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PII: S0925-8388(13)01752-0

DOI: <http://dx.doi.org/10.1016/j.jallcom.2013.07.127>

Reference: JALCOM 29051

To appear in:

Received Date: 26 April 2013

Revised Date: 18 July 2013

Accepted Date: 19 July 2013



Please cite this article as: O. Shpotyuk, L. Calvez, E. Petracovschi, H. Klym, A. Ingram, P. Demchenko, Thermally-induced crystallization behaviour of 80GeSe₂-20Ga₂Se₃ glass as probed by combined X-ray diffraction and PAL spectroscopy, (2013), doi: <http://dx.doi.org/10.1016/j.jallcom.2013.07.127>

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Thermally-induced crystallization behaviour of 80GeSe₂-20Ga₂Se₃ glass as probed by combined X-ray diffraction and PAL spectroscopy

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Abstract

Crystallization behaviour of 80GeSe₂-20Ga₂Se₃ glass caused by thermal annealing at 380°C for 10, 25 and 50 h are studied using X-ray diffraction and positron annihilation lifetime spectroscopy. It is shown that the structural changes caused by crystallization can be adequately described by positron trapping modes determined within two-state model. The observed changes in defect-related component in the fit of experimental positron lifetime spectra for annealed glasses testifies in a favour of structural fragmentation of larger free volume entities into smaller ones with preceding nucleation in the initial stage of thermal annealing. Because of strong deviation in defect-free bulk positron lifetime from corresponding additive values proper to boundary constituents, the studied glasses cannot be considered as typical representatives of pseudo-binary cut-section.

Keywords: chalcogenide glass, crystallization, positron annihilation, trapping, annealing

1. Introduction

The current state-of-the-art of the modern photonics indicates on significant importance of glassy-like multifunctional media with improved exploitation properties. Main developments concerning preparation of such media are known to include different methods of their technological and post-technological structural modification using external acting factors, such as thermal annealing, high-energy irradiation, laser-beam treatment, etc. However, technical possibilities of these methods are significantly restricted by physical-chemical peculiarities of vitreous state with effects of natural physical ageing, functional non-reproducibility and thermodynamic instability in view of high affinity to spontaneous crystallization and chemical reactivity. That is why, at the present, materials scientists and device manufacturers are more dealing with traditional methods of chemical-compositional modification using doping possibilities with additional components introduced in a glass matrix to reach new properties. Thus, for example, the principal functionality of chalcogenide glasses (ChG) revealed in their remarkable IR transparency in a wide spectral region, including both commercially-important atmospheric telecommunication windows at 3-5 and 8-12 μm up to space telecommunication domain at 20-25 μm can be effectively combined with excellent transparency of halide compounds in a visible range by developing mixed chalcogenide-halogenide (chalcohalide) glassy-like alloys and ceramics such as GeSe₂-Ga₂Se₃-MX (M – alkali, X – halide) [1].

The optimized inner-pore structure of base $\text{GeSe}_2\text{-Ga}_2\text{Se}_3$ ChG is a determinant factor of their final glassy-like state connected with a possibility to accommodate alien atoms and some atomic groups. By adding halide additives, these ChG can easily formed chalcogenide glass-ceramics transparent in IR region up to 16 μm owing to over- T_g isothermal annealing in, as it was well demonstrated by Zhang et al. [2]. The similar functionality is proper also to other ChG systems like Ge-Sb-Se , Ge-As-Se , Ge-In-Se [3,4]. To ensure optimal exploitation properties in such mixed alloys, their “pure” atomic sub-system should be effectively interbalanced with atomic-deficit (void-type) structure, caused by absence of atoms in some network sites.

