THE STRUCTURAL PROPERTIES OF Sb_2Se_3-As_2Se_3 AND Sb_2Te_3-As_2Se_3 GLASSES

M. LEH DELI[*], D. HOUPHOUET BOIGNY, G. KRA
*Laboratoire de Chimie des Matériaux Inorganiques, UFR-SSMT,
Université de Cocody, 22 Bp 582 Abidjan 22. Côte d'Ivoire*

The general formulas of studied vitreous compositions of the Sb_2Se_3-As_2Se_3 and Sb_2Te_3-As_2Se_3 systems are: (1-x) Sb_2Se_3+x As_2Se_3 + ySb_2Te_3 $\rightarrow$ $Sb_{2(1-x+y)}As_{2x}Se_3Te_{3y}$ where $0 \leq x \leq 1$ and $0 \leq y \leq 1$ x and y represent respectively the molar fractions of As_2Se_3 and Sb_2Te_3. Glass-forming region of the Sb_2Se_3-As_2Se_3 system is wider than that of the Sb_2Te_3-As_2Se_3 system. The Ordered Bond Network Model shows that all glasses of the above systems are stoichiometric vitreous compositions with only heteronuclear bonds: Sb_2Se_3-As_2Se_3 glasses contain mainly Sb-Se and As-Se bonds while the Sb_2Te_3-As_2Se_3 system consists of Se-Te, Sb-Se and As-Se bonds. For these vitreous compositions, the average coordination number (Z) determined by the constraints model is equal to 2.4.

1. Introduction

Chalcogenide glasses are vitreous materials whose composition contains one or more chalcogen elements S, Se or Te, as well as elements of the groups IV and V of periodic classification. These glasses are interesting materials because of their technological applications [1] and commercial importance [2]. In this study, the glass-forming regions of Sb_2Se_3-As_2Se_3 and Sb_2Te_3-As_2Se_3 systems, the nature of chemical bonds in their glasses determined by the Ordered Bond Network Model (OBNM) [3], the calculated average coordination number (Z) of antimony (Sb) and arsenic (As) atoms by the constraints model [4] and the stability of glasses quantified by numerical parameter $K_{WO}=(Tc_1 /Tf_1)$[5] is discussed. The correlation between the glass transition temperature (Tg), the optical gap (Eg) and the average coordination number (Z) in each system was investigated in order to find the possible structural modifications in the Sb_2Se_3-As_2Se_3 and Sb_2Te_3-As_2Se_3 glasses.

2. Synthesis and characterization of glasses

Glasses of Sb_2Se_3-As_2Se_3 and Sb_2Te_3-As_2Se_3 systems, whose formulas are
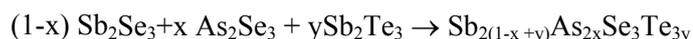
(1-x) Sb_2Se_3+x As_2Se_3 + ySb_2Te_3 $\rightarrow$ $Sb_{2(1-x+y)}As_{2x}Se_3Te_{3y}$

where $0 \leq x \leq 1$ and $0 \leq y \leq 1$
x and y represent respectively the molar fractions of As_2Se_3 and Sb_2Te, were prepared by direct synthesis from pure starting elements such as arsenic (As), antimony (Sb), tellurium (Te) and selenium (Se). Quartz ampoules were filled with ~ 1 g of the mixed elements and then evacuated to ~ 10^{-3} Torr, sealed and heated to 900°C at the rate of 3°C /minute. The ampoules were held at this temperature for 24 hours and quenched in ice-water. The glassy state in the quenched samples was confirmed by X-ray diffraction at room temperature using Cu-Kα radiation (λ=1.5405 Å). The thermal characteristics such as the glass transition temperature Tg , the first crystallization temperature Tc_1 and the first melting temperature Tf_1 , were measured by using DSC 121 Setaram

apparatus at a heating rate of 1°C/minute in the studied temperature range (from 25°C to 650°C). The thermal stability of Sb_2Se_3-As_2Se_3 and Sb_2Te_3-As_2Se_3 glasses was estimated using K_{WO} parameter defined above. Measurements of optical absorption of the studied compositions were carried out in diffuse reflexion using a U.V-Visible-PIR spectrometer doubles beam CARY 5th (Varian) equipped with an integral sphere of which the interior is covered with polytetrafluoroethylene (PTFE). The range accessible wavelength with this apparatus is 250-2500 nm. The detectors, specific to the integral sphere, are for the infra-red a PbS cell and visible photomultiplier. The resolution depends on the selected slit and is to the maximum of 0.01nm in the visible one and 0.04nm in the PIR. The base line is carried out starting from a PTFE spectrum, white compound reflecting the near total of the incidental light on all the range of work. The reduced samples, out of powder are placed in a door sample of diameter interns 20mm. The side in contact with the sphere is closed by a quartz plate.

