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Structural investigation and selected properties of $Zn_{2.5-x}Co_xVMoO_8$ lyonsites

Joseph N. Tang, Jun Li, M.A. Subramanian*

Department of Chemistry, Oregon State University, Corvallis, OR 97331, United States

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ABSTRACT

The lyonsites are an underexplored crystal structure type; with precedent for compositional flexibility, this family of compounds has potential uses as inexpensive functional materials. This work examines cationic substitutions into $Zn_{2.5-x}Co_xVMoO_8$ and the subsequent effect on the Zn site preference. All samples were annealed between 700 and 1000 °C, resulting in green-colored pastilles. Powder X-ray diffraction (PXRD) and neutron powder diffraction (NPD) confirmed the solid solution range to be $0 \leq x \leq 2.5$, with all members isostructural with the parent compound. Magnetic susceptibility measurements indicated Curie-Weiss behavior in the high T region, confirming the presence of Co(II). Diffuse reflectance measurements are also presented to explain the color mechanisms of this series.

1. Introduction

Exploratory work in solid state chemistry has involved many structure types in the past century; while some structures are more ubiquitous in the literature, the understudied systems are no less worthy of investigation. In 2006, one of these lesser known families, the lyonsites, was given a thorough treatment in a seminal review [1], and what follows here is a brief recapitulation of that work. While the perovskite [2], pyrochlore [3], and spinel [4] families have extensive histories, the lyonsite had its beginnings in the laboratory, being first synthesized in 1960 [5], and a general structure determination carried out in 1964 [6]. Contrary to the typical trend of mineralogy inspiring chemistry, a natural lyonsite was not discovered until 1987, in which the iron-copper vanadate was found in El Salvador [7]. Since then, various lyonsite compounds have found potential uses as optical filters [8], photocatalytic materials [9,10], and microwave dielectrics [11–13].

The lyonsites takes the general formula $A_4M_3O_{12}$; other common formula expressions involve simple multipliers to clarify stoichiometric features or to facilitate ease of reading, as in the case of $A_{2.5}M_2O_8$. The connectivity within this oxygen framework consists of face- and edge-shared AO_6 polyhedra, the vertices of each polyhedron connected to isolated MO_4 tetrahedra. Typically, two cations occupy the A sites, the ionic radius range of which are empirically generalized to 0.46 to 1.02 Å [1]. The oxidation states of these cations can range between +1 and +5 [1]. The M sites are limited to smaller, highly charged cations that prefer four-fold coordination environments [14,15]. The A sites are further distinguished by polyhedral sharing: A1 (face-shared octahedra), A2 (edge-shared octahedra), and A3 (edge-shared trigonal prisms) (Fig. 1).

Known lyonsites typically contain two cations in the A site, usually Li(I), a transition metal (TM), and vacancies, the ratios and distribution of which are dictated primarily by charge separation [16–20]. The related compound $Zn_{2.5}VMoO_8$ is one of the few known lyonsites in which only one cation (and corresponding vacancies) occupy the A site [14,15,21,22]. Currently, the site preference for Zn(II) in this structure is unknown. This study therefore explores the structural behavior when the A site undergoes isovalent substitution with Co(II). Conventionally, Co(II)-containing oxides are blue in color, such as in the case of $CoAl_2O_4$ (spinel structure) [23]. The coloration is due to *d*-*d* transitions in the Co-containing tetrahedral site; in addition, the geometric arrangement of the Co(II) ions allows for atypical magnetic behaviors. The other end member, $Co_{2.5}VMoO_8$, has been reported, but no physical properties have been explored [24]. Thus, this work will also detail some physical properties of the solid solution.

2. Experimental

Stoichiometric ratios of ZnO (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 decarbonated at 500 °C for 6 h prior to annealing. All samples were annealed between 700 and 1000 °C.

X-ray diffraction data were collected using a benchtop Rigaku MINIFLEX II diffractometer using Cu Kα radiation and a graphite

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* Corresponding author.
E-mail address: mas.subramanian@oregonstate.edu (M.A. Subramanian).

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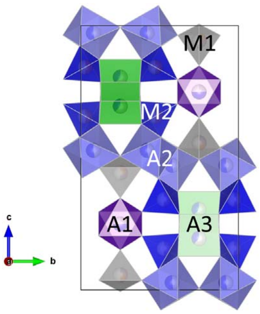

Fig. 1. Lyonsite crystal structure (A1 =purple, A2 =blue, A3 =green, M1 =gray, M2 =navy).

monochromator. Le Bail refinements were performed with KCl as an internal standard. A sample at the midpoint of the solid solution was loaded in a 6 mm vanadium sample can, and room temperature time-of-flight (TOF) neutron powder diffraction data were obtained from Oak Ridge National Laboratory, on the BL-11A POWGEN beamline. Subsequent Rietveld analysis was performed via the General Structure Analysis System (GSAS) software with the EXPGUI interface [25].

