Atomic ordering in $Bi_4Ge_3O_{12}$ melt by reverse Monte Carlo simulations

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Abstract. A three-dimensional structure model which well reproduces experimental structure functions for molten $Bi_4Ge_3O_{12}$ and agrees with the results of EXAFS experiments has been constructed by reverse Monte Carlo simulations. From the model atomic configuration the partial atomic distribution functions, the partial coordination numbers and distances of molten $Bi_4Ge_3O_{12}$ have been extracted. It has been found that, on an atomic scale, molten $Bi_4Ge_3O_{12}$ may well be described as an assembly of disconnected GeO_4 tetrahedra dispersed in a medium of weakly correlated Bi and O atoms. The structural differences between molten and crystalline $Bi_4Ge_3O_{12}$ have also been discussed in an attempt to clarify the reasons that make the process of pure $Bi_4Ge_3O_{12}$ crystals growth from the melt difficult.

1. Introduction

Crystalline $Bi_4Ge_3O_{12}$ (BGO) has recently attracted much attention because of its potential as an energy detector for electrons and photons. That is why several studies have dealt with improving the efficiency of the growth process of BGO single crystals [1–3]. Despite the research efforts exercised, however, the growth process has shown poor reproducibility and often inclusions of Bi_2O_3 have been found to persist in the BGO crystals obtained. A hypothesis has been put forward that the difficulties encountered in growing pure (stoichiometric) BGO single crystals arise from the fact that the atomic ordering of molten and solid BGO are completely different. In particular, it has been suggested that, by contrast with crystalline BGO, which is a regular arrangement of GeO_4 tetrahedra sharing all their vertices with distorted BiO_6 octahedra [4] (see figure 4 introduced later in the text), molten BGO contains chains of GeO_4 tetrahedra and large-scale layered-like atomic grouping of Bi_2O_2 units [5]. Because of this structural resemblance the melt has been suggested to dissociate easily into Bi-rich and Ge-rich phases upon crystallization and thus the difficulties encountered in obtaining pure BGO crystals have been explained [2, 5]. It has even been suggested that, in order to grow pure BGO crystal, extra energy should be supplied to the melt, i.e. it should be overheated well above the point of crystallization, in order to break down its layered structure and thus to enable it to solidify into stoichiometric BGO [2].

On the other hand, recent EXAFS studies have found no indication for the presence of well defined Bi–O atomic configurations, such as Bi_2O_2 layers but have found the presence of stable GeO_4 tetrahedral units in BGO melt [6]. On the basis of these findings, it has been suggested that the BGO melt structure is a kind of a random mixture of GeO_4 tetrahedra,

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bismuth and oxygen atoms. Thus two model pictures for the atomic arrangement in molten BGO which contradict each other have been suggested which justifies carrying out a new structural study aimed at clarifying the situation.

In the present paper the results of such a study on the BGO melt structure are reported. A three-dimensional structure model based on structure data obtained by energy-dispersive x-ray diffraction (EDXD) experiments has been constructed by reverse Monte Carlo (RMC) simulations. The model has been analysed in detail in order to reveal clearly the characteristics of atomic ordering in the BGO melt.

2. Preliminary analysis of the diffraction structure data from $Bi_4Ge_3O_{12}$ melt used in the reverse Monte Carlo simulations

The structure functions used in the construction of the three-dimensional structure model for the BGO melt have been obtained by EDXD experiments. A brief account of the results of these experiments has already been published elsewhere [7]. Here, some important experimental details are given once more for clarity. The EDXD experiments were carried out by utilizing x-rays with a continuous energy spectrum produced by a sealed x-ray tube with a W anode. The radiation source was mounted on one arm of a θ–θ-type goniometer device and an energy-sensitive Ge solid state detector on the other. The detected x-ray photons of different energies were processed with a multichannel pulse-height analyser and stored in a computer-readable format. During the measurements, the BGO melt was kept in a platinum container placed in an evacuated high-temperature chamber mounted on the centre of the goniometer axis. The temperature of the BGO melt was controlled to within ∓ 5 K and monitored with a thermocouple inserted into a hole in the side of the heating block supporting the platinum container. The measurements were carried out at 1373 K, i.e. quite close to the melting point of BGO ($T_m \simeq 1328$ K). A more detailed description of the experimental EDXD set-up can be found in [7]. Seven EDXD spectra at fixed diffraction angles of $2\theta = 8°$, $12°$, $17°$, $25°$, $34°$, $60°$ and $80°$ were collected from the open surface of the BGO melt. Each spectrum was gathered over a period of approximately 10 h to ensure sufficient counting statistics. By applying proper corrections the only x-ray intensities coherently scattered by molten BGO were extracted from each of the spectra measured. These intensities were reduced to corresponding segments of the structure factor $S(q)$ where q is the amplitude of the wavevector. By matching the different segments a total structure factor for molten BGO was constructed. The thus-obtained experimental structure factor for the BGO melt is shown in figure 1. It Fourier transform, the pair atomic distribution function $g(r) = \rho(r)/\rho_0$, where r is the radial distance, and $\rho(r)$ and ρ_0 are the local and average atomic number densities, respectively, is shown in figure 2. It may be added that all steps of the experimental EDXD data processing briefly outlined here have been described in full detail in [8].

