

Magnetic properties of perovskite-type oxide  $\text{BaBiO}_3$  and of  $\text{BaBi}_{1-x}\text{M}_x\text{O}_3$  with M identical to In, Mo or La

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# Magnetic properties of perovskite-type oxide $\text{BaBiO}_3$ and of $\text{BaBi}_{1-x}\text{M}_x\text{O}_3$ with $\text{M} \equiv \text{In, Mo or La}$

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**Abstract.** The magnetic properties of  $\text{BaBiO}_3$  and the metal-substituted compounds  $\text{BaBi}_{0.5}\text{In}_{0.5}\text{O}_3$ ,  $\text{BaBi}_{0.85}\text{Mo}_{0.15}\text{O}_3$  and  $\text{BaBi}_{0.5}\text{La}_{0.5}\text{O}_3$  were measured. A combined behaviour of temperature-dependent Curie-like paramagnetism and of independent diamagnetism was observed. The diamagnetic contribution is about  $8 \times 10^{-5} \text{ emu mol}^{-1}$  almost independently of the metal impurities. The paramagnetic contribution, on the other hand, shows markedly different behaviours for different impurities. The number of Bohr magnetons included in a molecule is larger by one order of magnitude for the compound with indium than for those without and with transition-metal impurities. It was concluded that the paramagnetic behaviour comes from the holes on the Bi 6s and O 2p bonding orbits, while the diamagnetic behaviour mainly comes from the core electrons on barium or on the other ions. A deviation from the Curie law in the low-temperature region was observed. In the case of  $\text{BaBi}_{0.85}\text{Mo}_{0.15}\text{O}_3$  and  $\text{BaBi}_{0.5}\text{La}_{0.5}\text{O}_3$  the behaviour could not be explained by the simple idea of saturation in a field. For  $\text{BaBi}_{0.5}\text{In}_{0.5}\text{O}_3$  a phase-transition-like behaviour at around 10 K was observed. It is pointed out that there is some correlation between the number of Bohr magnetons and the number of electric current carriers.

## 1. Introduction

The perovskite-type compound  $\text{BaBiO}_3$  is known to be an activation-type semiconductor. The electrical properties have been discussed in relation to the valence of bismuth. According to Cox and Sleight [1, 2], the oxidation state in  $\text{BaBiO}_3$  is described as  $\text{Ba}^{2+}\text{Bi}_{0.5}^{3+}\text{Bi}_{0.5}^{5+}\text{O}_3^{2-}$  rather than  $\text{Ba}^{2+}\text{Bi}^{4+}\text{O}_3^{2-}$ . They suggested that  $\text{Bi}^{3+}$  and  $\text{Bi}^{5+}$  construct an ordered structure accompanied by alternative expansion and contraction of the oxygen octahedra around the respective bismuth sites. This configuration is called the static charge density wave (CDW) or breathing-mode distortion, as a whole. CDW order creates a band gap at the Fermi level, and then the semiconductor-like property arises. The idea of a CDW gap has been supported by many workers [3–9].

Different ideas have also been described by other workers. In order to control the oxidation state, de Hair and Blasse [10] substituted lanthanum, terbium or lead in the place of bismuth in the compound. By means of infrared absorption spectrum measurement they suggested that the valence of bismuth changes depending on the substituted element and the concentration. Some workers studied the effect of oxygen vacancies [11–17]. Chaillout and Remeika [14] suggested that the bismuth valence in  $\text{BaBiO}_3$  depends on the oxygen stoichiometry. Suzuki and Murakami [15] measured the resistivity and Hall coefficients in the superconducting compound  $\text{BaPb}_{0.7}\text{Bi}_{0.3}\text{O}_3$  with oxygen vacancies. They described the fact that the oxygen vacancies induce excess  $\text{Bi}^{3+}$  ions and concluded that the Anderson localization around Bi ions bring about a metal–insulator transition. In our previous work we

studied the metal substitution effect through the crystal structure, electrical resistivity and x-ray photoelectron spectroscopy [18–20]. The electrical resistivity and the carriers' activation energy markedly changed, depending on the doped impurities. The lattice parameters also changed, while the valence band structure at the Fermi level was insensitive to substitution.

