International Journal of Innovative Technology and Exploring Engineering (IJITEE)
ISSN: 2278-3075 (Online), Volume-7 Issue-7, April 2018

Thermal Analysis of $In_xTe_{10}Se_{90-x}$ Glasses

S.R. Alharbi, E. S. Al-Zahrani, M. Y. Alharbi, W. Alharbi, K.A. Aly

Abstract: ***measurements of differentially scanning calorimeter (DSC)*** $In_xTe_8Se_{92-x}$ $0 \le x \le 9$ ***under non isothermal technique (at heating rates (α) ranging from 2 to 32 K/min.) have been carried out. The (α) value is found to affect the characteristic temperatures (the temperature of glass transition (T_g), the onset temperature of crystallization (T_c) and the temperature of crystallized peak (T_p)) that helping us to investigate the Avrami's exponent (n) and the activation energy for glass transition (E_g) and crystallization (E_c). The investigated results are discussed in terms of the chemical bond approach, the cohesive energy (CE) and the average heats of atomization (H_s). The X- ray diffractograms confirmed the amorphous state of the as-prepared glasses.***

Keywords: Chalcogenides; DSC; XRD.

I. INTRODUCTION

Chalcogenide type of glasses has a lot of attention due to their wide range of technologically applications. Binary as Se-Te and In-Se glasses have many advantages in comparison with a-Se [1-3]. The In-Se system is attractive because of their uses in solar cell [4, 5]. On the other hand, Se-Te system is characterized by their large crystallization temperature, high hardness, good photosensitive as well as small ageing effects than a-Se [1]. Whereas these glasses are characterized by low thermos-mechanical properties, thus their applications can be enlarged through improving their soften temperature and mechanically strength. The Addition of third element to binary glass system (In in our case) not only enlarge their region of glass formation but, also makes compositional and configuration disorder in the glass system, the structure modification and improving the electrical as well as thermal characterization of the Se-Te glasses [6-9].

In the literature, many research papers [8, 10-12] deals with the study of electrical, photoelectrical and thermally properties of In-Se-Te glasses. From an application point of view, it is necessity to study the thermal properties of like glasses. The current study deals with the effect of In amount on the thermal analysis of different compositions of) $In_xTe_8Se_{92-x}$ $0 \le x \le 9$ halcogenides.

Manuscript published on 30 April 2018.
*Correspondence Author(s)
S.R. Alharbi, Physics Department, Faculty of Science- Al Faisaliah Campus, King Abdulaziz, University, Jeddah, Saudi Arabia. E-mail: srfalharbi@kau.edu.sa
E. S. Al-Zahrani, Physics Department, Faculty of Science- Al Faisaliah Campus, King Abdulaziz, University, Jeddah, Saudi Arabia.
M. Y. Alharbi, Physics Department, Faculty of Science- Al Faisaliah Campus, King Abdulaziz, University, Jeddah, Saudi Arabia
W. Alharbi, Physics Department, Faculty of Science- Al Faisaliah Campus, King Abdulaziz, University, Jeddah, Saudi Arabia.
K.A. Aly, Physics Department, Faculty of Science and Arts Khulais, University of Jeddah, Saudi Arabia, Physics Department, Faculty of Science, Al - Azhar University, P.O. 71452, Assiut, Egypt.

II. THEORETICAL BASES:

Explanation of the DTA and/or DSC results is retired through the formal kinetic transformations theory in terms of the crystallized fraction (volume) (χ) in the time interval (t) by using the Johnson, Mehl and Avrami's experssion [13]

$$\chi = 1 - e^{-(k.t)^n} \quad (1)$$

where n is the Avrami's exponent (is an integer or half integer depending on the mechanisms of growth and the crystal dimension), k is the effective reaction rate,

$$k = k_0 . e^{-E_c/RT} \quad (2)$$

where E_c is the crystallization activation energy.