As one can see in figure 1 the experimental structure factor of BGO exhibits peaks whose amplitudes rapidly decrease with increase in the wavevector q and almost vanish when q-values are higher than 15 Å^{-1}, a picture typical for most molten materials. Some high-frequency ripples, due to the insufficient statistical accuracy of EDXD data, are seen at high q-values as well.

The experimental $g(r)$ for molten BGO exhibits a first peak centred at 1.8 Å, a second peak of larger amplitude at 3.6 Å, a third broad peak at 7 Å and subsequent low-amplitude low-frequency oscillations extending up to 20 Å. By referring to the crystal structure of BGO and having in mind that the contribution of oxygen atoms to the experimental atomic
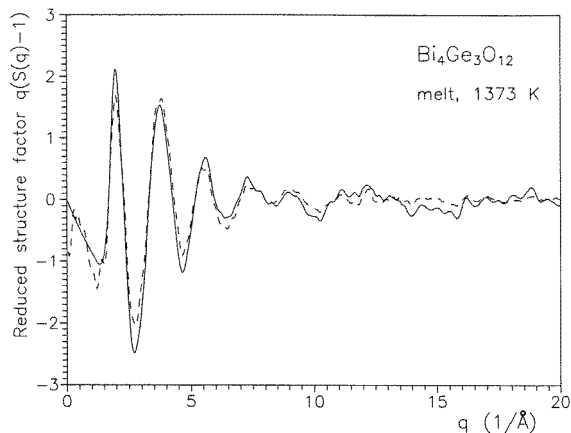
Figure 1. Total reduced structure factor $q(S(q) - 1)$ for molten BGO: ——, experimental EDXD data; – – –, RMC results. The RMC results are a Fourier transform of the model atomic distribution function of figure 2.
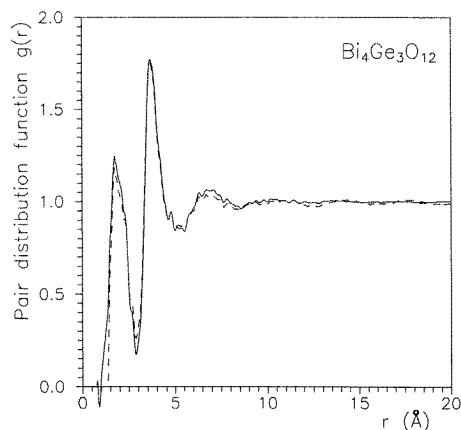
Figure 2. Pair distribution function $g(r)$ for molten BGO: ——, experimental data; – – –, RMC fit. The RMC results have been obtained from a structure model where some of the features of the local atomic ordering of crystalline BGO, namely the Ge involving atomic correlations, have been preserved and others, namely the Bi involving atomic correlations, considerably modified.

distribution function in the case of x-ray diffraction experiments is relatively small the first peak in $g(r)$ for molten BGO has been attributed to Bi–O and Ge–O, and those at 3.6 Å to the Bi–Bi and Bi–Ge atomic pairs present in the melt [9]. However, a more detailed analysis of the experimental atomic distribution function for molten BGO carried out by us showed that this assumption is only an approximation to the specific atomic-scale structure of the melt.

The analysis has been carried out by comparing the present experimental atomic pair distribution function for molten BGO with first coordination spheres of crystalline BGO appropriately substituted for Gaussians. According to literature sources [4], in crystalline BGO, each Bi atom has three oxygen neighbours at 2.16 Å and three further, more distant
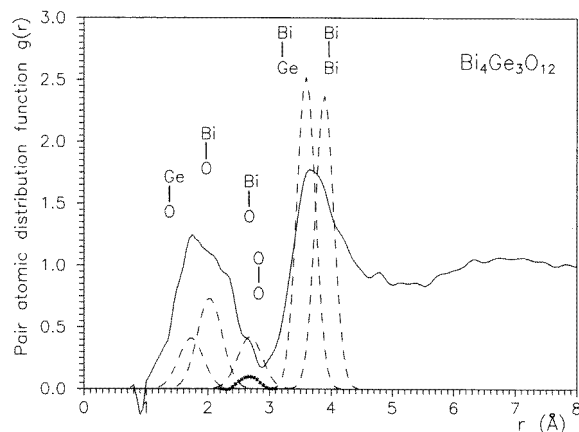
Figure 3. Experimental pair distribution function for molten BGO (——) and smeared-out first coordination spheres in crystalline BGO (– – –). The calculated O–O first coordination sphere has been indicated by symbols for clarity.