In the present work we measured the magnetic properties in some  $\text{BaBi}_{1-x}\text{M}_x\text{O}_3$  compounds ( $\text{M} \equiv \text{In}, \text{Mo}$  or  $\text{La}$ ). From the paramagnetic susceptibility obtained, a discussion about the valence electron states will be given in the following sections.

## 2. Experimental procedure

Two kinds of  $\text{BaBiO}_3$  crystals were grown with starting materials and a crucible of different purities. One was grown from 99.99%  $\text{BaCO}_3$  and  $\text{Bi}_2\text{O}_3$  in the purest crucible of SSA-S with 99.5% alumina by Nihon Chemical Ceramics (C.C.) Co., and the other from 99.9% reagent in a crucible of SSA-H with 95.4% alumina. This will be described in section 3, and no detectable difference between the magnetic and x-ray data for samples in both groups was found. The other compounds were synthesized by the use of the latter group.  $\text{BaBi}_{0.85}\text{Mo}_{0.15}\text{O}_3$  was also grown in the form of a crystal, where  $\text{Mo}_2\text{O}_3$  was added as one of the starting materials. Crystal growth was made by slowly cooling the molten mixture of starting materials with the cationic stoichiometry. Single crystals of size greater than  $3 \text{ mm} \times 3 \text{ mm} \times 1 \text{ mm}$  were cut from the solidified block. The details of crystal growth have been described elsewhere [18, 19].  $\text{BaBi}_{0.5}\text{In}_{0.5}\text{O}_3$  and  $\text{BaBi}_{0.5}\text{La}_{0.5}\text{O}_3$  were synthesized by sintering. A mixture of powdered  $\text{BaCO}_3$ ,  $\text{Bi}_2\text{O}_3$  and  $\text{In}_2\text{O}_3$  (or  $\text{La}_2\text{O}_3$ ) with the desired cationic ratio was calcined at  $790^\circ\text{C}$  for 24 h. Then it was pressed at  $160 \text{ kg cm}^{-2}$  and finally sintered at  $800^\circ\text{C}$  for 24 h in oxygen gas flowing at  $5 \text{ l min}^{-1}$ .

Quantitative analysis was carried out using a JEOL JED-2001 electron probe microanalyser. The results showed that the compositions of metallic elements were spatially distributed within  $\pm 3\%$  of the intended compositions, and that the oxygen stoichiometry range was  $2.8 \pm 0.05$  in all the samples. The mean valence of bismuth was calculated as four.

Powder x-ray diffraction measurements were carried out at room temperature. All the compounds showed a perovskite-type crystal structure.  $\text{BaBiO}_3$  and  $\text{BaBi}_{0.5}\text{La}_{0.5}\text{O}_3$  were accompanied by a monoclinic strain, and  $\text{BaBi}_{0.85}\text{Mo}_{0.15}\text{O}_3$  by a tetragonal strain. Only  $\text{BaBi}_{0.5}\text{In}_{0.5}\text{O}_3$  was cubic. No traces of impurities or primary oxides were detected in the spectra of all samples.

The magnetization was measured using a Quantum Design Co. SQUID magnetometer. The temperature region was 2–300 K and the field was up to 50 kG.