3. Results and discussion

3.1. Chemical composition of glasses.

The chemical composition of the investigated glasses is indicated in Table 1.

In the Sb_2Se_3-As_2Se_3 system the atomic percentage of arsenic (As) increases from 10 % to 20 %. The one of antimony (Sb) decreases from 10 % to 0 %). For selenium (Se) atom, the atomic percentage remains equal to 30 %. As replaces Sb, the number of As-Se bonds increases at the expense of Sb-Se. In the Sb_2Te_3-As_2Se_3 system, the atomic percentages of As and Se increase respectively from 13 % to 20 % and from 19.5 % to 30 %. Those of Sb and tellurium (Te) decrease from 7 % to 0 % and from 10.5 % to 0 %, respectively. As replaces Sb and Te is substituted by Se. It is suggested that the number of As-Se bonds increases at the expense of Sb-Te.

3.2. Glass-forming regions

The domain of glass formation in the Sb_2Se_3-As_2Se_3 system extends from 50 to 100 mol % As_2Se_3. Sb_2Se_3-rich compositions having contents lower than 30 mol %As_2Se_3 do not form glasses. The domain of Sb_2Se_3-As_2Se_3 system extends from 35 to 45 mol % As_2Se_3 the compositions are partially crystallized.

The maximal solubility of Sb_2Se_3 in the glasses is 30 mol % As_2Se_3. The glass-forming region of Sb_2Se_3-As_2Se_3 system obtained in this study is wider (from 50 to 100 mol %As_2Se_3). The glass-forming region of Sb_2Te_3-As_2Se_3 system is between 65 and 100 mol % As_2Se_3. Sb_2Te_3-rich compositions having contents less than 35 mol %As_2Se_3 are crystalline. The domain of Sb_2Te_3-As_2Se_3 system extends from 45 to 60 mol % As_2Se_3 the compositions are partially crystallized.

The maximum solubility of Sb_2Te_3 in the Sb_2Te_3-As_2Se_3 glasses is 35 mol % As_2Se_3. By comparing the domains of glass formation obtained in the two binary systems one observes that glass-forming region is reduced when one passes from Sb_2Se_3-As_2Se_3 system to Sb_2Te_3-As_2Se_3 system. The substitution of selenium (low atomic mass equal to 78.96 g/mol) by tellurium (high atomic mass equal to 127.6 g/mol) involves the reduction of glass-forming region.

The glass-forming ability of selenium is higher than that of tellurium. This is in agreement with A. R. Hilton[6]. According to [6], the glass-forming tendency decreases in the order: S>Se>Te and P>As>Sb. From the above considerations, an analysis concerning the glass-forming ability of As_2Se_3, Sb_2Se_3 and Sb_2Te_3 compounds can be done. In the As_2Se_3 compound, the environment of arsenic atoms is given by a trigonal pyramid $AsSe_3$ (three selenium atoms located at 2.42Å from arsenic atom) and its structural arrangement is two-dimensional (2D) with covalent As-Se bonds. Glassy As_2Se_3 is easily synthesized[7]. For the Sb2Se3 compound the coordination number for antimony atoms is larger than 3 when they form bonds with selenium atoms. The average coordination number for antimony is greater than the topological threshold for glasses (2.4)[8]. This is in agreement with the results of a Sb2Se3 study where antimony is on two crystallographic sites[9]:

one is of the pyramidal type $SbSe_3$ with bonds Sb-Se average length 2.85 Å and the other is the square-based pyramid type $SbSe_5$ with bonds Sb-Se average length 2.95 Å. The structural arrangement of Sb_2Se_3 is one-dimensional (1D) with Sb-Se bonds less covalent than the As-Se bonds. The preparation of Sb_2Se_3 glass requires high cooling rates[7]. Sb in the Sb_2Te_3 compound is found on poorly deformed octahedral sites constituted by three tellurium atoms located at 2.98Å and three others at 3.17 Å. Sb_2Te_3 is a semi-metal with a compact three-dimensional (3D) structure. It does not form glass with usual hardening. It can be concluded that the glass-forming ability of As_2Se_3, Sb_2Se_3 and Sb_2Te_3 compounds is due to the structural arrangement resulting from the condensation of coordination polyhedra (constituent elements) of the framework.

