The Effects of cation arrangement on band gap: Theoretical studies of highly polar semiconductor $PbTi_{1-x}Ni_xO_{3-x}$ solid solutions

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We use a combination of first-principles density functional theory (DFT) and the post-DFT methods LDA+U and PBE0 to study the electronic properties of d^8 Ni-substituted $PbTiO_3$ (Ni-PT) solid solutions. We find that LDA calculations yield unreasonable band structures, especially for Ni-PT solid solutions that contain an uninterrupted NiO_2 layer. The correct treatment of $3d$ states within Ni-PT requires calculations using post-DFT methods. Compositional effects of B-site Ni and Ti cation ordering, are also investigated. Our calculated band gaps of Ni-PT systems depend strongly upon the B-site cation arrangement, altering the bonding between Ni and O. We predict that Ni-PT solid solutions have direct band gap within the visible light energy range, while maintaining the large polarization of parent $PbTiO_3$. This combination of properties could make these solid solutions promising candidate materials for solar energy conversion devices.