PCCP

PAPER



Cite this: Phys. Chem. Chem. Phys., 2022, 24, 17289

Received 23rd October 2021, Accepted 17th June 2022

DOI: 10.1039/d1cp04851a

rsc.li/pccp

Introduction

Since their first synthesis in 1971,¹ Chevrel Phases (CPs), $M_xMo_6T_8$ (M = metal; T = S, Se, Te), have demonstrated remarkable properties. Most notably, these properties lend themselves toward the use of CPs as high-temperature superconductors,^{2,3} thermoelectrics,⁴ multivalent cathode materials,⁵⁻⁸ and catalysts.⁹⁻¹¹ Indeed, its unique pseudo-molecular structure endows CPs with a high degree of tunability of its electronic structure, including its valence and

^d Department of Chemical and Biological Engineering, University of Colorado Boulder, Boulder, Colorado 80303, USA

‡ These authors contributed equally.

X-ray absorption spectroscopy insights on the structure anisotropy and charge transfer in Chevrel Phase chalcogenides[†]

Forrest P. Hyler, (D) ‡^a Brian A. Wuille Bille, (D) ‡^a Jessica C. Ortíz-Rodríguez, (D)^a Ana Sanz-Matias, (D)^{bf} Subhayan Roychoudhury,^b Joseph T. Perryman, (D)^e Christopher J. Patridge, (D)^c Nicholas R. Singstock, (D)^d Charles B. Musgrave,^d David Prendergast (D) *^b and Jesús M. Velázquez (D) *^a

The electronic structure and local coordination of binary (Mo_6T_8) and ternary Chevrel Phases ($M_xMo_6T_8$) are investigated for a range of metal intercalant and chalcogen compositions. We evaluate differences in the Mo L₃-edge and K-edge X-ray absorption near edge structure across the suite of chalcogenides $M_xMo_6T_8$ (M = Cu, Ni, x = 1-2, T = S, Se, Te), quantifying the effect of compositional and structural modification on electronic structure. Furthermore, we highlight the expansion, contraction, and anisotropy of Mo₆ clusters within these Chevrel Phase frameworks through extended X-ray absorption fine structure analysis. Our results show that metal-to-cluster charge transfer upon intercalation is dominated by the chalcogen acceptors, evidenced by significant changes in their respective X-ray absorption spectra in comparison to relatively unaffected Mo cations. These results explain the effects of metal intercalation on the electronic and local structure of Chevrel Phases across various chalcogen compositions, and aid in rationalizing electron distribution within the structure.

conduction band positions, band gaps, and orbital interactions with participating species in surface reactions. Hence, the electronic properties of these materials are sensitive to the identity and stoichiometry of the metal ion intercalant, M, as well as by the chalcogen identity, T.¹² However, while numerous studies have been performed by our group^{10,11,13–15} and by the larger community exploring the electronic structure of sulphide binary and ternary CPs, comparatively less is known about their selenide and telluride analogs.^{4,13,15–17}

The structure of CPs can be described as a network of cubic chalcogen cages that enclose a distorted octahedron of Mo atoms. As a result of their arrangement, the cage and octahedron that form each $M_xMo_6T_8$ cluster share a 3-fold rotational axis, rendering two chalcogen ions (T₂) of each cluster along this axis of symmetry as chemically distinguishable from the remaining six chalcogen ions due to their unique coordination environment (as seen in Fig. 1).¹⁸ In the extended CP structure, clusters are linked together by their chalcogen cages, which enable strong intercluster Mo-T and T-T interactions to yield a framework with voids that can host a range of metal cation stoichiometries.

