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From Total Scattering to Total Understanding: Structure-Functionality Relationships in Scheelite-Type Oxides

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The development of carbon-neutral energy-generation and storage is critical to combatting climate change. Various technologies are currently being developed for sustainable energy generation, such as next-generation ion conductors for solid-oxide fuel cells (SOFCs), industrial catalysts for sustainable processing, and materials capable of safely storing radioactive waste. Scheelite-type ABO_4 materials have become a focus for these technological advances, with $RbReO_4$ emerging as a potential solid electrolyte, $Bi_3FeMo_2O_{12}$ as a viable oxidation catalyst, and $TlTcO_4$ as a model for highly mobile nuclear fission products. Paramount to the development of these technologies is a deep understanding of their structure-functionality relationships. In this work, we have investigated materials that show unusual temperature dependent structural properties and use total scattering techniques to fully understand the structural origins of such behavior.

$RbReO_4$ undergoes a continuous phase transition from $I41/a$ to the true $I41/amd$ scheelite aristotype upon heating. This phase transition is particularly important as it changes the number of possible interstitial sites, potentially leading to higher ionic conductivity. Rietveld refinements using synchrotron X-ray diffraction data shows an anomalous reduction in the Re-O bond lengths upon heating towards the phase transition temperature. This is unexpected, as the BO_4 scheelite tetrahedra are traditionally considered rigid with 'fixed' B-O bond distances. Combining synchrotron X-ray diffraction and X-ray total scattering data, we uncovered a unique symmetry-lowering process on the local scale involving incoherent tetrahedra rotations. By manipulating the size of the A-site cation, local scale disorder can be tuned to tailor the physical properties of the material [1].

$Bi_3FeMo_2O_{12}$ is a rare example of a transition metal oxide that undergoes a symmetry-lowering 2:1 cation ordering upon heating. Synchrotron X-ray and neutron powder diffraction demonstrate that this is a consequence of a first-order tetragonal-to-monoclinic phase transition that occurs at temperatures below 600 °C. Neutron pair distribution function analysis revealed that the transition does not involve a rearrangement of the cation sublattice but showed that the $Bi^{3+} 6s_2$ lone pairs are stereochemically active in both phases. The observed phase transition is a result of changes in the correlation length of the of the $Bi^{3+} 6s$ electrons from short range in the tetragonal structure to long range in the monoclinic structure. This is then used to understand the magnetization of the different phases [2].

$TlReO_4$ is a rare example of a non-magnetic oxide displaying a re-entrant phase transition. The symmetry changes from tetragonal $I41/a$ to monoclinic $P21/c$, and then back to tetragonal $I41/a$ upon heating. Using neutron total scattering, we describe this behavior in terms of the correlation length of the $Tl^{+} 6s_2$ lone pairs. Whilst the long-range average structure experiences emphanitic behavior (that is, the emergence of a lower-symmetry phase upon heating), the local structure is best fitted with monoclinic distortions to the unit cell due to the Tl^{+} lone pairs. This study presents a possible method of tuning the energy landscape of lone pair-containing functional materials [3].

[1] Marlton, F. *et al.*; Tetrahedral Displacive Disorder in the Scheelite-Type Oxide $RbReO_4$. *Inorg. Chem.*, In Press.

Saura-Múzquiz, M. *et al.*; Cation and Lone Pair Order-Disorder in the Polymorphic Mixed Metal Bismuth Scheelite $Bi_3FeMo_2O_{12}$. *Chem. Mater.*, To be Submitted.

Saura-Múzquiz, M. *et al.*, Understanding the Re-Entrant Phase Transition in a Non-Magnetic Scheelite. *J. Am. Chem. Soc.*, <https://doi.org/10.1021/jacs.2c05620>.

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