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## LETTER TO THE EDITOR

# Fast-ion conduction and the structure of $\beta$ - $\text{Mg}_3\text{Bi}_2$

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**Abstract.** The structure of  $\beta$ - $\text{Mg}_3\text{Bi}_2$  has been determined by neutron powder diffraction. The results show this is a superionic phase, with a fixed body-centred cubic bismuth sub-lattice and mobile  $\text{Mg}^{2+}$  ions. From analysis of the radial distribution function obtained from the diffraction pattern, it is concluded that the magnesium ions occupy the tetrahedral and triangular symmetry sites of the bismuth lattice in a similar way to the silver ions in the anion lattices of  $\alpha$ -AgI and  $\alpha$ - $\text{Ag}_2\text{Se}$ . This material is an example of a new type of superionic conductor in which the metallic mobile ion is small and doubly charged.

Superionic conductors have been studied for many years because of their interesting condensed matter properties (part solid-like, part liquid-like) and for their important technological applications as electrodes and electrolytes in solid state batteries. It has been noted (Armstrong 1972) that in a material in which the cation is the mobile ion, the following conditions should be met.

- (i) There must be a large number of connected and vacant sites in the crystal structure.
- (ii) The difference in the energies of the cation-anion interactions on different sites should be small.
- (iii) The cations should be stable with a coordination number of 4 or less.
- (iv) The fast ion should be small and singly charged.

In this work we give an example of a new superionic material  $\beta$ - $\text{Mg}_3\text{Bi}_2$ , which satisfies all these requirements with the notable exception that the mobile cation is divalent.

$\alpha$ - $\text{Mg}_3\text{Bi}_2$  is a semiconducting compound with the anti- $\text{La}_2\text{O}_3$  structure (Zintl and Husemann 1933). Band structure calculations using the tight-binding approximation (Robertson 1979) show that it is characterized as an essentially ionic material composed of  $\text{Mg}^{2+}$  and  $\text{Bi}^{3-}$  ions. In the liquid state  $\text{Mg}_3\text{Bi}_2$  remains semiconducting (Enderby and Collings 1970). The liquid is, however, very unusual as it rapidly becomes metallic for small deviations away from stoichiometry, and has a thermopower that never exceeds  $\pm 10 \mu\text{V K}^{-1}$ . This is extremely unusual for a liquid semiconductor. A knowledge of the structure of this liquid is important in understanding its electronic properties. Enderby and Barnes (1990) showed that the crystal structure of a material just below its melting point is often closely related to the structure of the liquid. However,  $\alpha$ - $\text{Mg}_3\text{Bi}_2$  does not melt directly but undergoes a phase transition to the  $\beta$  phase at a temperature of 703 °C. The  $\beta$  phase melts congruently at 821 °C and has an unknown structure. It is the structure of this phase which is most important when considering the local structure in the liquid. As part of a study of this and similar liquids we have been investigating the high-temperature crystal

phases of some of these materials. Here we present the first structure determination of  $\beta$ - $\text{Mg}_3\text{Bi}_2$ . This was obtained by neutron powder diffraction and demonstrates the superionic properties of this high-temperature material.

A sample of  $\text{Mg}_3\text{Bi}_2$  was prepared by direct mixing of the pure elements at a temperature of 1000 °C. The neutron diffraction experiments were carried out using the LAD diffractometer at the ISIS pulsed neutron source at the Rutherford Appleton Laboratory. The sample was contained in a vanadium can and the diffraction pattern recorded at a temperature of 730 °C. The data were corrected for the effects of absorption and multiple scattering and normalized to an absolute scale using a vanadium reference using the ATLAS data analysis package (Soper *et al* 1989).