In the binary CPs, the Mo_6 cluster is better described as a trigonal antiprism, which decreases in anisotropy as intercalant ions are inserted into the frameworks. This symmetry change has been previously explained as being the result of the electron

View Article Online

^a Department of Chemistry, University of California, One Shields Avenue, Davis, California, 95616, USA. E-mail: jevelazquez@ucdavis.edu

^b Molecular Foundry, Lawrence Berkeley National Laboratory, Berkeley, California, 94720, USA. E-mail: dgprendergast@lbl.gov

^c Department of Chemistry, D'Youville College, 320 Porter Avenue, Buffalo, New York, 14201, USA

^e Department of Chemical Engineering, Stanford University, 443 Via Ortega, Stanford, California, 94305, USA

^f Joint Center for Energy Storage Research, Lawrence Berkeley National Laboratory, Berkeley, California, 94720, USA

[†] Electronic supplementary information (ESI) available: Detailed experimental methods, including synthesis, characterization and XAS data analysis. See DOI: https://doi.org/10.1039/d1cp04851a



Fig. 1 Crystal structure of the rhombohedral (R-3) CPs studied herein (Cu₂Mo₆T₈ T = S, Se) depicting (a) an individual Mo₆T₈ cluster where the Mo atoms are represented in blue, and chalcogen atoms in gold, (b) adjacent Mo₆T₈ clusters detailing a 3-fold rotational axis where cluster-linking undercoordinated chalcogens (T₂) are represented in white, and an intercluster cavity into which metals can be intercalated, and (c) the M_xMo₆T₈ framework where intercalant metal atom sites are represented by magenta.

density distribution within the Mo₆ octahedra (electronic factor)¹⁹ as well as intercluster chalcogen repulsion that affects intracluster Mo-Mo bonding (geometric factor).²⁰ These electronic and geometric factor hypotheses agree with the observed contraction of the Mo₆ cluster upon intercalation of metal ions, which derives from the filling of Mo-Mo bonding states and the weakening of intercluster Mo-Mo and Mo-T bonds, respectively. A more detailed bond valence study that explored the nature of Mo6-cluster anisotropy and its evolution upon cation insertion identified non-uniformity in anion charge distribution as the primary driver of intrinsic electronic instability of the binary sulphide phases, as well as the decrease in nonuniformity upon intercalation of small ions.²¹ To provide additional insight regarding the aforementioned electronic structure and bonding formalisms for CPs, we present a detailed X-ray spectroscopic analysis of the interplay between electronic structure and local Mo-Mo and Mo-T coordination across an entire suite of binary and ternary CP chalcogenides.

X-ray absorption spectroscopy (XAS) is a uniquely well-suited technique for the study of these complex multinary systems, owing to its high elemental specificity and ability to provide valuable structural and electronic information. By means of X-ray absorption near-edge structure (XANES) analysis, exciton transitions are observed that can reveal critical information regarding the coordination environment of an absorbing species, as well as its oxidation and density of unoccupied electronic states.²²⁻²⁴ Although intensity of the L₁ quadrupole transition edge (2s \rightarrow 4d) is low, the more intense L_{2,3} (2p \rightarrow 4d) electric dipole transitions can instead be used to probe the oxidation state and electronic density around absorbing Mo ions in CPs without convolution from p-d mixing, and can thereby serve as a direct probe of covalency of transition metals regardless of their crystal field.²⁵ Furthermore, lattice geometry can be determined through extended X-ray absorption fine structure (EXAFS) analysis that reveals structural distortions and bond distance information. This is accomplished through

excitation by photons of energy greater than the absorption edge, which produces photoemitted electrons. Interference between outgoing wave components of the photoemitted electron from the X-ray excited atom and backscattered components from neighbouring atoms provides information related to the interatomic distances between the absorber atom and those in its surrounding coordination shells. The combination of analyses in both regions of the XAS spectrum helps explain the charge transfer phenomena and differences in the structural properties of intercalated and binary Mo₆T₈ frameworks.

Herein, we report the analyses of XANES and EXAFS experiments that corroborate arguments regarding how metal intercalation into the CP sulphide, selenide, and telluride frameworks control cluster anisotropy, cavity deformation, and charge transfer. This work highlights the intricate effects of ternary intercalation on structure and electronic properties for a highly versatile material family, and thereby provides valuable insights that may inform and accelerate the design of new compositions with a variety of applications.