2.1. Afify's Method

Using Afify condition [14, 15] at $\chi = 0.63205$ the term $\ln(1-\chi) = -1$ and the eq. 1 rewritten as:

$$\ln(1-\chi) = -1 = -(k_{0.63}\, t_{0.63})^n \quad (3)$$

i.e

$$k_{0.63} = t_{0.63}^{-1} \quad (4)$$

Using equation (4) the $k_{0.63}$ at $\chi = 0.63205$ can be estimated at every heating rate. Then the reaction rate $k_{0.63}$ in the logarithmic form is given by:

$$\ln(k_{0.63}) = \ln(k_0) - E_c/RT_{0.63} \quad (5)$$

The values E_c *and* k_0 can be estimated without any dependence on the Avrami's exponent (n) from the slope and intersect of the relationship between $\ln(k_{0.63})$ *and* $1000/T_{0.63}$. Furthermore, eq.5 satisfied for isothermal and non-isothermal technique [13]. rewriting Eq. 3 in the logarithmic form as

$$\ln(\ln(1-\chi)) = n.\ln(k) + n.ln(t) \quad (6)$$

where k is constant at constant temperature, plotting $\ln(\ln(1-\chi))$ versus $ln(t)$ a straight line with slope equal to the n value. In iso-thermal technique, Eq. 6 is carried out for only one DSC curve whereas, in non-isothermal technique, Eq. 6 is carried out, at constant temperature for different DSC curves.

2.2. Bansal's Method

Bansal's method detail is quoted approximation which may cause an 3% error in the value of E_c/R in the worst cases [16] and the final relationship can be written as:

$$\ln(T_p^2 / \alpha) = -E_c / RT_p - \ln(K_0 R / E_c) \quad (7)$$

Depending on Bansal's analysis the kinetic exponent can be estimated by the use of the following relation:

Published By:
Blue Eyes Intelligence Engineering
and Sciences Publication (BEIESP)

$$\chi_P = n(0.37\alpha E_C)/(RT_P^2) \qquad (8)$$

and exponent that based on the crystal growth dimensionality (m) also may be estimated by :

$$\left[\frac{d\chi}{dt}\right]_p = mE\alpha(1-\chi_p)/RT_p^2 \qquad (25)$$

At study the kinetics of crystallization in the glass, $n = m$ if the nuclei are formed through any previous heat treatment prior to DSC or DTA scan. Whereas, in the case of the nuclei are formed through the heating at constant rate α are dominant and $n = m+1$ [6, 17].

III. EXPERIMENTAL

$In_xTe_8Se_{92-x}$ $(0 \le x \le 9)$ glasses were prepared starting with highly purity In, Te and Se (99.999 %) using the well-known melt quench technique. The amorphous state of the as-prepared samples was checked using a Philips (1710) X-ray diffract meter. The elemental composition was investigated using energy dispersive X-ray spectroscopy (Link analytical EDS). The as-prepared samples as well as that starting calculation based on their ratios and atomic percentage with small error only ± 0.4 at %.

10 mg in powder form for each sample was sealed in Al boat and scanned through the temperature range 300-450 K at different heating rates (α = 2, 4, 8, 16 and 32 K min^{-1}) using Shimadzu 50 DSC. The characteristic temperatures T_g, T_c, and T_p (the temperature of glass transition, the onset of the crystallization peak, and the temperature of the crystallized peak, respectively) were estimated using the microprocessor of the thermal analyser with accuracy (±1 K). T_g, T_c, and T_p, are

IV. RESULTS AND DISCUSSION

Figure 1 shows the DSC curves for $In_xTe_8Se_{92-x}$ different compositions of the (where x = 0, 2.5, 5, 7.5 and 9 at.%) glasses measured at heating rate 10 K.min^{-1}. The characteristic temperatures, T_g, T_c and T_p are increases with the increase of In content.

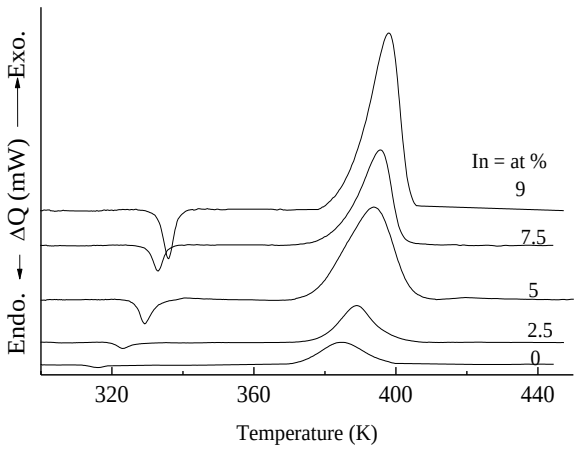

Figure 1. DSC curves for powdered $In_xTe_8Se_{92-x}$ chalcogenides scanned at α = 8 K/ min.