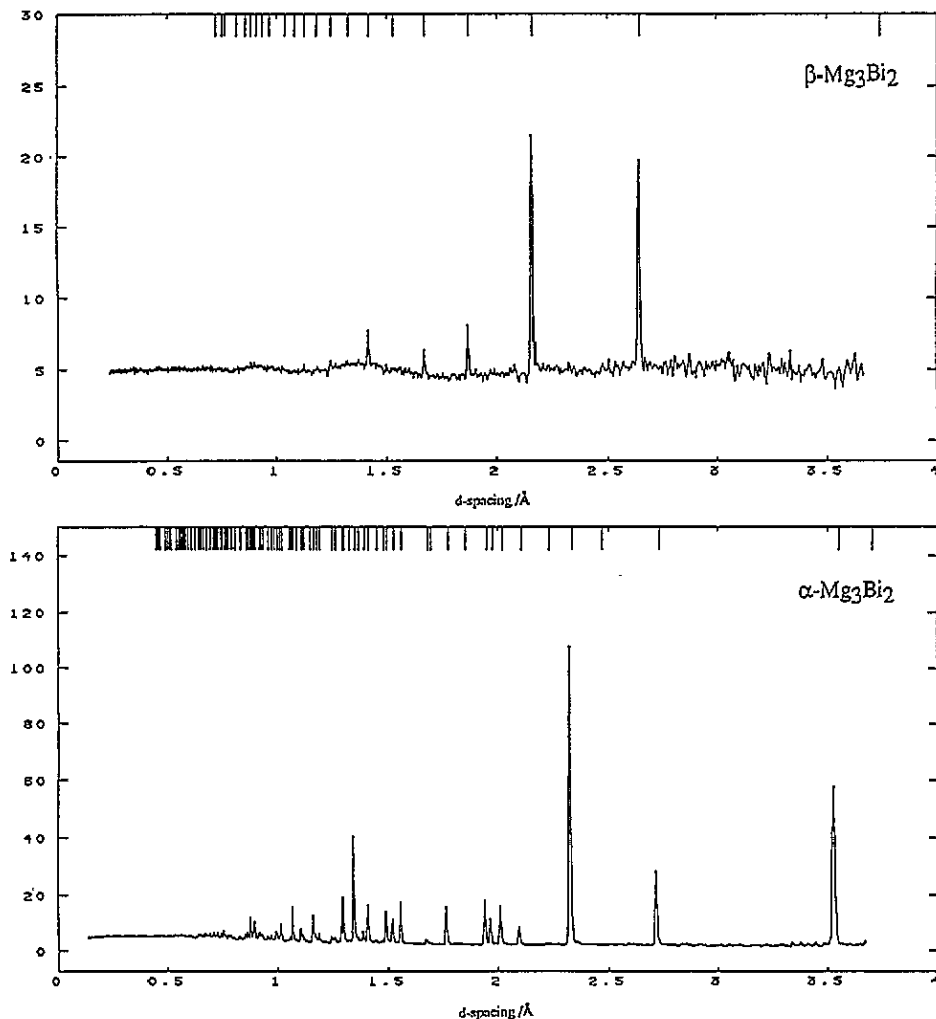


Figure 1. The neutron diffraction pattern obtained from  $\alpha\text{-Mg}_3\text{Bi}_2$  at 730 °C as a function of  $d$ -spacing.

The diffraction pattern obtained from the  $\alpha$  phase (at room temperature) and the  $\beta$  phase (at  $T = 730 \pm 10$  °C) for the LAD 150° scattering angle is shown in figure 1 as a function of  $d$ -spacing. The diffraction peaks of the  $\alpha$  phase are tagged according to the