Results and discussion

Synthesis and structural characterization

Pure-phase binary and metal-intercalated CPs with the Mo_6S_8 , Mo₆Se₈, Mo₆Te₈, Cu₂Mo₆S₈, Cu₂Mo₆Se₈, and NiMo₆Te₈ compositions were obtained through a rapid microwave-assisted solidstate synthesis approach described in our previous work,^{10,11,13–15} with this being the first expansion of the synthesis approach to produce metal-intercalated CP selenides. Scanning electron microscopy (SEM) images reveal the faceted, polycrystalline morphology of these phases (Fig. 2(a)-(c) and Fig. S1a-c, ESI⁺). A slight decrease in crystallinity was observed for the telluride phase, which agrees with the broader and less intense diffraction peaks for NiMo6Te8 compared to Cu2MoS8 and Cu₂Mo₆Se₈. The powder X-ray diffraction (PXRD) patterns for each CP are in close agreement with literature and indicate a rhombohedral crystal phase for Cu₂Mo₆Se₈, Cu₂Mo₆S₈, Mo_6S_8 , Mo_6Se_8 and Mo_6Te_8 (Fig. 2(d), (e) and Fig. S1d-f, ESI[†]). Additional diffraction peaks associated with a triclinic distortion are observed for NiMo₆Te₈, which agrees with results



Fig. 2 (a) SEM micrographs of (a) $Cu_2Mo_6S_{8,}$ (b) $Cu_2Mo_6Se_8$ and (c) $NiMo_6Te_8$ along with their corresponding PXRD diffractograms (d)–(f).

reported for the similar Ni_{0.85}Mo₆Te₈ composition (Fig. 2(f)).²⁶ All the phases synthesized in this work share a diffraction peak at $2\theta \cong 12^\circ$, which is characteristic of CPs and corresponds to diffraction from the (101) and (010) planes for the rhombohedral and triclinic phases, respectively. A noticeable shift of this peak to lower 2θ values (Te < Se < S) was observed as the ionic radius of the chalcogen increases (S < Se < Te), agreeing with the increase in the unit cell volume (Fig. S2. ESI⁺). Additionally, a slight shift in 2θ to lower values for the rhombohedral structures was observed upon metal intercalation-a feature that is noticeably more pronounced for CP selenides $(Mo_6Se_8 < Cu_2Mo_6Se_8)$ than sulphides $(Mo_6S_8 < Cu_2Mo_6S_8)$ (Fig. S2, ESI[†]). This appears to be the result of reduced chalcogen-intercalant attraction in Cu2Mo6Se8 relative to Cu₂Mo₆S₈, which arises due to the decreased chalcogen electronegativity and resultant lack of electrostatic attraction between the Mo₆Se₈ cluster and the interstitial cation species linking them together.¹⁵

Local structure distortion upon intercalation

As previously mentioned, metal intercalation has a marked effect on the electronic and geometric structures of CPs. More specifically, insertion of metal ions into the cavities between Mo_6T_8 clusters induces alterations not only to the intercluster Mo-Mo, Mo-T, and T-T distances, but also to the intracluster Mo-Mo distances of the Mo_6 trigonal antiprism. Thus, to understand the extent to which the host structure is modified by the ternary intercalant species, Mo K-edge EXAFS analysis was performed for Mo_6S_8 , $Cu_2Mo_6S_8$, Mo_6Se_8 , $Cu_2Mo_6Se_8$, Mo_6Te_8 , and $NiMo_6Te_8$ CPs. Fourier-transformed EXAFS data, including magnitudes and real components, and corresponding fitted plots for the binary and intercalated sulphides, selenides, and tellurides are showcased for comparison in Fig. 3.

Upon X-ray irradiation above the Mo K-edge energy (20 keV), generated photoelectrons scatter from the neighbouring atoms surrounding the absorbing element. Due to the overlapping edges of the sulphur K-edge and molybdenum L_3 -edge, the Mo K-edge was chosen for EXAFS fitting due to the non-interferent nature of the photoelectrons produced at the energy utilized, as well as the wealth of structural information extractable for the intercluster and intracluster Mo–Mo and Mo–T bonding land-scape. Contributing scattering paths to the EXAFS signal are represented in Fig. 4 and extracted distances from fitted data are detailed in Table S1 (ESI†). Cu₂Mo₆Se₈ and especially Cu₂Mo₆S₈ demonstrate appreciable increases in their intercluster Mo–T distances relative to their binary analogues of 0.1 and 0.03 Å, respectively. This increase in path length is consistent with the incorporation of multiple ions per cavity.

