org/10.1021/ic051741+).
- (59) J. W. Heo, J. Hyoung, S.-T. Hong, Unveiling the intercalation mechanism in $\text{Fe}_2(\text{MoO}_4)_3$ as an electrode material for Na-ion batteries by structural determination, Inorg. Chem. 2. [doi:10.1021/acs.inorgchem.8b01244](https://doi.org/10.1021/acs.inorgchem.8b01244).
- (60) V. F. Sears, Neutron scattering lengths and cross sections, Neutron News 3 (1992) 26–37. [doi:10.1080/10448639208218770](https://doi.org/10.1080/10448639208218770).
- (61) J. Wang, B. H. Toby, P. L. Lee, L. Ribaud, S. M. Antao, C. Kurtz, M. Ramanathan, B. Von Dreele, M. A. Beno, A dedicated powder diffraction beamline at the Advanced Photon Source: Commissioning and early operational

- results, *Rev. Sci. Instrum.* 79 (8) (2008) 085105. [doi:10.1063/1.2969260](https://doi.org/10.1063/1.2969260).
- (62) B. H. Toby, EXPGUI, a graphical user interface for GSAS, *J. Appl. Crystallogr.* 34 (2001) 210–213. [doi:10.1107/S0021889801002242](https://doi.org/10.1107/S0021889801002242).
- (63) A. C. Larson, R. B. Von Dreele, General Structure Analysis System (GSAS), Tech. rep., Los Alamos National Laboratory Report LAUR 86-748 (2000).
- (64) P. Kubelka, F. Munk, An article on optics of paint layers, *Z. Tech. Phys.* 12 (1931) 593–601.
- (65) R. D. Shannon, Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides, *Acta Crystallogr., Sect. A: Found. Crystallogr.* 32 (1976) 751–767. [doi:10.1107/S0567739476001551](https://doi.org/10.1107/S0567739476001551).
- (66) S. F. Solodovnikov, Z. A. Solodovnikova, E. S. Zolotova, L. I. Yudanov, T. Y. Kardash, A. A. Pavlyuk, V. A. Nadolnny, Revised phase diagram of Li_2MoO_4 - ZnMoO_4 system, crystal structure and crystal growth of lithium zinc molybdate, *J. Solid State Chem.* 182 (7) (2009) 1935–1943. [doi:10.1016/j.jssc.2009.04.036](https://doi.org/10.1016/j.jssc.2009.04.036).
- (67) M. C. Viola, M. J. Martínez-Lope, J. A. Alonso, J. L. Martínez, J. M. De Paoli, Pagola, J. C. Pedregosa, M. T. Fernández-Díaz, R. E. Carbonio, Structure and magnetic properties of Sr_2CoWO_6 : an ordered double perovskite containing $\text{Co}^{2+}(\text{HS})$ with unquenched orbital magnetic moment, *Chem. Mater.* 15 (2003) 1655–1663. [doi:10.1021/cm0208455](https://doi.org/10.1021/cm0208455).
- (68) F. E. Mabbs, D. J. Machin, *Magnetism and Transition Metal Complexes*, Chapman and Hall, London, 1973.
- (69) A. E. Smith, M. C. Comstock, M. A. Subramanian, Spectral properties of the UV absorbing and near-IR reflecting blue pigment, $\text{YIn}_{1-x}\text{Mn}_x\text{O}_3$, *Dyes Pigm.* 133 (2016) 214–221. [doi:10.1016/j.dyepig.2016.05.029](https://doi.org/10.1016/j.dyepig.2016.05.029).
- (70) R. Köferstein, L. Jäger, S. G. Ebbinghaus, Magnetic and optical investigations on LaFeO_3 powders with different particle sizes and corresponding ceramics, *Solid State Ionics* 249-250 (2013) 1–5. [doi:10.1016/j.ssi.2013.07.001](https://doi.org/10.1016/j.ssi.2013.07.001).
- (71) R. López, R. Gómez, Band-gap energy estimation from diffuse reflectance measurements on sol-gel and commercial TiO_2 : A comparative study, *J. Sol-Gel Sci. Technol.* 61 (1) (2012) 1–7. [doi:10.1007/s10971-011-2582-9](https://doi.org/10.1007/s10971-011-2582-9).
- (72) J. Tauc, R. Grigorovici, A. Vancu, Optical properties and electronic structure of amorphous germanium, *Physica Status Solidi B* 15 (2) (1966) 627–637. [doi:10.1002/pssb.19660150224](https://doi.org/10.1002/pssb.19660150224).
- (73) A. R. West, *Solid State Chemistry and its Applications*, 2nd Edition, Student Edition, Wiley, Chichester, 2014.
- (74) W. D. Kingery, H. K. Bowen, D. R. Uhlmann, *Introduction to Ceramics*, 2nd Edition, Wiley, New York, 1976.

