

## Optical and electrical properties of the wide gap, n-type semiconductors: $\text{ZnBi}_2\text{O}_6$ and $\text{MgBi}_2\text{O}_6$

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Characterization of polycrystalline samples of the trirutile oxides  $\text{ZnBi}_2\text{O}_6$  and  $\text{MgBi}_2\text{O}_6$  reveals temperature independent conductivity ( $0.4$  and  $0.01 \text{ S cm}^{-1}$ ), a negative Seebeck coefficient ( $-0.035$  and  $-0.025 \text{ mV K}^{-1}$ ), and an optical band gap that falls at the low energy end of visible region ( $1.7$  and  $1.8 \text{ eV}$ ), this combination of attributes, indicating that these compounds are degenerate n-type semiconductors, has not previously been observed in a  $\text{Bi}^{5+}$  oxide.

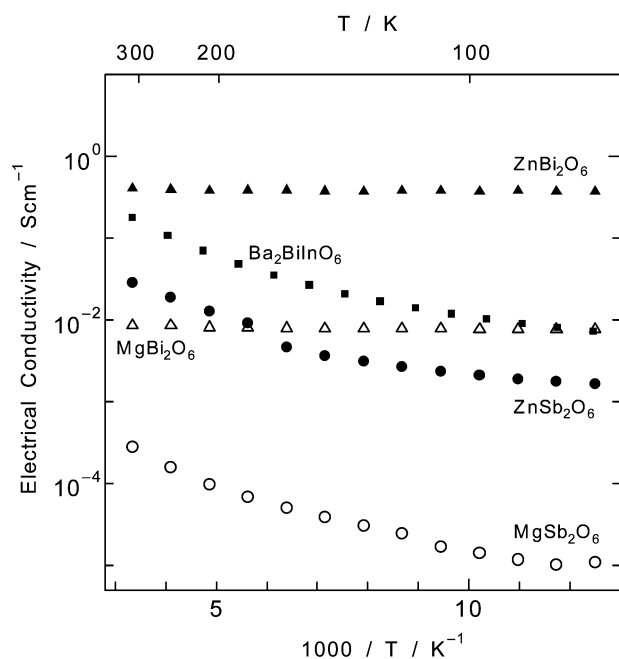
Materials that can be classified as transparent conducting oxides (TCO's)<sup>1</sup> possess an unusual combination of properties; high transparency across some or all of the visible spectrum, coupled with high electrical conductivity. TCO's have a wide variety of applications, including use in flat panel displays, solar cells, energy-efficient windows, gas sensors, antistatic coatings, and heating elements. Almost all TCO materials contain p-block cations with an  $(n-1)d^{10}ns^0$  electronic configuration, such as  $\text{Zn}^{2+}$ ,  $\text{Ga}^{3+}$ ,  $\text{Cd}^{2+}$ ,  $\text{In}^{3+}$ ,  $\text{Sn}^{4+}$ ,  $\text{Tl}^{3+}$  and  $\text{Pb}^{4+}$ .<sup>2</sup> The conduction band (CB) in these materials originates primarily from the antibonding interaction between the cation s-orbital and oxygen 2p-orbitals. The strong overlap produces a CB with large dispersion. This feature along with the high degree of s-character of the CB lead to high electron mobility, which is an essential characteristic for any transparent conductor. Among these oxides, attractive properties are known to exist among compounds which adopt the rutile structure. For example doped  $\text{SnO}_2$  is widely used as a window coating, while  $\beta\text{-PbO}_2$  is known to show one of the highest mobilities of any TCO material.<sup>3</sup> Therefore, it is interesting to examine the effects of replacing  $\text{Sn}^{4+}$  and  $\text{Pb}^{4+}$  with their group 15 analogues,  $\text{Sb}^{5+}$  and  $\text{Bi}^{5+}$ , while maintaining the topology of the rutile structure. While the pentavalent oxidation states of  $\text{Sb}^{5+}$  and  $\text{Bi}^{5+}$  do not allow one to prepare compounds that are truly isostructural with the  $\text{Sn}^{4+}$  and  $\text{Pb}^{4+}$  compounds, antimony and bismuth ions can be incorporated into the trirutile structure, with stoichiometry  $\text{AM}_2\text{O}_6$ . In these compounds the increased electronegativity of the group 15 elements increases the covalency of the M 5s/6s–O 2p interaction, which in the absence of other effects will increase the CB dispersion. However, the introduction of a more electropositive divalent cation on 1/3 of the octahedral sites will tend to reduce the long range connectivity of the  $\text{MO}_6$  octahedra, thereby decreasing CB dispersion. The net effect of these competing interactions is not entirely clear. While there have been some investigations of the electrical and optical properties of  $\text{Sb}^{5+}$  oxides, such as  $\text{CdSb}_2\text{O}_6$ ,  $\text{Cd}_2\text{Sb}_2\text{O}_7$ ,  $\text{ZnSb}_2\text{O}_6$ ,  $\text{AgSbO}_3$ , and  $\text{InSbO}_4$ ,<sup>4</sup> to our knowledge the only previous report of electronic conductivity in a  $\text{Bi}^{5+}$  oxide, was for the disordered perovskite compound  $\text{Ba}_2\text{InBiO}_6$ .<sup>5</sup> Therefore, we have synthesized and characterized  $\text{ABi}_2\text{O}_6$  ( $\text{M} = \text{Mg}^{2+}$ ,  $\text{Zn}^{2+}$ ) in order to investigate the prospects for achieving transparent conductivity in a  $\text{Bi}^{5+}$  oxide.

