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Abstract. A positron annihilation study has been carried out on $Bi_{12}XO_{20}$ (X = Ge, Si, Ti) structures with the aim of identifying the nature of native defects in these structures. The positron lifetimes have been measured at room temperature for the three structures, and a long component which depends on the type of cation has been obtained. Moreover, theoretical calculations have been carried out for the bulk lifetime in these materials and for several types of vacancy-like defect. From both the experimental and the theoretical results the native defects are tentatively identified as cation–vacancies complexes.

1. Introduction

The $Bi_{12}XO_{20}$ compounds (X = Ge, Si, Ti) are a well known group of materials from among the sillenite compounds. Their importance derives from their use in optical applications, as has been recently reviewed [1]. For this reason, there is increasing interest in the growth of high-quality crystals [2, 3], and in the knowledge of the nature of the intrinsic defects, mainly related to cation vacancies.

The positron annihilation technique is highly sensitive to vacancy-type defects and has been very successfully used to reveal the presence of vacancy-like defects such as small clusters or vacancy–impurity complexes. Theoretical calculations of the annihilation characteristics and positron states for defects also play a very important role as regards achieving the correct interpretation of the experimental results and they are crucial when one is dealing with very complex materials such as sillenites. Positron annihilation is thus expected to be a powerful tool for identifying the defects present in $Bi_{12}XO_{20}$ (X = Ge, Si, Ti) materials. Recently Misheva, Toumbev and Gospodinov [4] used this technique to study native and irradiation-induced defects in $Bi_{12}GeO_{20}$, concluding that positrons are trapped at some kind of defect, presumably connected with oxygen.

In this paper we report on a systematic positron study of the native defects in three bismuth oxides containing Ge, Si, and Ti for which both lifetime measurements and theoretical calculations have been carried out.

2. Experimental details

The $Bi_{12}XO_{20}$ (BXO in the following) single crystals studied in this work were grown using computerized Czochralski equipment developed at the Crystal Growth Laboratory of

the Universidad Autónoma de Madrid. The equipment was provided with an automatic diameter control via a weighing of the melt contained in the crucible [2, 3, 5]. Resistance-heated furnaces, pure platinum crucibles and $\langle 100 \rangle$-oriented seeds were utilized to grow the crystals. The starting materials used were from Johnson–Matthey (Grade Al, Puratronic). The crystals were grown in air from stoichiometric mixtures of oxide powders ($6Bi_2O_3:1XO_2$ for X = Ge, Si) or in a flux of Bi_2O_3 for the case of $Bi_{12}TiO_{20}$. Boules of about 20 mm diameter were pulled at 2.5–0.3 mm h^{-1} and rotation rates of 70–30 rpm up to approximately 50% of the charge. The crystals were cooled to room temperature over a period of 60–100 h in the growth environment to reduce strain. The boules were sectioned, and the samples were mechanically polished plates of about $15 \times 15 \times 1.5$ mm^3 in dimension.

The positron annihilation measurements were performed at room temperature with a conventional fast spectrometer having a resolution (FWHM) of 220 ps. As a positron source a ^{22}NaCl aqueous solution evaporated onto a Kapton foil was used. The specimen surface was polished in order to minimize the surface effects.

In order to extract the correct source contribution, a preliminary analysis was carried out for all of the samples in which one lifetime was fixed to 382 ps, i.e., the value currently assigned to the Kapton foil [6]. The NaCl lifetime component due to positrons annihilating in the salt crystals can be included in the Kapton characteristic positron lifetime, and thus the source spectrum is reduced to only one component. Four components (one constrained to 382 ps lifetime and three unconstrained ones) were necessary to obtain satisfactory fits. The intensity corresponding to the fixed lifetime, 382 ps, oscillates between 17.0 and 19.1% with an average value of 18.5%. We have thus assigned the 382 ps component with an intensity of 18.5% to annihilations both in the salt and in the support Kapton foil and have repeated the data analyses by subtracting the above-mentioned component as a source value. Satisfactory fits were obtained with three components. For all of the spectra a very long component ranging from 1.4 to 2 ns with low intensity (0.2–0.5%) was present. This long lifetime originates very probably from surface effects and it is not characteristic of the bulk specimens; thus it will be neglected in the following.