4.1. Glass Transition

The glass transition temperature dependence on the heating rate (α) obey the following relationship [18]:

$$T_g = A + B \ln(\propto) \qquad (26)$$

where A and B with the same meaning written here [19]. The A and B values were estimated by plotting T_g values versus ln (∝) as shown in Fig.2. The deduced values of A and B for $In_xTe_8Se_{92-x}$ glasses in excellent agreement with eq. (26) and are listed in Table 1.

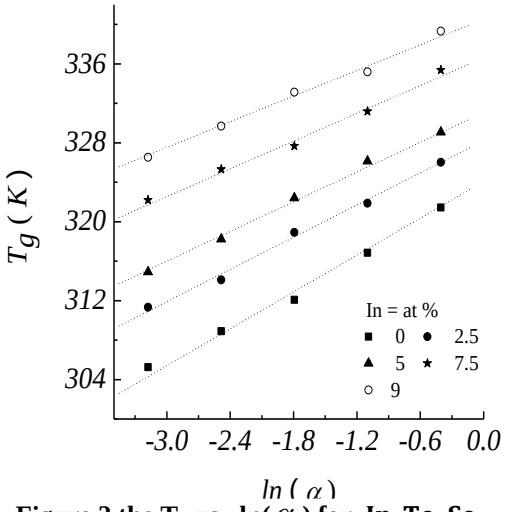

Figure.2 the T_g vs. ln(α) for $In_xTe_8Se_{92-x}$ $(0 \le x \le 9)$ chalcogenides.

On the other side, Eq.7 can be rewritten for the glass transition temperature, T_g as [20]:

$$\ln(T_g^2/\alpha) = E_g/RT_g + const. \qquad (27)$$

By plotting $\ln(T_g^2/\alpha)$ versus 1000/T_g, the slope can be used to determine the E_g value as well as demonstrated in Figure 3.

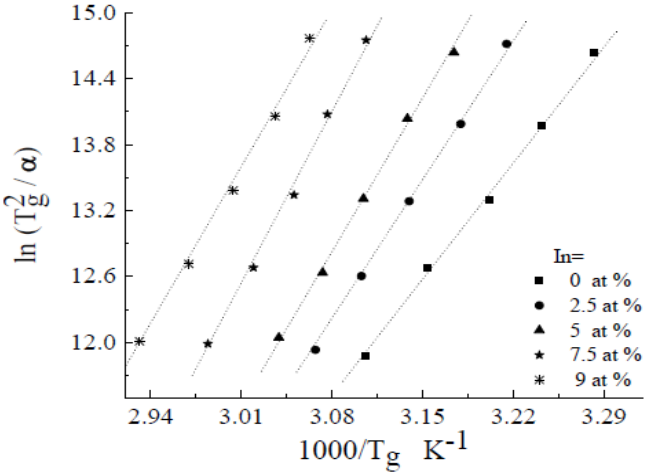

Figure 3: the values of $\ln(T_g^2/\alpha)$ against 1000/T_g, for $In_xTe_8Se_{92-x}$ $(0 \le x \le 9)$ chalcogenides.

Published By:
Blue Eyes Intelligence Engineering
and Sciences Publication (BEIESP)

The estimated values of E_g are agree with that was observed for chalcogenide glasses [21-23]. The E_g values increases with the increase of In content which can be considered as a result of increasing the T_g values consequentially the glass rigidity also are increased.

The glass transition temperature is strongly affected by many independent parameters for example the effective molecular weight, the optical, bonding energy, the fraction and type for different structural units formed, the average heats of atomization, cohesive energy, the mean coordination number [24, 25]. For heteronuclear bonds the bonding energy between to different atoms $D(C-E)$ can be estimated using Pauling's relationship [26]:

$$D(C-E)=[D(C-C).D(E-E)]^{1/2}+30(\chi_C-\chi_E)^2 \quad (28)$$

where $D(C-C)$ and $D(E-E)$ are the homonuclear bond energies in units kcal mol^{-1} [27], χ_C and χ_E are the electronegativity values for C and E atoms [28]. Bond formation tack place in sequence of decreasing bond energy up to the available atom valences are satisfied [29]. For In-Se-Te glasses, bonds of In-Se are expected to occur firstly because of their highly possible energy (54.321 kcal mol^{-1}) then, Se-Te bonds (44.19 kcal mol^{-1}) in try to saturate all available Se valences but, the Te atoms isn't enough to do this. Therefore, Se-Se defect homopolar bonds are formed. In accordance with approach of chemical bond, the bond energies are assumed to be additive. Therefore, the summation of bond energies over all the bonds expected in glass gives cohesive energy (CE). The calculated values of CE for the glasses under study are listed in Table 1 and it were increases with the increase of indium content.