trigonal ( $P\bar{3}m1$ ) structure reported by Zintl and Husemann (1933) and show good agreement with the reported structure. There is a very clear change on moving to the  $\beta$  phase. It is immediately apparent that in this phase there is a high-symmetry structure with a large diffuse background. Figure 2 shows the diffraction pattern of the  $\beta$  phase as a function of momentum transfer  $Q$  along with the diffraction pattern of the sample after melting. Clear similarities between the diffuse background in the  $\beta$  phase and the liquid are observed. Table 1 shows the  $d$ -spacings for the diffraction peaks observed in the  $\beta$  phase. These can be indexed to a body-centred cubic structure with the peak assignments as shown in figure 2 (and tagged in figure 1). The 222 reflection is predicted to have a low intensity and is not resolvable within the statistics of the experiment. The unit cell dimension corresponds to  $a = 5.297 \pm 0.004$  Å. The very large and liquid-like diffuse background observed in this phase is characteristic of a superionic (fast-ion) conductor and is similar to that of  $\alpha$ -AgI and  $\alpha$ -Ag<sub>2</sub>Se which also have body-centred cubic structures (Salamon 1979). Due to the large size of the Bi<sup>3-</sup> ion and the smallness of the Mg<sup>2+</sup> ion we conclude that  $\beta$ -Mg<sub>3</sub>Bi<sub>2</sub> is a superionic conductor in which magnesium is the mobile ion with the bismuth ions forming the rigid lattice. This assignment is fully consistent with the atomic number density of the system.

Table 1. The  $d$ -spacings and assignments of the Bragg peaks observed in  $\beta$ -Mg<sub>3</sub>Bi<sub>2</sub>.

$d$ -spacing/Å	Assignment
3.741	110
2.647	200
2.162	211
1.874	220
1.675	310
Unresolvable	222
1.417	321

Figure 3 shows the radial distribution function obtained by direct Fourier transform of the fully corrected  $\beta$ -Mg<sub>3</sub>Bi<sub>2</sub> data. This shows a first coordination peak at 2.80 Å which is much smaller than the Bi-Bi nearest neighbour distance of 4.58 Å in the BCC structure. This distance must therefore be associated with the Mg-Bi and Mg-Mg correlations. Given the bismuth lattice, the Mg ions can only occupy certain, preferred positions within the lattice or the interstitial regions between them. The possibilities are essentially the octahedral, tetrahedral and triangular positions marked in figure 4. If the magnesium only occupied the octahedral positions then these would all be fully occupied at stoichiometry. Therefore if fast-ion conduction is to take place it must occur through the tetrahedral or triangular sites. Occupation of the octahedral sites gives rise to Mg-Bi distances of 2.65 Å and 3.75 Å, and a Mg-Mg distance of 3.75 Å. These are not strongly observed in the radial distribution function, and we conclude that the octahedral sites are not heavily populated in  $\beta$ -Mg<sub>3</sub>Bi<sub>2</sub>.

There are twelve tetrahedral sites per unit cell. Occupation of some of these sites by Mg ions would give a Mg-Bi distance of 2.96 Å and Mg-Mg distances of 1.87 Å (which is physically implausible) and 2.65 Å. Occupation of the triangular sites gives a Mg-Bi distance of 2.81 Å and Mg-Mg distances of 2.81 Å and 3.972 Å, distances consistent with the observed peak in the radial distribution function at 2.80 Å. With the current diffraction data we cannot say which of these two positions is preferred, but the absence of Mg ions in the octahedral positions leads us to conclude that the predominant channel for ion motion in this material is between the tetrahedral and triangular sites in the lattice.

