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Band gap tuning of lead-substituted $BaSnO_3$ for visible light photocatalysis

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The Pb substitution effect was investigated experimentally and theoretically on the crystal structure of $BaSnO_3$ and on the photo-oxidation activity of H_2O. The chemically doped Pb in $BaSnO_3$ induced a concentration-dependent redshift of the experimental band gap (BG). The $BaPb_{0.8}Sn_{0.2}O_3$ system produced 32 μmol/h of O_2 under $\lambda \geqslant 420$ nm photons, but no O_2 for $BaSnO_3$. The DFT calculations of $BaPb_xSn_{1-x}O_3$ ($x=0,0.5,1$) by using generalized approximation, implying the BG alteration and the photocatalytic activity of $BaPb_xSn_{1-x}O_3$, are due to the induced Pb 6*s* orbital in the BG of $BaSnO_3$. Thus Pb modified the insulating nature of $BaSnO_3$ to semiconducting and semimetallic. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2430932]

Recently, we proposed and demonstrated that the doping of Pb in perovskite structures[1] could convert a visible light (VL) inactive system into a VL active photocatalyst (PC). We demonstrate here that $BaSnO_3$ (a cubic perovskite structure), a photocatalytically inactive material under VL radiation, is converted to an active PC via Pb substitution. $BaSnO_3$ is an insulating metal oxide (MO) containing *B*-site metal ion (Sn^{4+}) with d^{10} electronic configuration. Such MOs containing Sn^{4+}, Ga^{3+}, Ge^{4+}, In^{3+}, Sb^{5+}, etc., have been predicted to be comparatively efficient PCs.[2] In spite of such perception of d^{10} systems, investigations on Sn^{4+} containing MOs are lacking. Herein we attempt a systematic tailoring of the band structure (BS) of $BaSnO_3$ for their utilization in the photochemical applications.

The best known PCs[3,4] such as TiO_2, $SrTiO_3$, $KTaO_3$, etc., are wide band gap (BG) semiconductors or insulators, and thus not suitable for solar energy conversion applications as visible light PCs and photovoltaics. The known approaches, viz., dye sensitization, external surface modifications, or BS tuning, can be used to achieve the long wavelength absorption in the pure semiconductors. Doping-induced BG tailoring is the most efficient and popular approach especially for the purpose of VL photocatalysis and similar kind of solar applications. This is because the doping can prolong the lifetime of charge carriers as dopant levels may serve as acceptor or donor levels. In addition, BG narrowing is also possible if the electronic coupling effect between dopant and host lattice is strong enough to change the BS. Consequently, there are several reports on the anionic and cationic substitution of metal ions in the host lattice to reduce the BG.[4,5]

Here, we systematically attempt Pb substitution at the *B* site in cubic $BaSnO_3$ and further study its effect on the physicochemical properties of obtained $BaPb_xSn_{1-x}O_3$. Thus, $BaPb_xSn_{1-x}O_3$ was chemically synthesized and calcined at a much lower temperature than 1000 °C. This is the salient feature of this letter and an important achievement as general solid state reaction methods used for producing Pb containing MOs require high calcination temperatures ($\geqslant$1000 °C), thereby posing the problem of Pb phase segregation or evaporation. The study is mainly designed to obtain a photoactive material which will show VL absorption and photocatalysis by Pb-induced BG tuning in the cubic perovskite. Thus $BaPb_xSn_{1-x}O_3$ with different Pb concentrations [$Pb/(Sn+Pb)=0.1-0.8$ mol/mol] are synthesized and characterized for structural, photoelectronic, and photocatalytic properties.

$BaPb_xSn_{1-x}O_3$ samples were synthesized by a modified citrate complex method,[5] in which typically (say, for $BaPb_{0.5}Sn_{0.5}O_3$) 20 mmol of $Ba(NO_3)_2$, 10 mmol of $Pb(CH_3CO_2)_4$ and $SnCl_4{\cdot}SH_2O_1$, 0.4 mol ethylene glycol, and 0.1 mol of citric acid were mixed and stirred at 60 °C. The thus obtained thick yellow gel was heated for more than 10 h at 130–140 °C to obtain brown color gel, and later to 350 °C for 8 h and 700 °C for 10 h to obtain the oxide. Similarly, other $BaPb_xSn_{1-x}O_3$ samples were prepared by variation of the Pb/(Sn+Pb) mole ratios from 0.1 to 0.8 to obtain pale white, yellow, and red, brown, and black colored powders.

