

# Cation order in mixed metal bismuth scheelite Bi<sub>3</sub>FeMo<sub>2</sub>O<sub>12</sub>

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The scheelites are a family of compounds with chemical formula  $ABO_4$  where A and B can represent a variety of different cations. The highly versatile scheelite crystal structure consists of  $AO_8$  dodecahedra and  $BO_4$  tetrahedra and gives rise to a variety of interesting properties depending on the combination of cations.<sup>1</sup> Scheelite-type oxides including  $CaWO_4$ ,  $BiVO_4$  and  $NaLa(MoO_4)_2$  have been extensively studied for applications exploiting some of these properties including luminescence, ferroelectricity, ionic conductivity and photocatalytic activity. In particular,  $Bi^{3+}$  containing molybdates are efficient photocatalysts<sup>2, 3</sup> due to the strong repulsive force of the 6s<sup>2</sup> lone pair of  $Bi^{3+}$ , resulting in distortion of the  $BO_4$  tetrahedra and alteration of the band gap.

The compound of interest in the present study,  $Bi_3FeMo_2O_{12}$  (BFMO), was reported by Sleight et al. in 1974 as the first scheelite-type compound containing trivalent cations on the tetrahedral site.<sup>4</sup> Notably, two different polymorphs of BFMO can be isolated.<sup>5</sup> The ideal tetragonal scheelite-type structure in space group  $I4_1/a$  (#88) can be prepared by a wet chemical route from aqueous solution of the constituent elements. Jeitschko et al. reported in 1975 that, when the tetragonal scheelite structure is heated above 600 °C for ~10 h, a 2:1 ordering of the Mo and Fe cations occurs, which lowers the symmetry to monoclinic in space group  $C2/c$  (#15), and gives rise to a tripling of the a axis. Here, phase pure BFMO in the disordered tetragonal structure was synthesized by a wet chemical route. The conversion from the disordered tetragonal to the ordered monoclinic structure was examined by in situ neutron powder diffraction in order to understand the temperature dependence of the phase transition and cation order in the mixed metal bismuth scheelite. The study shows no amorphization prior to the formation of the ordered monoclinic phase. Given the substantial cation movement involved in such a transformation, the lack of structural break-down suggests that a certain degree of local cation order may already exist in the tetragonal phase, facilitating the conversion into a fully ordered monoclinic structure. This hypothesis is further supported by an opening in the field-dependent magnetization curve of the tetragonal phase at 1.8 K.

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Level of Expertise

Early Career <5 Years

Speakers Gender

Female

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No

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