The nearest atomic arrangement in a glass can be adequately studied with numerous experimental measuring techniques (like vibration and Raman scattering spectroscopy, XRD, SEM, XPS, NMR, etc.) [5,6]. However, the row of probes available to study atomic-deficient distribution is rather limited, especially at sub-nanometer scale. One of the best (if not unique) techniques capable to probe such finest free volumes is the positron annihilation lifetime (PAL) spectroscopy, the method grounded on physical phenomena of positron-electron interaction in a matter [7-15]. It is frequently used to identify spatial heterogeneities in crystals (dislocations, vacancies, vacancy-like clusters and agglomerates, etc.) [7-9], free volume evolution in organic polymers (size and number of open-volume holes, inner pores) [10,11], light metallic alloys (cracks, bubbles, etc.) [13,14], zeolites [7-9], gels [14], but less commonly for network glasses. The reason is that normally in glassy materials like ChG we do not observe bounded positron-electron state known as positronium Ps (at least in a considerable amount), which typically needs to quantify free-volume entities [7-9]. Under such conditions, a strict analysis is possible only in terms of average positron lifetime τ_{av} , defined as a measured mass centre of one- or two-component fitted PAL spectrum [15]. The most effective positron traps in ChG were identified as sub-nanometer voids based on bond-free solid angles (free of charge spaces and their agglomerations appeared because of strong directionality in covalent bonding) having an effective negative charge excess near chalcogen atoms within heteropolar covalent chemical bonds [16]. If ChG composition do not change significantly (being within the same bond statistics), we still consider the evolution of average positron lifetime τ_{av} , caused by below- T_g structural relaxation as a direct signature of trends in a total molar volume [15]. In this case, an exact quantitative analysis of free-volume structural entities demands an appropriate trapping model to decompose unambiguously the measured PAL spectra into individual components and associate them with physically real positron trapping channels [7-9,15].

In the present paper, we imply, for the first time, the PAL method to reveal changes in free-volume structure of $80\text{GeSe}_2\text{-}20\text{Ga}_2\text{Se}_3$ ChG subjected to thermally-activated crystallization (ceramization) owing to above- T_g annealing.

2. Experimental

ChG of $80\text{GeSe}_2\text{-}20\text{Ga}_2\text{Se}_3$ composition were prepared from melting mixture of highly pure raw materials (Ge, Ga, and Se: 99.999%) in sealed silica ampoule kept under 10^{-6} Pa vacuum [1,17]. The ampoule of 9 mm inner diameter was placed in a rocking furnace. The raw materials were heated from 20 to 850 $^{\circ}\text{C}$ using 2 $^{\circ}\text{C}/\text{min}$ heating rate and maintained at this temperature for 12 h at least. Then, the silica tube was quenched in water at room temperature, annealed 30 $^{\circ}\text{C}$ below the glass transition temperature ($T_g=370$ $^{\circ}\text{C}$) for 3 h to minimize inner strains, and finally slowly cooled down to room temperature. Glass rods were cut into slices of 1 mm thickness and polished for further optical measurements [1].

The crystallization of the $80\text{GeSe}_2\text{-}20\text{Ga}_2\text{Se}_3$ was performed with a single step of heat treatment at T_g+10 $^{\circ}\text{C}$. This temperature has been chosen as an optimal temperature of ceramization as it permits to control the generation by simultaneous nucleation and growth of nanoparticles within the glassy matrix according to the heat treatment time. Thus, glass samples were placed in a ventilated furnace where the accuracy of temperature is ± 2 $^{\circ}\text{C}$ for various time varying from 10 to 50 hours.

XRD measurements with $\text{CuK}_{\alpha 1}$ radiation were performed to determine crystalline phases in the studied samples. Solid-rock plates of powdered $80\text{GeSe}_2\text{-}20\text{Ga}_2\text{Se}_3$ ChG deposited on amorphous substrate were prepared to arrange experiments in optimal transmittance geometry. The measured X-ray beam intensities and reflection angles 2θ were obtained using automatic STOE STADI P diffractometer (“STOE & Cie GmbH, Germany) with a linear position-precision detector.

Experimental linear absorption coefficients were determined as logarithmic ratio of primary beam intensities after passing through background and studied samples. All measurements were conducted in 2θ -step regime, the profiles of peaks being refined using WinPLOTR software [18].

The PAL spectra were recorded with conventional fast-fast coincidence system (ORTEC) of 230 ps resolution (full width at half maximum FWHM of a single Gaussian, determined by ^{60}Co isotope measuring) at the temperature $T = 22\text{ }^{\circ}\text{C}$ and relative humidity $RH = 35\%$, provided by special climatic installation. Contribution intensity of source is 18 %. Two identical ChG samples were used to build a character sandwich arrangement needed for PAL measurements. Isotope ^{22}Na of slow activity ($\sim 50\text{ kBq}$) sandwiched between two identical tested samples was used as a source of positrons.

A series of a few independent experiments were assembled with samples of the same thermal prehistory to exclude data scatter because of differences between actual status of samples and uncontrolled instabilities in the experimental setting of PAL spectrometer. The obtained results agreed well with each other within experimental uncertainties, being no more than $\pm 0.005\text{ ns}$ in lifetimes and ± 0.01 in component intensities. Each spectrum was measured with a channel width of 6.15 ps (the total number of channels was 8000) and contained at least $\sim 10^6$ coincidences in a total, which can be considered as conditions of normal PAL measurement statistics.