Figure 1 shows the effect of Pb substitution on the x-ray diffraction pattern of different $BaPb_xSn_{1-x}O_3$ ($x=0-1$) samples. The spectra reveal that as the Pb concentration increased from $x=0$ to 1, the (110) reflection of cubic $BaSnO_3$ structure shifted towards lower 2θ values, finally yielding a structure close to the cubic $BaPbO_3$. This clearly indicates that the degree of Pb incorporation in the $BaSnO_3$ structure increases with the increase in Pb doping concentration. The concentrations of Pb as found by energy dispersive spectroscopy were also in line with the intended doping concentrations. The additional impurity peaks are due to the existence of different amounts (1%–10%) of $BaSnO(OH)_4$ or PbO phases. A further analysis shows that there is a concentration-dependent increase in the lattice constant from $BaSnO_3$ ($a=4.1163$ Å) (Ref. 6) to $BaPbO_3$ ($a=4.262$ Å) (Ref. 7) as displayed by the left hand side ordinate on the graph of Fig. 2. The increase in lattice constant (a) is expected due to the difference in the ionic radii of Sn^{+4} (0.83 nm) and Pb^{+4} (0.91 nm). The right hand side ordinate of Fig. 2 shows the result of O_2evolution from the photo-oxidation of water on the $BaPb_xSn_{1-x}O_3$, which will be discussed later.

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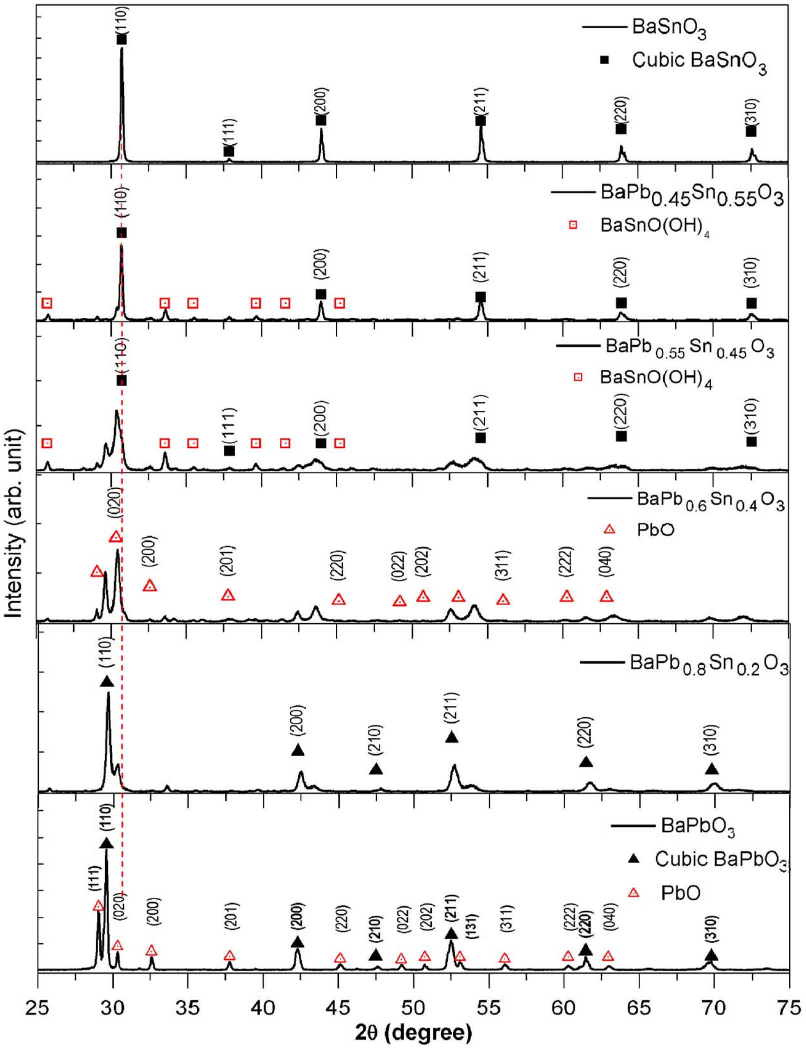

FIG. 1. (Color online) Diffraction spectra for BaPb$_x$Sn$_{1-x}$O$_3$ $(0>x>1)$ prepared by chemical method.