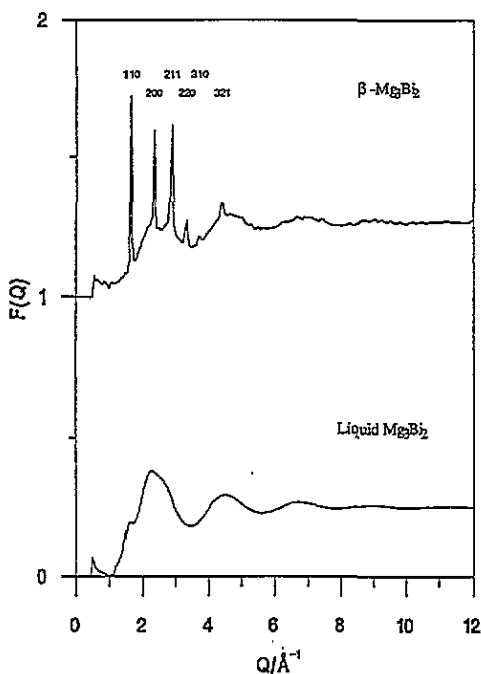


Figure 2. The neutron diffraction pattern from  $\beta\text{-Mg}_3\text{Bi}_2$  at 730 °C as a function of  $Q$ . The assignment of the peaks for the bcc Bi lattice is shown.

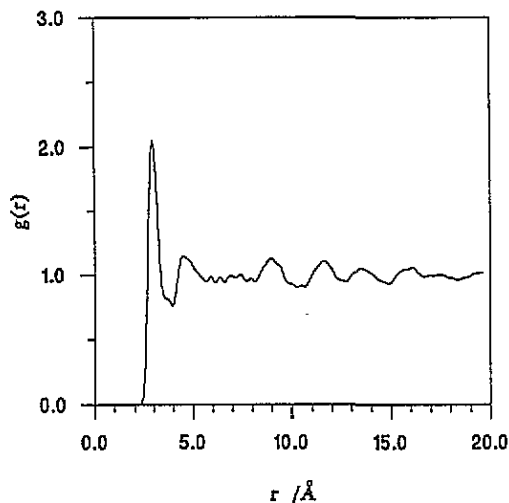


Figure 3. The radial distribution function  $g(r)$  of  $\beta\text{-Mg}_3\text{Bi}_2$  at 730 °C.

This material represents a new family of superionic conductors in which the mobile ion is a doubly charged metallic ion moving in a lattice of triply charged anions. Its structure appears to be closely analogous to that of  $\alpha\text{-AgI}$  and  $\alpha\text{-Ag}_2\text{Se}$  which both have BCC anionic sublattices in which the Ag ions move between tetrahedral sites via the triangular sites. The number of cations (Mg) in the unit cell is exactly midway between the numbers for the

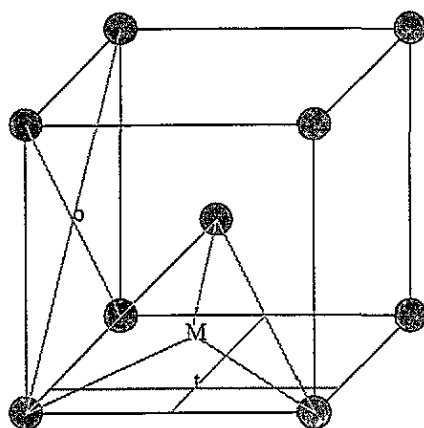


Figure 4. The unit for  $\beta$ - $\text{Mg}_3\text{Bi}_2$  showing the Bi BCC lattice and the octahedral (o) tetrahedral (t) and triangular (M) lattice positions for the Mg ion.

silver cations in the two silver superionics  $\alpha$ -AgI and  $\alpha$ -Ag<sub>2</sub>Se. The existence of high ionic mobility in this material is of considerable interest in the study of superionic conduction processes.

The high mobility of the  $\text{Mg}^{2+}$  ions in the high-temperature phase may be relevant to the study of the liquid  $\text{Mg}_3\text{Bi}_2$ . Its rather unusual properties are difficult to understand in terms of the model for liquid semiconductors proposed by Enderby and Barnes (1990). Similar difficulties appear in the electronic properties of liquid Ag<sub>2</sub>S (Ohno *et al* 1990) and Ag<sub>2</sub>Se (Ohno *et al* 1994). Both of these materials are superionic before melting. Further investigation of the relationships between the ionic mobility and the electronic properties of these materials may be crucial in our understanding of liquid semiconductors generally.

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