Neutron diffraction study of φ-Bi$_8$Pb$_5$O$_{17}$: structure refinement and analysis of cationic ordering

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The triclinic crystal structure of the φ phase in the structure of the Bi$_2$O$_3$–PbO phase diagram has been recently solved by the synergetic use of electron and X-ray diffraction on a polycrystalline Bi$_8$Pb$_5$O$_{17}$ sample. In the present work the problem is re-examined on the basis of powder neutron diffraction data: the structure has been confirmed and refined by the Rietveld method. The increased accuracy of the O-atom positions allowed the study of the cationic ordering in this structure by means of bond-valence calculations and charge distribution analysis. The results, confirmed by the refinement of the site occupancies, indicate that the structure is ordered to a large extent, with Bi and Pb atoms occupying preferentially different lattice sites. In this frame, the φ phase being the most ordered one in the considered region of the Bi$_2$O$_3$–PbO phase diagram, it should represent the thermodynamically stable low-temperature polymorph.

1. Introduction

Fast ionic conductors are characterized by typical structures involving tunnels or layers through which mobile ions may move. Some phases of the PbO–Bi$_2$O$_3$ system showing high conductivity belong to this class of material (Honnart *et al.*, 1983; Fee & Long, 1996; Boivin & Mairesse, 1998, and references therein). Recently great interest has been focused on the composition Bi$_8$Pb$_5$O$_{17}$ corresponding to a 4Bi$_2$O$_3$:5PbO ratio (Fee *et al.*, 1997; Santarosa *et al.*, 1999; Watanabe *et al.*, 1999). Above 863 K this compound is stable as a cubic solid solution labelled β. By quenching the β phase, another modification (β_2) appears, which has been described for a long time as a disordered structure with a partially vacant oxygen arrangement. Recently it has been discovered (Santarosa *et al.*, 1999) that β_2 is an incommensurate modulated phase with an average structure with tetragonal symmetry. The transformation β_2–β occurs on heating *via* an intermediate material named φ (or β_L), whose thermal stability ranges from 733 to 833 K. The φ phase can also be directly produced by heating a mixture of Bi$_2$O$_3$ and PbO in appropriate amounts above 773 K. Its powder X-ray diffraction (PXRD) pattern is extremely complex, so that this material has been erroneously believed to be a mixture of different phases. This, together with the impossibility to grow crystals suitable for single-crystal X-ray analyses, prevented for a long time the structure solution.

The lack of detailed structural information on this phase, associated with the relatively slow β_2–φ transition kinetics, which results in broad and very weak thermal effects,

complicates the comprehension of the thermodynamic stability of the different phases, and the relation between ionic conductivity and structural features. The structural problem of the φ phase has been tackled recently by an original structure solution method, based on the combination of both electron diffraction (ED) and PXRD (Gemmi *et al.*, 2000), which led to a satisfactory structural model. Unfortunately, the small contribution, with respect to the heavy metals, of O atoms to the total scattered amplitude resulted in a high uncertainty (0.1 Å) in their coordinates, which prevented deeper analysis of a structure that seems to be characterized by cationic ordering. In this work the problem is re-examined through the additional complementary use of neutron powder diffraction data, confirming this phase as an ordered solid solution, where Bi and Pb atoms are arranged in the (110) plane in stripes parallel to the *c* direction.

2. Experimental

A sample of composition $Bi_8Pb_5O_{17}$ was obtained by solid-state reaction at 833 K starting from Bi_2O_3 and PbO. The reagents were mixed in a stoichiometric amount, grounded, pelletized and heat-treated in air for 72 h with intermediate grinding.

Powder XRD patterns were collected with conventional θ–2θ laboratory equipment (Philips X'pert powder diffractometer), using Ni-filtered Cu $K\alpha$ radiation, 0.02° steps and 10 s counting time. Transmission electron microscopy (TEM) investigations were performed with a Philips CM30T microscope operating at 300 kV. The samples were prepared by mild grinding of the powder, suspension in isopropilic alcohol and deposition on a holey carbon film. ED data were collected in a selected area mode with a Gatan slow-scan CCD camera. The neutron diffraction experiment has been performed at room temperature at the beamline D2B at ILL, Grenoble, with a wavelength of λ = 1.594 Å. The conditions of the pattern acquisition were: 2θ angular range 5–155°, step scan 0.02°.