The measured PAL spectra of ChG were processed with standard LT 9.0 computer program [19], the obtained curve being fitted by two components with τ_1 , τ_2 lifetimes and I_1 , I_2 intensities ($I_1 + I_2 = 1$). Introducing a third component into the envelope of the fitting curves did not improve decomposition goodness significantly. So the Ps formation is not proper to any of the studied ChG in full agreement with previous data [20,21]. Therefore, the positron trapping modes in the studied ChG, e.g. average positron lifetimes τ_{av} , positron lifetime in defect-free bulk τ_b , positron trapping rate in defects κ_d and fraction of trapped positrons η were calculated using a formalism of two-states trapping model [7,15].

A strict analysis of positron annihilation inputs, however, strongly depends on the correct understanding of τ_b nature, especially in case of complicated compositional tendencies associated with significant changes in the type of glass-forming structural units [15]. Since a general procedure of PAL spectra deconvolution includes some uncertainties [22], the proper data processing algorithms should be developed to unambiguously compare physically-real annihilation channels and mathematically-fitted components. For present analysis, we have developed special algorithm based on appropriate error analysis of PAL measurements geometry and background removal. In addition, the $(\tau_2 - \tau_b)$ difference was accepted as a size measure for extended free-volume defects where positrons are trapped (in terms of equivalent number of monovacancies), as well as the τ_2/τ_b ratio was taken in a direct correlation to the nature of these defects [22,23].

3. Results and discussion

Results of XRD measurements for $80\text{GeSe}_2\text{-}20\text{Ga}_2\text{Se}_3$ glasses before and after thermal annealing at $380\text{ }^{\circ}\text{C}$ during different time periods are shown in Fig. 1.

Polythermal and isothermal cut-sections of crystalline phases possible in Ge-Ga-Se system were studied [24-27]. In part, the ternary GeGa_4Se_8 phase ($\text{Ga}_{0.5}\text{Ge}_{0.13}\text{Se}$) having polymorph transformation near $\sim 898\text{ K}$ ($625\text{ }^{\circ}\text{C}$) was identified, the high temperature modification being crystallised in ZnS structural type (cubic syngony, $F\text{-}43m$ space group, lattice parameter $a \sim 5.45\text{ \AA}$, most essential XRD reflexes of $\text{CuK}_{\alpha 1}$ radiation being grouped near $2\theta = 28^{\circ}, 47^{\circ}, 56^{\circ}, 68.5^{\circ}, 76^{\circ}, 87.5^{\circ}$), while low-temperature one being of unknown structure but of close subcell parameter $a \sim 5.461\text{ \AA}$ type (main XRD reflexes of $\text{CuK}_{\alpha 1}$ radiation are observed near $2\theta = 28^{\circ}, 47^{\circ}, 56^{\circ}$) [24]. Two other ternary phases GeGa_2Se_3 [26] and GeGaSe_3 [27] were also detected after 25 or 50 hours of annealing. General structural similarity between these phases, as well as binary Ga_2Se_3 (main XRD reflexes of $\text{CuK}_{\alpha 1}$ radiation are observed near $2\theta = 28^{\circ}, 47^{\circ}, 55.5^{\circ}$) and GeSe_2 phases (main XRD reflexes of $\text{CuK}_{\alpha 1}$ radiation are observed near $2\theta = 15^{\circ}, 25^{\circ}, 29^{\circ}$) of different modifications is their tetrahedral arrangement based on $(\text{Ge,Ga})[\text{Se}_4]$ tetrahedra.

It was established previously [28] that reproducible glass-ceramics based on $80\text{GeSe}_2\text{-}20\text{Ga}_2\text{Se}_3$ alloy can be obtained using appropriate heat-treatment at the temperature of $380\text{ }^{\circ}\text{C}$. At short heating durations up to 25-50 h, the small nanosized particles of GeGa_4Se_8 of about 10 nm appear.

These crystallized inclusions aggregates in larger ones of about 100 nm in size uniformly distributed within the glass structure, the nanocrystallites of GeSe₂ phase being detected in addition to growing content of GeGa₄Se₈ ones [28,29]. Our XRD results confirm, in principal features, these conclusions.

