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Crystallization ability of $80GeSe_2$-$20Ga_2Se_3$ glasses caused by thermal treatment studied by XRD method

Halyna Klym
Specialized Computer System Dpt.,
Lviv Polytechnic National University,
Lviv, Ukraine
e-mails: klymha@yahoo.com

Oleh Shpotyuk
Vlokh Institute of Physical Optics,
Lviv, Ukraine
e-mail: shpotyuk@novas.lviv.ua

Laurent Calvez
Equipe Verres et et Céramiques, UMR-CNRS 6226,
Institute des Sciences chimiques de Rennes,
Université de Rennes,
Rennes, France
e-mail: laurent.calvez@univ-rennes1.fr

Andriy Ivanusa
Lviv State University of Life Safety,
Lviv, Ukraine
e-mail: ivaaanusa@gmail.com

***Abstract*—Crystallization ability of the $80GeSe_2$-$20Ga_2Se_3$ chalcogenide glasses caused by annealing at 380 °C during different duration are studied using X-ray diffraction method. It is established that $GeGa_4Se$ phase of low- and high-temperature modification, Ga_2Se_3 phase (α- and γ-modification) and $GeSe_2$ phases are crystallized during this process. It is shownnoen that annealing duration over 50 h does not lead to further internal structural crystallization.**

Keywords— chalcogenide glass; crystallization; annealing; phase composition; modification

I. Introduction

Modern development of IR photonics and sensor electronics put forward an actual task to search new functional media for effective transfer of wide-spectra electro-magnetic radiation and to develop novel miniaturization technologies of passive and active photonic elements (optical waveguides, resonators, splitters, multiplexers, detectors, signal amplifiers and converters, comparators, etc). One of the most perspective media for such applications are special chalcogenide glasses (ChG) – non-oxide glassy-like materials with high content of chalcogens (S, Se, Te) [1,2]. To a great extent, the further success in this field relies on chemical-technological resolutions in development of ChG-based media with unique properties. Thus, principal functionality of ChG revealed in their excellent IR transparency (including both commercially-important atmospheric telecommunication windows at 3-5 and 8-12 μm up to space telecommunication domain at 15-25 μm) can be effectively combined with transparency of halide compounds in a visible range by developing mixed chalcogenide-halogenide glasses and glass-ceramics [3-7].

Basic conceptions receipt of such media based on the varied methods technological and post-technological structural modification using external factors such as thermal annealing, high-energy radiation treatment laser beams. It is known that in the nearest atomic environment glass matrix can adequately studied using numerous experimental methods like vibration and Raman scattering spectroscopy, X-ray diffraction (XRD) scanning electron microscopy, etc. [4,9].

The aim of this work is investigation of crystallization processes and features formation of crystalline phases in $80GeSe_2$-$20Ga_2Se_3$ chalcogenide glasses under different durations of thermal annealing above the glass transition temperature using XRD method.

II. Experimantal

The $80GeSe_2$-$20Ga_2Se_3$ samples were prepared from high pure Ge, Ga and Se (99.999%) components in silica ampoule kept under 10^{-6} vacuum. Raw materials were heated from 20 to 850 °C at 2 °C/min and maintained at temperature for 12 h. Then silica tube was cooled in water at room temperature and annealed at 30 ° C below the glass transition temperature (370 °C) for 3 h and slowly cooled at room temperature. Samples with thickness of 1 mm were polished for further investigations [4,10-18].

The crystallization of the $80GeSe_2$-$20Ga_2Se_3$ ChG was performed with a single step of heat treatment at T_g+10 °C [8,9,12,14]. 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 °C for various time varying from 10 to 100 h [9].

The XRD measurements ($CuK_{\alpha 1}$ radiation) were carried out to determine crystalline phases in the studied glasses. Powdered $80GeSe_2$-$20Ga_2Se_3$ glasses were deposited on amorphous substrate and prepared to arrange experiments in optimal geometry. The automatic STOE STADI P diffractometer ("STOE & Cie GmbH, Germany) with a linear position-precision detector were used for XRD measurements. 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 [8].

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III. Results and Discussion

Combined results obtained by XRD method for $80GeSe_2$-$20Ga_2Se_3$ chalcogenide glasses before and after thermal annealing at 380 °C for 10, 25 and 50 h compared with the theoretical reflexes of the known $GeGa_4Se_8$, $GeSe_2$ phases are represented in Fig. 1 and Fig. 2.