The introduction of intercalant metal ions causes structural transformations in both the chalcogen cage and the Mo_6 cluster. To quantify this structural shift, we monitored cluster anisotropy. The cluster anisotropy is defined here as the quotient between the longest and shortest Mo–Mo bond distances in the trigonal antiprism (Table 1). In conjunction with the elongation of intercluster Mo–T bonds, our results indicate



Fig. 3 Mo K-edge FT-EXAFS data (circles) and fits (solid lines) showing the non-phase-corrected magnitude (top lines) and real (bottom lines) components of the Fourier transform of $k^3\chi(k)$ in radial space for the sulphide, selenide, and telluride binary CPs (a), (c), and (e), and the Cu intercalated sulphide and selenide (b), (d), and Ni intercalated telluride CPs (f).



Fig. 4 Graphic representation of the intracluster and intercluster scattering paths observed in Fig. 3 for 1s photoelectrons between an absorbing Mo and its neighbouring Mo and T ions in the CP framework. Information for each path is detailed in Table S1 (ESI \dagger).

a reduction in cluster anisotropy between the binary CPs and their respective ternary analogues, in good agreement with previous reports (Table 1).²¹ In binary CPs, the two chalcogen ions located along the 3-fold rotation axis have a lower coordination number than the remaining 6 of the Mo_6T_8 cluster (Fig. 1(b)). Thus, the lack of dative interactions from the

Table 1 Cluster anisotropy relationship to the cluster valence electron count (VEC). The anisotropy was calculated following ref. 21, as ($R_{long} - R_{short}$) × 100/ R_{long} , where R depicts the interatomic distance between intracluster Mo atoms as obtained from Mo K edge EXAFS data (distances can be visualized in the blue polyhedron with each vertex representing a Mo atom). VEC was calculated according to ref. 21

Chevrel Phase C	Cluster e-count	t Cluster anisotropy (%	6)
MO_6S_8	20	8.85 ± 1.63	Rshort
Cu ₂ Mo ₆ S ₈	22	4.44 ± 1.64	
Mo ₆ Se ₈	20	5.55 ± 2.15	t t
Cu ₂ Mo ₆ Se ₈	22	3.70 ± 1.52	R _{long}
Mo ₆ Te ₈	20	4.73 ± 0.50	
NiMo ₆ Te ₈	22	11.04 ± 0.43	
0 0			

chalcogen to neighbouring clusters induces the undercoordinated chalcogens to bare a more negative charge, as demonstrated by Hughbanks and Hoffmann.²⁷ Upon intercalation, the occupation of intercluster cavities mitigates the undercoordination of these chalcogen sites and distributes their valency more evenly amongst the other chalcogen atoms.

In the case of the intercalated telluride phase (NiMo₆Te₈), the cluster anisotropy shows a remarkable increase in comparison to the binary. This could be rooted in the lower electronegativity of the Te ions, thus leading to a lower degree of charge transfer with the intercalant cations, as well as in the distinct space groups between the binary and ternary telluride CPs. The triclinic crystal structure of NiMo₆Te₈, which lacks the 3-fold rotation axis of symmetry present in Mo₆Te₈, may impose a lower symmetry on the entire chalcogen cage, thus resulting in an inherently asymmetric Mo₆ cluster. To attain a clear understanding of the structural symmetry of the intercalated CP tellurides, additional EXAFS studies over a large composition spectrum are required.