oxygen neighbours at 2.62 Å, all forming a distorted octahedral coordination polyhedron; each Ge atom has four immediate oxygen neighbours at 1.75 Å located at the vertices of a tetrahedral structural unit and, correspondingly, each O atom has three immediate oxygen neighbours at 2.7 Å; the first-neighbour Bi–Ge and Bi–Bi distances are 3.60 Å and 3.89 Å and the corresponding numbers of atomic neighbours are 6 and 5, respectively.

The approximating Gaussians were calculated according the expression

$$g_{ij}(r) = \frac{C_{ij}}{2(2\pi)^{3/2}\rho_0 r_{ij}\beta_{ij}r} \exp\left(-\frac{(r-r_{ij})^2}{2\beta_{ij}^2}\right) \tag{1}$$

where r_{ij} is the position of a given first coordination sphere of crystalline BGO and C_{ij} is the corresponding effective first coordination number. The effective coordination numbers C_{ij} were derived from the actual first coordination numbers Z_{ij} given above, as follows:

$$C_{ij} = Z_{ij}w_{ij}/c_j \tag{2}$$

where c_j is the atomic concentration of atomic species of type j (j =Bi, Ge or O) and w_{ij} are the corresponding weighting factors. In our case of x-ray diffraction experiments on BGO melt the weighting factors are as follows: $w_{Bi-Bi} = 0.399$, $w_{Bi-Ge} = 0.117$, $w_{Bi-O} = 0.115$, $w_{Ge-Bi} = 0.117$, $w_{Ge-Ge} = 0.035$, $w_{Ge-O} = 0.033$, $w_{O-Bi} = 0.115$, $w_{O-Ge} = 0.033$ and $w_{O-O} = 0.033$. It may be added that the widths β_{ij} of all Gaussians have been selected so as to match the actual width of the peaks in the experimental $g(r)$ data.

The results of the comparison are shown in figure 3. As one can see in the figure the first peak in $g(r)$ of molten BGO spreads over real space distances corresponding well to the Ge–O and Bi–O first-neighbour interatomic distances occurring in crystalline BGO. The second largest-amplitude peak in $g(r)$ is positioned exactly at the Bi–Ge and Bi–Bi first-neighbour distances occurring in crystalline BGO. These observations indicate that the geometrical features of the local atomic ordering in crystalline BGO are preserved in the structure of molten BGO to a great extent. However, as one can also see in figure 3 the number of atoms separated at short distances, from 1 up to 3 Å, in molten BGO is larger than that of the atoms separated at the same short distances in crystalline BGO. Furthermore,

the number of atomic pairs with pair distances between 3 and 4.5 Å in molten BGO is somewhat smaller than that of the atomic pairs occurring in this region of real space in crystalline BGO. In other words, there are some pairs of atoms separated at approximately 1–3 Å which do not occur in crystalline BGO but do occur in molten BGO and contribute to the first peak in it atomic distribution function. Besides, the number of Bi–Bi and Bi–Ge first neighbours in molten BGO seems to be reduced when compared with that in crystalline BGO. These findings play an important role in the construction of a structure model that accounted well for all details in the experimental atomic distribution function for molten BGO.