$\text{ABi}_2\text{O}_6$  ( $\text{A} = \text{Mg}^{2+}$ ,  $\text{Zn}^{2+}$ ) samples were synthesized by hydrothermal methods as reported by Kumada *et al.*<sup>6</sup> Source materials,  $\text{NaBiO}_3$  and  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  for  $\text{A} = \text{Mg}$  or  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  for  $\text{A} = \text{Zn}$ , were placed with water in a Teflon lined autoclave and kept at 390 K and 370 K, respectively, for 2 days. The obtained powder was filtered and washed twice with

water and once with acetone, then dried at 320 K in air. For comparison  $\text{ASb}_2\text{O}_6$  ( $\text{A} = \text{Mg}$ ,  $\text{Zn}$ ) and  $\text{Ba}_2\text{MBiO}_6$  ( $\text{M} = \text{In}$ ,  $\text{Y}$ ,  $\text{La}$ ) were also synthesized and characterized.  $\text{MgSb}_2\text{O}_6$  samples were synthesized by solution method through  $\text{Sb}_2\text{O}_5$  sol.<sup>7</sup>  $\text{Sb}_2\text{O}_3$  (0.8 g) and  $\text{H}_2\text{O}_2$  (20 ml) were added to water (100 ml) and kept at 360 K with stirring for 1 h. Stoichiometric  $\text{MgCl}_2$  in aqueous solution was poured into the antimony oxide sol slowly and heated until evaporation of the solvent was achieved. After drying, the samples were pressed into pellets and sintered at 1320 K.  $\text{ZnSb}_2\text{O}_6$  and  $\text{Ba}_2\text{MBiO}_6$  samples were synthesized using conventional ceramic methods. The chemical composition of the samples was confirmed using energy dispersive X-ray analysis (EDX), while oxygen contents were found by thermogravimetric analysis to be quite close to their stoichiometric values.