Figure 1. The NASICON structure, as viewed along the c axis, with unit cell outline shown in dotted lines. Na = white, ZrO_6 octahedra = green, SiO_4 tetrahedra = blue.

Figure 2. The lyonsite crystal structure as viewed along the a axis (A1 = blue, A2 = green, A3 = gray, M1, M2 = purple). Left: primary tunnel motif of the lyonsite. Right: representation of broader structure, with unit cell outline shown in dashed lines.

Figure 3. The primary tunnel motif of the $\text{Al}_7\text{BO}_3(\text{SiO}_4)_3\text{O}_3$ (*Pmcn*) member of the dumortierite mineral family. AlO_6 face-sharing octahedra = red, AlO_6 edge-sharing octahedra = purple, black, AlO_6 face- and edge-sharing octahedra = dark green, SiO_4 tetrahedra = gray, BO_3 trigonal planes = green, Al = pale blue, Si = blue, B = green.

Figure 4. Powder X-ray diffraction patterns for $\square_{0.25-1/8 x}\text{Li}_x\text{Co}_{3.75-7/8 x}\text{V}_{1.5-3/4 x}\text{Mo}_{1.5+3/4 x}\text{O}_{12}$. Reference *hkl* tick marks: $x = 0$ end member (green), $x = 2$ end member (blue).

Figure 5. Lattice parameters for $\square_{0.25-1/8} \text{Li}_x \text{Co}_{3.75-7/8} \text{V}_{1.5-3/4} \text{Mo}_{1.5+3/4} \text{O}_{12}$. The ranges for the a , b , and c parameters are set to the same size (0.7 Å) for direct comparisons.

Figure 6. CW neutron diffraction pattern (top) and synchrotron X-ray diffraction pattern (bottom) for $\square_{0.25-1/8} \text{Li}_x \text{Co}_{3.75-7/8} \text{V}_{1.5-3/4} \text{Mo}_{1.5+3/4} \text{O}_{12}$ at $x = 1.25$. Display includes calculated intensities (red), difference curve (blue), and allowed reflections for $Pnma$ (magenta).

Figure 7. Magnetic susceptibility and inverse susceptibility (designated by arrow) plots for $\square_{0.25-1/8} \text{Li}_x \text{Co}_{3.75-7/8x} \text{V}_{1.5-3/4x} \text{Mo}_{1.5+3/4x} \text{O}_{12}$ as a function of temperature T in K.

Figure 8. Derivative of magnetic susceptibility plots for $\square_{0.25-1/8} \text{Li}_x \text{Co}_{3.75-7/8x} \text{V}_{1.5-3/4x} \text{Mo}_{1.5+3/4x} \text{O}_{12}$ as a function of temperature T in K.

Figure 9. Powder pictures for $\square_{0.25-1/8} \text{Li}_x \text{Co}_{3.75-7/8x} \text{V}_{1.5-3/4x} \text{Mo}_{1.5+3/4x} \text{O}_{12}$, arranged as a function of x (left to right).

Figure 10. Visible wavelength diffuse reflectance spectra for $\square_{0.25-1/8 x}\text{Li}_x\text{Co}_{3.75-7/8 x}\text{V}_{1.5-3/4 x}\text{Mo}_{1.5+3/4 x}\text{O}_{12}$. Absorbance values were normalized to the high energy peak.

Figure 11. Vis-NIR diffuse reflectance spectra for $\square_{0.25-1/8 x}\text{Li}_x\text{Co}_{3.75-7/8 x}\text{V}_{1.5-3/4 x}\text{Mo}_{1.5+3/4 x}\text{O}_{12}$.

Figure 12. McLean analysis for $\square_{0.25-1/8} \text{Li}_x \text{Co}_{3.75-7/8x} \text{V}_{1.5-3/4x} \text{Mo}_{1.5+3/4x} \text{O}_{12}$.