The structural refinement was performed using *GSAS* (Larson & Von Dreele, 1995). Bond valence and charge distribution calculations were performed using the program *CHARDIS*99 (Nespolo *et al.*, 1999).[1]

2.1. Structure solution and refinement

The lattice parameters and the crystal symmetry of the φ phase were found by an extensive electron diffraction study (Santarosa *et al.*, 1999). 33 different selected area diffraction (SAD) patterns, taken on different crystals, were indexed using the software package *QED* (Belletti *et al.*, 2000). The structure was found to be triclinic and the lattice parameters, determined by ED, were used as starting values for indexing the PXRD pattern. The extraction routine (EXTRA) used in *EXPO* (Altomare, Burla, Camalli, Carrozzini *et al.*, 1999) was

used in a simultaneous attempt to refine the cell parameters and to extract the reflection intensities. Unfortunately, the frequent peak overlapping produced by the low symmetry and by the similarity of the lattice parameters prevented a faithful intensity extraction of most PXRD reflections (only 16% of the total number were considered extracted as independent observations). As a result, any structure resolution attempt using either Patterson analysis or direct methods (EXPO) on PXRD data failed. The possibility of deriving a starting model from the dynamic ED intensities was therefore taken into account as the unique way to solve the structure.

The application of direct methods (DM) to ED data is clearly complicated by the unavoidable dynamic effects that destroy the simple relation between the observed intensity and the modulus of the structure factor. However, the application is made possible for two principal reasons:

(i) the ED intensities are differently affected by dynamic effects (depending on the sample thickness, zone axis and scattering vector); however, since the reflections related to the strongest normalized structure factors are often located at high angle and are usually less perturbed by multiple scattering, the starting set of phases could therefore be correctly assigned;

(ii) the dynamic effects can be taken into account by using the approximation $|F_{hkl}| \propto I_{hkl}$ (Vainshtein, 1964; Cowley, 1992). Although this approximation was used for correcting ED data from mosaic crystals and polycrystalline specimens, it has been demonstrated that the results are useful in improving the quality of ED data to be used by DM (Weirich *et al.*, 2000). However, in solving structure by ED data, it must be considered that the dynamic amplitudes are linearly correlated with the Fourier transform of $\zeta(\mathbf{r}) = |\Psi(\mathbf{r}) - 1|$, where $\Psi(\mathbf{r})$ is the electron exit wavefunction (Sinkler *et al.*, 1998; Sinkler & Marks, 1999). $\zeta(\mathbf{r})$ fulfils the DM requirements for phase reconstruction, but any interpretation of the final model should take into account that the quantity reconstructed by DM using ED data is not the projected crystal potential $V(\mathbf{r})$ but $\zeta(\mathbf{r})$. While most peaks are correctly located on atomic sites, their assignment on the basis of relative height becomes uncertain since the relative peak height of $\zeta(\mathbf{r})$ varies with the thickness and depends on the alignment of the atoms along columns in the considered projection. A careful investigation of the E maps is therefore required in order to correctly assign the atomic species on the basis of crystal chemistry requirements.

Taking into account the previous considerations, ED intensities derived from single ED patterns (*i.e.* the fundamental ones) have been successfully used for solving layered structures (Weirich *et al.*, 2000) by DM. The incommensurate composite structure of $Ba_{0.70}CuO_2$ has been solved using DM on three-dimensional sets of ED data (Migliori *et al.*, 1999), obtained by recording a set of ED patterns in a different zone axis and by scaling the plates on the basis of common row intensities.

The structure solution of the φ phase was found in a similar way. A three-dimensional set of intensities was extracted with the program *QED* and merged together using a common row

of reflections (Gemmi *et al.*, 2000). The merged ED data were processed in space group $P\bar{1}$ by DM using the program *SIR*97 (Altomare, Burla, Camalli, Cascarano, Giacovazzo *et al.*, 1999). A partial structure solution, consisting of five heavy atoms, having consistent distances and arrangements, was found in the first E-map proposed by the program by automatically using pseudo-translation information and random phase assignment. The remaining three heavy atoms were located simultaneously by a difference Fourier (ΔF) map, performed using the unrefined partial model. In spite of the relatively high R value (0.36) resulting from a structure factor calculation, the heavy atoms model, showing an atomic arrangement closely related to that of the cubic β structure, was considered realistic and used as a starting set in the Rietveld refinement of powder XRD data. The refinement, performed with the program *GSAS* (Larson & Von Dreele, 1995), demonstrates the correctness of the direct method solution on ED data. $R_p = 0.0575$, $R_{wp} = 0.0836$ were obtained, indicating that the high R value obtained with ED data was attributable to the dynamic nature of the measured ED intensities rather than to errors in the atomic positions. The O atoms were successively located *via* ΔF maps on both electron and XRD data and further processing of DM on electron and XRD data starting with partial structures.