## 3. Results and discussions

Figure 1 shows the temperature and field dependences of magnetic properties for a  $\text{BaBiO}_3$  single crystal. They are typical behaviours for the present series of compounds, which show overlap of Curie-like paramagnetism and temperature-independent diamagnetism. From the temperature dependence (figure 1(a)) the susceptibility should be written

$$\chi(T) = \chi_p(T) + \chi_d \quad (1)$$

Here,  $\chi_d$  is a negative constant of the compound. The temperature-dependent term  $\chi_p(T)$  is assumed to behave according to the Curie law and is written

$$\chi_p(T) = Nn^2\mu_B^2/3k_B T$$

so that

$$\chi(T) = Nn^2\mu_B^2/3k_B T + \chi_d \quad (2)$$

where  $\mu_B$  is the Bohr magneton,  $n$  is the number of Bohr magnetons on a molecule and  $N$  is the number of molecules.  $k_B$  is the Boltzmann constant. From the field dependence seen in figure 1(b) the gradient of the linear part gives  $\chi_d$ .  $M - \chi_d B$  gives the paramagnetic contribution,  $M_p$ . Figure 2(a) shows that  $BaBiO_3$  has a spin paramagnetic moment of about  $1.5 \text{ emu mol}^{-1}$ . To check the influence of magnetic impurities the reproducibility was ascertained by using crystals grown from two groups of starting materials and the crucibles as described in section 2.

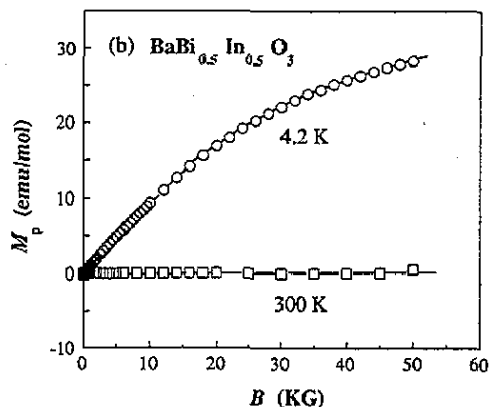
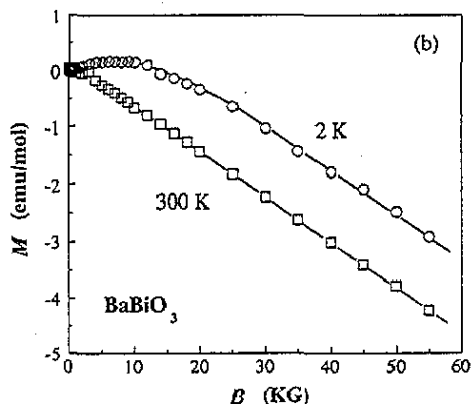
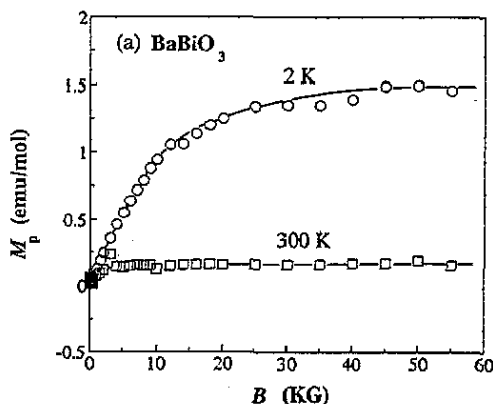
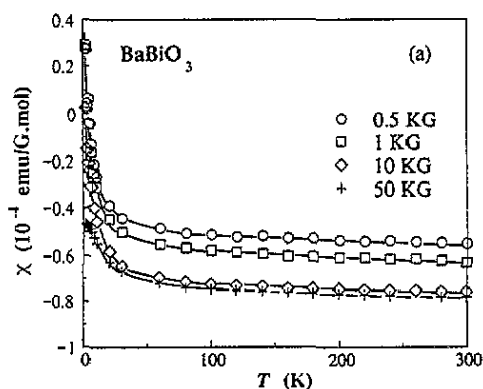


Figure 1. (a) Temperature dependence of the molar magnetic susceptibility of  $BaBiO_3$ . The parameters are the magnetic field values. Curie-like behaviour is clearly seen here. (b) Field dependence of the molar magnetization. The parameters are the mean temperatures. The gradient of the linear part gives the diamagnetic susceptibility  $\chi_d$ .