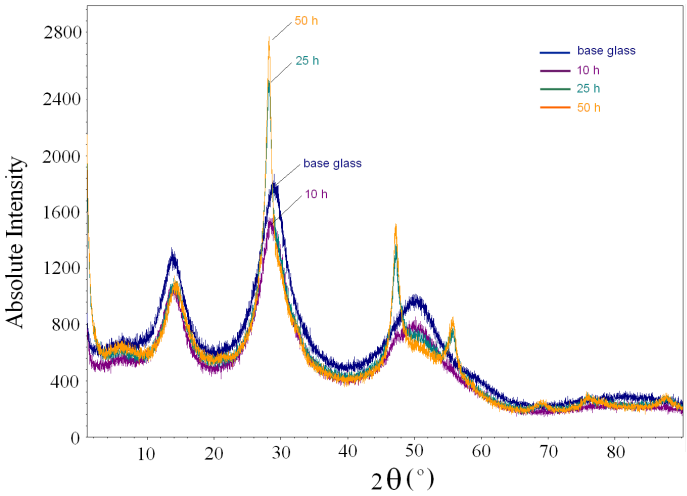

Fig. 1. Experimental XRD patterns for $80GeSe_2$-$20Ga_2Se_3$ glasses before (base glass) and after annealing for 10, 25 and 50 h

It is shown that annealing at 380 °C for 10 h almost does not change the structure of glasses. However, in the diffraction angles of $2\theta < 1{,}5°$ there is the increase of intensity that testifies to formation of fractals aggregates and structures. It is possible to assume that basic transformations can be related to inwardly-phase stratification in the $80GeSe_2$-$20Ga_2Se_3$ cut-section on individual components (stoichiometric $GeSe_2$ and Ga_2Se_3) which set the stage for further reaction forming of $GeGa_4Se_8$ triple phase [8]. This indicates that the stoichiometric $80GeSe_2$-$20Ga_2Se_3$ cut-section creates terms for crystallization of $GeGa_4Se_8$ phase due to segregation of preliminary selected $GeSe_2$ and Ga_2Se_3 phases with additional formation of $GeSe_2$-enriched residues. Since the stoichiometric $GeSe_2$ phase is outside glass formation [8,9,14] then in future it will be formed in a separate crystalline phase.

The Ge-Ga-Se system (polythermal and isothermal cut-sections, crystal structure of intermediate phase) was studied in [19,20]. The existence of $GeGa_4Se_8$ ($Ga_{0.5}Ge_{0.13}Se$) phase is in two modifications with polymorphic transformation temperature of ~898 K (625 °C). High-temperature modification is crystallized in ZnS structural type (cubic crystal system, *F*-43*m* space group, *a* ~5,45 Å), whereas for low-temperature modification ($GeGa_2Se_5$) structure precision has not been established, however, parameter a is ~ 5,461 Å [19] indicating affinity in structures of these two modifications. It was also reported about existence of $GeGa_2Se_3$ but $GeGaSe_3$ phases [21]. Total structural relationship between these phases and binary Ga_2Se_3 $GeSe_2$ phases and various modifications are Ga [Se_4] and Ge [Se_4] tetrahedrons.

In non-annealed ChG and annealed for 10 h semi-amorphous halo testify dipped ordering of these tetrahedrons in the glass structure without clear their belonging to some of the mentioned phases. However, with increasing annealing time from 25 to 50 h the well-formed peaks of $GeGa_4Se_8$, Ga_2Se_3 and $GeSe_2$ phases appear. The maximal reflection corresponding to $GeSe_2$ phase is semi-amorphous halo while reflections from $GeGa_4Se_8$ and Ga_2Se_3 are relatively well formed, especially at maximum of $2\theta \sim 28.22°$ (Fig. 2).

It should be noted that semi-amorphous halo presented in diffraction pattern of non-annealed ChG and annealed for 10 h does not disappear. Overall, the picture is completely consistent with the results given in [5]. For samples annealed for 25 h and 50 h raising intensity at low diffraction angles of 2θ is shown suggesting that the fractal formation in the glass during annealing will not disappear, but become larger (Fig. 2).