Charge transfer in Chevrel Phases

Mo L_{3} -, S K-, Se K-, and Te L_{3} -edge excitations were probed to evaluate metal-chalcogen interactions and electron density distribution in each CP. It is known that Mo 4d orbitals play a critical role in previously observed S pre-edge features due to hybridization between Mo 4d and S 3p orbitals.^{6,19} Vacant hybrid orbitals enhance the pre-edge region observed in the S K-edge. The addition of electron density to these hybridized orbitals from a ternary intercalant acting as an electron donor results in a depressed pre-edge peak, as observed in Fig. 5(b). Additionally, interactions between Mo and T have a substantial effect on the Mo L_{3} -edge absorption edge position and can provide additional electronic information for the Se and Te congeners, allowing for further analysis of the role that chalcogen electronegativity has on electron distribution within the cluster.

Inspection of the Mo L_3 -edge position shown in Fig. S4 (ESI[†]) reveals the effect of ion intercalation on the valency of the Mo₆ host. Both sulphide and selenide CPs exhibit a red-shifted Mo L_3 -edge after 2 equivalents of Cu have been intercalated into the cavities. This lower absorption energy indicates a more reduced Mo species following electron donation from



Fig. 5 Molybdenum and chalcogen XANES spectra for binary and ternary Chevrel phases. (a) Mo L₃-edge of sulphide, selenide and telluride CPs, (b) S K-edge of Mo₆S₈ and Cu₂Mo₆S₈, the calculated spectra are shown with dashed lines (c) Se K-edge of Mo₆Se₈ and Cu₂Mo₆Se₈, and (d) Te L₃-edge of Mo₆Te₈.

the intercalant into the cluster, subsequent redistribution of chalcogen valency, and resultant contraction of the clusters (Fig. 3). Conversely, the telluride CP displays an opposite trend, with a small blue shift in the Mo L3-edge following Ni intercalation. This observation is in good agreement with the previously described expansion of the Mo6Te8 cluster after intercalation (vide supra and detailed in Table S1, ESI⁺). Bond lengthening upon metal intercalation of Mo₆Te₈ clusters develops a lower overall electron density of the molybdenum atoms. While perceptible, these energy shifts are small in magnitude, which is consistent with the general low redox activity of the Mo centers upon intercalation.^{17,28} It is noteworthy that the effect of chalcogen composition and-more importantly-chalcogen electronegativity manifests itself in the electronic structure of the Mo₆ trigonal antiprism, as seen in the progressively blueshifted Mo L₃-edge centroids in Fig. 5(a) along the series Mo₆Te₈ < Mo₆Se₈ < Mo₆S₈. Specifically, and perhaps intuitively, a more oxidized molybdenum species predominates as the chalcogen electronegativity increases. This result is of high importance, as Mo atoms are known to be the adsorption site of small molecules in catalytic applications,^{9,13} hence selectively engendering programmable valency to these sites may afford a fine level of control over reactivity for a suite of applications. As a result of this promise for tuning Mo reactivity based upon chalcogen electronegativity, additional in situ and operando Mo XANES measurements are warranted that may elucidate the nature of Mo-adsorbate interactions during relevant reactions such as the CO₂ reduction and C-C coupling reactions.

Much like the Mo edges, chalcogen absorption edges provide valuable insight into the charge transfer phenomenon that occurs during ternary intercalation into CPs. Among these edges, the S K-edge illustrates the pronounced effect of intercalant-to-chalcogen charge transfer. As can be seen in Fig. 5(b), a modest red shift of the white line position is

detected upon intercalation, although a rather abrupt decrease in the pre-edge (located around 2470.5 eV) intensity is observed, indicating significant population of previously unoccupied hybridized S 3p/Mo 4d states that are responsible for the preedge feature intensity. This population of 3p states by Cudonated electron density effectively depresses the pre-edge feature in the intercalated Cu2Mo6S8 structure relative to the binary Mo₆S₈ that retains its unoccupied S 3p states that can accept excited electrons during the S 1s \rightarrow S 3p/Mo 4d transition. This effect is more clearly visible from the analysis of the second derivatives of the corresponding spectra shown in Fig. S6a (ESI[†]) where the binary sulphide CP exhibits two well-resolved peaks centred around 2470 eV. These peaks merge into a single signal upon intercalation of two copper equivalents and subsequent introduction of the intercalant electron density. Small metal cations such as Cu⁺ are known to occupy the cavity in a perpendicular fashion to the 3-fold rotation axis of the CP framework highlighted in Fig. 1(b) and (c),¹⁷ in closest proximity to undercoordinated S sites. Upon intercalation, electron density from the ternary cation is transferred to empty (4d hybridized) S 3p orbitals that are responsible for the preedge feature. As a result of orbital occupation from intercalantinduced electron transfer, the spectra show a reduced intensity in the absorption pre-edge signal in the S K-edge XANES. The two resolved peaks at 2470 eV for the S-K 2nd derivative are merged to a single broad feature and this can be interpreted as a more uniform S valency distribution and coordination environment and, consequently, a less anisotropic Mo₆ trigonal antiprism.18,19