## 3. Reverse Monte Carlo simulations on the $Bi_4Ge_3O_{12}$ melt structure

In brief, the RMC method for modelling disordered structures involves random movements of atoms placed in a simulation box with periodic boundary conditions. Moves are accepted if the difference between the model calculated and experimentally derived structure-sensitive data, usually given in terms of structure factors and atomic distribution functions, is reduced. If necessary, appropriate constraints on the atomic moves may be imposed in order to comply with additional structure-relevant information based on strong experimental or theoretical evidence. The process is repeated until an almost perfect fit to the experimental data is achieved. The resulting three-dimensional atomic configuration is considered to be a possible model of the material under study. From the configuration, important structural characteristics such as partial structure functions, coordination numbers, bond angles, etc, are determined by geometrical analyses of the atomic coordinates [10–13]. The present simulations on the atomic-scale structure of molten BGO were started from an atomic configuration with the structure of crystalline BGO. This choice was based on the finding that the features of the local atomic ordering of crystalline BGO are preserved in molten BGO to a great extent. The starting configuration consisted of 4392 atoms (920 Bi, 688 Ge and 2784 oxygen atoms) placed in a cubic box of appropriate edge length (approximately 42.6 Å), resulting in an experimental atomic number density ρ_0 of molten BGO of 0.0572 Å^{-3}. A fragment of the starting atomic configuration is given in figure 4. It may be noted that the size of the atomic configuration used in the present simulations is large enough to account for the atomic correlations present in molten BGO up to approximately 20 Å. During the simulations the random moves of the atoms from the model atomic configuration were limited by 'cut-off' distances which prevented the atoms from approaching each other to an unrealistically close distance. The following 'cut-off' distances of 3.4 Å, 3.3 Å, 1.7 Å, 3.45 Å, 1.6 Å and 2.6 Å, estimated by referring to all available structure data for BGO, were used for the Bi–Bi, Bi–Ge, Bi–O, Ge–Ge, Ge–O and O–O atomic pairs, respectively. In order to ensure that the basic structural features of the starting atomic configuration are not completely lost in the course of the simulation process some extra constraints on the atomic moves were imposed. Namely, it was required that the numbers of first Ge–O and Bi–O atomic neighbours are always 4 and 6, respectively, so that all atomic moves violating these constraints were rejected. Furthermore, the amplitude of the random atomic moves was deliberately kept small with a maximum value of 0.1 Å initially and a minimum value of 0.01 Å at the final stages of the simulation process. The probability of accepting an atomic move was determined by comparing the model calculated with the experimental atomic pair distribution function $g(r)$ for molten BGO obtained by the EDXD experiments discussed already. The simulation process was terminated when approximately 10^5 atomic moves were completed and it was not possible to achieve any further improvement in the fit to the experimental data. A comparison between the experimental atomic distribution function
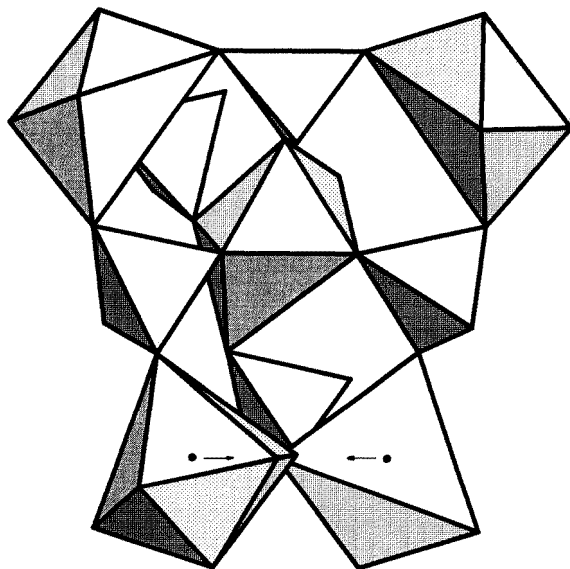
Figure 4. Fragment of the starting atomic configuration used in the present RMC simulations. The configuration is for the structure of crystalline BGO. A typical structural motif seen is a GeO_4 tetrahedron sharing its vertices with distorted BiO_6 octahedra. A direction in which two neighbouring Bi atoms (●), eventually having lost their loosely bound O nearest neighbours, could approach each other and form a Bi–Bi couple in molten BGO is indicated by arrows.

and $g(r)$ calculated from the thus-constructed structure model is shown in figure 5. As one can see in the figure the so-constructed model of the molten BGO structure, where all local structural characteristics of crystalline BGO have been deliberately preserved, reproduces well only the basic features but not the fine details of the experimental structure data. In particular, the model results in an atomic distribution function with the first peak at 1.8 Å of amplitude much lower and the second peak at 3.6 Å of amplitude somewhat higher than those of the corresponding peaks in the experimental atomic distribution function. This result is not greatly surprising if one recalls the findings of the preliminary analysis of the experimental data carried out in section 2 of this paper. Obviously, some modifications in the structure model considered up to now should be made or some other structure model, not based on the crystalline structure of BGO, should be looked for in order that a better fit to the experimental structure data is achieved. To check the latter possibility, two other independent structure models, one with a random arrangement of the constituent Bi, Ge and O atoms and the other with the structure of crystalline Bi_2GeO_5, which sometimes has been encountered as a byproduct of the $Bi_4Ge_3O_{12}$ melt crystallization process [2, 3], have been tested. However, these two models have been found to be incapable of reproducing even the basic features of the experimental $g(r)$ data and that is why further efforts have been directed towards modifying the structure model considered up to now.