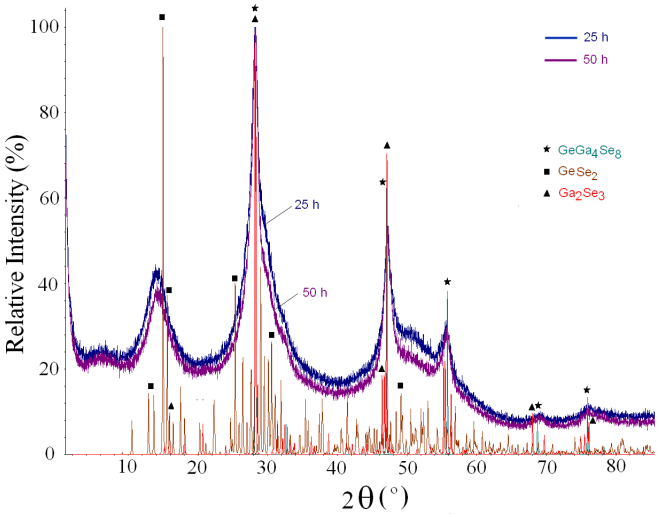

Fig. 2. Experimental and theoretical XRD patterns for $80GeSe_2$-$20Ga_2Se_3$ glasses after annealing for 25 and 50 h

However, at detailed analysis of maximum halo, it is possible to notice that even at insignificant time of heat treatment (10 h), the changes in glass structure are performed (Fig. 3).

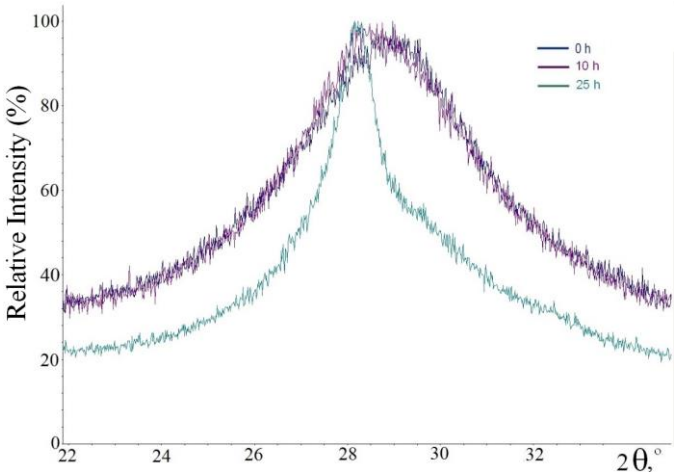

Fig. 3. Comparison of maximum of diffraction peaks for ChG before and after annealing for 10 and 50 h

This process is accompanied by crystallization of $GeGa_4Se_8$ phase (in the structure of glass from chaotic arrangement of Ga [Se_4] and Ge [Se_4] tetrahedrons characterized by only short-range order, the transition to the formation of long-range order characteristic of crystalline structure of $GeGa_4Se_8$ with ZnS structural type ZnS occurs).

Further increasing in annealing duration to 80 and 100 h does not affect on the diffraction peaks, reflecting mainly the formation of double and triple $GeGa_4Se_8$ and Ga_2Se_3 phases, just as for $80GeSe_2$-$20Ga_2Se_3$ glass, annealed for 50 h (Fig. 2 and Fig. 4). Thus, further crystallization process registered by XRD and formation of long-range order in times of such annealing does not occurs. First maximum of semi-amorphous halo at ~14.6 °2θ (Fig. 4) corresponds to the maximum intensity reflection (002) of $GeSe_2$ phase (monoclinic syngony, $P2_1/c$ space group).

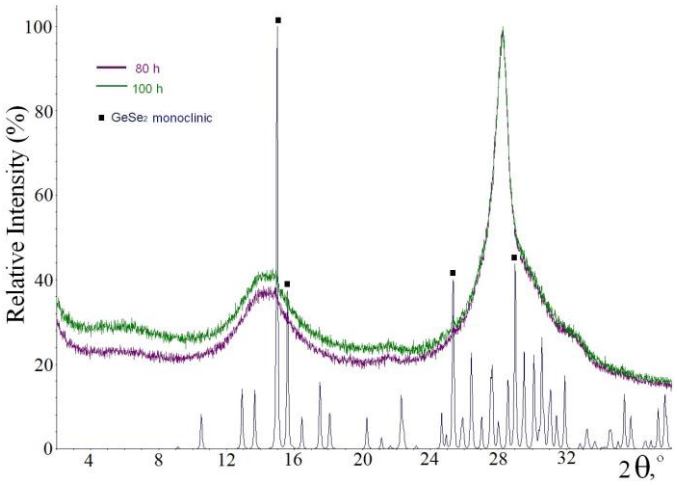

Fig. 4. Comparison of small-angle diffraction experimental plot for glasses annealed for 80 and 100 h with theoretical reflections of $GeSe_2$ phase

For ChG samples annealed at high duration of 80 and 100 h the additional analysis of Ga_4GeSe_8 and Ga_2Se_3 crystallization phase was performed. Taking into account the state diagram for the Ga-Se system, temperature of existence of cubic Ga_2Se_3 (high-temperature $Ga_{0.67}Se$) begins above T = 730 °C. Below this temperature is low-temperature monoclinic modification of Ga_2Se_3. Distinguish monoclinic and cubic modification of Ga_2Se_3 phases is possible only on samples with the high degree of crystalline.