All the residuals found in ΔF and E maps, having a geometry consistent with expectations, were carefully checked. Starting with a few common peaks and performing refining cycles and an oxygen search in an iterative way, the model was slowly completed by carefully taking into account the stereochemical requirements of Bi and Pb atoms. The final refinement, with Bi and Pb distributed on the same sites in fractions consistent with the phase stoichiometry (0.615/0.385), gave $wR_p = 0.0414$, $R_p = 0.0310$ and $R(F^2) = 0.0925$. However, the poor sensitivity of XRD to a small variation of the oxygen positions in a system containing heavy scatterers such as Bi and Pb, as well as the strong overlapping of the diffraction peaks in the experimental PXRD pattern, result in a large uncertainty ($\sim$0.1 Å) in the refined oxygen coordinates. In spite of this the results suggested, on the basis of bond distances, the occurrence of cationic ordering.

A neutron diffraction experiment consequently has been carried out to unambiguously confirm the proposed structure and to improve the accuracy of the oxygen coordinates, which is needed for a deeper discussion on ordering phenomena. The neutron diffraction study began with a structural model consisting of the heavy-atom positions refined previously on PXRD data. For each site the occupancies were initially fixed to a Bi/Pb ratio consistent with the phase stoichiometry (0.615/0.385). After refining the scale factor, the background and the zero-shift position, the O atoms were located by an iterative succession of Rietveld refinements and ΔF maps. Only the 11 sites previously assigned to the O atoms were found in this way, confirming the reliability of the structure determined by electron and PXRD data. The existence of partially vacant oxygen sites was then tested by refining their occupancy factors, but convergence to values close to one, associated with the absences of significant residuals in the ΔF map, convinced

us to carry on the refinement using full occupancies for oxygen sites. By using isotropic displacement parameters for all the atoms and statistic occupancy of the cationic (M) sites, the structure was refined to $wR_p = 0.0511$, $R_p = 0.0399$, $R(F^2) = 0.0501$ and g.o.f. = 1.42.

2.2. Structural ordering

Inspection of the structure geometry shows that all the cationic sites display the typically distorted coordinations usually found in Bi^{3+} and Pb^{2+} oxides, where the presence of a localized $6s^2$ lone pair determines the occurrence of short metal–oxygen interactions (usually three) only on the opposite side with respect to $6s^2$ localized electrons. One site is threefold coordinated, with the metal atom at the top of a trigonal pyramid and $M-$O distances in the range 2.21–2.25 Å. Three M sites display a fourfold coordination arranged as a monocapped trigonal pyramid, with the heavy atom at the top; the $M-$O distances (three short and a longer one, corresponding to the capping oxygen) range from 2.09 to 2.72 Å. The remaining four M sites are fivefold coordinated, with the oxygen forming a distorted square pyramid, whose basal plane is occupied by the cation. The $M-$O distances range from 2.08 to 2.61 Å. By taking into account the shortest bond lengths, the coordination is arranged as previously in the form of a trigonal pyramid, with the heavy atom at the top; this atom is capped by two additional O atoms at longer distances.

At this stage the refinement of the cationic occupancy has been considered untimely, since the neutron form factors of Pb and Bi do not differ so significantly to assure the convergence of the Rietveld refinement to the global minimum. Therefore, a preliminary analysis of the possible ordering of lead and bismuth in the structure was considered by taking into account the correlation between bond lengths and bond valences, the so-called 'R–s' curves (Brown & Shannon, 1973; Brown & Wu, 1976; Brown & Altermatt, 1985). However, in most cases the application of the bond-valence (BV) approach to cations such as Pb^{2+} and Bi^{3+} is not straightforward. In fact, as discussed previously, their coordination is usually very distorted, without a clear separation between first and second coordination sphere, so that the interatomic distances are not deducible as the sum of the atomic radii. In order to evaluate the efficiency of BV in the treatment of the φ-phase structure, α-Bi_2O_3 (Harwig, 1978) was at first analysed as a reference structure; this choice is justified not only by the crystal-chemical similarity, but also by the presence of two symmetry-independent Bi^{3+} sites, which should reasonably present very similar bond length–bond valence characteristics. The parameters given by Brown & Wu (1976) for the R–s curve of bismuth produce in this structure a calculated valence of 2.54 and 2.80 for the two independent Bi^{3+} cations. The valence increases to more acceptable values (2.88 and 3.11) by using parameters given successively (Brown & Altermatt, 1985). However, since also in this case the parameters defining the R–s curve depend upon the cation, but are independent from the geometry of the specific site, significant deviations persist between the two independent Bi^{3+} cations.

Table 1
CD calculations for the φ-Bi$_8$Pb$_5$O$_{17}$ structure performed on the intermediate disordered model and on the final of the φ structure.