Recalling that in crystalline BGO each Bi atom has six oxygen nearest neighbours, three of which are relatively strongly and three that are not so strongly bound to the Bi atom at distances of 2.16 Å and 2.62 Å, respectively, one may expect that because of the thermal impact of the melting process some of the loosely bound Bi and oxygen atoms dissociate, i.e. some of the longer Bi–O bonds break, so that in molten BGO some of the Bi atoms
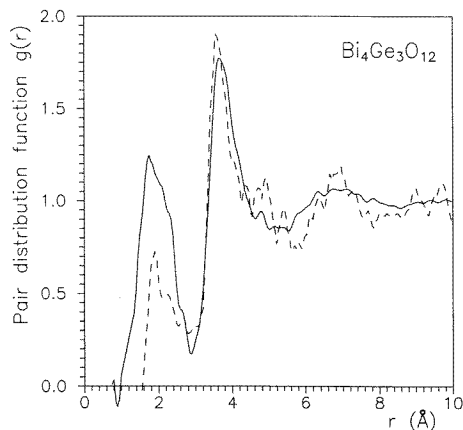
Figure 5. Comparison between experimental (——) and calculated (– – –) pair distribution functions for molten BGO. The calculated $g(r)$ has resulted from a structure model for molten BGO where the features of the local atomic ordering of crystalline BGO have been deliberately introduced and preserved.

lack sixfold oxygen coordination. One may further expect that some neighbouring Bi atoms which have lost their loosely bound oxygen nearest neighbours may simply approach each other close enough to form Bi–Bi couples which do not occur in crystalline BGO. As a result the number of Bi–Bi first neighbours mediated by common oxygen atoms in molten BGO may be expected to be reduced and, as a consequence, the corresponding peak in the atomic distribution function at 3.6 Å may not be so strong as predicted (see figures 3 and 5) by a model based on the intact crystalline structure of BGO. Also, some Bi–Bi atomic pairs, not mediated by oxygen atoms, may emerge in molten BGO and thus give an extra contribution to the atomic distribution function in the region around 2 Å where the immediate-neighbour Bi–Bi atomic separations are most frequently found to occur in the molten state [14]. Thus it seems that, if the structure model considered up to now, based on the BGO crystalline structure, is so modified that the changes in the local coordination of the Bi atoms suggested above are accounted for, much better agreement with the experimental atomic distribution function of molten BGO may be achieved. This modification was done by removing the constraint imposing a sixfold oxygen coordination of the Bi atoms and allowing Bi–Bi distances of closest approach as short as 1.35 Å, which is the low-r limit of the first peak in the atomic distribution function for molten BGO, to occur. It may be noted that the undertaken modification of the Bi atomic correlations involved in the structure model being constructed is quite in line with the findings of the recent EXAFS experiments of Omote and Waseda [6] which have unambiguously shown that, while the tetrahedral coordination of Ge atoms (GeO_4 units) is well preserved, the local coordination of Bi atoms is so considerably changed on melting crystalline BGO that BiO_6 octahedral or other polyhedral units involving Bi atoms could no longer be identified in molten BGO.

With the new constraints which are looser with respect to the Bi coordination, the model rapidly relaxed and the experimental $g(r)$ data for molten BGO were almost perfectly fitted. The success of the thus-constructed RMC model in reproducing the atomic distribution function for molten BGO is well demonstrated in figure 2 where a comparison between the RMC derived and experimental data is made. For reference, the goodness-of-fit indicator achieved in real space is 4.5% only. The thus-modified RMC model has also been found

to reproduce the reduced structure factor for molten BGO well, as one can see in figure 1. Given the good consistency of the simulations with the experimental EDXD data in both real and reciprocal space achieved, one may expect that all important structural characteristics of molten BGO are likely to be well accessed from the three-dimensional configuration constructed.

4. Discussion

The analyses of the present RMC model for molten BGO structure started with the derivation of the partial atomic distribution functions $g_{ij}(r)$, ($i, j = $ Bi, Ge or O). These are shown in figure 6. As one can see in figure 6(a), the $g_{Bi-Ge}(r)$ distribution function has a dominant first peak at 3.65 Å, a second peak at 7.5 Å with a shoulder at 6.05 Å and a hardly discernible third peak centred around 12 Å. The finding that the first-Bi–Ge-neighbour separation in the model atomic configuration is 3.65 Å, as it is in crystalline BGO, suggests that, similarly to the corresponding crystal, all Bi–Ge pairs in molten BGO are mediated by oxygen atoms. The partial distribution function $g_{Bi-O}(r)$ exhibits only one well defined peak at 2.05 Å followed by a small maximum at 3.98 Å. The peak reflects the correlations between the first-neighbour Bi–O atoms and its position is quite close to the Bi–O separation in molten BGO determined by EXAFS experiments [6]. This close agreement is strong evidence in support of the reliability of the previous EDXD [7] and present RMC studies on molten BGO. The pair distribution function $g_{Bi-Bi}(r)$ has its first peak positioned at 1.9 Å and the second peak at 3.95 Å. Some low-frequency low-amplitude oscillations are also seen in $g_{Bi-Bi}(r)$ up to 20 Å. The first peak in $g_{Bi-Bi}(r)$ is due to the Bi atoms from the model atomic configuration which have lost all or some of their first oxygen neighbours and have approached each other close enough to form Bi–Bi couples which, otherwise, do not occur in crystalline BGO. The second peak, the position of which is close to the first-neighbour Bi–Bi separation in crystalline BGO, may be attributed to the Bi–Bi atomic pairs mediated by O atoms. The fact that the Bi atoms from the present structure model have been found to have both Bi and oxygen atoms as first neighbours at distances from approximately 1.35 to 3.05 Å (see the positions and the spatial extent of the first peaks in $g_{Bi-O}(r)$ and $g_{Bi-Bi}(r)$ in figure 6(a)) suggests that it is quite possible for the Bi-centred coordination polyhedra in molten BGO to be not well defined which may explain well the weakness of the amplitude of the Bi EXAFS oscillations measured by Omote and Waseda [6].