In respect to our results, the extended gallous in XRD patterns of non-annealed 80GeSe₂-20Ga₂Se₃ glasses near $2\theta = 12^\circ$, 30° and 50° (Fig. 1) can be ascribed to typical signatures of amorphous structure. Obviously, these peaks are predetermined by cumulative inputs of some precursors caused by different phases possible in this cut-section.

Annealing at 380 °C for 10 h does not change significantly the structure of ChG, since no sharp crystalline patters appear in their XRD patterns apart from noticeable decrease in gallous. Therefore, we can assume that even under this short-time heat treatment there are some transformations in the intrinsic structure of ChG, which do not contribute essentially to crystallization ordering. Nevertheless, slight decrease in the gallous intensities indicates that some changes are still occurred in these ChG. We can speculate that underlying transformations can be probably associated with inner phase separation in 80GeSe₂-20Ga₂Se₃ cut-section on individual boundary components (stoichiometric binary GeSe₂ and Ga₂Se₃), which serve as prerequisites for further disproportionality reaction to form ternary GeGa₄Se₈ phase:



It means that stoichiometry of base 80GeSe₂-20Ga₂Se₃ cut-section provides an excellent condition for crystallization of GeGa₄Se₈ phase through segregation of previously extracted GeSe₂ and Ga₂Se₃ phases accompanied by formation of GeSe₂-rich remainder. Since stoichiometric germanium selenide GeSe₂ is out of glass-forming region [30], under quite large amount of latter it will be extracted in a separate crystallized phase.

With increasing annealing time from 10 h to 25 h and further to 50 h, the well-pronounced crystalline peaks at $2\theta \sim 28^\circ$ are observed (see Fig. 1). The positions of this peak are in good agreement with GeGa₄Se₈ and Ga₂Se₃ phase indexation. Both phases have sharp reflexes near $2\theta \sim 28^\circ$, which cannot be well separated [25]. In fact, all principal XRD peaks of GeGa₄Se₈ and Ga₂Se₃ phases coincide [31], so we are consider them in crystallized 80GeSe₂-20Ga₂Se₃ glass as signatures of both these phases (Ga₂Se₃ and GeGa₄Se₈). The broadness of this peak ($2\theta \sim 28^\circ$) confirms presence of dispersed nanoparticles in a glassy matrix as nanocrystalline inclusions of near 9-10 nm in sizes (determined in respect to Debay-Scherrer equation [32,33]) which is in good agreement with previous results [28,34-36].

The maximums associated with GeSe₂ phase appear on the XRD patterns of thermally annealed 80GeSe₂-20Ga₂Se₃ glass too, but (in contrast to [28]) it cannot be well distinguished as separate crystalline peaks even for long annealing durations (50 h). It means that GeSe₂ crystals appear only in a small amount, probably as surface inclusions [28]. It can be imagined that GeSe₂ crystals grow among glass remainder after Ga₂Se₃ and GeGa₄Se₈ crystals extraction as a result of ceramization process governed by reaction (1).

The XRD peaks of ChG annealed during 25 and 50 h reveal quick enhancement at small scattering angles $2\theta < 1.5^\circ$, that can be probably attributed to some kinds of fractal structures [25].

Undoubtedly, these changes in the atomic structure of 80GeSe₂-20Ga₂Se₃ glasses can be somehow reflected in the corresponding changes of their free-volume structure. The results of PAL experiments obtained for the first time for these ChG confirm these assumptions. Best-fit positron trapping parameters along with error-bars of corresponding fitting procedure and trapping modes for PAL spectra of 80GeSe₂-20Ga₂Se₃ glasses are given in Tables 1 and 2, respectively.

Assuming two-state positron trapping model like as for typical ChG systems [7,15,22,37], two components in the fit of experimental PAL spectra can be provided with reduced bulk positron lifetime τ_l which itself has no physical meaning, positron lifetime in free-volume entities (positron traps) τ_2 and corresponding intensities I_1 and I_2 . Within formalism of this model [7,15], the open volume holes free of electron density are treated as specific positron trapping “defects”, while structural domains without them is related to intrinsic “defect-free” bulk (represented by τ_b value).

