Structural, physical and photocatalytic properties of mixed-valence double-perovskite Ba$_2$Pr(Bi,Sb)O$_6$ semiconductor synthesized by citrate pyrolysis technique

Arisa Sato, Michiaki Matsukawa, Haruka Taniguchi, Shunsuke Tsuji, Kazune Nishidate, Akiyuki Matsushita, and Kun Zhang

Faculty of Science and Engineering, Iwate University, Morioka 020-8551, Japan
National Institute for Materials Science, Ibaraki 305-0047, Japan

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We demonstrated crystal structures, magnetic, optical, and photocatalytic properties of the B-site substituted double perovskite Ba$_2$Pr(Bi$_{1-x}$Sb$_x$)O$_6$ ($x=0, 0.1, 0.2, 0.5$ and $1.0$) synthesized by the citrate pyrolysis method. The single-phase polycrystalline samples with the light Sb substitution crystallized in a monoclinic structure ($I2/m$). Magnetization measurements on all the samples showed that the effective magnetic moments are concentrated around $3\mu_B$, indicating the valence mixing states between Pr$^{3+}$ and Pr$^{4+}$. The magnitudes of band gap energy for the two end member samples were estimated from the optical measurements to be $E_g=1.06\ eV$ at $x=0$ and $2.71\ eV$ at $x=1.0$. The Ba$_2$Pr(Bi$_{1-x}$Sb$_x$)O$_6$ ($x=0$, and $0.1$) powders obtained by the present technique exhibited enhanced photocatalytic activities when compared to the same compounds prepared by the conventional solid state method. Our findings suggest that the higher photocatalytic activities strongly depend on powder preparation methods as well as the band gaps and photogenerated charge separation.

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I. INTRODUCTION

A large number of double perovskite oxides $A_2B'B''O_6$ have been widely studied due to their attractive physical properties and potential applications. For example, the $A_2$FeMoO$_6$ compound shows negative tunneling magnetoresistance effect at room temperature, which is of great interest with a wide range of applications in magnetic devices. Furthermore, multiferoic double perovskite oxides with a coupling between spontaneous ferroelectric polarization and ferromagnetic ordering are promising materials from view points of physics and its applications. Some of semiconducting $A_2B'B''O_6$ compounds exhibit photocatalytic properties such as hydrogen generation by water splitting and are taken as alternative materials for TiO$_2$ oxide. In particular, Ba$_2$PrBiO$_6$ has been shown to possess high photocatalytic activity, which is probably related to the valence mixing. A previous study on the magnetic states of the Ba$_2$PrBiO$_6$ compound suggests an anomalous valence situation for Pr ions. The complicated ground states of rare earth ions such as the Pr ion under the crystal field effect remain open question, not only in the physical properties of the double perovskite compound, but also from the view point of physics of the 4$f$ electron systems.

There are significant factors such as charge and size differences between $B'$ and $B''$ sites, to determine the B-site ordering of the double perovskite oxide. Increase in lattice strain and/or increase in the electrostatic repulsion overcome the entropy contribution toward disordering, causing the alternate arrangement. For $A_2^{2+}B'^{3+}B''^{5+}O_6$ composition, the $B'$ sites tend to order with increasing the ion size difference $\Delta r_B=r_{B'}-r_{B''}$. If $\Delta r_B>0.2\ \text{Å}$, it is well known that the $B'$ sites of the compounds are almost ordered alternately in the all crystallographic axes. In the Ba$_2^{2+}$Pr$^{3+}$Bi$^{5+}$O$_6$ compound, the B-site ionic radius difference $\Delta r_B=0.23\ \text{Å}$ meets the above condition, suggesting the B-site ordering, $(r_{B'}(\text{Pr}^{3+})=0.99\ \text{Å}$ and $r_{B''}(\text{Bi}^{5+})=0.76\ \text{Å}$).