The inspection of figure 6(b) shows that the model $g_{Ge-O}(r)$ has a dominant peak at 1.75 Å followed by a weak maximum at 3.95 Å. The position of the peak, which reflects the correlations between the first-neighbour Ge–O atoms, is again quite close to the Ge–O separation in molten BGO determined by EXAFS experiments [6]. The atomic distribution function $g_{Ge-Ge}(r)$ exhibits low-amplitude oscillations up to 20 Å the first of which is centred at 5.5 Å. The fact that the position of the first oscillation in the model $g_{Ge-Ge}(r)$ is quite close to the first-neighbour Ge–Ge separation in crystalline BGO, where no Ge–Ge couples exist, suggests that all Ge–Ge pairs in the present structure model for molten BGO are mediated by Bi and O atoms. The persistence of oscillations in $g_{Ge-Ge}(r)$ up to 20 Å also suggests that the Ge–Ge correlations in the thus-simulated molten BGO exhibit some specific medium-range order regularities which may be considered to be inherited from the crystalline state since the maxima of the oscillations, 5.5 Å, 7.1 Å, 10.0 Å, 14.5 Å and 17 Å, coincide with the positions of the corresponding Ge coordination spheres in crystalline BGO.

As one can see in figure 6(c) the model $g_{O-O}(r)$ has only one sharp peak at 2.70 Å followed by a hardly discernible bump at 5.5 Å. There are almost no correlations between
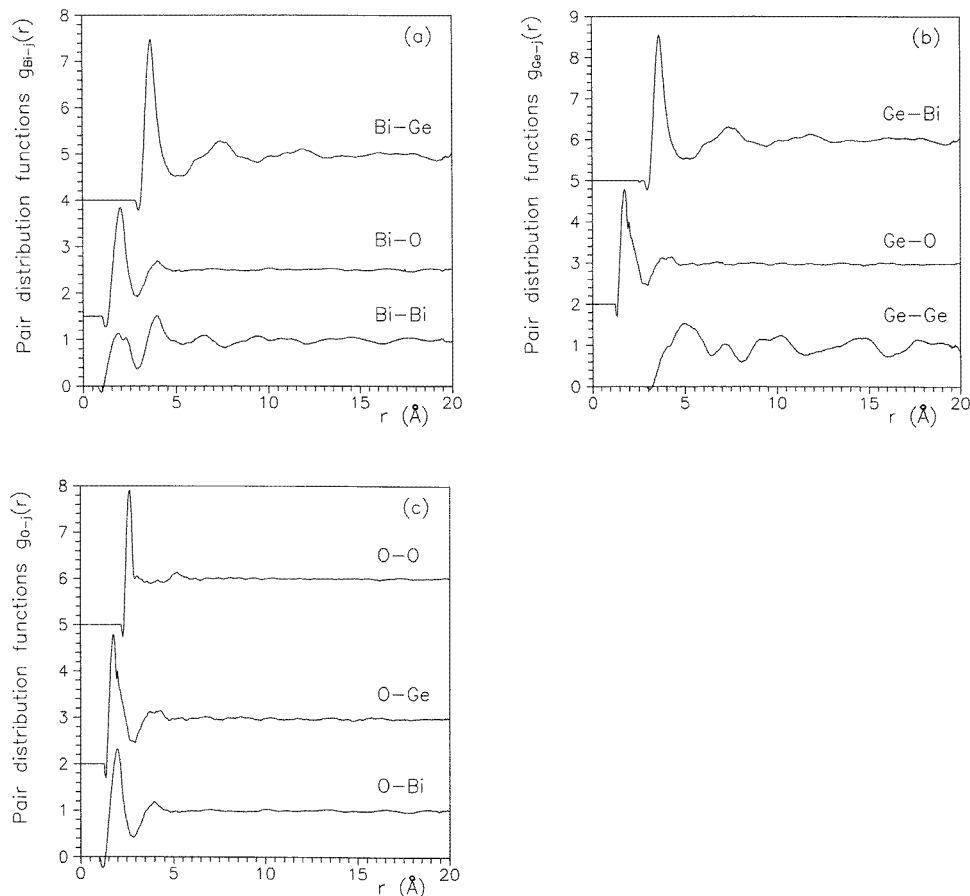
Figure 6. Partial atomic distribution functions $g_{ij}(r)$ for molten BGO according to the present RMC model: (*a*) $g_{Bi-j}(r)$; (*b*) $g_{Ge-j}(r)$; (*c*) $g_{O-j}(r)$ (j =Bi, Ge or O).