In case of phase separated and pseudo-binary solid state systems, the τ_b value reveals additional behaviour in respect to boundary ingredients [7,15]. By assuming at the basis of experimental PAL data ($\tau_l = 0.31$ ns, $\tau_2 = 0.45$ ns, $I_2 = 0.60$) [38] that bulk positron lifetime τ_b for crystalline Ga₂Se₃ is

near 0.38 ns, and accepting $\tau_b = 0.28$ ns proper for glassy GeSe₄ ($\tau_1 = 0.24$ ns, $\tau_2 = 0.42$ ns, $I_2 = 0.32$) [39] or Ge₃₀Se₇₀ ($\tau_1 = 0.20$ ns, $\tau_2 = 0.35$ ns, $I_2 = 0.65$) [40] as quite close to bulk positron lifetime of GeSe₂ component, we should expect $\tau_b \approx 0.30$ ns as quite responsible value for pseudo-binary 80GeSe₂-20Ga₂Se₃ solution. But this value is obviously greater than experimentally measured $\tau_b = 0.25$ -0.26 ns for base 80GeSe₂-20Ga₂Se₃ glasses (see Table 2). It means that these glasses cannot be considered as belonging to typical pseudo-binary systems with structurally independent boundary component (GeSe₂ and Ga₂Se₃). Such complicated behavior is supposed to be associated with dual nature of Ga atoms incorporated in a glassy backbone in different atomic coordination [41,42].

Since (τ_1 , I_1) component has no strong physical meaning within accepted two-state positron trapping model, we will focus our further analysis on second (τ_2 , I_2) component [7,15,37].

With increase of annealing duration from 80GeSe₂-20Ga₂Se₃ glass to samples annealed for 10 h, the lifetimes τ_2 increases and I_2 intensities decreases to 0.29 because of void expansion. This trend correspondingly reduces the positron trapping rate in defect κ_d without significant changes in τ_{av} and τ_b lifetimes. With further annealing duration proceeding to 25 and 50 h, the I_2 intensity ceases to increase, while lifetime τ_2 appreciably decreases to 0.426 and 0.416 ns, respectively. These changes result in increase of positron trapping rate in defect κ_d . Other positron trapping parameters (τ_2/τ_b , η) behave at the annealing in a harmony with these (Table 2), but ($\tau_2 - \tau_b$) difference, accepted as a size measure for extended free-volume defects where positrons are trapped, naturally decreases with annealing duration.

It was shown [16] that coupling of open volumes created by bond free solid angles, belonging to different chalcogen chains or coordination polyhedrons, can be effective positron traps in ChG. During crystallization, the glass structure relaxes towards more thermodynamically favourable state (crystallization shrinkage or densification), eliminating the excess of free volume of neighbouring voids. It means that existing free volume voids either disappear or convert into a greater number of smaller ones. We can argue that crystallization in 80GeSe₂-20Ga₂Se₃ glass induced by long-term annealing (25-50 h) is accompanied by void growth because their expansion and appearance of new tiny voids due to mismatch between glassy and crystalline regions. So the fragmentation of larger free-volume entities into smaller ones occurs like as during natural physical ageing [43]. Such process is accompanied by essential decrease in τ_2 lifetime and corresponding increase in I_2 intensity in full agreement with above scenario. The described crystallization precedes opposite changes caused by nucleation in 80GeSe₂-20Ga₂Se₃ glasses at lower annealing times (10 h) like as it occurs in [44].

In contrast to above fitting PAL parameters (τ_2, I_1, τ_2, I_2), the changes in the positron trapping rate of free-volume defects κ_d are more pronounced, especially at long annealing durations, when a specific fragmentation behaviour revealed a decrease in dimensions of free-volume entities accompanied by simultaneous increase in their amount (see Table 2). In principle, these changes in κ_d can be caused by charge state of trapping centres too [6,15]. However, the constant τ_2/τ_b ratio close to 1.7 for all ChG samples despite their treatment duration, testified that corresponding positron-trapping centres are rather of the same type, being most probably as large as di- or tri-atomic vacancies [16].

4. Conclusions

Crystallization behavior of 80GeSe₂-20Ga₂Se₃ glasses during annealing at 380°C for 10, 25 and 50 h indicates on the possibility of formation of GeGa₄Se₈ and Ga₂Se₃ crystals. These crystallites modify free-volume structure of ChG leading to specific fragmentation of larger free-volume entities (positron trapping voids) into greater number of smaller ones with nucleation in the initial stage of annealing. Such effect reveals an increase of the second lifetime component τ_2 and simultaneous I_2 decrease in the initial stage of annealing (10 h) because of preliminary void expansion and further decrease of τ_2 lifetimes with simultaneous I_2 increase during more prolonged annealing (25 and 50 h) testifying in a favour of increased number of smaller free volumes. In respect to PAL spectroscopy, these ChG cannot be attributed to typical pseudo-binary system

because of non-additivity of defect-free bulk lifetimes τ_b of its constituting components (GeSe₂ and Ga₂Se₃).

