

Oral Contributions

[MS15-05] Effect of Lone Pair Cations on the Orientation of Crystallographic Shear Planes in Anion-deficient Perovskites

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Anion deficiency in perovskite-based ferrites containing lone electron pair cations (i.e. Pb^{2+} , Bi^{3+}) can be accommodated by the formation of crystallographic shear (CS) planes [1-4]. The structure and the orientation of the CS plane in these compounds significantly vary depending on the A-cations. If the perovskite A-positions are occupied exclusively by the lone pair cations, the compounds exhibit incommensurately modulated structures with a $(h0l)_p$ orientation of the CS planes ($\sim(104)_p$ and $\sim(305)_p$ in " $\text{Pb}_2\text{Fe}_2\text{O}_5$ " [1]; $\sim(509)_p$ in the $(\text{Pb},\text{Bi})_{1-x}\text{Fe}_{1+x}\text{O}_{3-y}$ family [2]). When Pb^{2+} and $3+ 2+2+ \text{Bi}^{3+}$ are partially replaced by Ba^{2+} or Sr^{2+} , the $(101)_p$ CS planes are stabilized resulting in the structure of the $\text{A}_n\text{B}_n\text{O}_{3n-2}$ homologous series [3,4]. In this contribution we investigate the effect of the lone pair cations on the structure and the orientation of the CS planes using $(\text{Pb}_{1-z}\text{Sr}_z)_{1-x}\text{Fe}_{1+x}\text{O}_{3-y}$ perovskites as a model system. The

isovalent substitution of Pb^{2+} by Sr^{2+} highlights the influence of the A-cation electronic structure owing to very close ionic radii of these cations. Employing a combination of transmission

electron microscopy and X-ray and neutron powder diffraction, we systematically study the structure evolution of the compounds with z . Two compositional ranges with distinct orientations of the CS planes have been identified in the system: $0.05 \leq z \leq 0.2$, where the CS planes orientation systematically varies but stays close to $(203)_p$, and $0.3 \leq z \leq 0.45$ with the $(101)_p$ CS planes. The incommensurate structure of $\text{Pb}_{0.792}\text{Sr}_{0.168}\text{Fe}_{1.040}\text{O}_{2.529}$, a representative compound of the first range, was refined from the neutron powder diffraction data (S.G. $X2/m(\alpha0\gamma)$, $X = [1/2, 1/2, 1/2, 1/2]$, $a = 3.9512(1)\text{\AA}$, $b = 3.9483(1)\text{\AA}$, $c = 3.9165(1)\text{\AA}$, $\beta = 93.268(2)^\circ$, $\mathbf{q} = 0.0879(1)\mathbf{a}^* + 0.1276(1)\mathbf{c}^*$, $R_F = 0.023$, $R_p = 0.029$, $T = 900\text{K}$). Comparing the structures with different CS planes we have elucidated the main factors governing the orientation of the CS planes and demonstrated that they are associated with the stereochemical activity of the A-cations in the perovskite blocks.

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