Table 1: The Glass Transition Parameters for $In_xTe_8Se_{92-x}$ ($0 \le x \le 9$) Chalcogenides.

In at. %.	A	B	E_g	E_c (Eq.6)	E_c (Eq.14)	CE	H_s
			kcal mol^{-1}		Kcal.mol^{-1}	(kcal atom^{-1})	(kcal g atom^{-1})
0	322	5.88	28.04	21	21.55	36.99	49.59
2.5	330	5.24	33.76	24.12	25.87	37.07	49.75
5	338	4.71	42.65	27.83	26.97	37.16	49.99
7.5	340	4.34	46.43	29.21	28.55	37.23	50.16
9	343	4.19	50.66	30.76	31.22	37.31	50.32

Extending Pauling's idea to the ternary glasses (In-Se-Te in the present study) according to Sadagopan et al. [30] and neglecting the heat of formation. Thus, the average heats of atomization may be calculating by using the H_S values for In, Se, and Te into the following relationship [31].

$H_s(In-Se-Te)$ is given by:

$$H_S(In-Se-Te)=\frac{1}{2}(H_S^{In}+H_S^{Se}+H_S^{Te}) \quad (31)$$

The deduced values of H_s for $In_xTe_8Se_{92-x}$ glasses were shown in Table 1,

4.2. Crystallization

Based on Eq.6 the crystallization activation energy (E_c) can be estimated by plotting the values of $\ln(k_{0.63})$ as a function of $10^3/T_{0.63}$ for $In_xTe_8Se_{92-x}$ ($0 \le x \le 9$) *chalcogenide g*lasses as shown in Fig. 4. The deduced values of E_c were listed in Table 2.

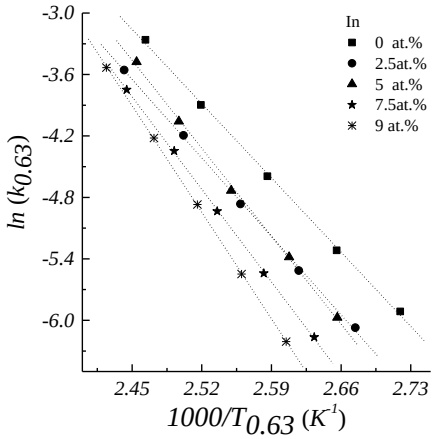

Figure 4: The $\ln(k_{0.63})$ vs. $1000/T_{0.63}$ for $In_xTe_8Se_{92-x}$ ($0 \le x \le 9$) chalcogenides.

On the other hand, according to Bansal's equation using the slope and intercept of the linear relation between $\ln[T_p^2/\alpha]$ and $10^3/T_p$, both the K_0 and E_c values can be deduced. Figure 5 shows this plot for $In_xTe_8Se_{92-x}$ glasses.

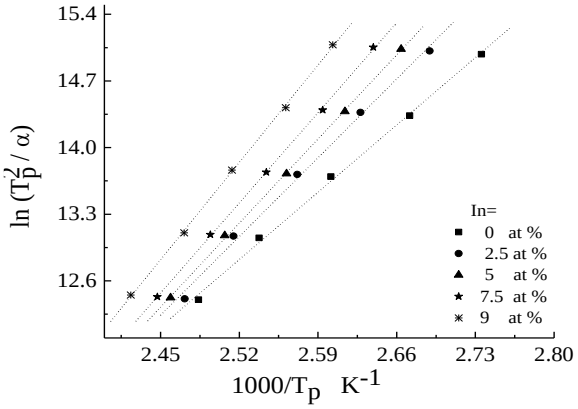

Figure5: $\ln[T_p^2/\alpha]$ vs. $1/T_p$ for $In_xTe_8Se_{92-x}$ ($0 \le x \le 9$) chalcogenides.