The UV-visible diffuse reflectance spectra for the BaPb$_x$Sn$_{1-x}$O$_3$ samples are displayed in Fig. 3. The absorption of BaSnO$_3$ is gradually extended to the whole visible region (even up to $\lambda > 750$ nm) with the increase in the Pb doping level, which is an important attribute required for solar active materials. With the doping level of Pb/(Sn+Pb)=0.45, the absorption is significantly enhanced in the wavelength of $\lambda > 450$ nm. For the higher Pb doping levels, the absorption is totally extended in the visible region of electromagnetic spectrum, indicating that BaPb$_x$Sn$_{1-x}$O$_3$ structures (for $x>0$) absorb the light necessary for a VL active PC. Inset of Fig. 3 displays the color chip showing the variation in the spectral color (hue) for the respective

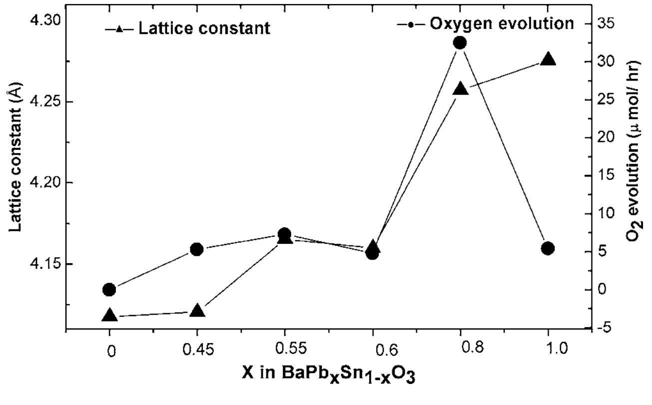

FIG. 2. Variation of lattice constants for BaPb$_x$Sn$_{1-x}$O$_3$ (-▲-) and rates of oxygen evolution (-●-) by photo-oxidation of water under $\lambda > 420$ nm, with different Pb doping concentrations. The photolytic oxidation of water was tested for 0.1 g of the sample in the presence of 0.01M of AgNO$_3$ as the electron scavenger,in an upper-irradiation-type vessel hooked up in a closed gas circulation system irradiated with 300W Xe lamp equipped with cutoff filter.

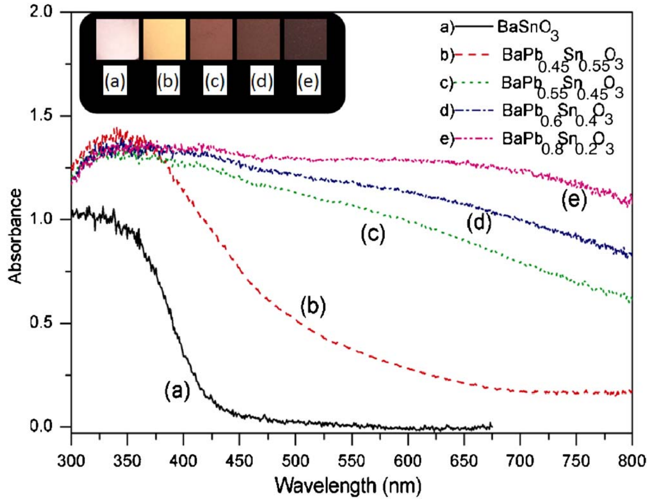

FIG. 3. (Color online) Diffuse reflectance spectra for BaPb$_x$Sn$_{1-x}$O$_3$ $(0>x>1)$ structures. Left side inset shows the spectral colors (hue) of the respective BaPb$_x$Sn$_{1-x}$O$_3$ $(0>x>1)$ structures.

$BaPb_xSn_{1-x}O_3$ structures. It can be seen that for $0 > x > 1$ in $BaPb_xSn_{1-x}O_3$, the white color of $BaSnO_3$ changes to yellow, reddish brown, dark brown, and finally to black. This clearly demonstrates the tunability of the spectral response in the $BaPb_xSn_{1-x}O_3$ structures and thereby their potential usefulness in the VL optical applications.

Due to this alteration of the optical response, we tested the $BaPb_xSn_{1-x}O_3$ samples for their photocatalytic activity under the longer wavelength irradiation, $\lambda \geqslant 420$ nm. As shown in Fig. 2 (the right hand side ordinate), the doped sample $BaPb_xSn_{1-x}O_3$ showed O_2 evolution as high as 32 μmol/h for $Pb/(Sn+Pb)=0.8$, in contrast to the nil photoactivity of $BaSnO_3$ under similar conditions. This indicates that the $BaPb_{0.8}Sn_{0.2}O_3$ seems to be an optimum concentration for producing a relatively high activity material as compared to other Pb concentrations. Possibly, the lower Pb doping concentrations than $BaPb_{0.8}Sn_{0.2}O_3$ are not sufficient to induce enough density of states (DOSs) needed for maximum O_2 evolution and on the other hand, the concentrations larger than that induce large population of DOSs due to Pb, enough to change completely the optical nature of the material. The validity of the above argument has been checked by theoretical BS calculation as will be discussed later. Furthermore, there was no loading of cocatalysts on these sample semiconductor materials. Loading of transition metals and MOs is a common practice to promote the gas evolution rate from water decomposition.[8]