3.3. Chemical bond determination

Ordered Bond Network Model suggests that the formation of the heteropolar bonds is favoured over the homopolar bonds. And they are formed in decreasing order of their energies. Each atom is then coordinated by (8-N) atoms where N is the number of valence electrons. In this case, glass is made of the structural units which are the most stable chemical components of the system. The nature of chemical bonds in the glasses can be determined by using the parameter (R) which represents the ratio of covalent bonding possibilities of chalcogen atoms to covalent bonding possibilities of non chalcogen atoms [10]. The value of R=1 represents the case of the existence of only heteronuclear bonds in a given system, which indicates the existence of a chemical threshold. The R_1 and R_2 parameters of Sb_2Se_3-As_2Se_3 and Sb_2Te_3-As_2Se_3 glasses can be calculated by using, respectively, the equations below:

$$R_1 = 2z(Se)/ (3z (As) + 3z (Sb)) \tag{1}$$

$$R_2 = (2z(Se) + 2z(Te))/(3z(As) + 3z(Sb)) \tag{2}$$

where z(Se), z(Te), z(As) and z(Sb) are the atomic fractions of Se, Te, As and Sb by considering Table 1 formulas, respectively. The atomic coordination number is 2 for chalcogens (Se, Te) and 3 for non-chalcogens (As, Sb). The calculation of R_1 and R_2 for each studied glass gives a value equal to 1. This means that all glasses can be then regarded as stoichiometric compositions in which only the heteropolar bonds are present. Stoichiometric glasses were found in As_2S_3-GeS_2 and Sb_2S_3-GeS_2 systems [11]. The bond energies DA-B for heteronuclear bonds are calculated on the basis of the relation postulated by Pauling [12]:

$$D_{A-B} = (D_{A-A} \times D_{B-B})^{1/2} + 30(X_A - X_B)^2 \text{ (kcal/mole)} \tag{3}$$

where, D_{A-A} and D_{B-B} are energies of the homonuclear bonds and X_A and X_B are the electronegativity values of the atoms involved. The values of the energies of the homopolar bonds Se-Se, Te-Te, As-As and Sb-Sb are 216 kJ/mole, 137.94 kJ/mole, 134.18 kJ /mole and 126.24 kJ /mole, respectively. The electronegativities according to Pauling are: As = 2.18; Sb=2.05; Se=2.55 and Te=2.10. The relative probability of chemical bonds formation can be calculated by the Boltzmann factors exp (-E/RT) = exp (D/RT), where D is the bond energy, R the gas constant and T the reaction temperature (at which the samples were prepared during their synthesis) in Kelvins (T = 900+273.15=1173.15 K).

Table 1.Chemical composition, values of thermal characteristics (Tg, Tc₁ and Tf₁), stability parameters (K_{WO}) and the optical gap (Eg) of Sb₂Se₃-As₂Se₃ and Sb₂Te₃-As₂Se₃ glasses.

Sb_2Se_3-As_2Se_3 system							Sb_2Te_3-As_2Se_3 system						
mol% As_2Se_3	Chemical composition	Tg	Tc_1	Tf_1	K_{wo}	Eg	mol%A s_2Se_3	Chemical composition	Tg	Tc_1	Tf_1	K_{wo}	Eg
50	$Sb_{10}As_{10}Se_{30}$	185	212	366	0.58	1.1							
55	$Sb_9As_{11}Se_{30}$	185	216	366	0.59								
60	$Sb_8As_{12}Se_{30}$	183	230	366	0.63	1.17							
65	$Sb_7As_{13}Se_{30}$	182	237	366	0.65	1.20	65	$Sb_7As_{13}Se_{19.5}Te_{10.5}$	149	183	307	0.59	
70	$Sb_6As_{14}Se_{30}$	181	242	366	0.66	1.24	70	$Sb_6As_{14}Se_{21}Te_9$	153	205	334	0.61	0.85
75	$Sb_5As_{15}Se_{30}$	182	264	366	0.72	1.23	75	$Sb_5As_{15}Se_{22.5}Te_{7.5}$	155	207	308	0.67	0.92
80	$Sb_4As_{16}Se_{30}$	182	291	367	0.79	1.26	80	$Sb_4As_{16}Se_{24}Te_6$	159	264	309	0.85	0.94
85	$Sb_3As_{17}Se_{30}$	178	285	368	0.77	1.30	85	$Sb_3As_{17}Se_{25.5}Te_{4.5}$	163	291	331	0.88	0.97
90	$Sb_2As_{18}Se_{30}$	180	274	370	0.74	1.32	90	$Sb_2As_{18}Se_{27}Te_3$	166	272	343	0.79	1.06
95	$SbAs_{19}Se_{30}$	170	283	367	0.77	1.37	95	$SbAs_{19}Se_{28.5}Te_{1.5}$	172	292	360	0.81	1.13
100	$As_{20}Se_{30}$	177	304	375	0.81	1.40	100	$As_{20}Se_{30}$	177	304	375	0.81	1.40