The X-ray diffraction patterns of  $\text{ABi}_2\text{O}_6$  samples showed only the peaks expected from the trirutile structure. Rietveld refinements confirmed the structural characterization of Kumada, *et al.*<sup>6</sup> Pressed green compacts were used for the electrical characterization, as all attempts to sinter pellets led to partial or complete thermal decomposition. The densities of  $\text{MgBi}_2\text{O}_6$  and  $\text{ZnBi}_2\text{O}_6$  pressed pellets were estimated to be 58% and 51% of theoretical X-ray density, respectively. Electrical contacts were applied using silver paste and standard four probe electrical conductivity measurements were made over the temperature range 300–80 K. Both samples showed temperature independent conductivity over the entire temperature range investigated, suggesting that these compounds are degenerate semiconductors. Seebeck coefficients were measured to be  $-0.025$  and  $-0.035 \text{ mV K}^{-1}$  at 300 K for  $\text{MgBi}_2\text{O}_6$  and  $\text{ZnBi}_2\text{O}_6$ , respectively. The negative Seebeck coefficients confirm that these compounds are n-type semiconductors, as are  $\text{SnO}_2$  and  $\beta\text{-PbO}_2$ . The electrical conductivities,  $\sigma$ , were measured to be  $0.4 \text{ S cm}^{-1}$  for  $\text{ZnBi}_2\text{O}_6$  and  $0.01 \text{ S cm}^{-1}$  for  $\text{MgBi}_2\text{O}_6$ , as shown in Fig. 1. While the measured conductivity values are much lower than typically required for application as a transparent conductor, it should be borne in mind that grain boundary resistance is likely to be high for cold-pressed compacts, so that the intrinsic conductivity is almost certainly much higher. As a comparison we have included our conductivity measurements on sintered pellets of the trirutile analogues  $\text{ZnSb}_2\text{O}_6$  and  $\text{MgSb}_2\text{O}_6$ , as well as the perovskites  $\text{Ba}_2\text{InBiO}_6$ ,  $\text{Ba}_2\text{YBiO}_6$  and  $\text{Ba}_2\text{LaBiO}_6$ . Note that conductivity of  $\text{ZnBi}_2\text{O}_6$  is higher than any other compound in this group, even  $\text{Ba}_2\text{InBiO}_6$ , which has a much smaller band gap as shown in Fig. 2. Perhaps more important is the observation that only the  $\text{Bi}^{5+}$  trirutile oxides have the temperature dependence of a degenerate semiconductor. Whereas, both the  $\text{Sb}^{5+}$  trirutile phases and the  $\text{Bi}^{5+}$  perovskite phases show behavior consistent with an activated transport mechanism, in agreement with previous reports.<sup>4b,5</sup> Therefore, we would expect the intrinsic carrier mobility of the  $\text{ABi}_2\text{O}_6$  phases to be rather large.

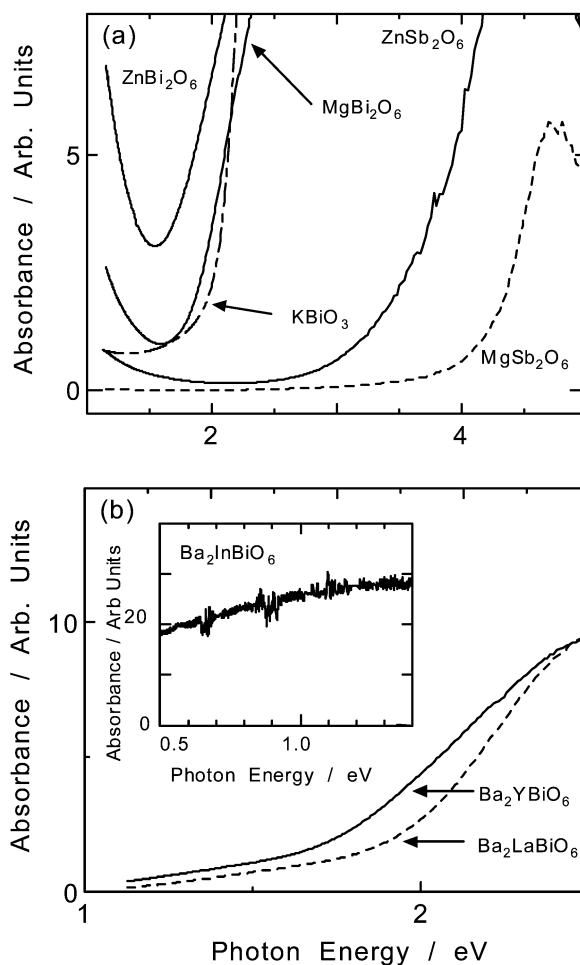
Diffuse reflectance spectra reveal that the reddish color of  $\text{MgBi}_2\text{O}_6$  and the brownish color of  $\text{ZnBi}_2\text{O}_6$  originate from optical band gaps of 1.8 and 1.7 eV, respectively, as shown in Fig. 2. These values are similar to the bandgap of  $\text{KBiO}_3$  (2.1 eV), and can be ascribed to the charge transfer electronic