3. Theoretical calculations

The calculations for perfect BXO lattices and those containing defects were performed by using the superimposed-atom model of Puska and Nieminen [7]. Details of the calculation method have been given elsewhere [8]. The BXO structures crystallize in the cubic system [9–11] and belong to the $I23$ space group. The X cations occupy the corners and the centre of the cubic cell and are surrounded by oxygens located at the corners of a tetrahedron. In this lattice we have considered several types of defect (see [9] for the site description): (i) bismuth vacancies (V_{Bi}); (ii) cation vacancies (V_X); (iii) oxygen vacancies in the three non-equivalent positions (V_{O_1}, V_{O_2}, V_{O_3}); (iv) three types of complex involving one cation vacancy and oxygen vacancies in tetrahedral positions ($V_X V_{O_3}$, a cation vacancy plus one oxygen vacancy; $V_X 2V_{O_3}$, a cation vacancy plus two oxygen vacancies; and $V_X 4V_{O_3}$, a cluster formed of five vacancies in the X–$4O_3$ tetrahedron).

The results are shown in table 1, where the lifetime values for the bulk and the defects considered have been listed for the three structures. The positron–defect binding energy for the single vacancies is also shown in the table. In these calculations the high-frequency dielectric constant has been used for $Bi_{12}GeO_{20}$ [12]. Due to the lack of data for the high-frequency dielectric constants of $Bi_{12}SiO_{20}$ and $Bi_{12}TiO_{20}$ the results presented in the table for these materials were obtained by using the lowest values available in the literature for this magnitude, which is the low-frequency value [13, 14]. The use of larger dielectric

Table 1. Calculated positron annihilation lifetimes in bulk and vacancy defects in BXO (X = Ge, Si, Ti) structures. The quoted values refer to the positron–defect binding energy. The value of the dielectric constant ε used in each case is also listed.

τ (ps) (E_b (eV))	$Bi_{12}GeO_{20}$		$Bi_{12}SiO_{20}$		$Bi_{12}TiO_{20}$	
	$\varepsilon = 5$	[12]	$\varepsilon = 56$	[13]	$\varepsilon = 47$	[14]
Bulk	186		175		178	
V_{Bi}	240	(−0.76)	223	(−0.80)	226	(−0.77)
V_X	188	(−0.08)	174	(−0.18)	182	(−0.31)
V_{O_1}	191	(−0.06)	179	(−0.06)	182	(−0.06)
V_{O_2}	188	(−0.04)	177	(−0.04)	179	(−0.04)
V_{O_3}	188	(−0.04)	177	(−0.04)	180	(−0.03)
$V_X V_{O_3}$	223	(−0.35)	200	(−0.29)	215	(−0.46)
$V_X 2V_{O_3}$	256	(−0.61)	230	(−0.59)	243	(−0.72)
$V_X 4V_{O_3}$	324	(−1.05)	291	(−1.10)	295	(−1.14)

constants, as in the present case, decreases the calculated positron lifetime values [8] and thus, in order to make a rough estimation of this decrease, we have carried out the same calculations for $Bi_{12}GeO_{20}$ by using the dielectric constant value in the microwave region [15]. The values obtained for the lifetime are lower by 15–20 ps than the ones presented in the table. In the light of these results, in the following it should be remembered that the lifetimes calculated for BXO (X = Si, Ti) and listed in the table are underestimated by 15–20 ps. It is worth remarking that the positron binding energy for oxygen single vacancies is very low and thus they are not likely to be traps for positrons, at least at room temperature.
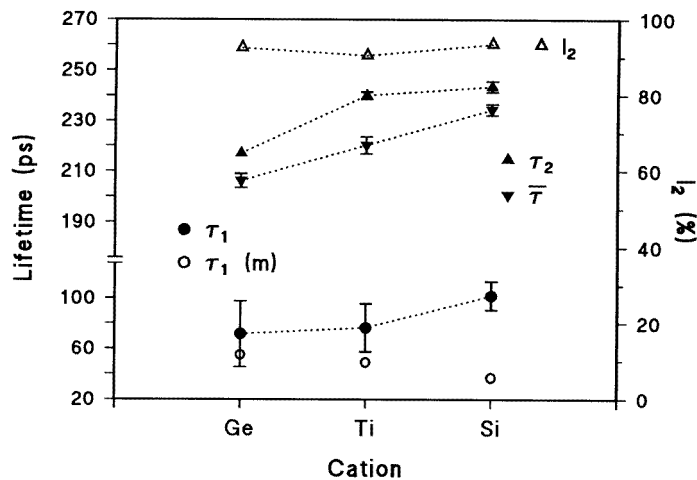

Figure 1. Experimental positron lifetime parameters in as-grown $Bi_{12}XO_{20}$ (X = Ge, Si, Ti) single crystals. The open circles denote the values for the shorter component τ_1 as extracted for the one-trap model (see the text for an explanation). The lines have been drawn as a guide for the eye.