The total amount of the alloy crystallized is directly proportional to area under DSC curve. The corresponding crystallization rates $(d\chi/dt)_p$ is the ratio between the ordinates and the total area of the peak. In accordance the preceding theory, the sample was reheated up to a temperature slight larger than T_g for 1 hour to forming a large number of nuclei. Based on the experimentally results, It was shown that,

Published By:
Blue Eyes Intelligence Engineering
and Sciences Publication (BEIESP)

The correlation coefficients of the corresponding straight regression lines show a maximum value for a given temperature, which is the most suitable to calculate the n using Eq.(21). The value of n for the as-prepared glass isn't equal to that for the treated glass. This confirms that, the as prepared glass is free from any nuclei thus, *n= m+1* for $In_xTe_8Se_{92-x}$ glasses. The kinetic parameters n and m are calculated depending on the crystallization mechanism. The n value decreases from 3 to 2 with increasing the content of indium. The value of n *=2* for the as prepared glass corresponding to the mechanism of volume nucleation with one dimensional growth and *n= 3* corresponding to volume nucleation mechanism with two dimensional growth. At the final it was worth mentioned that, Eq. 25 gives m values which confirm the rule of *n=m+1* for $In_xTe_8Se_{92-x}$.

V. CONCLUSIONS

Adding the In content into $Se_{92}Te_8$ glass results in: Increasing the T_g, T_c, and T_p with the increasing the content of In consequently both the activation energy of glass transition, E_g, and crystallization, E_c are increase. The observed results well explained in terms of the approach of chemical bonds, the mean heat of atomizations and cohesive energies (CE). Successful applied of Afify's method gives accurate values of E_c, and *n*.