The S K-edge spectra of Mo₆S₈ an Cu₂Mo₆S₈ (Fig. 5(b), dashed lines) were calculated using the many-body X-ray absorption spectroscopy method (MBXAS),²⁹⁻³¹ a density functional theory-based methodology that computes the absorption cross-section by approximating each electronic state (i.e., the initial state and each of the final states) as a Slater determinant (see Computational details in the ESI[†]). The anisotropy of the simulated structural models is, respectively, 5.76% and 3.31%, in excellent agreement with experiment (Table 1), as are the spectra. Bader charge analysis of the Mo₆S₈ and Cu₂Mo₆S₈ structures confirms that the intercalant-induced electron transfer is mostly to the previously undercoordinated S_2 sites (see Table S9, ESI[†]), which are reduced by 0.16 e⁻. On the other hand, the Mo and the tetracoordinated S₁ sites are reduced by less than 0.08 e⁻. The charge on S_1 and S_2 sites equalizes to $\sim -0.80 \, e^-$ in the intercalated phase, reflecting the reduced cluster anisotropy of Cu₂Mo₆S₈ and their corresponding atomic contributions to the overall spectrum bear closer resemblance to one another (Fig. S8, ESI⁺), leading to the disappearance of the pre-edge. The strong-blue shift in the S₂ spectra is mainly due to the presence of the Cu, rather than the geometric changes associated with it. Counterintuitively, the steepness of the pDOS near the Fermi level indicates a decrease in charge carriers when Cu is added and the Fermi level raised. This results in decreased screening, hence the blue-shift (see ESI⁺ Section Effect of geometric changes and charge transfer on spectra). We note that, in contrast to the expected greater

negativity of the undercoordinated S_2 atom, Bader charges indicate less negative charge on these sites. However, the associated atomic volume for these atoms is quite large, due to the open structure of the lattice, and a more localized charge estimate (Löwdin charge) does indeed indicate that S_2 is slightly more reduced than S_1 (Table S8, ESI†).

In the case of the Se K-edge, there is no appreciable pre-edge feature and no change in intensity of the edge is noticeable upon intercalation. This may be rooted in a lower degree of Mo d–T p orbital hybridization as a result of a larger orbital energy mismatch between the elements. In addition, the lack of welldefined pre-edge absorption peaks in the heavier chalcogens is consistent with the decrease in the core-hole lifetime of their corresponding high energy edges compared to sulphur.

Cu-intercalated selenide and Ni-intercalated telluride CPs both demonstrate a decrease in absorption onset energies in their respective chalcogen XANES spectra, in good agreement with more reduced Se and Te species. In comparing the Mo L₃edge spectra for the CPs studied here (Fig. S4, ESI†), the electronic structure changes as evidenced by shifting chalcogen absorption edges indicate that charge transfer occurs primarily from the intercalant to the chalcogen cages, rather than directly to the Mo₆ core, despite the redistribution of Mo valency upon intercalation. However, this M-to-T electron transfer shows good agreement with previous results published by Prendergast *et al.*³² These changes in absorption edge positions and intensities highlight the significance of identifying useful sites within the CP structure that are amenable to selectively accepting electron density during intercalation by a ternary species.