4. Experimental results

In figure 1 the annihilation parameters as a function of the cation X in the BXO have been plotted; each value is the mean of two measurements. In this plot we have omitted the very long component due to surface effects.

It is shown that the long lifetime τ_2 depends on the type of X cation whereas its associated intensity I_2 is the same in all three cases. The intensity is very high and trapping is almost at saturation. From these results it is apparent that positrons are trapped at some type of vacancy-like defect which depends on the X cation. The defect concentration is very high and roughly the same for the three structures as reflected by the the intensity I_2 corresponding to the long component τ_2. To check the validity of the one-trap model [16] we have extracted the τ_1-value predicted by the model from the very well known expressions

$$\tau_1 = \frac{\tau_f}{1 + \kappa \tau_f} \qquad \kappa = \frac{I_2}{I_1}(\lambda_f - \lambda_2)$$

with $\lambda_f = 1/\tau_f$ and $\lambda_d = 1/\tau_2$, where τ_f is the bulk lifetime, τ_2 is the lifetime associated with the trap, I_1 and I_2 are the intensities corresponding to lifetimes τ_2 and τ_1, and κ is the rate of trapping to the positron traps. To obtain the trapping rate and the τ_1-value predicted by the one-trap model, we have used the experimental values for the intensities and for the τ_2-component and the calculated bulk lifetime for each structure. The results have also been plotted in figure 1 for comparison. The agreement between the experimental τ_1-values and the ones predicted by the one-trap model is very poor. This could be an indication that several kinds of trap are present in the samples.

It is to be noted that our results for $Bi_{12}GeO_{20}$ differ noticeably from the ones obtained by Misheva *et al* [4] for the same material. In our case the component τ_2 with a value of 444 ps is absent and the intensity for the very-long-lived component ($\sim$2 ns) is about 0.5% whereas Misheva *et al* obtain a higher value of 7.4%.

5. Discussion

The positron results reveal clearly that native defects in the BXO materials studied are vacancy-like defects. Moreover, it can be concluded that the concentration of these defects is very high since the intensity associated with the long component is around 90%. It is to be recalled that the one-trap model does not fit the experimental results, indicating that there is more than one kind of trap in the three compounds studied.

According to the data available in the literature, it is well established that the defect responsible for the optical properties in BXO (X = Ge, Si) has trigonal symmetry [17]; candidates are the Bi_{Ge} antisite and some kind of vacancy complex involving vacancies in the cation sublattice [17, 18]. Two kinds of positron trap in BXO materials have been proposed: complexes formed by one Bi atom, one oxygen vacancy and X cation (X = Ge, Si, Ti) vacancies [4]. By inspection of table 1 the oxygen vacancies can be excluded from consideration because they have very low binding energies and positron-bound states will not be formed at room temperature. The substitution of a Bi atom at a Ge site would very probably give rise to a decrease in the lifetime associated with the O_3 vacancy; thus the Bi_{Ge} antisite plus an oxygen vacancy can be excluded from consideration. The rest of the defects presented in the table can act as traps for positrons. In order to identify the nature of the traps for positrons it is instructive to compare the experimental values for the τ_2-component with the lifetime values calculated for several vacancy-type defects listed in the table. When doing this, one has to recall that the values corresponding to X = Si and