REFERENCES

1. D.C. Jain, K.S. Jerath, H.S. Chauhan, K.B. Garg, U. Chandra, R.K. Singhal, K.V. Ramanna Rao, G. Parthasarathy, E.S.R. Gopal, XANES STUDY OF Se-Te GLASSES, Key Eng Mater, 13 (1986) 148.
2. V. Sharma, A. Thakur, Phase transition in Se-Te thin film on UV illumination, Journal of Optoelectronics and Advanced Materials, 9 (2007) 3097-3099.
3. C. Allen, G. Belev, R. Johanson, S.O. Kasap, Relaxation of electrical properties of stabilized amorphous selenium based photoconductors, Journal of Non-Crystalline Solids, 354 (2008) 2711-2714.
4. T.T. Nang, T. Matsushita, M. Okuda, A. Suzuki, PHOTOVOLTAIC EFFECT OBSERVED ON THE CONSTRUCTION OF METAL-AMORPHOUS In//xSe//1// minus //x THIN FILM-SnO//2 SYSTEM, Jpn J Appl Phys, 16 (1977) 253-257.
5. S. Singh, R.S. Sharma, R.K. Shukla, A. Kumar, Steady state photoconductivity in a-Se90Ge10-xIn x thin films, Journal of Optoelectronics and Advanced Materials, 6 (2004) 769-776.
6. A.M. Abd Elnaeim, K.A. Aly, N. Afify, A.M. Abousehlly, Glass transition and crystallization kinetics of $In_x(Se0.75Te0.25)_{100-x}$ chalcogenide glasses, Journal of Alloys and Compounds, 491 (2010) 85-91.
7. V.A. Kulbachinskii, Z.M. Dashevskii, M. Inoue, M. Sasaki, H. Negishi, W.X. Gao, P. Lostak, J. Horak, A. De Visser, Valence-band changes in Sb2-xInxTe3 and Sb2Te3-ySey by transport and Shubnikov-de Haas effect measurements, Physical Review B, 52 (1995) 10915-10922.
8. A.S. Maan, D.R. Goyal, Study of crystallization kinetics of Te5(InxSe100-x)95 glassy alloys, Chalcogenide Letters, 4 (2007) 89-96.
9. A.S. Maan, D.R. Goyal, A. Kumar, Investigation of optical absorption in Te5(InxSe100-x)95 glassy alloys, Chalcogenide Letters, 4 (2007) 48-53.
10. N. El-Kabnay, E.R. Shaaban, N. Afify, A.M. Abou-sehly, Optical and physical properties of different composition of InxSe1-x thin films, Physica B: Condensed Matter, 403 (2008) 31-36.
11. K.A. Aly, A.M. Abousehly, A.A. Othman, Photoelectrical properties of $(Sb_{15}As_{30}Se_{55})_{100-x}Te_x$ ($0 \le x \le 12.5$ at.%) thin films, Journal of Non-Crystalline Solids, 354 (2008) 909-915.
12. K.A. Aly, A.M. Abd Elnaeim, N. Afify, A.M. Abousehly, Improvement of the electrical properties of Se_3Te_1 thin films by in additions, Journal of Non-Crystalline Solids, 358 (2012) 2759-2763.
13. (!!! INVALID CITATION !!!).
14. N. Afify, A new method to study the crystallization or chemical reaction kinetics using thermal analysis technique, Journal of Physics and Chemistry of Solids, 69 (2008) 1691-1697.
15. K.A. Aly, M.Y. Hassaan, Y.B. Saddeek, Thermal features and physical properties of sulfur modified barium vanadate glasses, Phase Transitions, 86 (2013) 477-489.
16. K.A. Aly, A. Dahshan, F.M. Abdel-Rahim, Thermal stability of Ge-As-Te-In glasses, Journal of Alloys and Compounds, 470 (2009) 574-579.
17. A.A. Abu-Sehly, Variation of the activation energy of the glass transition in amorphous Se thin film: Isoconversional analysis, Thermochimica Acta, 501 (2010) 103-107.
18. N.B. Maharjan, D. Bhandari, N.S. Saxena, D.D. Paudyal, M. Husain, Kinetic studies of bulk $Se_{85-x}Te_{15}Sb_x$ glasses with x = 0, 2, 4, 6, 8 and 10, Physica Status Solidi (A) Applied Research, 178 (2000) 663-670.
19. A.A. Othman, K.A. Aly, A.M. Abousehly, Glass transition and crystallization kinetics of Sb 14.5As 29.5Se 53.5Te 2.5 amorphous solid, Physica Status Solidi (A) Applications and Materials Science, 203 (2006) 837-843.
20. A.A. Othman, K.A. Aly, A.M. Abousehly, Crystallization kinetics in new Sb14As29Se52Te5 amorphous glass, Solid State Communications, 138 (2006) 184-189.
21. K.A. Aly, F.M. Abdel Rahim, A. Dahshan, Thermal analysis and physical properties of Bi-Se-Te chalcogenide glasses, Journal of Alloys and Compounds, 593 (2014) 283-289.
22. A. Dahshan, K.A. Aly, M.T. Dessouky, Thermal stability and activation energy of some compositions of Ge-Te-Cu chalcogenide system, Philosophical Magazine, 88 (2008) 2399-2410.
23. A.A. Othman, H.H. Amer, M.A. Osman, A. Dahshan, Non-isothermal crystallization kinetics study on new amorphous Ga 20Sb5S75 and Ga20Sb 40S40 chalcogenide glasses, Journal of Non-Crystalline Solids, 351 (2005) 130-135.
24. V. Dimitrov, T. Komatsu, Communication: Coordination number changes of tellurium and group optical basicity of ZnO-TeO2 glasses, Physics and Chemistry of Glasses: European Journal of Glass Science and Technology Part B, 50 (2009) 395-398.
25. M.M. El-Samanoudy, A.H. Ammar, Some Physical and Optical Properties of the a-Se85SbxS15-x Film System, Physica Status Solidi (A) Applied Research, 187 (2001) 611-621.
26. K.A. Aly, A. Dahshan, A.M. Abousehly, Compositional dependence of the optical properties of amorphous $Se_{100-x}Te_x$ thin films, Philosophical Magazine, 88 (2008) 47-60.
27. L. Tichý, H. Tichá, M. Frumar, J. Klikorka, A. Tříska, C. Barta, A. Němečková, Index of refraction and d. c. electrical conductivity in Ge40-xSbxS60 glasses, Czechoslovak Journal of Physics, 32 (1982) 1363-1373.
28. J. Bicerano, S.R. Ovshinsky, Chemical bond approach to glass structure, Journal of Non-Crystalline Solids, 75 (1985) 169-175.
29. D. Adler, S.R. Ovshinsky, AMORPHOUS PHOTOVOLTAICS, CHEMTECH, 15 (1985) 538-546.
30. V. SADAGOPAN, H.C. GATOS, on the relationship of semiconductor compound properties and the average heats of atomisation, Solid-State Electronics, 8 (1965) 529-534.
31. L. Pauling, The dependence of bond energy on bond length, Journal of Physical Chemistry, 58 (1954) 662-666.

Published By:
Blue Eyes Intelligence Engineering and Sciences Publication (BEIESP)