MS15 Mineralogical and inorganic crystallography

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Epitaxial intergrowths and local oxide displacements in natural bixbyite

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Abstract

The naturally occurring mineral bixbyite, $Fe_{2-x}MnxO_3$, was recently studied due to its low temperature transition to a disordered spin-glass state [1,2]. However, the mineral also exhibits correlated disorder of structural origins as evidenced by elastic room-temperature single crystal neutron diffuse scattering, Fig. 1(left), and single crystal X-ray diffuse scattering, Fig. 1(right). The one-dimensional nature of the single crystal X-ray scattering suggests the presence of two-dimensional order and one-dimensional disorder. Here we show that this disorder arises from epitaxial intergrowths of the mineral braunite. This is consistent with reports of such intergrowths in natural bixbyite samples based on transmission electron microscopy experiments [3]. Additional short-range order is indicated by the presence of broad diffuse scattering features in the room temperature single crystal neutron scattering data. As these features are not observed in the X-ray data it is natural to expect them to originate from correlations involving Fe^{3+} and Mn^{3+} which have low X-ray but high neutron contrast. We show that the diffuse scattering can be modelled by a size effect where the displacements of oxide ions are correlated with the substitutional disorder on the cation sites. This can be rationalized by the approximately octahedral sites being occupied by Jahn-Teller inactive (Fe^{3+}, d^5) and active (Mn^{3+}, d^4) ions which results in preferences for local octahedral or tetragonally distorted octahedral coordination, respectively. The different contrasts and experimental requirements in single crystal X-ray and neutron scattering experiments allow us to analyze the two modes of disorder in natural bixbyite separately giving a more complete overview of the structure of disordered bixbyite.

References

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Figure 1