

# Iodine intercalation in the oxide-ion conductor $\text{BaBi}_8\text{O}_{13}$

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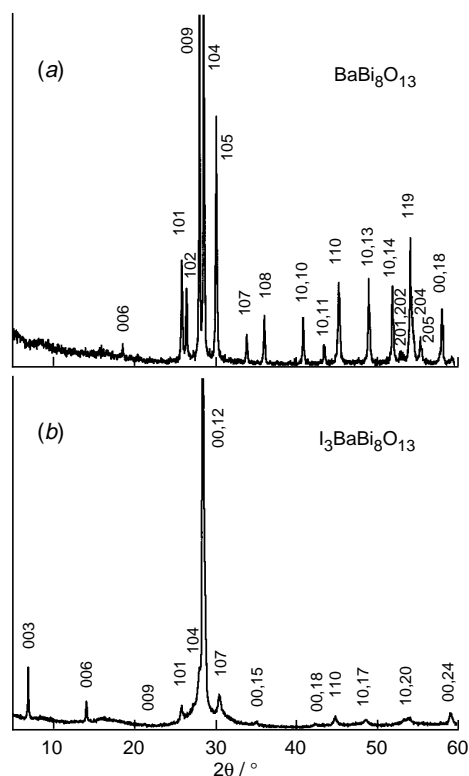
**The intercalation compound  $\text{I}_3\text{BaBi}_8\text{O}_{13}$  forms on reaction of iodine with the layered oxide-ion conductor  $\text{BaBi}_8\text{O}_{13}$ ; the location of iodine within the structure and the ac conductivity of the iodine intercalated phase are described.**

Intercalation reactions of neutral molecules with neutral layered host lattices are restricted to a few guest–host combinations.<sup>1</sup> In insulating host lattices, host–guest interactions include hydrogen bonding, for example in formamide–kaolinite intercalation compounds,<sup>2</sup> and coordination of a base to a metal centre in pyridine– $\text{VOPO}_4$ .<sup>3</sup> In conducting host lattices, intercalation of neutral molecules is usually accompanied by oxidation of the host lattice and reduction of the guest species. The formation of graphite intercalation compounds with bromine and arsenic pentafluoride are among the most studied examples of neutral molecule intercalation reactions that proceed by this mechanism.<sup>4</sup> A closely related recent example was provided by the observation of iodine intercalation in bismuth cuprate high  $T_c$  superconductors, for example,  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ .<sup>5</sup> Iodine is intercalated by direct reaction with the oxide to form a stage 1 structure with iodine located between the double Bi–O sheets and the composition  $\text{IBi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ . The nature of the intercalated iodine species remains controversial though the preponderance of the evidence from Raman, XPS, and XAS measurements suggests that the intercalated species is  $\text{I}_3^-$  charge balanced by the formation of holes in the  $\text{CuO}_2$  planes.<sup>6–12</sup> Here, we describe a new example of the intercalation of iodine into the layered bismuth oxide host lattice,  $\text{BaBi}_8\text{O}_{13}$ . In this case, the host lattice is a good oxide ion conductor but is electronically insulating.

The composition  $\text{BaBi}_8\text{O}_{13}$  is part of the solid solution series observed in the  $\text{Bi}_2\text{O}_3$ – $\text{BaO}$  phase diagram between *ca.* 20 to 25 mole%  $\text{BaO}$  that is characterized by a rhombohedral layer structure.<sup>13</sup> The same layered structure type is also observed in the  $\text{Bi}_2\text{O}_3$ – $\text{MO}$  ( $\text{M} = \text{Ca}, \text{Sr}$ ) systems.<sup>14</sup> Each macrolayer is composed of a slab built of octahedrally coordinated (Ba,Bi)–O units sandwiched between two planar hexagonal Bi–O sheets. The structure of each complex layer can be related to that of fluorite and is distinctly different from the structure of the square-planar BiO layers in  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ . In each rhombohedral unit cell of  $\text{BaBi}_8\text{O}_{13}$  (space group  $R\bar{3}m$ ) three interlayer spaces are located between the hexagonal Bi–O sheets (a significant fraction of the oxygen atoms in the Bi–O layers are missing). The macrolayers are held together by van der Waals forces and there are no interlayer ions in the pristine host lattice. The rhombohedral phase has been studied in detail because of its very high oxide ion conductivity.<sup>13–19</sup> Two previous structural studies have investigated possible oxygen transport pathways and have suggested that migration *via* the empty interlayer sites is important in the anionic conduction mechanism.<sup>16,19</sup> In this study, we have synthesized the new intercalation compound  $\text{I}_3\text{BaBi}_8\text{O}_{13}$  and measured its ac conductivity. The conductivity difference between the host and the intercalated lattice gives further insight into the conductivity mechanism.

The host material was prepared by reaction of a stoichiometric mixture of  $\text{Bi}_2\text{O}_3$  and  $\text{Ba}(\text{NO}_3)_2$  with repeated grinding and annealing at 710 °C in air. The lattice parameters of the single-phase product ( $\text{BaBi}_8\text{O}_{13}$ ) were determined from the powder