	Disordered model			Final refinement			
Cation	q_{ij}	Q_{ij}	q_{ij}/Q_{ij}	Cation	q_{ij}	Q_{ij}	q_{ij}/Q_{ij}
M(1)	2.62	2.87	0.91	Bi(1)	3.00	3.09	0.97
M(2)	2.62	2.63	0.99	M(2)	2.54	2.54	1.00
M(3)	2.62	2.49	1.05	Pb(3)	2.00	2.18	0.92
M(4)	2.62	2.70	0.97	Bi(4)	3.00	3.04	0.99
M(5)	2.62	2.62	1.00	Bi(5)	3.00	2.88	1.04
M(6)	2.62	2.40	1.09	Bi(6)	3.00	2.85	1.05
M(7)	2.62	2.43	1.08	Pb(7)	2.00	1.94	1.03
M(8)	2.62	2.86	0.91	M(8)	2.37	2.49	0.95

This problem may be overcome by the charge distribution (CD) method, introduced as a development of the BV approach (Hoppe, 1979) and utilized to analyse the distribution of charges in crystalline structures (Hoppe *et al.*, 1989). Recently it has been shown (Nespolo *et al.*, 1999) that the CD method represents a suitable alternative to BV to analyse the distribution of bond strength/bond valence, as well as a suitable tool to check the presence of structural anomalies. Differently from BV, the CD descriptions depend upon the geometry of each coordination polyhedron, which is defined by a non-integer effective coordination number (ECoN) through the scaling of each bond distance to the shortest bond length of each polyhedron (instead of an empirical normalization parameter as in BV). CD explicitly use the formal oxidation number of cations $q(ij)$ and anions $q(k)$ as input variables and the corresponding calculated charges $Q(ij)$ and $Q(k)$ are the results of the distribution of $q(ij)$ and $q(k)$ as a function of ECoN in each polyhedron.

The application of CD to the analysis of the α-Bi$_2$O$_3$ structure was found to be satisfactory. The computed charges $Q(ij)$ of the two Bi^{3+} cations are 3.03 and 2.97, indicating CD as a useful tool in the analysis of this type of compound. The ratio $q(ij)/Q(ij)$ is close to 1 (0.99 and 1.01, respectively) and this can be interpreted as a measure of the correctness of the structure. On the contrary, the CD calculations performed on the refined disordered model of the φ structure [$q(ij)$ = +2.62 for all the cations] are quite unsatisfactory (Table 1). Five of the eight $q(ij)/Q(ij)$ ratios deviate significantly (5–10%) from the expected value. Since negative (positive) deviations from 1 can be interpreted as a request for increasing the Bi (Pb) content of the site, the CD analysis suggests a higher Bi occupancy for three cationic sites, whereas three sites seem to be more occupied by Pb. However, a quantification of the real cationic occupancies through CD is complicated: since the calculated charges $Q(ij)$ and $Q(k)$ are the results of the distribution of $q(ij)$ and $q(k)$ (input variables) as a function of ECoN, a modification of a single q in the input data will influence all the calculated charges.

From this point of view the BV method would be more simply applicable. In fact, even if the computation also depends in this case upon $q(ij)$ through the choice of the parameters of the R–s curve, the calculated bond valences are

mutually independent. In the Brown & Altermatt (1985) approach the oxidation state of the cation i (V_i) is given by