Figure 2. Paramagnetic contribution to the magnetization: (a)  $BaBiO_3$ ; (b)  $BaBi_{0.5}In_{0.5}O_3$ . The numerical value in (b) at 4.2 K is larger by a factor of 20 than in (a) at a field of 50 kG. It does not seem to saturate, yet.

A considerable difference was observed depending on the metal element substituted. The most characteristic behaviour is seen for  $BaBi_{0.5}In_{0.5}O_3$ , which has no magnetic metal element. It has a larger paramagnetic contribution by a factor of almost 20 than  $BaBiO_3$  at 50 kG. On the contrary the compounds with transition elements substituted, namely  $BaBi_{0.85}Mo_{0.15}O_3$  and  $BaBi_{0.5}La_{0.5}O_3$ , have rather smaller paramagnetic contributions. This

Table 1. Magnetic data.

Compound	$\chi_d$ ( $10^{-6}$ emu G $^{-1}$ mol $^{-1}$ )	Effective number of $\mu_B$ (formula unit $^{-1}$ )	Sample
BaBiO <sub>3</sub>	-79.5	0.0413	Crystal
BaBi <sub>0.5</sub> In <sub>0.5</sub> O <sub>3</sub>	-77.7	0.1850	Ceramic
BaBi <sub>0.85</sub> Mo <sub>0.15</sub> O <sub>3</sub>	-72.3	<0.0330	Crystal
BaBi <sub>0.5</sub> La <sub>0.5</sub> O <sub>3</sub>	-19.9	<0.00537	Ceramic

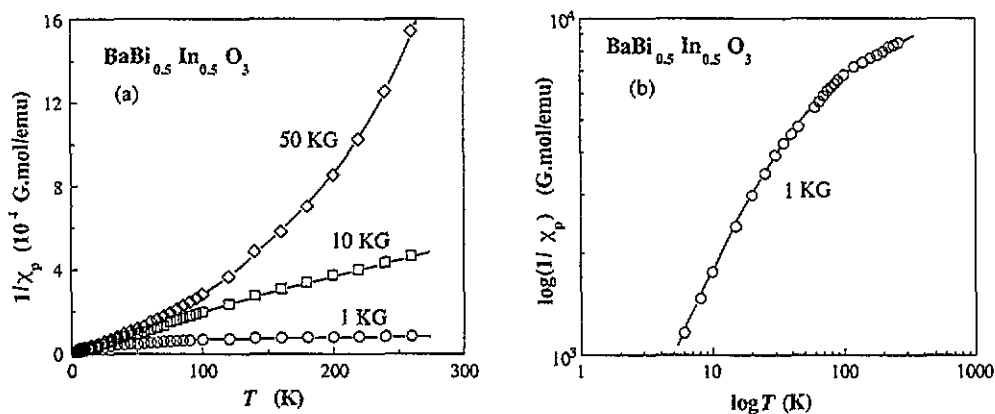
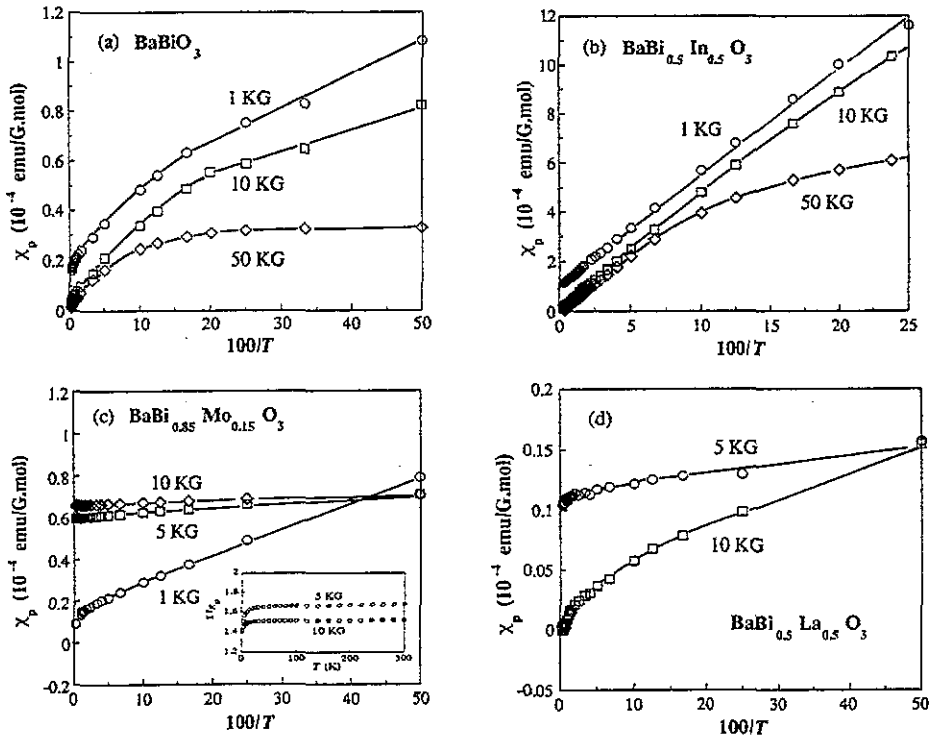


