

Effect of A-site cation radius on ordering of BX₆ octahedra in (K,Na)MgF₃ perovskite

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ABSTRACT

We present a structural model for (K,Na)MgF₃ perovskite using results from high-resolution synchrotron X-ray powder diffraction and nuclear magnetic resonance (NMR) spectroscopy. (K,Na)MgF₃ perovskite is found to transition from orthorhombic (*Pbnm*) to tetragonal (*P4/mbm*) to cubic (*Pm $\bar{3}$ m*) as potassium concentration is increased. These phase transitions are not accompanied by a discontinuity in pseudo-cubic unit-cell volume and occur close to compositions (K_{0.37}Na_{0.63})MgF₃ and (K_{0.47}Na_{0.53})MgF₃, respectively. ¹⁹F NMR spectra indicate that the Na⁺ and K⁺ cations do not occupy the A cation site at random and end-member local environments are favored for all compositions. Based on results from both X-ray diffraction and NMR, we propose that diffuse diffraction is the result of strain between coexisting regions of different octahedra (MgF₆) tilts brought about by the ionic radius mismatch of Na⁺ and K⁺ cations. We suggest A-site cations group with like cations as neighbors to reduce excess volume and total strain.