the positions of oxygen and the other atomic species (Ge and Bi) above 6 Å as well (see the $g_{Ge-O}(r)$ and $g_{Bi-O}(r)$ partial atomic functions) which suggests that there are no large-scale atomic groupings involving oxygen which could exist in the present structure model for molten BGO.

Other important characteristics of the local atomic ordering in molten BGO derived from the RMC constructed model were the partial coordination numbers. These were obtained by counting all atomic pairs falling into coordination shells with boundaries of 5.1 Å, 2.8 Å, 5.3 Å, 5.1 Å, 2.85 Å, 6.45 Å, 2.9 Å, 2.85 Å and 2.8 Å for the Bi–Ge, Bi–O, Bi–Bi, Ge–Bi, Ge–O, Ge–Ge, O–O, O–Ge and O–Bi atomic pairs, respectively. The boundaries of the coordination shells considered, except that for Bi–Bi pairs, coincide with the first deep minima in the corresponding partial distribution functions. For the Bi–Bi shell the second minimum in $g_{Bi-Bi}(r)$ has been considered as a first coordination boundary in order that all Bi–Bi pairs, mediated and not mediated by oxygen atoms, are accounted for. It has been found that each Ge atom from the model structure has 3.9 ± 0.1 nearest oxygen neighbours and that each O atom has 1 ± 0.1 Ge nearest neighbours. To clarify the spatial arrangement of these nearest Ge and O neighbours the distribution of the O–Ge–O 'bond angles', defined
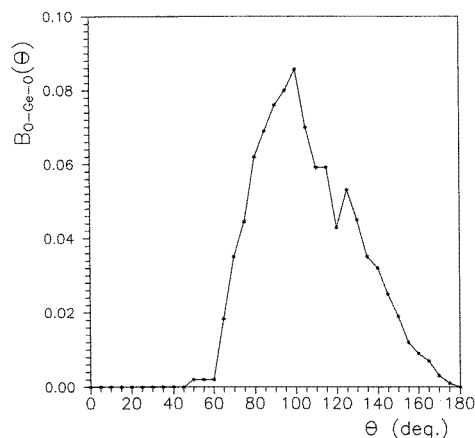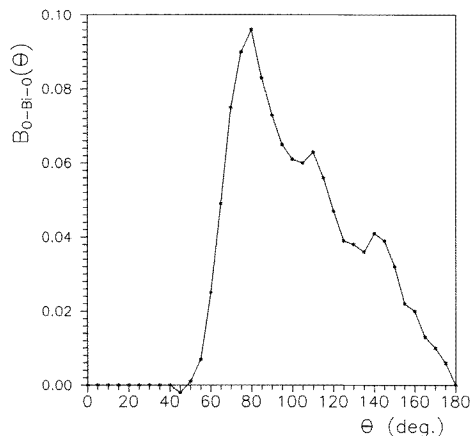
Figure 7. Distribution of the O–Ge–O 'bond angles' in molten BGO according to the present RMC model.

as the number of angles between the two vectors joining a central Ge atom with any two of its first O neighbours, has also been calculated. The results are shown in figure 7. As one can see in the figure, the O–Ge–O 'bond angle' distribution has a broad single peak centred at an angle of $103°$ which is quite close to the tetrahedral angle of $109°$. Having obtained the fact that there are approximately four Ge–O first neighbours and the most frequently occurring O–Ge–O angles involving these atoms are close to the tetrahedral angle, one may conclude that the GeO_4 tetrahedra from crystalline BGO, although quite distorted (see the width of the 'bond angle' distribution of figure 7), have survived in the present structure model for molten BGO as was required by the constraints imposed on the simulations carried out. This result fully complies with the findings of EXAFS experiments [6] which also suggest the presence of GeO_4 tetrahedra in molten BGO.

It is interesting to note that, since there have been found to be 3.4 ± 0.1 O–O nearest neighbours and, as shown by the data in figure 6(*c*), the distances between these neighbours are narrowly distributed around 2.70 Å, which is close to $2r_{Ge-O}\sqrt{\frac{2}{3}}$, one may well assume that the nearest O–O atomic neighbours in molten BGO are most frequently located at the vertices of tetrahedral units centred by Ge atoms. It may be added that the result of present analyses, namely that each oxygen atom has only one Ge first neighbour also suggests that there are no GeO_4 tetrahedra having common edges or vertices in the present structure model for molten BGO. Thus the present RMC model has been found not to support the theories [2, 5] suggesting the presence of chains of GeO_4 tetrahedra in the BGO melt.