X-ray diffraction (XRD) pattern shown in Fig. 1(a) [ $a = 3.984(1)$ ,  $c = 28.491(2)$  Å]. Iodine intercalation was carried out by reaction of single-phase  $\text{BaBi}_8\text{O}_{13}$  with  $\text{I}_2$  (4–5 molar excess) in a sealed evacuated (*ca.* 50 mTorr) Pyrex tube for 1–5 d. The optimum conditions for intercalation were investigated by varying reaction temperatures from 50 to 350 °C and analysing the reaction products by XRD. The yellow colour of the starting material changes to brown on intercalation. For temperatures  $\leq 150$  °C, the XRD patterns showed no reaction between the host material and excess iodine. Reactions at temperatures  $\geq 300$  °C resulted in a decomposition of the starting materials to  $\text{BiI}_3$  and other unidentified impurity phases. XRD patterns of samples reacted at 150–275 °C showed the formation of a single-phase layered iodine intercalated compound [Fig. 1(b)]. Electron microprobe analysis (EMPA<sup>†</sup>) was used to determine the stoichiometry of the reaction product. Analyses of elemental composition and the backscattered electron images indicated the formation of a single-phase product with an average composition  $\text{I}_{3.10}\text{Ba}_{0.98}\text{Bi}_{8.06}\text{O}_{13.42}$ .<sup>‡</sup> The stability of the iodine intercalated structure was studied by thermogravimetric analysis (TGA) under flowing  $\text{N}_2$  saturated with water at 298 K using a TA 2950 Instrument. TGA and XRD showed that the iodine intercalated structure is stable up to temperatures of *ca.* 450 °C, although this is accompanied by the evolution of 1.3 moles of iodine. Above 650 °C the host material is the majority phase observed together with small



**Fig. 1** Powder X-ray diffraction patterns for (a) the host compound  $\text{BaBi}_8\text{O}_{13}$  and (b) the iodine intercalated phase  $\text{I}_3\text{BaBi}_8\text{O}_{13}$

amounts of unidentified impurity phases. Single-phase host material is obtained only after heating at 700 °C for 10 h. In agreement with the EMPA data, the weight loss given by TGA indicates an iodine content of 3.15(2).

The X-ray diffraction data for the iodine intercalation compound [Fig. 1(b)] show several (*h*0*l*) and a well defined series of (00*l*) reflections. The mixed reflections are weak relative to the (00*l*) series most probably due to a combination of preferred orientation effects and some stacking disorder. We note that the observed (*h*0*l*) reflections obey rhombohedral absences suggesting that the layer stacking sequence is preserved. The *a* axis expands from 3.984(1) to 4.01(1) Å on intercalation. The X-ray data show no evidence of any superstructure.

The positions of the (00*l*) reflections were used to determine the *c* axis of the intercalation compound. A value of *c* = 38.46(5) Å was obtained corresponding to an increase of 9.97 Å per unit cell assuming that the rhombohedral symmetry is preserved. Each unit cell contains three layers and therefore each iodine layer expands the *c* axis by *ca.* 3.32 Å. Refinement of the intensities of the observed (00*l*) reflections was used to confirm a structural model in which the intercalated iodine species form a stage 1 compound with a monolayer of iodine located in the van der Waals gap mid-way between the Bi–O layers. In the refinement, the Ba, Bi and O atom positions were fixed at positions corresponding to the host structure. A scale factor, iodine atom *z* coordinate, occupancy and thermal parameters were refined. The best fit to the data gave an iodine stoichiometry of 3.12(4) corresponding to approximately one iodine atom intercalated into each interlayer space within the unit cell of the host material. Because only a limited number of mixed reflections are observed, the nature and the arrangement of iodine species within the *ab* plane is not yet known. Further studies on single crystal samples are in progress.

Conductivity measurements were made using a two-probe ac impedance technique in the temperature range 260–440 °C. The conductivities of the pristine host material and the iodine intercalated phase are shown in Fig. 2 in the form of an Arrhenius plot. The conductivity of the intercalated phase is approximately 1.5–2 orders of magnitude lower than the host material. The lower conductivity supports previous suggestions

that oxide-ion conductivity involves the participation of interlayer sites. At higher temperatures, the difference between the conductivities of the two materials decreases possibly due to the increase in the number of vacant interlayer sites available to oxide ions as iodine is removed from the structure. A larger value of the activation energy due to the migration of oxide ions *via* intralayer sites is a further possibility.

At present, the nature of the intercalated iodine species (*e.g.* I<sub>3</sub><sup>−</sup>, I<sup>−</sup>, I<sub>2</sub>), and its structural arrangement within the *ab* plane are not known. Further studies are required in order to determine the nature of the host–guest interactions and the extent of charge transfer in this new example of an intercalation compound formed by reaction of a neutral guest species with a neutral insulating host lattice. Iodine intercalation experiments in compounds with different Bi:Ba ratios and in the related rhombohedral phases in which Ba is substituted with Sr, Ca or La are in progress.

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## Footnotes

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‡ Electron microprobe analysis (EMPA) was carried out with a JEOL JXA-8600 instrument operated at 15 keV with a 10 µm beam diameter and a beam current of 30 nA. Counting times in the range of 40–100 s were used for both peaks and background. The uncertainties in the data are approximately ±1% (relative) for the cations and ±10% (relative) for oxygen.

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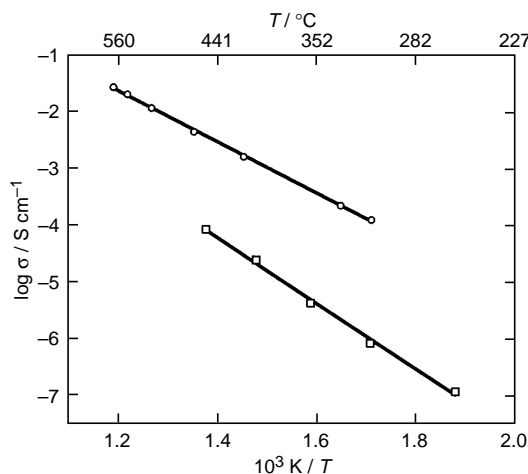


Fig. 2 Ac conductivity vs.  $10^3/T$  for BaBi<sub>8</sub>O<sub>13</sub> (○) and I<sub>3</sub>BaBi<sub>8</sub>O<sub>13</sub> (□)

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