In this paper, we report x-ray diffraction measurements, magnetic susceptibilities, diffuse reflectance spectra, and 2-propanol (IPA) degradation for the Ba$_2$Pr(Bi$_{1-x}$Sb$_x$)O$_6$ compounds, to determine the crystal structures, magnetic, optical, and photocatalytic properties of B-site substituted double perovskite oxides. A citrate pyrolysis technique is similar to nitrate combustion synthesis method and an unique route to prepare reactive precursor mixtures through an ignition process of concentrated aqueous solution including metallic ions of stoichiometric composition. For $A_2^{2+}B_1^{2+}Cu^{2+}$O$_8$ with $T_c=80\ \text{K}$ and its related cuprate oxide compounds, it has been reported that high-quality single-phase polycrystalline materials are synthesized under ambient pressure of oxygen gas at lower annealed temperatures. We expect that this procedure enables to synthesize highly homogeneous and fine powders.

As for one approach to developing efficient visible light driven photocatalysts, it is desirable to adjust the band gaps of their semiconductors to utilize a wide range of visible light. According to this approach, they are controlled by the effect of Sb substitution on the parent material. In addition to it, another approach for high performance is to enhance the photogenerated charge separation in the photocatalytic materials, to avoid charge recombination between electron and hole. In our research, the valence mixing states between Pr$^{3+}$ and Pr$^{4+}$ are closely related to the photo induced charge separation.
TABLE I: Physical and photocatalytic properties for Ba$_2$Pr$_x$(Bi$_{1-x}$,Sb$_x$)$_6$O$_6$ compounds ($x$=0, 0.1, 0.2, 0.5 and 1.0). Synthetic method, crystal symmetry, effective magnetic moment, energy gap, surface area, and gas evolution of CO$_2$ are listed as a function of Sb content. The value of evolved CO$_2$ is evaluated after a visible light irradiation of 120 min. (In details, see the text)

| Sb content $x$ | Synthetic method | Crystal symmetry | $\mu_{\text{eff}}$ ($\mu_B$) | $E_g$ (eV) | BET (m$^2$/g) | CO$_2$ (ppm/m$^2$) |
|---------------|------------------|------------------|---------------------|--------|-------------|----------------|
| 0.0           | citrate pyrolysis | monoclinic       | 3.08                | 1.06   | 1.31        | 111            |
| 0.1           | citrate pyrolysis | monoclinic       | 3.05                | -      | 2.88        | 102            |
| 0.5           | citrate pyrolysis | monoclinic       | 3.07                | 1.43   | 2.72        | <5             |
| 1.0           | citrate pyrolysis | rhombohedral     | 3.0                 | 2.71   | -           | <5             |
| 0.0           | solid-state reaction | monoclinic | 3.15$^a$          | 1.1$^a$ | 1.23        | 42             |
| 0.1           | solid-state reaction | monoclinic | 3.15$^a$          | 1.17$^a$ | 1.58        | 33             |
| 0.2           | solid-state reaction | monoclinic | 3.12$^a$          | 1.24$^a$ | 1.49        | 22             |
| 1.0           | solid-state reaction | rhombohedral | -                  | 2.22$^a$ | -           | ~5             |

$^a$ see ref.[22]

II. EXPERIMENT

Polycrystalline samples of Sb-substituted Ba$_2$PrBiO$_6$ were synthesized by using the citrate pyrolysis technique. In the first step, stoichiometric mixtures of high purity BaCO$_3$, Pr$_6$O$_{11}$, Bi$_2$O$_3$, and Sb were dissolved in a nitric acid solution at 70-80 $^\circ$C. After adding citric acid and neutralizing it by aqueous ammonia, we then obtained the porous products through the self-ignition process using halogen lamp stirrer. In the next step, the precursors were ground and resultant fine powders were annealed in air at 900-1000 $^\circ$C for 48-96h, in order to synthesize the Ba$_2$PrBiO$_6$ double perovskite phase. For scanning electron microscope measurements, the Ba$_2$PrBiO$_6$ polycrystalline film on Ag substrate was fabricated from the single-phase powders by an electrophoretic deposition technique. The electrophoretic deposition was conducted in the acetone and iodine bath under the application of electric voltage up to 300 V for 120 s$^{16}$. We set Pt and Ag plates as anode and cathode electrodes, respectively. We performed X-ray diffraction measurements on the produced samples at room temperature with an Ultima IV diffractometer (Rigaku) using Cu-Ko radiation. The lattice parameters were estimated from the x-ray diffraction data using the RIETAN-FP program. The Brunauer-Emmett-Teller (BET) surface area of the powder samples was evaluated using a surface area analyzer (BELSORP-mini II, Microtrac).