Conclusions

We have presented an extensive XAS study on the atomistic and electronic structure of Chevrel Phases and on their evolution upon intercalation by a ternary species. Results extracted from Mo K-edge EXAFS confirm the reduction of Mo₆ cluster anisotropy after metal insertion, which we attribute to a more evenly distributed chalcogen valency. Modulated charge density of the Mo₆ cluster as a function of chalcogen electronegativity was also evidenced by a red shift in the Mo L₃-edge absorption edge centroid for the binary series Mo₆T₈ with a decrease in energy as the electronegativity of the chalcogen decreases. Additionally, by comparing the Mo L₃- and chalcogen K- and L₃-edge XANES of binary and metal-intercalated CPs, it was concluded that charge transfer is mediated by the chalcogen, with the most noticeable effects observed for the S K pre-edge feature and Te L3-edge red-shift after metal intercalation. The results of this work provide a detailed view of the effect of intercalation on the atomic structure and anisotropy of Chevrel Phase sulphide, selenide and tellurides. Furthermore, the effect of the chalcogen identity on the Mo cluster electronic structure and its change after interaction with the ternary cation in M_xMo₆T₈ phases suggest how the ternary CPs may be rationally tuned for their applications of interest.

Author contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Conflicts of interest

The authors declare no conflicts of interest.

Acknowledgements

JMV thanks the University of California, Davis for start-up funding. JMV also acknowledges support from the Cottrell Scholars program supported by the Research Corporation for Science Advancement (RCSA 26780), as well as support from the National Science Foundation through the Faculty Early Career Development Program (DMR-2044403). JOR was funded by the National Science Foundation Graduate Research Fellowship (NSF 1650042). Part of this study was carried out at the UC Davis Center for Nano and Micro Manufacturing (CNM2). Use of the Stanford Synchrotron Radiation Lightsource, SLAC National Accelerator Laboratory, is supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences under Contract No. DE-AC02-76SF00515. This research used resources of the National Synchrotron Light Source, a U. S. Department of Energy (DOE) Office of Science User Facility operated for the DOE Office of Science by Brookhaven National Laboratory under Contract No. DE-AC02-98CH10886. DFT calculations and X-ray spectral analysis were performed by ASM, SR, and DP using resources of the National Energy Research Scientific Computing Center (NERSC), a U.S. Department of Energy Office of Science User Facility located at Lawrence Berkeley National Laboratory, operated under Contract No. DE-AC02-05CH11231. Work by ASM was supported by the Joint Center for Energy Storage Research (JCESR), an Energy Innovation Hub funded by the U.S. Department of Energy, Office of Science, Basic Energy Sciences. Spectral analysis was facilitated through a user project at the Molecular Foundry at Lawrence Berkeley National Laboratory, which is supported by the Office of Science, Office of Basic Energy Sciences, of the U. S. Department of Energy under Contract No. DE-AC02-05CH11231. NRS and CBM acknowledge support by the National Science Foundation (CBET-2016225).

References

- 1 R. Chevrel, M. Sergent and J. Prigent, *J. Solid State Chem.*, 1971, 3, 515–519.
- 2 G. V. Subba Rao and G. Balakrishnan, *Bull. Mater. Sci.*, 1984,
 6, 283–316.
- 3 Ø. Fischer, Appl. Phys., 1978, 16, 1-28.
- 4 X. Ya Shi, L. Wang, L. D. Chen and X. H. Chen, *Trans.* Nonferrous Met. Soc. China, 2009, **19**, 642–645.
- 5 A. Mitelman, M. D. Levi, E. Lancry, E. Levi and D. Aurbach, *Chem. Commun.*, 2007, 4212–4214.