$$V_i = \sum_j s_{ij} = \sum_j \exp((r'_0 - r_{ij})/B), \qquad (1)$$

where s_{ij} is the valence of the bond between the cation i and the anion j, r_{ij} the corresponding bond length, whereas r'_0 and B are parameters depending upon the cation (the contraction and the scaling parameter, respectively). In reality it has been shown that B varies very little from an atom pair to another and a value of 0.37 can be accepted in almost all cases. The major problem in the application of the BV method in the present study results from the contraction parameter r'_0 (the theoretical bond length of unitary bond strength), which has been derived from literature data and tabulated for each cation–anion pair. In particular, for the Pb^{2+}—O^{2-} pair the tabulated r'_0 value (2.112 Å), averaged by Brown & Altermatt (1985) on 174 structures, is too high for a satisfactory description of both the orthorhombic and tetragonal modifications of the simple binary oxide PbO (Hill, 1985; Boher *et al.*, 1985). Owing to the crystal-chemical similarity, a comparison with PbO (rather than with all the structures that include Pb and O atoms) should be considered probably more appropriate in the present analysis. Therefore, rather than selecting tabulated r'_0 values to calculate V_i, we decided to treat it as a parameter. Consequently, (1) must be interpreted as the functional dependence, characteristic of each particular site, of V_i *versus* r'_0 and the shape of the corresponding curve $V_i = V_i(r'_0)$ should represent the fingerprint of the occupying cation. The $V_i = V_i(r'_0)$ curves, calculated on the basis of (1) for all the M sites in the φ structure (numbered 1–8), are reported in Fig. 1 compared with the corresponding curves calculated in the same way for PbO and Bi$_2$O$_3$, chosen as reference behaviour for Pb^{2+} and Bi^{3+}. For Bi$_2$O$_3$ both curves relative to the two independent Bi^{3+} sites are reported, whereas for PbO the two curves refer to the orthorhombic and tetragonal modifi-
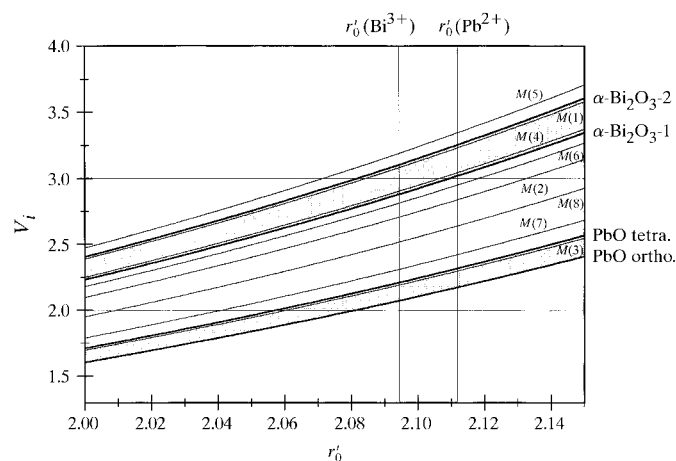
Figure 1
$V_i = V_i(r'_0)$ curves calculated for the eight M sites of the φ structure (thin lines), compared with the corresponding curves calculated for PbO and Bi$_2$O$_3$ (thick lines) chosen as the reference behaviour for Pb^{2+} and Bi^{3+}. The r'_0 given by Brown & Altermatt (1985) for Pb^{2+} and Bi^{3+} are marked by vertical lines. See text for details.

Table 2

Crystal data, fractional atomic coordinates and displacement parameters (Å^2) for φ-Bi$_8$Pb$_5$O$_{17}$.

Crystal data: $a = 7.4507$ (1), $b = 14.1768$ (2), $c = 7.2101$ (1) Å; $\alpha = 97.190$ (1), $\beta = 118.473$ (1), $\gamma = 80.643$ (1)°; $V = 659.55$ (1) Å^3; chemical formula: Bi$_8$Pb$_5$O$_{17}$, $M = 2979.83$, refined cell content = Bi$_{9.83}$Pb$_{6.17}$O$_{21}$, $D_x = 9.186$ g cm^3 (calculated on the basis of the refined structural model); space group = $P\bar{1}$; no. of reflections: 2799; $R_{wp} = 0.0490$; $R_p = 0.0383$; $R_{F^2} = 0.0480$; $S = 1.38$.

	x	y	z	U_{iso} ($\times$ 100)	s.o.f.
Bi(1)	0.2277 (9)	0.0276 (4)	0.2937 (9)	0.81 (13)	1.00
Bi(2)	0.0586 (9)	0.1900 (4)	0.7163 (8)	1.17 (13)	0.54 (06)
Pb(2)	0.0586 (9)	0.1900 (4)	0.7163 (8)	1.17 (13)	0.46 (06)
Pb(3)	0.2143 (8)	0.5560 (4)	0.2380 (8)	0.76 (11)	1.00
Bi(4)	0.4825 (9)	0.3249 (4)	0.2355 (10)	1.00 (13)	1.00
Bi(5)	0.6857 (8)	0.0719 (4)	0.1979 (8)	0.68 (12)	1.00
Bi(6)	0.7577 (9)	0.5449 (4)	0.2723 (9)	1.08 (12)	1.00
Pb(7)	0.9851 (8)	0.2928 (4)	0.2585 (8)	1.42 (12)	1.00
Bi(8)	0.5309 (9)	0.2039 (4)	0.7298 (9)	1.21 (15)	0.37 (10)
Pb(8)	0.5309 (9)	0.2039 (4)	0.7298 (9)	1.21 (15)	0.63 (10)
O(1)	0.9645 (12)	0.9773 (6)	0.2761 (14)	1.23 (17)	1.00
O(2)	0.2618 (13)	0.1207 (6)	0.5961 (14)	1.30 (18)	1.00
O(3)	0.4035 (13)	0.2125 (6)	0.9856 (14)	1.58 (19)	1.00
O(4)	0.0546 (12)	0.4699 (6)	0.3355 (13)	0.79 (17)	1.00
O(5)	1/2	1/2	1/2	3.72 (40)	1.00
O(6)	0.5995 (13)	0.0847 (6)	0.5069 (13)	1.44 (19)	1.00
O(7)	0.6794 (13)	0.3742 (6)	0.1417 (14)	1.63 (20)	1.00
O(8)	0.2371 (14)	0.4270 (6)	0.0293 (14)	1.34 (19)	1.00
O(9)	0.2513 (14)	0.8979 (7)	0.0556 (16)	2.30 (22)	1.00
O(10)	0.8279 (13)	0.1912 (6)	0.3603 (14)	1.64 (21)	1.00
O(11)	0.0811 (15)	0.3257 (7)	0.5939 (15)	2.15 (21)	1.00