Optical spectra were measured by a diffuse reflectance method using a spectrophotometer (Hitachi U-3500) and BaSO$_4$ was used as the reference material. The optical band gaps for the powder samples were evaluated from reflectance spectral data using the conventional Kubelka-Munk functions$^{6,13}$. The dc magnetization was measured at a magnetic field of 0.1 T under the field cooling process using a superconducting quantum interference device magnetometer (MPMS, Quantum Design). We conducted the gaseous 2-propanol (IPA) degradation experiment, to evaluate photocatalytic activities of the powder samples. (In detail, refer to$^{6,15}$). The powder (about 1g) was placed on the bottom of a small glass cell and its cell was set in a 0.5-L glass reactor vessel. After removing impurities from the vessel through filling a dry air, the dilute IPA gas (5cc) was injected into its vessel using a syringe. We started illuminating the visible light after the IPA concentration remained constant, which implied that the IPA gas finished absorbing on the surface of particles. The visible light was obtained using a 300W Xe lamp (Cermax LX300F, Excelitas Technologies). It is well known that the IPA gas under photocatalytic reaction is finally decomposed into CO$^2_{19}$. Accordingly, the CO$_2$ concentration was measured as a function of irradiation time using a gas chromatography system (GC-2014, Shimazu Co.)

III. RESULTS AND DISCUSSION

The X-ray diffraction patterns for the two end-member oxides, Ba$_2$PrBiO$_6$ and Ba$_2$PrSbO$_6$, are shown in Fig.1(a) and (b), respectively. For the parent Ba$_2$PrBiO$_6$ with a monoclinic structure (the space group $I2/m$), the lattice parameters are estimated to be $a = 6.2038$ Å, $b = 6.1689$ Å, $c = 8.7011$ Å and $\beta = 89.7303^\circ$ from the x-ray diffraction data using RIETAN-FP program, which are in good agreement with previous data$^{6,17}$. The emergence of (101) reflection (the inset of Fig.1(a)) indicates B-cation ordering which is characteristic of the ordered double-perovskite structure. The polycrystalline samples for $x < 0.5$ are formed in almost single phases of the monoclinic structure, while the $x = 1.0$ sample crystallizes in a rhombohedral structure with the space group $R3$. Substitution of the smaller Sb$^{5+}$ (0.60 Å) ion at the Bi$^{3+}$ (0.76 Å) site causes a monotonic decrease in the lattice parameters as displayed in the inset of Fig.1(b). Upon further increasing Sb content, the x-ray diffraction patterns for $x=0.5$ sample exhibit a two-phase mixture of monoclinic and rhombohedral structures. (data not shown) The double main peaks responsible for the monoclinic and rhombohedral phases are almost compa-
Fig. 1: (color online) X-ray diffraction patterns for the two end-member citrate samples, (a) $\text{Ba}_2\text{PrBiO}_6$ and (b) $\text{Ba}_2\text{PrSbO}_6$. The calculated profiles based on the monoclinic and rhombohedral structure models are shown in (a) and (b), respectively. The insets of (a) and (b) display the enlarged diffraction profiles and the lattice parameters as a function of Sb content. In the inset of (b), $c^* = c/\sqrt{2}$.

Fig. 2: (color online) (a) Crystal structures for the two end-member samples, $\text{Ba}_2\text{PrBiO}_6$ and $\text{Ba}_2\text{PrSbO}_6$. The left and right pictures represent the monoclinic and rhombohedral structures, respectively. Bi(or Sb)O$_6$ and PrO$_6$ octahedra are connected by corner-sharing with each other. (b) Charge separation model for the coexistence between trivalent and tetravalent states of Pr ions. The band gap at the cluster region occupied by the Pr$^{4+}$O$_6$ octahedra is assumed to be narrower than that at its neighboring region occupied by the Pr$^{3+}$O$_6$ octahedra. (see the text)
number of magnetic atom per mol, and the Bohr magneton, respectively. Performing the calculation for the parent and lightly Sb substituted samples, we obtain that $\mu_{\text{eff}} = 3.07 \mu_B$ and $3.05 \mu_B$ in $x=0$ and $x=0.1$ cases, respectively. As shown in the inset of Fig. 4 (a), the magnetic moment is almost stable against the Sb substitution. Next, we try to estimate the ratio of the Pr$^{3+}$ and Pr$^{4+}$ ions using the equation