**Fig. 1** Temperature dependence of electrical conductivity of  $\text{ABi}_2\text{O}_6$ ,  $\text{ASb}_2\text{O}_6$  ( $A = \text{Mg, Zn}$ ) and  $\text{Ba}_2\text{InBiO}_6$ .

transition between the valence band maximum, which is largely O 2p in character, and the conduction band minimum, which has predominantly Bi 6s orbital character. Band structure calculations, which will be published elsewhere, are in agreement with this description. In addition to the band gap transition, additional absorption was observed around 1.2 eV in both spectra. This feature is ascribed to excitations originating from the plasma frequency, which give further evidence for the existence of free carriers. The bandgaps of  $\text{ZnBi}_2\text{O}_6$  and  $\text{MgBi}_2\text{O}_6$  are similar to the bandgap of  $\beta\text{-PbO}_2$  (~1.7 eV) and smaller than that of  $\text{SnO}_2$  (~3.6 eV) or the  $\text{Sb}^{5+}$  trirutile oxides. In contrast,  $\text{Ba}_2\text{InBiO}_6$  is highly absorbing across the entire spectral range investigated.  $\text{Ba}_2\text{YBiO}_6$  and  $\text{Ba}_2\text{LaBiO}_6$  have optical band gaps similar to the trirutile  $\text{Bi}^{5+}$  compounds but cannot be made conducting through doping, presumably due to the narrow conduction band width that results from isolating the  $\text{Bi}^{5+}$  centered octahedra in the ordered perovskite structure.

These results show that the electronic structure of the  $\text{Bi}^{5+}$  trirutile oxides shares a number of common characteristics with well known TCO materials. The findings demonstrate it is possible to tune the  $\text{Bi}^{5+}$  6s–O 2p interaction in order to produce a disperse conduction band which is located so as to produce an optical band gap that extends into the visible region of the spectrum. While the  $\text{Sb}^{5+}$  trirutile oxides have larger band gaps, which is attractive for TCO applications, it appears that they cannot easily be doped to such an extent that they become degenerate semiconductors. Direct determination of the carrier concentration and mobility is difficult due to the lack of good single crystals or thin films. However, it is possible to make a crude estimate of the carrier concentration from the plasma frequency ( $\omega_p$ ). From the diffuse reflectance spectra, we can estimate  $\omega_p = 0.2\text{--}1.0$  eV. If we take a minimum value of 0.2 eV for the plasma frequency, assume a value of  $5 \epsilon_0$  for the permittivity ( $\epsilon_0$ : permittivity in vacuum), and  $0.3 m_0$  for the effective mass of the carriers ( $m_0$ : mass of free electron in vacuum), we obtain a value of  $\sim 4 \times 10^{19} \text{ cm}^{-3}$  for the carrier



**Fig. 2** Optical absorption spectra of  $\text{Bi}^{5+}$  and  $\text{Sb}^{5+}$  trirutile-type oxides,  $\text{Ba}_2\text{MBiO}_6$  perovskites and  $\text{KBiO}_3$  as a reference.

concentration. Typically a carrier concentration of this magnitude in a degenerate semiconductor would lead to a conductivity in excess of  $10 \text{ S cm}^{-1}$ .<sup>8</sup> Thus our measured conductivities are 2–4 orders of magnitude smaller than expected. These considerations lead us to the conclusion that the measured conductivities are much smaller than the intrinsic value due to a relatively large grain boundary resistance that would be expected for measurements on pressed powders. Therefore, high quality films of  $\text{MgBi}_2\text{O}_6$  and especially  $\text{ZnBi}_2\text{O}_6$  are likely to show relatively high conductivities.

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