Assuming that in studied samples pure high-temperature Ga_2Se_3 phase is crystallized, then most likely this is modification of α-Ga_2Se_3 (a ~ 5.44 Å).However, taking into account that the peaks are extended, along with α-modification γ-modification of Ga_2Se is possible (Fig. 5).

However, it should pay attention to raising of background on diffraction pattern (indicated by ellipses in Fig. 6).

These raising correspond to peaks from experimental diffraction pattern for high- and low- temperature modification of Ga_4GeSe_8 (Fig. 7).

Otherwise, we can assume that crystallized high-temperature α-Ga_2Se_3 phase (stabilization with minor Ge impurities lowers the temperature of its existence from 730 °C to 385 °C, which despondence for glass annealing) and amorphous phase of glass, which is responsible for halo circled ellipses, are present in ChG.

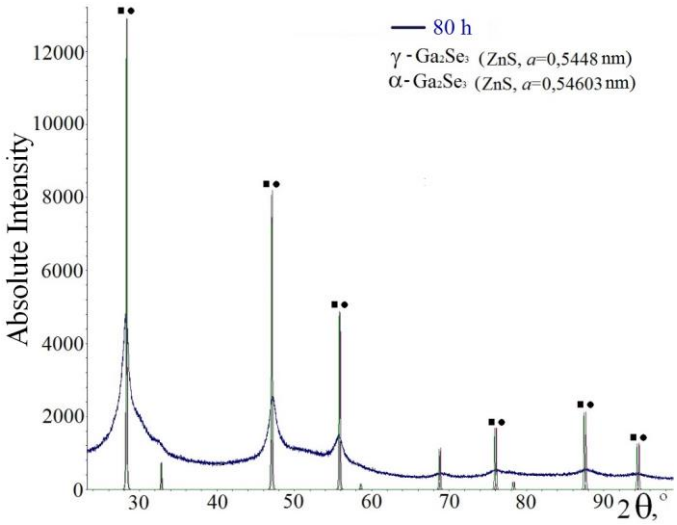

Fig. 5. Comparison of experimental XRD patterns for ChG annealed for 80 h with theoretical reflexes of α-Ga_2Se_3 and γ-Ga_2Se_3 phases

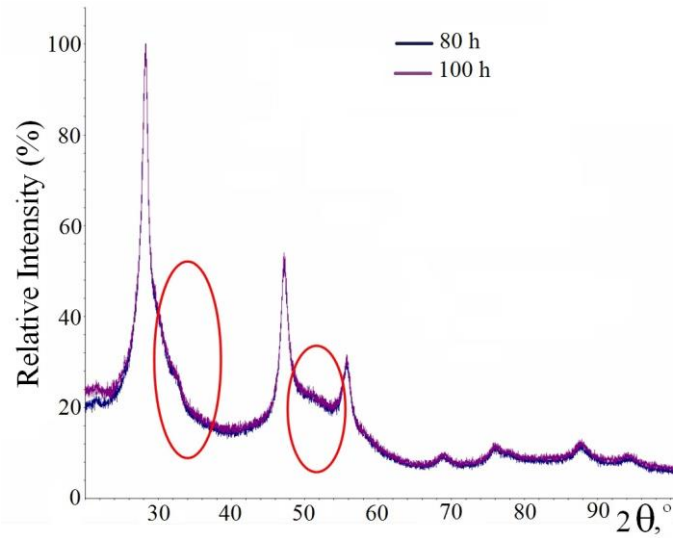

Fig. 6. Raising of background on experimental XRD patterns for samples annealed for 80 and 100 h

The width of the peak at 2θ ~ 28,22° indicates the presence in the crystal matrix of nanoparticles dispersed in the form of nanocrystalline including by a size of 9-10 nm (determined by the Debye-Scherrer equation [8,24]).