For the Bi–O pairs it has been found that each Bi atom has on average 3.5 ± 0.1 oxygen nearest neighbours, and each O atom has 1.2 ± 0.1 Bi neighbours. These findings suggest that the Bi atoms in molten BGO may have lost almost half of their six O neighbours from the crystalline state and, as a result, may have lost their octahedral oxygen coordination. However, the fact that the O–Bi–O 'bond-angle' distribution, presented in figure 8, peaks close to $90°$, which is the O–Bi–O 'bond angle' in crystalline BGO [4], suggests that the angular correlations between the neighbouring Bi and O atoms in crystalline and molten BGO are quite likely to exhibit some similarities. Here, it may also be added that the present model does not support the previous theories [2, 5] suggesting the presence of Bi_2O_2 layers in molten BGO since each O atom has been found to have so few Bi nearest

Figure 8. Distribution of the O–Bi–O 'bond angles' in molten BGO according to the present RMC model.

neighbours (1.2 only) that the existence of well connected large-scale Bi–O atomic groupings seems quite improbable. These theories are also not supported by the fact that no Bi–O atomic correlations of spatial extent longer that 5 Å have been found in the model atomic configuration (see $g_{Bi-O}(r)$ in figure 6(*a*)).

The following results for the rest of the partial coordination numbers have been obtained: 6.9 ± 0.1 for Ge–Bi, 10.6 ± 0.1 for Ge–Ge, 5.2 ± 0.1 for Bi–Ge and 7.8 ± 0.1 for Bi–Bi. These partial coordination numbers in the present structure model for molten BGO are not very different from the corresponding coordination numbers in crystalline BGO. It may be noted that, of the 7.8 like neighbours around each Bi atom, only 0.8 have been found to be immediate, i.e. to correspond to Bi–Bi couples, while the rest (seven) are not immediate but correspond to Bi–Bi pairs mediated by O-atoms. This result suggests that a great portion of but not all the Bi atoms in molten BGO are quite likely to be coordinated to another Bi atom.

In summary, the findings of the present analyses suggest that, on an atomic scale, molten BGO may well be described as an assembly of disconnected GeO$_4$ tetrahedral units dispersed in a medium of weakly correlated Bi and O atoms. It should be emphasized, however, that this assembly may not be considered as a completely random mixture of its constituents since the spatial arrangement of the GeO$_4$ tetrahedra and the orientational correlations between the Bi and O atoms have been found to be similar to those encountered in crystalline BGO. According to the present model, the substantial difference between the atomic arrangements in crystalline and molten BGO is that in the molten state the Bi–O first coordination number is reduced to approximately 3; the reduction makes it possible for some of the Bi atoms to approach each other at distances shorter than usually found in crystalline state and, as a result, some couples of Bi atoms emerge. This possible model picture for molten BGO may well explain the difficulties encountered with the growth of pure BGO crystals as being due to the presence of Bi couples in the melt which could serve as seeds for the formation of Bi-rich phases (Bi$_2$O$_3$) upon crystallization. Thus, according to the findings of the present study, any further overheating of the melt well above the point of crystallization would certainly not help the crystal growth process, as speculated in [2], since it would eventually increase the number of Bi–Bi couples and make it even more difficult to obtain pure BGO single crystals. Extensive stirring of the melt, which has been

empirically found to promote the obtaining of pure BGO crystals [2], would eventually not allow the Bi–Bi couples to coalesce and, from this point of view, at least would not make the BGO crystal growth process more difficult.

5. Conclusions

The results of the present studies, which are in full accord with the previous EXAFS experiments of Omote and Waseda [6], have found no evidence to support the theories suggesting that the atomic arrangements in molten and crystalline BGO are completely different. On the contrary, they suggest that molten and crystalline BGO exhibit a number of similar structural features which could be summarized as follows.

(i) Most of the local geometrical characteristics (including most of the pair atomic distances and coordination numbers) of the atomic arrangements in molten and crystalline BGO are quite similar.

(ii) There are well defined GeO_4 tetrahedral units, which are similarly spatially arranged up to 20 Å, in both crystalline and molten BGO.

(iii) The angular correlations between the neighbouring Bi and O atoms in molten and crystalline BGO are also similar.

The present study also suggests that the substantial structural difference between molten and crystalline BGO, which makes the growth of pure BGO single crystals from the melt difficult, is quite likely to be the complete lack of BiO_6 octahedral units and the resulting emergence of couples of Bi atoms in the melt.

Acknowledgments

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