Zero-field-cooled (ZFC) DC magnetization experiments were conducted using a Quantum Design PPMS, from 5 to 300 K, and a Quantum Design SQUID MPMS. Determination of the effective magnetic moments (in Bohr magnetons, μ_B) were done by fitting the inverse susceptibility curves to the reciprocal of the Curie-Weiss Law (Eq. (1)),

$$\frac{1}{\chi_M} = \frac{T-\theta}{C}, \tag{1}$$

extracting the Curie constant C, and subsequent conversion to magnetic moment via $\mu_{eff} = 2.84\sqrt{C}$. UV–Vis diffuse reflectance data were obtained using an Ocean Optics HR-4000 spectrophotometer, with an MgO reference. The data, R, were then converted to absorbance units A via the Kubelka-Munk relationship (Eq. (2)). Vis-NIR reflectance data were collected via a Jasco V-670 spectrophotometer (out to 2500 nm).

$$A = \frac{(1-R)^2}{2R} \tag{2}$$

3. Results/Discussion

3.1. Crystal structure

A full solid solution was found to exist along the $0 \le x \le 2.5$ range. However, due to the similarity in Shannon radii (Zn(II): 0.74 Å and Co(II): 0.745 Å) [26], lattice shifts are difficult to notice upon visual inspection of the XRD patterns (Fig. 2). The a and b parameter are shown to be relatively constant, while the c parameter (and in extension, the unit cell volume) decreases (from 17.63 Å to 17.52 Å) with increasing Co content (Fig. 3). The decrease along the c axis is counterintuitive, considering the Shannon radius for Co(II) is larger than that of Zn(II). Initially, this atypical behavior was attributed to the unknown ionic radii of Co(II) and Zn(II) in the trigonal prismatic site. This lack of reliable radii data for the TP site is due to the small number of known compounds exhibiting this coordination environment. Therefore, it is conjectured that if the Co(II) radius is smaller than that of Zn(II) in that coordination environment, it is conceivable that the unit cell would shrink. Radius determination is difficult, though, due to the asymmetric nature of the trigonal prism in this structure.

TOF neutron diffraction analysis was conducted on the $x = 1.25$ composition. The Rietveld refinement yielded a refined formula of $Zn_{1.20}Co_{1.30}V_{0.98}Mo_{1.02}O_8$ (or if adhering to the $A_4M_3O_{12}$ formula, $\square_{0.25}Zn_{1.80}Co_{1.95}V_{1.47}Mo_{1.53}O_{12}$), correlating well to the nominal composition (Fig. 4). Due to the presence of unavoidable vacancies in this system, several considerations had to be made. As a starting point, Zn, Co, and a vacancy, $\square$, were equally distributed across the three A sites, and V and Mo across the M sites. Vacancies were refined to localize on the A1 site, which consists of face-sharing octahedra. Localization along this chain of octahedra makes intuitive and chemical sense, as vacancies would stabilize the cationic repulsion that would result from the close proximity of Zn(II) and Co(II). This behavior is also corroborated from prior work on vanadomolybdate lyonsites [1,21,22].

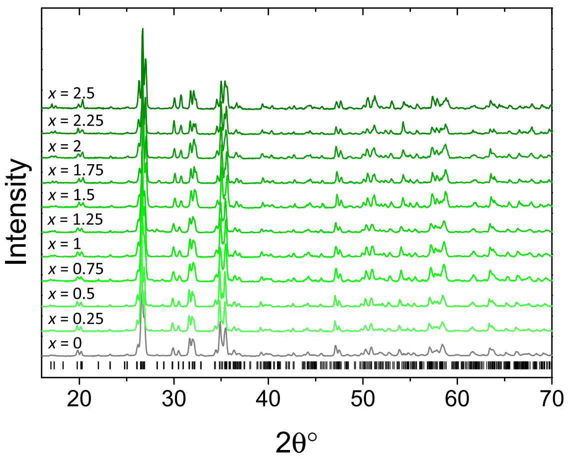

Fig. 2. Powder X-ray diffraction patterns for $Zn_{2.5-x}Co_xVMoO_8$.

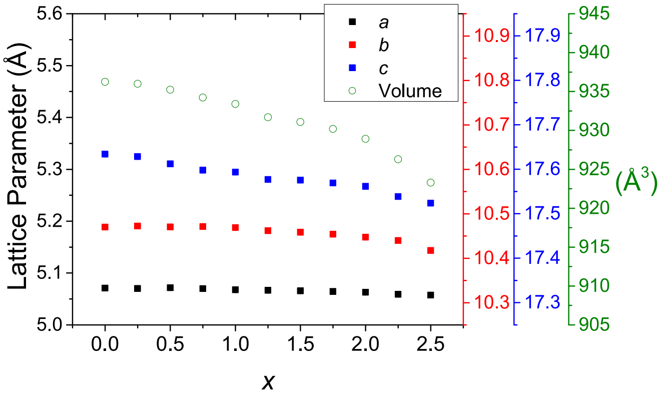

Fig. 3. Lattice parameters for $Zn_{2.5-x}Co_xVMoO_8$. The ranges for the a, b, and c parameters are set to the same size (0.6 Å) for direct comparisons.

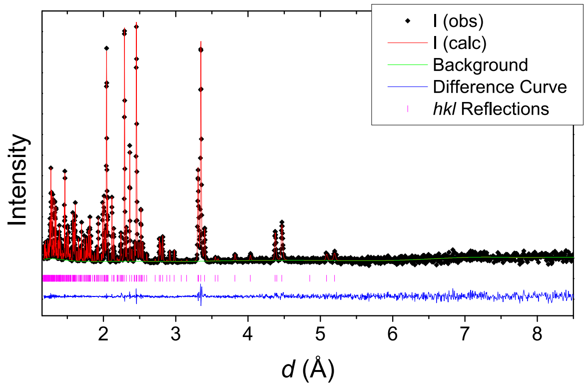

Fig. 4. TOF neutron diffraction pattern for $Zn_{1.25}Co_{1.25}$ $VMoO_8$. Display includes calculated intensities (red), difference curve (blue), and allowed reflections for *Pnma* (magenta).

The O sites were determined to be fully occupied from the lack of impurity phases in the X-ray analysis, and subsequent refinement was performed with these sites' occupancies fixed at 1. The face-sharing octahedral site A1 extends through the center of the tunnel structure,