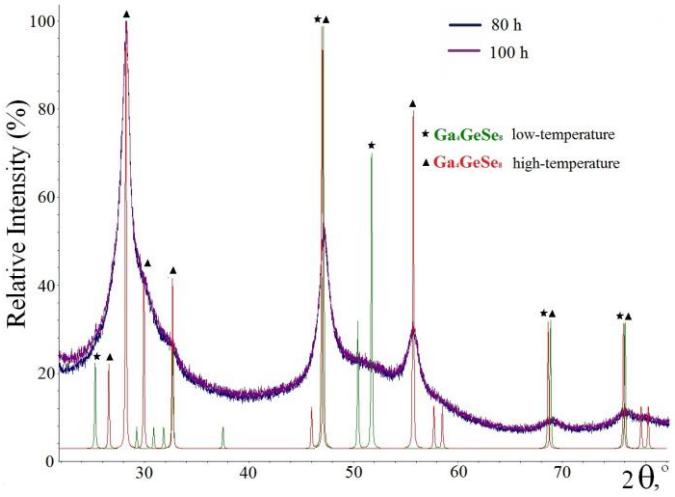

Fig. 7. Comparison of experimental XRD patterns for ChG annealed for 80 and 100 h with theoretical reflexes of Ga_4GeSe8 phase low- and high-temperature modifications

CONCLUSIONS

It is established that crystallization processes in the $80GeSe_2$-$20Ga_2Se_3$ ChG caused by annealing at 380 ° C for 10, 25, 50, 80 and 100 h indicating the formation of $GeGa_4Se$ (high- and low-temperature modification), Ga_2Se_3 (α- and γ-modification) and $GeSe_2$ crystals with size of 9-10 nm. Increasing duration of thermal treatment for $80GeSe_2$-$20Ga_2Se_3$ glasses leads to obtaining of thermal-stabile glasses and glass-ceramic media.

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REFERENCES

[1] M. Rozé, L. Calvez, M. Hubert, P. Toupin, B. Bureau, C. Boussard-Plédel, and X.H. Zhang, "Molded glass–ceramics for infrared applications", *International Journal of Applied Glass Science*, vol. 2, No 2, 2011, pp. 129-136.

[2] L. Calvez, H.L. Ma, J. Lucas, and X.H. Zhang, "Selenium-based glasses and glass ceramics transmitting light from the visible to the far-IR", *Advanced materials*, vol. 19, No 1, 2007, pp. 129-132.

[3] L. Calvez, P. Lucas, M. Rozé, H.L. Ma, J. Lucas, and X.H. Zhang, "Influence of gallium and alkali halide addition on the optical and thermo-mechanical properties of $GeSe_2$-Ga_2Se_3 glass", *Applied Physics A*, vol. 89(1), 2007, pp. 183-188.

[4] L. Calvez, C. Lin, M. Rozé, Y. Ledemi, E. Guillevic, B. Bureau, M. Allix, and X. Zhang, "Similar behaviors of sulfide and selenide-based chalcogenide glasses to form glass-ceramics", *Proc. of SPIE*, vol. 7598, 2010, pp. 759802-1-16.

[5] M. Rozé, L. Calvez, Y. Ledemi, M. Allix, G. Matzen, and X.H. Zhang "Optical and mechanical properties of glasses and glass–ceramics based on the Ge–Ga–Se system", *Journal of the American Ceramic Society*, vol. 91, No 11, 2008, pp. 3566-3570.

[6] J. Ren, T. Wagner, M. Bartos, M. Frumar, J. Oswald, M. Kincl, B. Frumarova, and G. Chen, "Intense near-infrared and midinfrared luminescence from the Dy^{3+}-doped $GeSe_2$–Ga_2Se_3–MI (M= K, Cs, Ag) chalcohalide glasses at 1.32, 1.73, and 2.67 μm", *Journal of Applied Physics*, vol. 109(3), 2011, pp. 033105.

[7] L. Calvez, M. Roze, Y. Ledemi, H.L. Ma, J. Lucas, M. Allix, and X.H. Zhang, "Controlled crystallization in Ge-(Sb/Ga)-(S/Se)-MX glasses for infrared applications", *Journal of the Ceramic Society of Japan*, vol. 116, No 1358, 2008, pp. 1079-1082.

[8] O. Shpotyuk, L. Calvez, E. Petracovschi, H. Klym, A. Ingram, and P. Demchenko, "Thermally-induced crystallization behaviour of $80GeSe_2$-$20Ga_2Se_3$ glass as probed by combined X-ray diffraction and PAL spectroscopy", *Journal of Alloys and Compounds*, vol. 582, 2014, pp. 323-327.

