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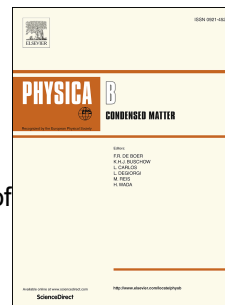
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Correlation between ionic size and valence state of tetra, penta and hexavalent B-site substitution with solubility limit, phase transformation and multiferroic properties of $\text{Bi}_{0.875}\text{Eu}_{0.125}\text{FeO}_3$

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Abstract

We present detailed comparative study of effect of isovalent i.e. Eu^{+3} substitution at A-site and tetra (Ti^{+4} , Zr^{+4}), penta (V^{+5}) and hexavalent (W^{+6}) substitutions at B-site in BiFeO_3 . Eu^{+3} substitution led to phase transformation and exhibited mixed phases i.e. rhombohedral and orthorhombic, while tetravalent substituents (Ti^{+4} and Zr^{+4}) led to stabilization of cubic phase. In higher valent (i.e. V^{+5} and W^{+6}) cases solubility limit was significantly reduced where orthorhombic phase was observed as in the case of parent compound. Phase transformation as a consequence of increase in microstrain and chemical pressure induced by the substituent has been discussed. Solubility limit of different B-site dopants i.e. Zr, W and V was extracted to 5%, 2% and 2%, respectively. Extra phases in various cases were $\text{Bi}_2\text{Fe}_4\text{O}_9$, $\text{Bi}_{25}\text{FeO}_{40}$, $\text{Bi}_{14}\text{W}_2\text{O}_{27}$, and $\text{Bi}_{23}\text{V}_4\text{O}_{44.5}$ and their fractional amount have been quantified. Ti was substituted up to 15% and has been observed to be completely soluble in the parent compound. Solubility limits depends on ionic radii mismatch and valence difference of Fe^{+3} and dopant, in which valence difference plays more dominant role. Solubility limit and phase transformation has been explained in terms of change in bond strength and tolerance factor induced by incorporation of dopant which depend on its size and valence state. Detail optical, dielectric, ferroelectric, magnetic and transport properties of Eu and Ti co-doped samples and selected low concentration B-site doped compositions (i.e. 2%) have presented and discussed. Two d-d transitions and three charge transfer transitions were observed within UV-VIS range. Both change in cell volume for the same phase and transformation in crystal structure affects the band gap. Increase in

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