Table 2. Bond energy D and relative probability of heteronuclear bonds at 900°C in Sb₂Se₃-As₂Se₃ and Sb₂Te₃-As₂Se₃ glasses

Sb_2Se_3-As_2Se_3 system			Sb_2Te_3-As_2Se_3 system		
Bond	Bond energy D (kJ/mole)[a]	Relative probability	Bond	Bond energy D (kJ/mole)[a]	Relative probability
As-Se	174.35	1	Se-Te	178.68	1
Sb-Se	172.63	0.84	As-Se	174.26	0.64
As-Sb	132.26	$1.053.10^{-4}$	Sb-Se	172.63	0.54
			As-Te	136.86	1.50×10^{-3}
			Sb-Te	132.276	9.40×10^{-4}
			As-Sb	132.263	9.40×10^{-4}

[a]Probability of the As-Se and Se-Te bonds was taken as unity

The orders of bond energies and the relative probabilities listed in Tables 2 indicate that the stronger the chemical bond is, the larger is its forming probability. According to the Ordered Bond Network Model, the chemical bonds in the Sb_2Se_3-As_2Se_3 glasses must be formed in the order of As-Se > Sb-Se > > As-Sb. When there is excess Sb and As atoms, the chemical bond As-Sb can be formed. The order established above indicates that the prior formation of the energetic bonds As-Se leads to pyramidal type structural units: based on $AsSe_3$. The remaining selenium will bind to arsenic to give trigonal pyramids units $AsSe_3$ by satisfying the 8-N rule where N is the number of valence electrons. The presence of the structural configurations $SbSe_3$ and $AsSe_3$ in the Sb_2Se_3-As_2Se_3 glasses was already confirmed by infrared and Raman spectroscopy [13]. This study has shown that these structural units ($SbSe_3$ and $AsSe_3$) are connected through selenium atoms.

In the Sb_2Te_3-As_2Se_3 system, the chemical bonds can be formed in the following order: Se-Te > As-Se >Sb-Se >> As-Te > Sb-Te = As-Sb (Table 2). The As-Te, Sb-Te and As-Sb bonds will be formed when there are excess of Te, As and Sb atoms. The energetic Se-Te bonds are probably used to connect the structural units $SbSe_3$ and $AsSe_3$ announced beforehand in the case of Sb_2Se_3-As_2Se_3 glasses and which would be found in Sb_2Te_3-As_2Se_3 glasses.

On the basis of the above discussion, one can deduce that the network structure of Sb_2Se_3-As_2Se_3 glasses mainly consists of the strongest As-Se and Sb-Se bonds, whereas the structure of Sb_2Te_3-As_2Se_3 glasses mainly consists of the strongest Se-Te, As-Se and Sb-Se bonds. A quantitative criterion for predicting which types of materials are likely to be good glass formers has been proposed by Phillips [4, 14], who used a topological viewpoint in which connectivity is measured by the average coordination number Z. One implication of this result is that alloys such as a-As_2Se_3, which have Z=2.4, have the ideal network rigidity to optimise both the bond lengths and the bond angles. They should thus be excellent glass formers, i.e, yield amorphous structures after quenching from the melt at a relatively modest rate. The average coordination number Z of the central atom of the coordination polyhedrons of Sb_2Se_3-As_2Se_3 and Sb_2Te_3-As_2Se_3 glasses can be obtained starting from the coordination numbers of the As, Sb, Se and Te elements and their atomic fraction by using the constraints model[4]. The average coordination numbers Z_1 and Z_2 of Sb_2Se_3-As_2Se_3 and Sb_2Te_3-As_2Se_3 glasses are calculated respectively by:

$$Z_1 = 3x(As)+3y(Sb)+2z(Se) \tag{4}$$

$$Z_2 = 3x(As)+3y(Sb)+2z(Se)+2t(Te) \tag{5}$$

where x(As), y(Sb), z(Se) and t(Te) are the respective atomic fractions of As, Sb, Se and Te by considering the formulas of Table 1. The calculation of Z_1 and Z_2 for each glass gives a value equal to 2.4. This result shows that when the content of As_2Se_3 increases on each binary system, the average coordination number Z does not vary. There are no structural phase transitions in these glasses. Z does not change because Sb (with a coordination number 3) is replaced by As (which also has the same coordination number) in the Sb_2Se_3-As_2Se_3 system. In the case of Sb_2Te_3-As_2Se_3 system with more Sb substitution by As announced above, Te replaces Se (both atoms have the same coordination number 2). The invariability of Z was observed in $As_{40}S_xTe_{(60-x)}$ system [15]. When x varies in this system, Z does not change as S (with a coordination number 2) is replaced by Te (which has the same coordination number). The Ordered Bond Network Model and the constraints model can enable us to conclude that, the most important short range order parameters in the description of structure and bonding in Sb_2Se_3-As_2Se_3 and Sb_2Te_3-As_2Se_3 glasses are the coordination number of the elements entering the glasses and bond energies between the elements.

3.4. Thermal and optical properties

The analysis of thermal properties (Table 1) show glasses for each system when the molar percentage of As_2Se_3 increases, have crystallization temperatures (Tc). Atoms of these materials although being mobile above Tg do not have any tendency to crystallize when they are heated. The characteristic structural disorder of these glasses is maintained. In these glasses, the thermal

stability against crystallization is probably due to the formation of stable structural units (SbSe$_3$ and AsSe$_3$) which constitute the framework of the vitreous networks when the molar percentage of As$_2$Se$_3$ increases.

The thermal and optical properties Tg and Eg, respectively, cannot be discussed in term of the average coordination number Z because they don't depend on Z=2.4. This is in agreement with[16] which showes that most physical properties of glasses are not universal functions of Z.

Contrary to the As-Te glasses, where Tg varies as a function of Z which is between 2.55 and 2.73[17], the optical gap (Eg) and Tg of the Ge20S80-xBix glasses decrease when Z increases from 2.4 to 2.52[18]. In the two quoted examples Tg and Eg depend on Z.

De Neufville and Rockstad[19] proposed and established the empirical relation between *Tg*, Eg and Z. They showed that these parameters can be connected by the relation:

$$Tg \approx T_g^0 + \beta(Z-2)E_{04} \tag{6}$$

Tg is the glass transition temperature, T_g^0 is the extrapolated value of *Tg* obtained when E_{04} is equal to 0. β is a linear proportionality constant for value of Z (the average coordination number). E_{04} is the energy at which the optical absorption coefficient is 10^4 cm^{-1} and is the measure of the optical gap Eg.
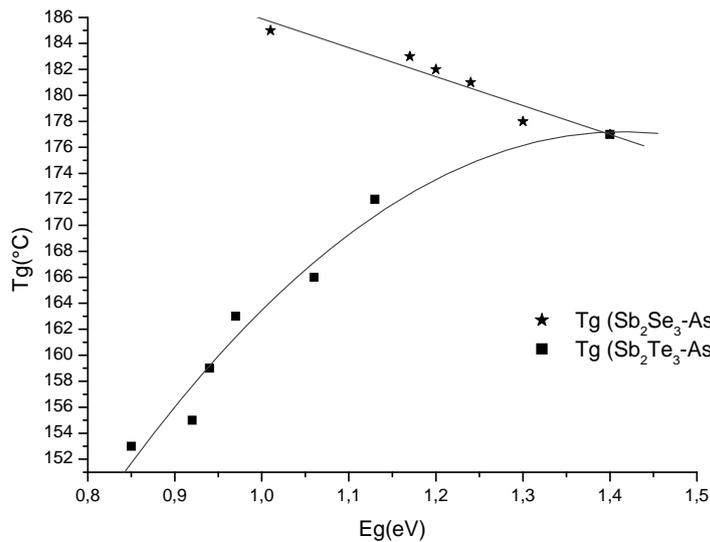
Fig. 1. The glass transition temperature Tg as a function of the optical gap Eg for Sb$_2$Se$_3$-As$_2$Se$_3$ and Sb$_2$Te$_3$–As$_2$Se$_3$ glasses with fixed value of the average coordination number Z= 2.4.