cations. Both in the case of PbO or Bi$_2$O$_3$, the $V_i = V_i(r'_0)$ curves differ significantly. However, it could be accepted that they define a region of the diagram, which can be considered as reasonably characteristic of the Pb^{2+} or Bi^{3+} behaviour, respectively. Following this idea, four sites of the φ structure seem to be occupied by Bi, whereas two other sites, whose behaviour approaches that of the PbO curves, seem to exhibit a Pb-type character. The two remaining sites present a behaviour intermediate between the two, suggesting a mixed occupancy.

A model based on these indications (two sites fully occupied by Pb, four sites occupied by Bi and two sites with a
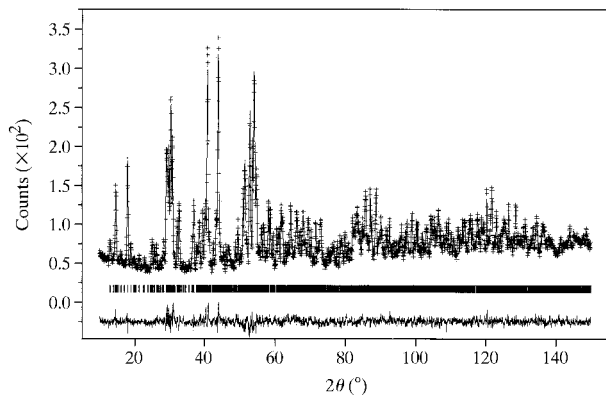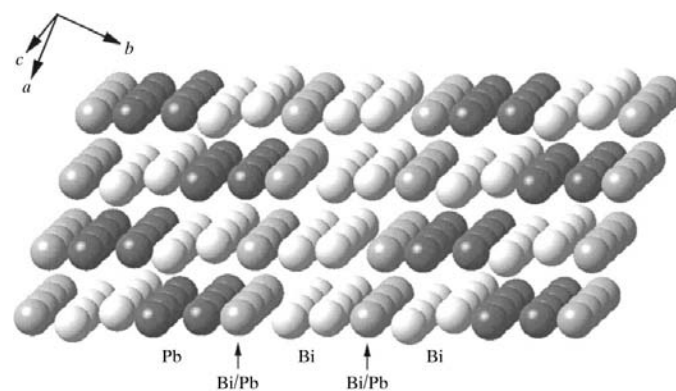
Figure 2
Final plot of the Rietveld refinement on powder neutron data showing observed (+) and calculated (solid line) profiles. The difference curve (observed − calculated) is shown on the bottom. Ticks refer to calculated peak positions. Final agreement factors are $R_{wp} = 0.0490$, $R_p = 0.0383$, $R_{F^2} = 0.0480$, g.o.f = 1.38.