The reason for the photoactivity of the $BaPb_xSn_{1-x}O_3$ structure was further investigated theoretically. Electronic structure computation based on density functional theory[9] using the generalized gradient approximation with linearized augmented plane wave method was used to explain the BG narrowing and thus the VL photocatalytic activity of $BaPb_xSn_{1-x}O_3$. Figure 4 shows the total DOSs of the $BaSnO_3$, $BaPb_{0.5}Sn_{0.5}O_3$, and $BaPbO_3$. The computed BG for $BaSnO_3$ (around 0.9 eV) is much less than the experimental BG of 3.4 eV,[9] yet the theoretical result is in good agreement with the earlier reports.[10] Though the underestimation of BG energy is a well known shortcoming of the single particle Kohn-Sham approach,[9] the predicted trends in the band gap and the qualitative features of band states can be used to interpret the physicochemical behavior of a system. As shown in Fig. 4(a) for the case of $BaSnO_3$, the dominant contribution to the top of valence band comes from the O 2*p* orbitals, while the states at the conduction band (CB) minimum are predominantly due to Sn 5*s* states. The unit cell of Pb-substituted $BaSnO_3$ was constructed by substituting Pb at the Sn site. The DOS of thus constructed structure corresponding to a fictitious composition of $BaPb_{0.5}Sn_{0.5}O_3$ is shown in Fig. 4(b). The computed BG (0.2 eV) is found to be reduced relative to the computed BG of $BaSnO_3$. In addition, the Pb substitution induces the Pb 6*s* states which are located close to the lower edge of the CB to form a lowest unoccupied band. Figure 4(c) shows DOS for cubic $BaPbO_3$, calculated to look at possible qualitative trend in DOS from $BaSnO_3$ and $BaPbO_3$. The total DOS of $BaPbO_3$ suggests that there is an overlap of valence band and CB there by revealing the semimetallic behavior of $BaPbO_3$. The calculation indicates that there is a finite overlap between the bands of O 2*p* and Pb 6*s* around the Fermi energy. The trend of variation of bands around the Fermi energy in $BaSnO_3$, $BaPb_xSn_{1-x}O_3$, and $BaPbO_3$ suggests that contribution of Pb 6*s* orbitals synchronously evolves near the bottom of CB, effectively reducing the BG to a greater extent with the increase in Pb concentration. In the extreme of complete substitution of Sn with Pb, the valence and CB overlap around the Fermi level, yielding a semimetallic BS. The photocatalytic activity for the photo-oxidation of water can be attributed to the suitable BS of $BaPb_xSn_{1-x}O_3$ that yields an active semiconductor with optimal BG for a significant absorption of VL irradiation.

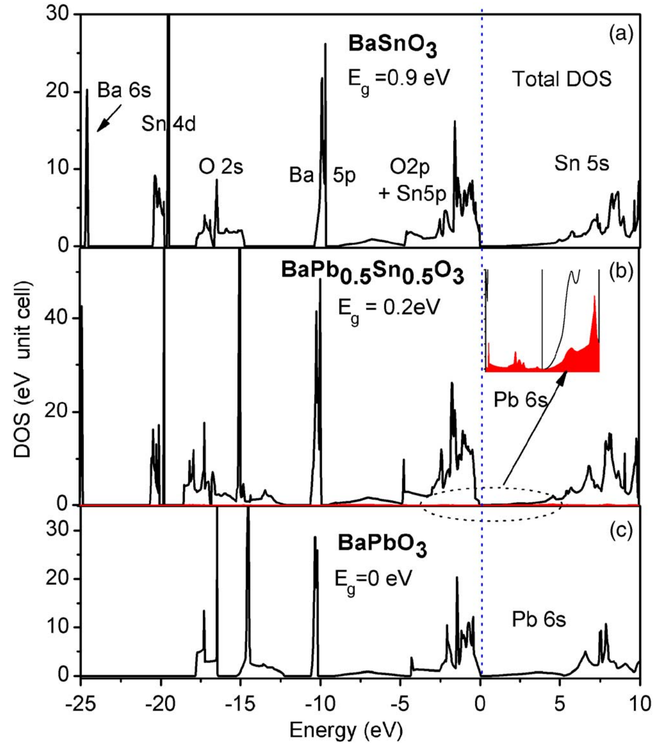

FIG. 4. (Color online) Theoretically calculated total density of states for $BaSnO_3$, $BaPb_xSn_{1-x}O_3$, and $BaPbO_3$. The Fermi level is set at 0 eV. The Pb 6*s* orbital is shaded in red. The inset shows the magnified view of DOS from −5 to +5 eV.

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