Designing the smallest bandgap bulk ferroelectric material

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A low band gap ferroelectric material with a sizable polarization at ambient conditions would constitute an ideal photovoltaic material to harvest solar energy owing to their efficient polarization driven charge carrier separation as well as generation of high, above band gap, photovoltage upon photoexcitation. Consequently, these materials in principle can overcome what is normally considered as the maximum theoretical limit of photoconversion efficiency. Unfortunately, all known ferroelectric materials tend to have very high bandgap with little overlap with the solar spectrum and the consequent inability to absorb most of the solar spectrum. Design and synthesis of reduced band gap ferroelectric transition metal oxides without compromising their polarization properties has been a longstanding challenge with little success. We achieve this elusive goal by co-doping a Jahn-Teller Mn^{3+} and Nb^{5+} pair for two Ti^{4+} ions, representing a charge-neutral dipole doping, in ferroelectric $BaTiO_3$, achieving for the first time a bulk ferroelectric oxide with the lowest bandgap of 1.66 eV with a sizable polarization of nearly 70% of $BaTiO_3$. We contrast with the analogous system with Mn^{3+} replaced by the non-Jahn-Teller Fe^{3+} ($3d^5$) ion, that, even at a much lower level of doping reduces the polarization to 25% without reducing the bandgap significantly, establishing the efficacy of the present strategy.

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Shyamashis Das, Somnath Ghara, Priya Mahadevan, A. Sundaresan, J. Gopalakrishnan, and D. D. Sarma, ACS Energy Lett. **3**, 1176 (2018)