Figure 13. Tauc plots for $\square_{0.25-1/8} \text{Li}_x \text{Co}_{3.75-7/8x} \text{V}_{1.5-3/4x} \text{Mo}_{1.5+3/4x} \text{O}_{12}$.

Figure 14. Dielectric constant κ and loss tangent $\tan \delta$ plots for the $x = 0$ member of the $\square_{0.25-1/8} \text{Li}_x \text{Co}_{3.75-7/8x} \text{V}_{1.5-3/4x} \text{Mo}_{1.5+3/4x} \text{O}_{12}$ solid solution.

Figure 15. Dielectric constant κ and loss tangent $\tan \delta$ plots for the $x = 2$ member of the $\square_{0.25-1/8x}\text{Li}_x\text{Co}_{3.75-7/8x}\text{V}_{1.5-3/4x}\text{Mo}_{1.5+3/4x}\text{O}_{12}$ solid solution.

Table 1. Unit cell coordinates, occupancies, and displacement parameters for $\square_{0.25-1/8} x\text{Li}_x\text{Co}_{3.75-7/8x}\text{V}_{1.5-3/4x}\text{Mo}_{1.5+3/4x}\text{O}_{12}$ ($Pnma$). $a = 5.0850(1) \text{ \AA}$, $b = 10.442(1) \text{ \AA}$, $c = 17.553(1) \text{ \AA}$, $V = 932.05(1) \text{ \AA}^3$. Reliability parameters $\chi^2 = 5.005$, $wR_p = 10.19 \%$.

Atom	Site	x	y	z	Occ.	$U_{iso} (\text{\AA}^2)$
Li/Co (A1)	4c	0.1066(4)	1/4	0.2486(1)	0.34(1)/ 0.57(1)	0.0188(8)
Li/Co (A2)	8d	0.2481(2)	0.0756(1)	0.5268(1)	0.21(1)/ 0.79(1)	0.0085(3)
Li/Co (A3)	4c	0.2496(8)	1/4	0.6965(2)	0.71(1)/ 0.29(1)	0.0098(10)
V/Mo (M1)	4c	0.2808(2)	1/4	0.0570(1)	0.31(1)/ 0.69(1)	0.0099(2)
V/Mo (M2)	8d	0.2796(1)	0.5283(1)	0.3432(1)	0.16(1)/ 0.85(1)	0.0121(1)
O1	4c	0.3615(8)	1/4	0.1517(2)	1.0	0.0218(11)
O2	4c	0.0586(9)	1/4	0.5044(2)	1.0	0.0180(11)
O3	8d	0.0838(6)	0.1156(3)	0.0371(2)	1.0	0.0197(8)
O4	8d	0.0650(6)	0.6164(3)	0.1264(2)	1.0	0.0172(7)
O5	8d	0.0799(7)	0.6240(3)	0.2849(2)	1.0	0.0233(8)
O6	8d	0.3574(6)	0.1144(3)	0.2956(2)	1.0	0.0212(8)
O7	8d	0.0854(6)	0.0102(3)	0.4254(2)	1.0	0.0211(8)

Table 2. Weiss constants and magnetic moments for $\square_{0.25-1/8} x\text{Li}_x\text{Co}_{3.75-7/8x}\text{V}_{1.5-3/4x}\text{Mo}_{1.5+3/4x}\text{O}_{12}$, along with the T range used in Curie-Weiss analysis. The T range corresponds to the most linear region of the inverse susceptibility curve, from 300 K down to at least twice that of the transition temperature T_N .

x	θ_W	$\mu_{\text{eff}} (\mu_B)$	Modeling T
0.5	-61.7	5.21	183–300K
1	-46.7	5.16	168–300K
1.5	-49.4	5.16	149–300K
2	-43.1	5.23	142–300K

Table 3. Possible band-to-band absorption transitions for a given material.

n	Type	Selection
2	Direct	Allowed
2/3	Direct	Forbidden
1/2	Indirect	Allowed
1/3	Indirect	Forbidden

Table 4. Estimated optical band gaps for $\square_{0.25-1/8} x\text{Li}_x\text{Co}_{3.75-7/8x}\text{V}_{1.5-3/4x}\text{Mo}_{1.5+3/4x}\text{O}_{12}$.

x	E_g (eV)
0.5	2.57
1	2.66
1.5	2.76
2	3.00