- 6 D. Muthuraj and S. Mitra, *Mater. Res. Bull.*, 2018, **101**, 167–174.
- 7 E. Lancry, E. Levi, Y. Gofer, M. Levi, G. Salitra and D. Aurbach, *Chem. Mater.*, 2004, 16, 2832–2838.
- 8 P. Yu, X. Long, N. Zhang, X. Feng, J. Fu, S. Zheng, G. Ren, Z. Liu,
 C. Wang and X. Liu, *J. Phys. Chem. Lett.*, 2019, **10**, 1159–1166.
- 9 K. M. Kadiev, S. N. Khadzhiev, M. K. Kadieva and E. S. Dogova, *Pet. Chem.*, 2017, **57**, 608–617.
- 10 J. T. Perryman, F. P. Hyler, J. C. Ortiz-Rodríguez, A. Mehta, A. R. Kulkarni and J. M. Velázquez, J. Coord. Chem., 2019, 72, 1322–1335.
- J. T. Perryman, J. C. Ortiz-Rodríguez, J. W. Jude, F. P. Hyler, R. C. Davis, A. Mehta, A. R. Kulkarni, C. J. Patridge and J. M. Velázquez, *Mater. Horiz.*, 2020, 7, 193–202.
- 12 O. K. Andersen, W. Klose and H. Nohl, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1978, **17**, 1209–1237.
- 13 J. C. Ortiz-Rodríguez, N. R. Singstock, J. T. Perryman, F. P. Hyler, S. J. Jones, A. M. Holder, C. B. Musgrave and J. M. Velázquez, ACS Appl. Mater. Interfaces, 2020, 12, 35995–36003.
- K. Lilova, J. T. Perryman, N. R. Singstock, M. Abramchuk, T. Subramani, A. Lam, R. Yoo, J. C. Ortiz-Rodríguez, C. B. Musgrave, A. Navrotsky and J. M. Velázquez, *Chem. Mater.*, 2020, 32, 7044–7051.
- 15 N. R. Singstock, J. C. Ortiz-Rodríguez, J. T. Perryman, C. Sutton, J. M. Velázquez and C. B. Musgrave, *J. Am. Chem. Soc.*, 2021, 143, 9113–9122.
- 16 F. J. Berry, E. M. Forgan and C. D. Gibbs, *Solid State Commun.*, 1988, **66**, 667–670.
- 17 F. J. Berry and C. D. Gibbs, *Solid State Commun.*, 1992, **83**, 517–520.
- 18 J. K. Burdett and J. H. Lin, Inorg. Chem., 1982, 21, 5-10.
- 19 F. Kubel and K. Yvon, J. Solid State Chem., 1988, 73, 188–191.
- 20 J. D. Corbett, J. Solid State Chem., 1981, 39, 56-74.
- 21 E. Levi and D. Aurbach, Chem. Mater., 2010, 22, 3678-3692.
- 22 T. K. Sham, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1985, **31**, 1888–1902.
- 23 F. Farges and G. E. Brown, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1997, **56**, 1809–1819.
- 24 M. Tromp, J. Moulin, G. Reid and J. Evans, AIP Conf. Proc., 2007, 882, 699–701.
- 25 M. L. Baker, M. W. Mara, J. J. Yan, K. O. Hodgson, B. Hedman and E. I. Solomon, *Coord. Chem. Rev.*, 2017, 345, 182–208.
- 26 K. Hönle and W. Yvon, J. Solid State Chem., 1987, 240, 235-240.
- 27 T. Hughbanks and R. Hoffmann, J. Am. Chem. Soc., 1983, 105, 1150–1162.
- K. Asokan, O. Peña, L. Le Polles, J. C. Jan, J. W. Chiou and W. F. Pong, *J. Cluster Sci.*, 2009, 20, 205–211.
- 29 Y. Liang, J. Vinson, S. Pemmaraju, W. S. Drisdell, E. L. Shirley and D. Prendergast, *Phys. Rev. Lett.*, 2017, **118**, 1–7.
- 30 Y. Liang and D. Prendergast, Phys. Rev. B: Condens. Matter Mater. Phys., 2019, 100, 1–12.
- 31 Y. Liang and D. Prendergast, Phys. Rev. B: Condens. Matter Mater. Phys., 2018, 97, 1–25.
- 32 L. F. Wan, J. Wright, B. R. Perdue, T. T. Fister, S. Kim, C. A. Apblett and D. Prendergast, *Phys. Chem. Chem. Phys.*, 2016, **18**, 17326–17329.