Acknowledgment

The authors acknowledge support from State Agency on Science, Innovation and Informatization of Ukraine and French EGIDE within common bilateral Program on scientific-technological cooperation “Dnipro” for years 2011-2012. The assistance from Science and Technology Centre in Ukraine under regular project # 5721 is also acknowledged.

References

1. Calvez L., Lucas P., Roze M., Ma H.L., Lucas J., Zhang X.H. Appl. Phys. A89 (2007) 183.
2. Zhang X.H., Calvez L., Seznec V., et al. J. Non-Cryst. Solids. 352 (2006) 2411.
3. Mahadevan, Sudha, A. Giridhar, J. Mater. Sci. 29(14) (1994) 3837.
4. Giridhar, S. Mahadevan, J. Non-Cryst. Solids. 126(1-2) (1990) 161.
5. G.N. Greaves, S. Sen, Adv. in Physics 56 (2007) 1.
6. Feltz, Amorphous inorganic materials and glasses, New York, VCH Publishers, 1993.
7. R. Krause-Rehberg, H. Leipner, Positron annihilation in semiconductors: defect studies, Springer, Heidelberg, 1999.
8. Y.C. Jean, P.E. Mallon and D.M. Schrader, Principles and application of positron and positronium chemistry, World Scientific, Singapore, 2003.
9. Mogenssen, Positron annihilation in chemistry, Springer, Berlin, Heidelberg, 1995.
10. G. Dlubek, A. Sen Gupta, J. Pionteck, R. Krause-Rehberg, H. Kaspar, K. H. Lochhaas, Macromolecules. 37 (2004) 6606.
11. G. Dlubek, A. Sen Gupta, J. Pionteck, R. Hassler, R. Krause-Rehberg, H. Kaspar, K. H. Lochhaas, Polymer. 46 (2005) 6075.
12. J. Banhart, M. D. H. Lay, C. S. T. Chang, A. J. Hill, Phys. Rev. B. 83 (2011) 014101.
13. Somoza, A. Dupasquier, R. Ferragut, Phys. Status Solidi C. 6 (11) (2009) 2295.
14. T. Goworek, K. Ciesielski, B. Jasinska, J. Wawryszczuk, Chem. Physics. 230 (1998) 305.
15. O. Shpotyuk, J. Filipceki, Free volume in vitreous chalcogenide semiconductors: possibilities of positron annihilation lifetime study, Wyd-wo WSP w Czestochowie, Czestochowa, 2003.
16. A. Ingram, R. Golovchak, M. Kostrzewa, S. Wacke, M. Shpotyuk, O. Shpotyuk, Physica B. 407 (2012) 652.
17. L. Calvez, C. Lin, M. Rozé, Ya. Ledemi, E. Guillevic, B. Bureau, M. Allix, X. Zhang, Proc. of SPIE. 7598 (2010) 759802-1.
18. T. Roisnel and J. Rodriguez-Carvajal, Mater. Sci. Forum, 378 – 381 (2001) 118.
19. J. Kansy, Nucl. Instr. Methods in Phys. Res. A 374 (1996) 235.
20. K.O. Jensen, Ph.S. Salmon, I.T. Penfold, P.G. Coleman, J. Non-Cryst. Solids. 170 (1994) 57.
21. O.K. Alekseeva, V.I. Mihailov, V.P. Shantarovich, Phys. Stat. Sol. A48 (1978) K169.
22. P.M.G. Nambissan, C. Upadhyay, H.C. Verma, J. Appl. Phys. 93 (2003), 6320.
23. M. Bigg, Engineering and Science. 36(6) (1996), 737.
24. A. Thiebault, L. Guen, R. Eholié, J. Flahaut, R. Ollitrault Fichet, Bull. Soc. Chim. Fr. (1975) 967.
25. A.M. Loireau Lozac'h, M. Guittard, Mater. Res. Bull. 12 (1977) 887.
26. I. Sidorov, R. Magunov, O. Zakolodyazhnaya, I. Kovalevskaya, Rus. J. Inorg. Chem. 22 (1977) 779.
27. R. Ollitrault-Fichet et al., Ann. Chim. (Paris), 2 (1977) 31.
28. M. Roze, L. Calvez, Ya. Ledemi, M. Allix, G. Matzen, X.-H. Zhang, J. Amer. Ceram. Soc. 91(11) (2008) 3566.
29. M. Hubert, G. Delaizir, J. Monnier, C. Godart, H. Ma, X. Zhang, L. Calvez, Optic Express 19(23) (2011) 23513.
30. A. Feltz, Amorphous and Vitreous Inorganic Solids, Mir, Moscow (1986) 556.
31. R. Ollitrault-Fichet et al., Ann. Chim. (Paris). 2 (1977) 31.
32. B.D. Cullity. Addison-Wesley (1978).
33. A.K. Keshari, A.C. Pandey, J. Nanoscience and Nanotechnology. 8 (2008) 1221.