[9] H. Klym, A. Ingram, O. Shpotyuk, L. Calvez, E. Petracovschi, B. Kulyk, R. Serkiz, and R. Szatanik, "'Cold' crystallization in nanostructurized $80GeSe_2$-$20Ga_2Se_3$ glass", *Nanoscale research letters*, vol. 10(1), 2015 pp. 1-8. doi:10.1186/s11671-015-0775-9

[10] A. Ingram, H.I. Klym, and O.I. Shpotyuk, "Ge-Ga-S/Se glasses studied with PALS technique in application to chalcogenide photonics", *Proc.* IEEE *International Conference on Advanced Optoelectronics and Lasers (CAOL)*, 2013, pp. 386-387.

[11] H. Klym, A. Ingram, O. Shpotyuk, R. Szatanik, E. Petracovschi, L. Calvez, and C. Lin, "Positron annihilation in IR transmitting GeS_2-Ga_2S_3 glasses", *Solid State Phenomena*, vol. 230, 2015, pp. 221.

[12] H. Klym, A. Ingram, and O. Shpotyuk, "Free-volume nanostructural transformation in crystallized GeS_2–Ga_2S_3–CsCl glasses, *Materialwissenschaft und Werkstofftechnik*, vol. 47(2-3), 2016, pp. 198-202.

[13] H. Klym, A. Ingram, O. Shpotyuk, and R. Szatanik, „Free-volume study in GeS_2-Ga_2S_3-CsCl chalcohalide glasses using positron annihilation technique", *Physics Procedia*, vol. 76, 2015, pp. 145-148.

[14] H. Klym, A. Ingram, and O. Shpotyuk, "Crystallization processes in Ge-Ga-Se glasses studied with positron annihilation technique", IEEE *29th International Conference on Microelectronics Proceedings (MIEL)*, 2014, pp. 277-278.

[15] H. Klym, A. Ingram, O. Shpotyuk, E. Petracovschi, and L. Calvez, "Positronics of IR transmitting chalcohalide glass-ceramics", *IEEE International Conference on Oxide Materials for Electronic Engineering (OMEE)*, 2014, pp. 176-177.

[16] H. Klym, I. Karbovnyk, M.C. Guidi, O. Hotra, and A.I. Popov, "Optical and vibrational spectra of CsCl-enriched GeS_2-Ga_2S_3 glasses", *Nanoscale research letters*, vol. 11(1), 2016, pp. 1-6.

[17] H. Klym, A. Ingram, O. Shpotyuk, and I. Karbovnyk, "Influence of CsCl addition on the nanostructured voids and optical properties of $80GeS_2$-$20Ga_2S_3$ glasses, *Optical Materials*, vol. 59, 2016, pp. 39-42.

[18] H. Klym, A. Ingram, O. Shpotyuk, O. Hotra, and A.I. Popov, "Positron trapping defects in free-volume investigation of Ge-Ga-S-CsCl glasses", *Radiation Measurements*, vol. 90, 2016, pp. 117-121.

[19] C. Thiebault, L. Guen, R. Eholié, J. Flahaut, and F.R. Ollitrault, "Contribution a l'étude du système ternaire Ga-Ge-Se", *Bull. Soc. Chim. Fr.*, 1975. pp. 967-972.

[20] A.M. Loireau Lozac'h, and M. Guittard, "Système ternaire La2Se3-Ga2Se3-GeSe2 diagramme de phase', *Mater. Res. Bull.*, vol. 12, 1977, pp. 887-893.

[21] J.C. Rouland, R. Ollitrault-Fichet, J. Flahaut, J. Rivet, and R. Ceolin, "The As-Te system: phase diagram and glass separation", *Thermochimica Acta*, vol. 161, No 1, 1990, pp. 189-200.

[22] A.K. Keshari, and A.C. Pandey, "Size and distribution: a comparison of XRD, SAXS and SANS study of II–VI semiconductor nanocrystals", *Journal of nanoscience and nanotechnology*, vol. 8(3), 2008, pp. 1221-1227.

[23] C. Lin, L. Calvez, M. Rozé, H. Tao, X. Zhang, and X. Zhao, "Crystallization behavior of 80GeS2·20Ga2S3 chalcogenide glass", *Applied Physics A*, vol. 97, No 3, 2009, pp. 713-720.

[24] A.K. Keshari, and A.C. Pandey, "Size and distribution: a comparison of XRD, SAXS and SANS study of II–VI semiconductor nanocrystals", *Journal of nanoscience and nanotechnology*, vol. 8, No 3, 2008, pp. 1221-1227.