mixed Bi and Pb occupancy) was considered a reliable starting point for a further Rietveld refinement of the cation occupancies. In order to maintain the overall stoichiometric ratio between Bi and Pb, a chemical composition constraint, fixing the total amount of both cations in the unit cell, was used during the refinement. Atomic coordinates, isotropic displacement parameters and occupancy factors were refined simultaneously and the system converged to a stable situation, not so different from the starting hypothesis. In fact, the refinement confirmed two sites as practically fully occupied by Pb and four sites fully occupied by Bi. The occupancy factors
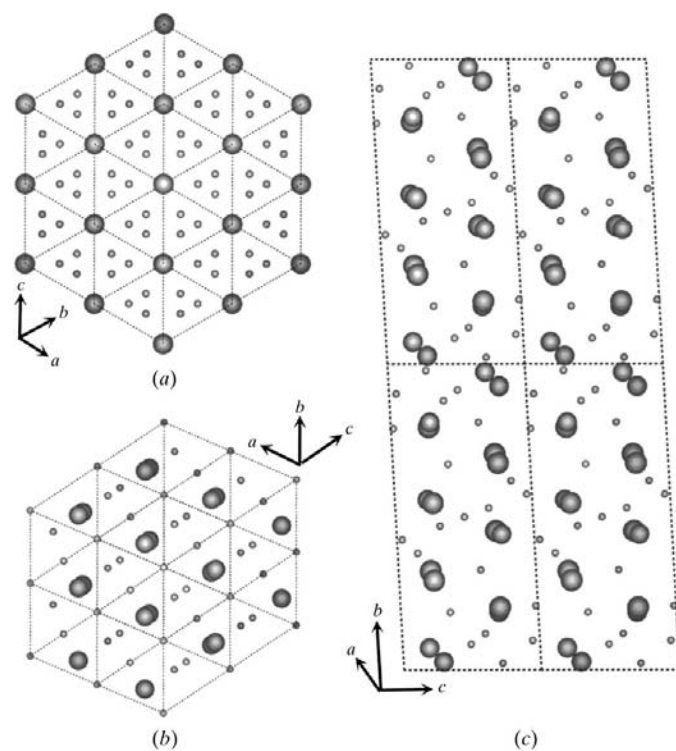
Figure 3
Comparison of the different Bi$_8$Pb$_5$O$_{17}$ polymorphs: (a) β; (b) β_2; (c) φ. Large and small balls represent cations and oxygen atoms, respectively. The oxygen sites are only partially occupied in the β and β_2 structures.
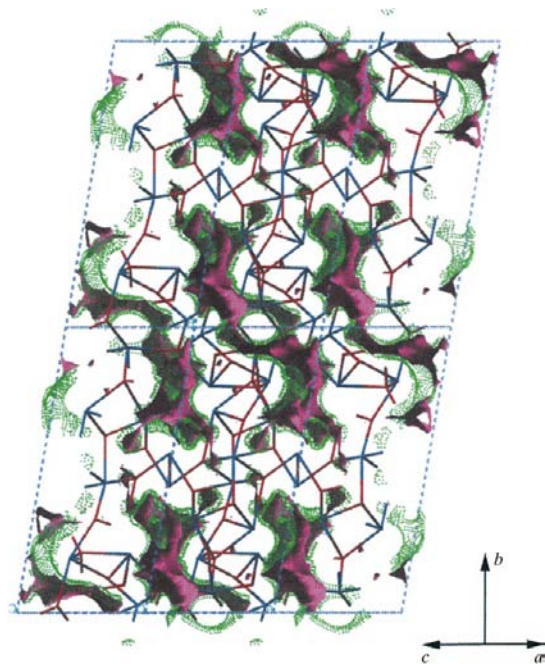
Figure 4
Cationic ordering in the (110) plane. Bi and Pb atoms tend to form stripes parallel to the c direction in the sequence Pb−Bi−Bi, separated by columns of sites with mixed occupancy.

Table 3
Selected bond distances (Å) for Bi$_8$Pb$_5$O$_{17}$.

Bi(1)—O(1)	2.137 (10)	M(2)—O(1)	2.414 (11)	Pb(3)—O(4)	2.209 (10)
Bi(1)—O(2)	2.328 (10)	M(2)—O(2)	2.136 (10)	Pb(3)—O(5)	2.173 (5)
Bi(1)—O(6)	2.655 (10)	M(2)—O(3)	2.415 (10)	Pb(3)—O(8)	2.256 (11)
Bi(1)—O(6)	2.098 (10)	M(2)—O(10)	2.311 (10)		
Bi(1)—O(9)	2.399 (12)	M(2)—O(11)	2.277 (11)		
Bi(4)—O(3)	2.169 (10)	Bi(5)—O(1)	2.145 (9)	Bi(6)—O(4)	2.151 (10)
Bi(4)—O(7)	2.120 (10)	Bi(5)—O(3)	2.659 (10)	Bi(6)—O(4)	2.505 (10)
Bi(4)—O(8)	2.176 (11)	Bi(5)—O(6)	2.576 (10)	Bi(6)—O(7)	2.539 (11)
Bi(4)—O(10)	2.767 (10)	Bi(5)—O(9)	2.196 (10)	Bi(6)—O(8)	2.278 (11)
		Bi(5)—O(10)	2.064 (11)	Bi(6)—O(11)	2.215 (12)
Pb(7)—O(4)	2.586 (11)	M(8)—O(2)	2.233 (10)		
Pb(7)—O(7)	2.188 (10)	M(8)—O(3)	2.428 (10)		
Pb(7)—O(10)	2.369 (10)	M(8)—O(6)	2.350 (11)		
Pb(7)—O(11)	2.181 (10)	M(8)—O(9)	2.125 (11)		

of these sites being close to one (well below their uncertainties) for a single atomic species meant they were fixed to unitary occupancies in the last refinement cycles. Final residuals were $wR_p = 0.0490$, $R_p = 0.0384$, $R(F^2) = 0.0480$ and g.o.f. = 1.38, showing a small but significant improvement with respect to the disordered situation. The average and maximum shifts of the atomic coordinates with respect to the previous model were found to lie within 1 and 3σ, respectively. The final Rietveld plot is shown in Fig. 2. Crystal data and structural parameters are reported in Table 2, and relevant bond distances in Table 3. The CD calculations performed on the refined structure are reported in Table 1, compared with those