Figure 3. (a) Inverse of the paramagnetic susceptibility  $\chi_p$  plotted as a function of temperature for BaBi<sub>0.5</sub>In<sub>0.5</sub>O<sub>3</sub>. (b) A logarithmic plot at 10 kG. A slight change in the gradient is seen at around 100 K.

can be seen from figures 4(c) and 4(d) or in table 1, as described later. The inverse of  $\chi_p (= \chi(T) - \chi_d)$  for BaBi<sub>0.5</sub>In<sub>0.5</sub>O<sub>3</sub> is plotted against  $T$  in figures 3(a) and 3(b), as an example. A marked deviation from the Curie law is observed in these figures. The classical law should hold at temperatures higher than 100 K under our experimental conditions. Despite this, no linearity is seen in the figures even at as low field as 1 kG. Moreover, some change in the temperature-dependent behaviours between fields of 10 and 50 kG is seen. The logarithmic plot of the behaviour in a field of 1 kG is shown in figure 3(b). This suggests some possible phase change at around 100 K.

The behaviour at low temperatures is rather clearer in the plots of  $\chi_p$  against  $1/T$  shown in figure 4. The tendency of saturation seen in figures 4(a) and 4(b) with increasing field at low temperatures is understood as it shows the deviation from the classical condition. On the contrary, the compounds substituted by the transition-metal elements molybdenum and lanthanum show a quite different behaviour, as seen in figures 4(c) and 4(d). In the crystal with 15 at.% Mo the susceptibility at low temperatures is almost independent of the applied field up to 10 kG, but the temperature dependence is considerably suppressed by the field. The paramagnetic susceptibility at room temperature is larger by a factor of 6 in a field of 5 kG than in a field of 1 kG. The behaviours independent of temperature in higher fields are clearer in the inset of figure 4(c). The compound doped with 50 at.% La has quite small susceptibilities  $\chi_d$  and  $\chi_p$ . The paramagnetic contribution shows a similar temperature dependence to that of BaBi<sub>0.85</sub>Mo<sub>0.15</sub>O<sub>3</sub>, but the field dependence is the opposite. Now the temperature dependence of  $\chi_p$  increases with increasing field. In the calculation of  $\chi_p$  we subtracted  $\chi_d$  at room temperature from the measured susceptibility. Although the absolute value of the latter slightly decreases with increasing temperature for BaBi<sub>0.85</sub>Mo<sub>0.15</sub>O<sub>3</sub> and BaBi<sub>0.5</sub>La<sub>0.5</sub>O<sub>3</sub>, the whole characteristics of the temperature dependence of  $\chi_p$  are not modified in practice at lower temperatures. The numbers  $n$  of Bohr magnetons per formula