34. A. Lin, L. Calvez, M. Rozé, H. Tao, X. Zhang and X. Zhao, Appl Phys A. 97 (2009) 713.
35. A. Lin, , L. Calvez, H. Tao, M. Allix, A. Moreac, X. Zhang and X. Zhao, J. Solid State Chem. 184 (2011) 584.
36. P. Mosselin, D. Le Coq, L. Calvez, E. Petracovschi, E. Lepine, E. Bychkov, X. Zhang, Appl. Phys. A. 106 (2012) 697.
37. H. Klym, A. Ingram, O. Shpotyuk, J. Filipecki, I. Hadzaman, J. Phys.: Conf. Ser. 289 (2011) 012010-1.
38. I.M. Askerov, S. Okuducu, J. Korean Phys. Soc. 42(6) (2003) 787.
39. B.V. Kobrin, V.P. Shandarovich, M.D. Mikhailov, E.Yu Turkina Phys. Scripta. 29 (1984) 276.
40. O. Shpotyuk, R. Golovchak, A. Ingram, V. Boyko, L. Shpotyuk, Phys. Stat. Sol. C10 (2013) 117.
41. R. Golovchak, L. Calvez, E. Petracovschi, B. Bureau, D. Savytskii, H. Jain, Mater. Chem. Phys. 138 (2013) 909.
42. K. Maeda, T. Sakai, K. Sakai, T. Ikari, M. Nunzar, D. Tonchev, S.O. Kasap, G. Lucovsky, J. Mater. Science: Mater. Electron 18 (2007) S367.
43. R. Golovchak, A. Kozdras, V. Balitska, O. Shpotyuk, J. Phys., Condens. Matter 24 (2012) 505106-1
44. J. Nie, F. Xia, R. Yu, B. Wang, Zh. Li , G. Chen, Measurement 44 (2011) 298.

Table 1.

Fitting parameters for PAL spectra of 80GeSe₂-20Ga₂Se₃ glasses

Sample, prehistory	Fitting parameters			
	τ_1	I_1	τ_2	I_2
	ns	a.u.	ns	a.u.
80GeSe ₂ -20Ga ₂ Se ₃ base glass	0.214±0.004	0.69±0.01	0.439±0.04	0.31±0.01
80GeSe ₂ -20Ga ₂ Se ₃ annealing for 10 h	0.218±0.004	0.71±0.01	0.453±0.004	0.29±0.01
80GeSe ₂ -20Ga ₂ Se ₃ annealing for 25 h	0.216±0.004	0.65±0.01	0.426±0.004	0.35±0.01
80GeSe ₂ -20Ga ₂ Se ₃ annealing for 50 h	0.209±0.004	0.65±0.01	0.416±0.004	0.35±0.01