$$\mu_{\text{eff}}^2 = y\mu_{\text{eff}}^2(\text{Pr}^{3+}) + (1-y)\mu_{\text{eff}}^2(\text{Pr}^{4+})$$

where $\mu_{\text{eff}}(\text{Pr}^{3+})=3.58 \mu_B$ and $\mu_{\text{eff}}(\text{Pr}^{4+})=2.54 \mu_B$. For the parent sample, we obtain that the ratio of Pr$^{3+}$ and Pr$^{4+}$ ions is $0.47 : 0.53$. For $x=0.1$, Pr$^{3+} : Pr^{4+} = 0.45 : 0.55$. For all the samples, the magnetic data strongly suggest the coexistence between trivalent and tetravalent states of Pr ions. The X-ray photoemission spectroscopy analysis of the solid-state parent sample revealed that a prominent peak of Pr$^{3+}$ is visible accompanied by a smaller shoulder structure of Pr$^{4+}$, which is consistent with the mixed valence state of the Pr ion.

We demonstrate the optical properties for the Ba$_2$Pr(Bi$_{1-x}$Sb$_x$)$_2$O$_6$ powder samples measured by the diffuse reflectance method. First, the observed reflectance data for the powder samples are transformed to the absorption coefficient $\alpha_{\text{KM}}$ by using the conventional Kubelka-Munk function. Next, for the Kubelka-Munk conversion data near the band edge, we extrapolate the tangent line to the $\varepsilon_p$ axis and evaluate the optical band gaps from the intersection according to the equation of

$$\alpha(\varepsilon_p) = \alpha \varepsilon_p$$

where $\alpha$, $\varepsilon_p$, and $E_g$ are the absorption coefficient, the photon energy, and the band gap energy. Here,
Fig. 5: (color online) Photocatalytic activities vs visible light irradiation time for Sb-substituted Ba$_2$PrBiO$_6$. (a) citrate pyrolysis samples, and (b) solid-state samples. The gaseous concentration is normalized by the surface area of the powder samples listed in Table 1.

it should be noted that the power exponent $n$ on the left hand side of the above formula decides the types of photon transition of optical absorption. For direct and indirect semiconductors, we assume that $n = 2$ and $n = 1/2$, respectively.\cite{01}
The optical measurements determine whether the energy gap is direct or indirect. Figure 4 (b) shows the absorption coefficient as a function of photon energy. For the $x=0$ sample, we adopt $(\alpha KM \varepsilon_p)^{1/2}$ vs $\varepsilon_p$ plot. In the inset of Fig. 4 (b), the square of the absorption coefficient for the $x=0.5$ and 1.0 samples, $(\alpha KM \varepsilon_p)^2$, is plotted as a function of $\varepsilon_p$. We estimate $E_g = 1.06$ eV at $x=0$ and 2.71 eV at $x=1.0$, assuming indirect and direct photon transitions, respectively. The magnitude of the energy band gap is substantially enhanced with increasing Sb content. When the Sb content exceeds 50\%, the nature of photon absorption is changed from the indirect to direct transitions.

Next, we conducted the gaseous IPA degradation experiment under a visible light irradiation, to evaluate photocatalytic activities of the powder samples. Figure 5 (a) shows the concentration of evolved CO$_2$ as a function of visible light irradiation time for the Sb-substituted Ba$_2$PrBiO$_6$. For comparison, the data for the solid state samples are presented. Here, we note that the concentration is normalized by the surface area of the powder samples listed in Table I. The CO$_2$ concentrations for both the parent and $x = 0.1$ citrate samples show a rapid rise at the initial 20 min under the visible light irradiation and then increase gradually with increasing irradiation time. On the other hand, for the Sb50\% and Sb100\% substituted samples we detect no clear evolution. We suspect that the band gap opening due to the heavy Sb substitution suppresses the formation of electron-hole pairs, causing a decrease of the photocatalytic reaction processes. In our previous study,\cite{22} the effect of the band gap opening due to the atomic substitution was examined by using first-principles electric structure calculation. The Sb substitution at Bi site gives rise to a reduction of the Bi-orbitals and then results in the enlarged band gap. The collapse of photocatalytic activity is probably originated from the larger band gap, which is closely related to the removal of Bi orbitals in the electric structures. The photocatalytic performance strongly depends on the Sb substitution, accompanied by an increase of the band gap energies. The photocatalytic data for the solid state samples with the same composition also show similar behaviors as the citrate samples. However, the evolved CO$_2$ values of the $x=0$ and $x=0.1$ citrate samples are more than twice as large as the data of the corresponding solid state samples, as shown in Fig. 5 (b). The enhanced photocatalytic properties in the citrate samples are attributed to their morphology, where fine particles are homogeneously distributed with a sub micron order. From the data listed in Table I we conclude that the parent and low Sb substituted samples exhibit good catalytic performance among the same synthesis based material members.