Figure 5
A *Cerius*^{2} (Molecular Simulations Inc., 1997) view of the φ-Bi$_8$Pb$_5$O$_{17}$ structure normal to the (101) plane, showing (exaggerated for clarity by using a probe with radius 0.5 Å) the free volume surface. The cavities are interconnected forming channels normal to the view direction, which can be related to possible migration paths for O atoms.

previously obtained for the fully disordered model. As can be seen, a general improvement of the $q(ij)/Q(ij)$ ratios is obtained for the ordered structure. Seven ratios lie within $\pm 5\%$ around the expected unitary value and this can be considered a satisfactory result in a situation in which eight highly distorted coordinations are taken simultaneously into account in the calculation. The main deviation involves the tricoordinated Pb(3) atom, which shows the most distorted environment and for which the description in terms of CD is deemed to be scarcely appropriate.

The structure is shown in Fig. 3(c) projected along the *a* axis, compared with the cubic β (Fig. 3a) and the tetragonal β_2 (Fig. 3b) modifications. The similarity of the heavy-atom arrangements in the three structures is evident and the φ structure can be considered as a distorted cubic β phase connected with oxygen and cationic ordering. As concerns the positions of the O atoms, some analogies with the β_2 arrangements can be found in the structural region showing the largest distortion from a cubic arrangement of the heavy atoms. The cationic ordering is illustrated in Fig. 4, showing the arrangement of the cations in the (110) plane, where Bi and Pb atoms tend to form stripes parallel to the *c* direction in the sequence Pb–Bi–Bi, separated by columns of sites with mixed occupancy.

As shown in Fig. 5, the atomic arrangement in the φ structure produces channels perpendicular to the (101) plane, which represent possible migration paths of O atoms and therefore can be related to the ionic conductivity of this material.

3. Conclusions

The crystal structure of the φ phase in the Bi$_2$O$_3$–PbO phase diagram has been determined by the synergetic use of electron and neutron diffraction on a polycrystalline Bi$_8$Pb$_5$O$_{17}$ sample. The crystal structure, solved with the determinant contribution of ED data in finding the heavy-atoms positions, was refined by Rietveld refinement on neutron powder data. Refinement of the site occupancies together with bond-valence and charge distribution analysis indicates that the structure is ordered to a large extent, with Bi and Pb atoms occupying preferentially different lattice sites. This frame, with the φ phase being the most ordered in the considered region of the Bi$_2$O$_3$–PbO phase diagram, should represent the thermodynamically stable low-temperature polymorph. In a recent work, Watanabe *et al.* (1999) reported the φ phase to be a well defined compound with the composition Bi$_{10}$Pb$_6$O$_{21}$ rather than a solid solution. They found, by indexing the X-ray powder pattern, a triclinic cell similar to the one we determined, but with a double *a* parameter for which no evidence has been found in ED patterns of our sample. The chemical formula given, Bi$_{10}$Pb$_6$O$_{21}$, agrees with the global cationic and anionic content of our unit cell and their measured density [9.219 (3) g cm^{-3}] is in agreement with a slightly richer Bi

composition. However, in the case of a well defined compound we should probably expect a complete structural ordering, whereas our data are consistent with a partially ordered solid solution in which the mixed columns separating the Pb and Bi stripes can adjust variations in composition. The solid solution hypothesis is supported by the absences of lead oxides segregation in the powder diffraction pattern used for the structural refinement, which has been obtained on a sample with a Pb-richer nominal composition $Bi_8Pb_5O_{17}$. The study of the compositional range of the φ phase in the phase diagram is in progress.

As far as the structure determination strategy is concerned, this work demonstrates that, even in the presence of dynamic effects, direct methods on ED data can be very useful in structure solution. Therefore, electron crystallography opens new possibilities in material science, in particular when good quality powder diffraction data (neutron or X-ray) are available for the structure refinement, that obviously cannot always be performed with dynamic electron data in a satisfactory way. The synergy between ED, X-ray and neutron diffraction could result in a breakthrough for solving difficult structural problems, in particular when appropriate software able to deal simultaneously with all types of data will become available.

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