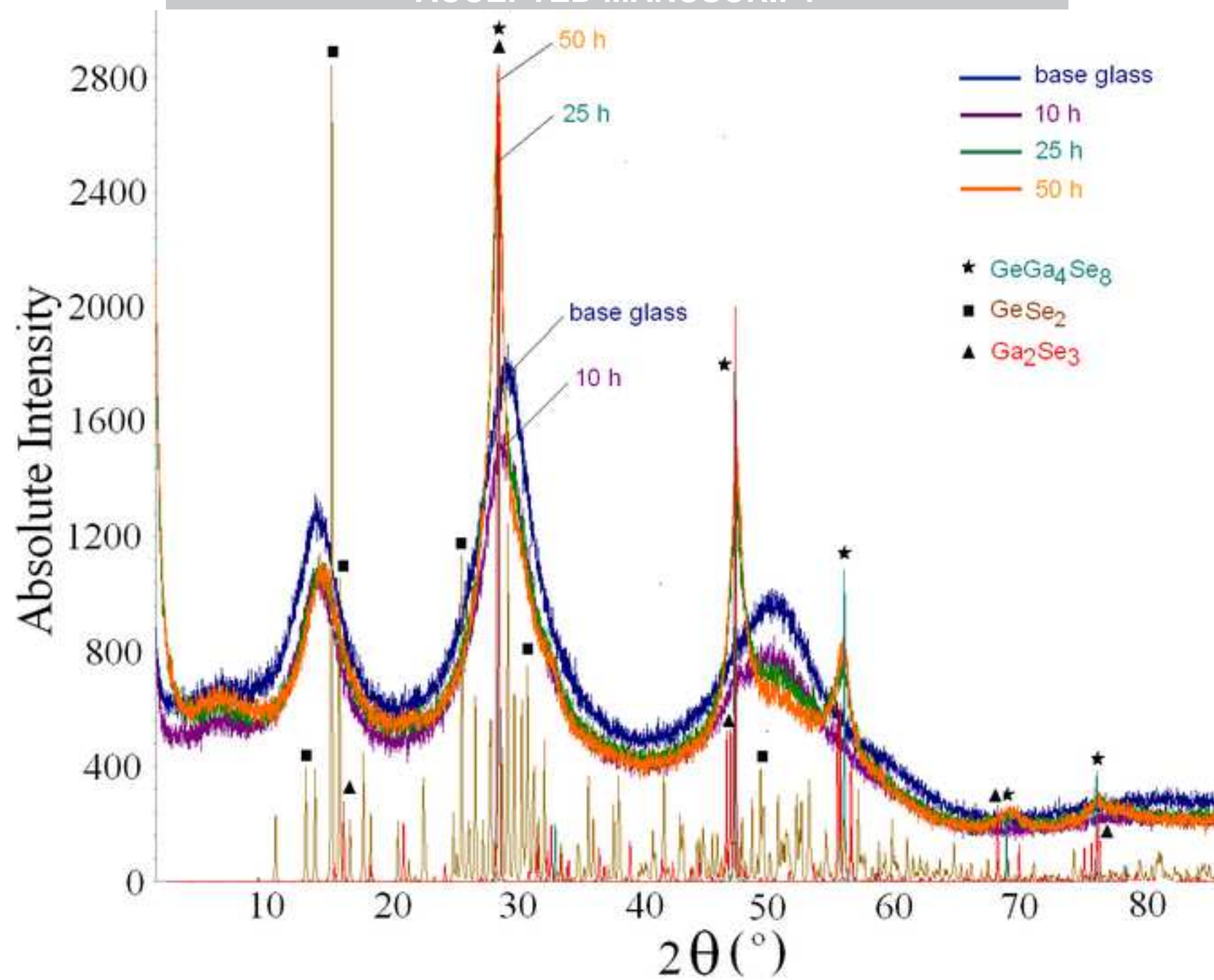
Table 2.

Positron trapping modes for PAL spectra of 80GeSe₂-20Ga₂Se₃ glasses

Sample, prehistory	Positron trapping modes					
	$\tau_{av.}$	τ_b	K_d	$\tau_2 - \tau_b$	τ_2/τ_b	η
	ns	ns	ns ⁻¹	ns	-	-
80GeSe ₂ -20Ga ₂ Se ₃ base glass	0.283	0.253	0.74	0.19	1.73	0.16
80GeSe ₂ -20Ga ₂ Se ₃ annealing for 10 h	0.287	0.257	0.70	0.20	1.76	0.15
80GeSe ₂ -20Ga ₂ Se ₃ annealing for 25 h	0.288	0.260	0.79	0.17	1.64	0.17
80GeSe ₂ -20Ga ₂ Se ₃ annealing for 50 h	0.281	0.252	0.83	0.16	1.65	0.17

Fig. 1. Comparison of XRD patterns of 80GeSe₂-20Ga₂Se₃ glass before annealing (base glass) and annealed at 380 °C for 10, 25 and 50 h with theoretical patterns of crystallized GeGa₄Se₈, GeSe₂ and Ga₂Se₃ phases

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Highlights

Chalcogenide Ge-Ga-Se glasses were annealed at 380°C for 10, 25 and 50 h.
Crystallization of glasses during annealing indicates formation of crystals.
Structural changes are described by two-state positron trapping model.
Modification leading to nucleation and fragmentation of free volume of glasses.
The Ge-Ga-Se systems cannot be classified as typical pseudo-binary system.