Stabilizing ferroelectricity in alkaline earth metal-based perovskites \(\text{ABO}_3\) via \(\text{A}(\text{Ca}^{2+}/\text{Sr}^{2+}/\text{Ba}^{2+})\) and \(\text{B}(\text{Ti}^{4+})\) site cationic radii ratio \((\text{R}_A/\text{R}_B)\)

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The structural distortions in the perovskites (\(\text{ABO}_3\)) lead them to exhibit various physical properties such as ferroelectricity [1], pyroelectricity [2], flexoelectricity [3], and many more. The relationship between the cationic radii of the A and B-sites (\(\text{R}_A\) and \(\text{R}_B\)), and various distortion parameters for alkaline earth metal-based perovskites \(\text{A}^2\text{B}^{4+}\text{O}_3\) has been studied. In this work, we have considered various \(\text{A}^2\text{B}^{4+}\text{O}_3\) perovskite structures grouped as \(\text{CaBO}_3\) (\(\text{B}=\text{Ti}, \text{Sn}, \text{and Zr}\)), \(\text{SrBO}_3\) (\(\text{B}=\text{Ti}, \text{Sn}, \text{and Zr}\)), \(\text{AZrO}_3\) (\(\text{A}=\text{Ca}, \text{Sr}, \text{and Ba}\)), and \(\text{ASnO}_3\) (\(\text{A}=\text{Ca}, \text{Sr}, \text{and Ba}\)) perovskite series. These perovskite series are analysed for their distinct variations in various distortion related parameters primarily tilt angles (\(\phi\) and \(\gamma\)) coupled with mode amplitudes (\(R_4^+\) and \(M_3^+\)), and many more. The measured octahedral rotations and related mode amplitudes showed a growing tendency toward bigger B-site cations, while a decreasing trend towards larger A-site cations. Furthermore, our analysis shows that for incipient ferroelectrics such as \(\text{CaTiO}_3\) [SG: \(\text{Pnma}\) (\(\bar{a}\bar{b}\bar{a})\) and \(\text{SrTiO}_3\) [SG: \(\text{Pm}\bar{3}m\) (\(\bar{a}\bar{b}\bar{a})\)], the ferroelectric displacements are obtained by cation manipulation guided by the \(\text{R}_A/\text{R}_B\) parameter, as shown in Figure 1. The findings are corroborated by the calculated amplitudes of several frozen phonon modes associated with the cubic Brillouin zone, which is responsible for symmetry breaking to tilt-oriented non-ferroelectric \(\text{Pnma}\) and ferroelectric \(\text{P4mm}\) phases. This study sets up a structure-property correlation among \(\text{A}^2\text{B}^{4+}\text{O}_3\) class of perovskites and eases the initial optimisation process [4].

![Figure 1. The stabilisation of ferroelectricity via increasing \(\text{R}_A/\text{R}_B\).](https://doi.org/10.1107/S1600576722009414)