Photo-response mechanisms in ferroelectric $Ba(Sn,Ti)O_3$ solid solutions

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In the framework of photoinduced (photovoltaic and photocatalytic) applications, ferroelectrics because of their internal electric dipole order are expected to favor charge separation. For solar cells, it could be possible to overcome the theoretical efficiency limit of p-n junction by using ferroelectrics, owing to their shift current flowing through them under illumination in short-circuit conditions, if optical and electronic properties are optimised [1]. Understanding how to improve these properties by chemical substitution is essential in view of new and more efficient devices exploiting light.

In this work, we focus on environmentally friendly $BaTiO_3$-based systems. In $Ba(Sn_xTi_{1-x})O_3$ solid solutions the electron mobility can be improved by Sn substitution, which would introduce Sn 5s 5p orbitals in the conduction band [2]. Our study of different $Ba(Sn_xTi_{1-x})O_3$ compositions in ceramic form showed the band gap increase by ~0.35 eV for intermediate compositions. The phase diagram of this system includes different polar arrangements, from ferroelectrics to relaxors. We used spectroscopic techniques (Raman and X-ray Photoelectron spectroscopy) to explain the band gap increase by local distortions structure due to disordered dipole state in relaxor phase. Such distortions can change the chemical bonding by narrowing the conduction band, and thus alternate the band gap and conductivity.

We further study the photo-response of $Ba(Sn_xTi_{1-x})O_3$ ceramics under lasers of different energy. From our measurements, it is possible to discriminate between pyro-current, transient component due to emptying of intrabandgap states, and steady intrinsic photocurrent. By fitting the photo-response of different compositions with this model, we make quantitative analysis of components, including the time-dependent recombination processes. Further, we study the charge trapping by distortion-related defects using ultraviolet-photoluminescence spectroscopy. We confront these two experiments and electric characterization with previous spectroscopic studies of local chemical environment. Our aim is to describe how the balance between different processes of photo-response is related to potential photovoltaic efficiency of $Ba(Sn_xTi_{1-x})O_3$.

[1] C. Paillard et al., Photovoltaics with ferroelectrics: Current status and beyond. Adv. Mat. 28(26), 5153-5168 (2016)
[2] B. G. Kim, J.Y. Jo, and S.W. Cheong, Hybrid functional calculation of electronic and phonon structure of $BaSnO_3$. J. Solid State Chem. 197, 134–138 (2013)