Finally, we discuss the charge separation model for higher activities of the parent Ba$_2$PrBiO$_6$ compound, as shown in Fig.2 (b). As far as we know, there are two approaches such as modification of the band gaps and improvement of the photogenerated charge separation in the photocatalytic materials, for completing high performance\cite{13,14,22}. We carried out the former approach by larger Sb substitution at Bi site in the double perovskite parent compounds as mentioned before. Here, we focus on the valence mixing states between Pr$^{3+}$ and Pr$^{4+}$ from the view point of charge separation. As shown in Fig.2 (b), it is assumed that the band gap at the cluster region occupied by the Pr$^{4+}$O$_6$ octahedra is narrower than that at its neighboring region occupied by the Pr$^{3+}$O$_6$ octahedra. For the Pr$^{4+}$ ions, the valence of their surrounding Bi ions is expected to change from 5+ to 3+ under electric neutral condition. Accordingly, the band gap becomes narrower in the presence of the Pr$^{4+}$O$_6$ octahedra because 6s electrons are added to empty orbitals of Bi$^{3+}$ contributing to a majority of valence and conduc-
tion band. The photoexcited electrons from the lower valence to upper conduction band do not recombine with holes, but transfer to its neighboring lower conduction band, resulting in charge separation. It has been reported that the Pr based compound with different valence states exhibits the highest efficiency among Ba$_2$ReBiO$_6$ series ($\text{Re}=\text{rare earth ions such as La, Pr, Ce, Nd, Sm, Eu, Gd, and Dy}$) in previous studies on the crystal structure and magnetic properties of Ba$_2$ReBiO$_6$, the Pr ion only is shown to exist in trivalent and tetravalent states (except for Ce). Therefore, we believe that our proposed model qualitatively describes one of the possible reasons for the efficient performance of the parent Ba$_2$PrBiO$_6$ compound.

IV. SUMMARY

We investigated the crystal structures, magnetic, and photocatalytic properties of the B-site substituted double perovskite Ba$_2$Pr(Bi$_{1-x}$Sb$_x$)O$_6$ ($x=0, 0.1, 0.2, 0.5$ and $1.0$) synthesized by the citrate pyrolysis precursor method. For comparison, the photocatalytic data for the solid-state sample were examined. The present synthesis procedure enabled to prepare highly homogeneous and fine powders. The single-phase poly crystalline samples with the light Sb substitution crystallized in a monoclinic structure ($I2/m$). Magnetization measurements showed that the effective magnetic moments are located around $3 \mu_B$, indicating the valence mixing states between Pr$^{3+}$ and Pr$^{4+}$.

The magnitudes of band gap energy for the two end member samples were estimated from the optical measurements to be $E_g =$1.06 eV at $x=0$ and 2.71 eV at $x=1.0$. The magnitude of the energy band gap is substantially enhanced with increasing Sb content. When the Sb content exceeds 50 %, the nature of photon absorption is changed from the indirect to direct transitions. The photocatalytic performance strongly depends on the Sb substitution accompanied by an increase of the band gap energies. The photocatalytic activities of the citrate powder samples with the light Sb substitution are considerably enhanced in comparison with those values of the samples prepared by the conventional solid state method. We believe that our charge separation model qualitatively describes one of the possible reasons for the efficient performance of the parent Ba$_2$PrBiO$_6$ compound in the presence of trivalent and tetravalent states of the Pr ions. We tried the two approaches to controlling the band gaps and realizing the photogenerated charge separation in the photocatalytic materials through larger Sb substitution and the valence mixing of the Pr ions. Our findings suggest that the higher photocatalytic activities strongly depend on the powder preparation method as well as the modification of band gaps and the photo-induced charge separation.

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