X = Ti have been obtained by using the low-frequency dielectric constant and, as a rough estimation, one can expect values for the lifetimes higher by 15–20 ps than the ones listed in the table, as pointed out in section 3. By comparing the experimental values for the τ_2-component for X = Ge (217 ps) with the theoretical ones, it can be seen that the closer value is the one corresponding to the defect labelled $V_X V_{O_3}$. As to BXO with X = Si and X = Ti, the experimental values for the lifetime τ_2 (238 and 240 ps respectively) seem to be very close to the lifetime associated with the bismuth vacancy, V_{Bi}. However, bearing in mind that ultrasonic attenuation measurements show that the native defects in these oxides have trigonal symmetry ([17] and references therein), it is not very likely that vacancies V_{Bi} are present in our samples. Thus, the traps giving rise to the τ_2-component should rather correspond to vacancy-type defects associated with the X–$4O_3$ tetrahedron. According to the results obtained for the one-trap model, there is more than one type of trap capable of trapping positrons, and thus the measured value for the long lifetime reflects an average of the lifetime values associated with the trapping centres. This average is very close to the divacancy lifetime value in the case of X = Ge, and thus we can conclude that they are the predominant defects in this material. In the case of BXO with X = Si, Ti it is not so straightforward. However, by inspection of table 1 it can be seen that the measured lifetimes take a value intermediate between the expected lifetimes for the defects labelled $V_X V_{O_3}$ and $V_X 2V_{O_3}$, which, under our hypothesis, should be higher by 15–20 ps than the values shown in the table. From this reasoning, it can be concluded that the X–oxygen divacancy and the X–oxygen trivacancy contribute to the observed τ_2-value in these materials.

6. Conclusions

(1) The positron lifetime has been measured in three as-grown compounds belonging to the family $Bi_{12}XO_{20}$, with X = Ge, Si and Ti. Only two lifetimes have been identified as originating from the samples, in disagreement with previous measurements assigning three characteristic lifetimes to $Bi_{12}GeO_{20}$ [4].

(2) The long lifetime depends on the type of cation X whereas the associated intensity has roughly the same value (90%) for the three samples.

(3) The bulk lifetimes and the lifetimes associated with several vacancy-like defects that can exist in the structures studied have been calculated. From the theoretical calculations concerning the positron–defect binding energy, it is found that trapping at oxygen vacancies can be excluded from consideration.

(4) By comparing both theoretical and experimental results we have tentatively assigned the long lifetimes to native defects involving cation–vacancies complexes.

Acknowledgments

References

[1] Arizmendi L, Cabrera J M and Agulló-López F 1992 *Int. J. Optoelectron.* **7** 2
[2] Santos M T, Rojo J C, Arizmendi L and Diéguez E 1994 *J. Cryst. Growth* **142** 103
[3] Santos M T, Rojo J C, Arizmendi L and Diéguez E 1996 *J. Cryst. Growth* at press
[4] Misheva M, Toumbev G and Gospodinov M 1993 *Phys. Status Solidi* a **135** K91
[5] Martínez-López J, Caballero M A, Santos M T, Arizmendi L and Diéguez E 1993 *J. Cryst. Growth* **128** 852

[6] MacKenzie I 1983 *Positron Solid State Physics, Proc. 83rd Int. 'Enrico Fermi' School of Physics* ed W Brandt
       and A Dupasquier (Amsterdam: North-Holland) p 210
[7] Puska M J and Nieminen R M 1983 *J. Phys. F: Met. Phys.* **13** 333
[8] Plazaola F, Seitsonen A P and Puska M J 1994 *J. Phys.: Condens. Matter* **6** 8890
[9] Abrahams S C, Jamieson P B and Bernstein J L 1967 *J. Chem. Phys.* **47** 4034
[10] Abrahams S C, Bernstein J L and Svenson C 1979 *J. Chem. Phys.* **37** 788
[11] Radaev S F and Simonov V I 1992 *Sov. Phys.–Crystallogr.* **37** 484
[12] Futro A T 1979 *J. Phys. Chem. Solids* **40** 201
[13] Aldrich R E, Hou S L and Harvill M L 1971 *J. Appl. Phys.* **42** 493
[14] Stepanov S I and Petrov M P *Photorefractive Materials and their Applications* ed P Günter and J P Huignard
       (Berlin: Springer) p 263
[15] Slodobnik A J and Sethares J C 1972 *J. Appl. Phys.* **43** 247
[16] Vehanen A, Hautojärvi P, Johansson J, Yli-Kauppila J and Moser P 1982 *Phys. Rev.* B **25** 762
[17] Grewal P K and Lea M J 1983 *J. Phys. C: Solid State Phys.* **16** 247
[18] Rehwald W, Frick K, Lang G K and Meier E 1976 *J. Appl. Phys.* **47** 1292