Fig. 1 indicates the Tg-Eg-Z correlation. The contrary evolution of Eg and Tg on the Sb$_2$Se$_3$-As$_2$Se$_3$ system and the increase in Eg and Tg on the Sb$_2$Te$_3$-As$_2$Se$_3$ system enable to suggest that the physical characteristics Tg and Eg are not dominated by the structural units of studied glasses because Tg and Eg don't vary with Z=2.4. One can deduce that glasses of Sb$_2$Se$_3$-As$_2$Se$_3$ and Sb$_2$Te$_3$-As$_2$Se$_3$ systems are effectively formed by the structural units SbSe$_3$ and AsSe$_3$ which do not change in each system.

4. Conclusions

The X-ray diffraction at room temperature is used to confirm the vitreous state of the investigated samples in the Sb$_2$Se$_3$-As$_2$Se$_3$ and Sb$_2$Te$_3$-As$_2$Se$_3$ systems. This study shows that the substitution of selenium by tellurium reduces the domain of glass formation because the glass-

forming region becomes smaller when one passes from Sb_2Se_3-As_2Se_3 system to Sb_2Te_3-As_2Se_3 system. The theoretical study by means of Ordered Bond Network Model indicates that, the studied glasses of the above systems are stoichiometric because of the existence of only heteronuclear bonds in these materials. Thus, Sb_2Se_3-As_2Se_3 and Sb_2Te_3-As_2Se_3 glasses are made up mainly of Sb-Se and As-Se bonds and Se-Te, Sb-Se and As-Se bonds, respectively. The calculated average coordination number (Z) of all studied glasses by using the constraints model is 2.4. The correlation between Tg , Eg and Z indicates that these thermal and optical properties are not dominated by the structural units ($SbSe_3$ and $AsSe_3$) because Tg and Eg do not vary with Z=2.4.

References

[1] K. Tanaka, Phys. Rev. **B39**, 1270 (1989).
[2] A. B. Seddon, J. Non-Cryst. Solids **44**, 184 (1995).
[3] J. Bicerano, S. Ovshinsky, J. Non-Cryst. Solids **74**, 75 (1985).
[4] J. C. Phillips, J. Non-Cryst. Solids 43 (1981) 37.
[5] T. Wakasugi, R. Ota, J. Fukuraya, J. Am. Ceram. Soc. 75 (1992) 29
[6] A. R. Hilton, J. Non-Cryst. Solids **2**, 28 (1970).
[7] L. Cervinka, A. Hruby, J. Non-Cryst. Solids **1**, 210 (1980).
[8] J. C. Phillips, J. Non-Cryst. Solids **34**, 835 (1979).
[9] P. Bayliss, W. Nowacki, Z. Kristallogr. **135**, 308 (1972).
[10] L. Tichy, H. Ticha, J. Non-Cryst. Solids **189**, 141 (1995).
[11] T. Kavetskyy, R. Golovchak, O. Shpotyuk, J. Filipecki, J. Swiatek, Chalc. Lett. **1**(10), 125 (2004).
[12] L. Pauling, The nature of the chemical bonds. Cornell University Press, Third edition. pp 85, 92 (1960).
[13] M. A. El Idrissi-Raghni, P. E. Lippens, J. Olivier-Fourcade, J. C. Jumas, J. Non-Cryst. Solids **192&193**, 191 (1995).
[14] J. C. Phillips, J. Non-Cryst. Solids **35&36**, 1157 (1980).
[15] P. K. Thiruvikraman, Bull. Mater. Sci. **29**(4), 371 (2006) -374.
[16] M. Tatsumisago, B. L. Halfpap, J. L. Green, S. M. Lindsay, C. A. Angell. Phys. Rev. Lett. **64**, 1549 (1990).
[17] G. Achamma, D. Sushamma, P. Predeep, Chalc. Lett. **3**(4), 33 (2006).
[18] P. Sharma, M. Vashistha, I. P. Jain, Chalc. Lett. **2**(11), 115 (2005).
[19] J. P. deNeufville, H. K. Rockstad, in Amorphous and Liquid Semiconductors, J. Stuke and W. Brenig, eds., Taylor and Francis, London, (1974) 419.

_____

*Corresponding author: lehdeli@netcourrier.com