**Figure 4.**  $\chi_p$  plotted against the inverse temperature: (a)  $\text{BaBiO}_3$ ; (b)  $\text{BaBi}_{0.5}\text{In}_{0.5}\text{O}_3$ ; (c)  $\text{BaBi}_{0.85}\text{Mo}_{0.15}\text{O}_3$ ; (d)  $\text{BaBi}_{0.5}\text{La}_{0.5}\text{O}_3$ . The number of Bohr magnetons  $\mu_B$  was calculated from the gradient of the line at 10 kG and in the temperature region below 10 K for every compound.

unit were calculated from figure 4. Here the gradient of the line at 10 kG was used in the range 5–10 K for every compound. These are summarized in table 1 together with  $\chi_d$  per mole calculated at room temperature. The numerical values of  $\chi_d$  are consistent with the results for  $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$  [21]. On the other hand the agreement of  $\chi_p$  with the data from previous studies is not good [12]. This is natural considering that  $\chi_d$  comes from the core states, and that  $\chi_p$  is from the valence states, which are sensitive to the oxidation state.

Nakamura *et al* [12] suggested that the paramagnetism is induced by spin pairing between 6s states on Bi ions. We also point out that the paramagnetic moments are situated on the holes in the hybridized Bi 6s–O 2p orbit. As the mean valence of bismuth is four for our  $\text{BaBiO}_3$  sample, the existence of unpaired 6s electrons is possible. Inevitable oxygen defects presumably cause some distribution in the value of  $\chi_p$ . The paramagnetism is markedly enhanced by the substitution of trivalent indium. This supports the above prediction, because the substitution may increase the unpaired electrons. It should also increase the interaction between spins, because the unit-cell volume is less by about 6% for  $\text{BaBi}_{0.5}\text{In}_{0.5}\text{O}_3$  than for  $\text{BaBiO}_3$  [19, 20]. Compounds substituted by molybdenum or lanthanum have larger cell volumes. Moreover, the valence of molybdenum in  $\text{BaBi}_{0.85}\text{Mo}_{0.15}\text{O}_3$  is probably four. In the case of  $\text{BaBi}_{0.5}\text{La}_{0.5}\text{O}_3$  the resistivity is higher by a factor of 1000 than for  $\text{BaBiO}_3$  [19], suggesting that the valence state is almost filled in the former. This explains the small paramagnetism in the two compounds with molybdenum or lanthanum. This interpretation is consistent with the Hall effect results [15, 22], where the current was carried by very few holes even at room temperature.

#### 4. Conclusions

The magnetic properties of  $\text{BaBiO}_3$ ,  $\text{BaBi}_{0.5}\text{In}_{0.5}\text{O}_3$ ,  $\text{BaBi}_{0.85}\text{Mo}_{0.15}\text{O}_3$  and  $\text{BaBi}_{0.5}\text{La}_{0.5}\text{O}_3$  have been measured. The magnetism in every compound is approximately given as the addition of almost constant diamagnetism and Curie-like paramagnetism. The value of the diamagnetic susceptibility is nearly common to all the compounds. This shows that the core electron states are little modified by the impurity substitution into bismuth sites. The paramagnetic susceptibility relates to the outermost electronic configuration. Its numerical value is much enhanced by the substitution of bismuth by trivalent indium. This is because the unpaired spins have increased with an increasing number of holes on the hybridized Bi 6s-O 2p orbit. The paramagnetic susceptibility is almost the same for  $\text{BaBi}_{0.85}\text{Mo}_{0.15}\text{O}_3$  as for  $\text{BaBiO}_3$ . This is consistent with the suggestion that molybdenum is tetravalent in the compound. For  $\text{BaBi}_{0.5}\text{La}_{0.5}\text{O}_3$ ,  $\chi_p$  is very small. It was suggested that some relation exists between  $\chi_p$  and the electrical transport properties. The anomalous behaviours of the susceptibilities which are seen at higher temperatures for  $\text{BaBi}_{0.85}\text{Mo}_{0.15}\text{O}_3$  and  $\text{BaBi}_{0.5}\text{La}_{0.5}\text{O}_3$  could not be explained.

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