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OBSERVATION OF COMPENSATION EFFECT FOR ISOTHERMAL CRYSTALLIZATION IN GLASSY $Se_{80-x}Ge_{20}In_x$ and $Se_{78-x}Ge_{22}Bi_x$ ALLOYS

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Many activated phenomena, including solid state diffusion in crystals and polymers, dielectric relaxation, conduction and thermally stimulated processes in polymers, and electronic conduction in amorphous semiconductors obey the compensation law or Meyer-Neldel rule. In the present paper, we discuss the results of investigation into the compensation effect observed under isothermal crystallization in glassy $Se_{70}Te_{30-x}Sb_x$ alloys. It is found that the relation between the pre-exponential factor K_o and activation energy of crystallization E_c follows the Meyer – Neldel rule for the alloys studied.

1. INTRODUCTION

In studying properties inherent in disordered materials, certain properties, e.g., conductivity and diffusion, are found to exhibit exponential thermally activated (Arrhenius) behavior

$$Z = Z_0 \exp\left(\frac{-\Delta E}{kT}\right) \tag{1}$$

Here Z is the absolute rate of a thermally activated process, Z_0 is the pre-exponential factor, ΔE is the activation energy, and k is the Boltzmann constant.

It was shown in [1] that Z_0 is related with ΔE by the following relation:

$$Z = Z_0 \exp\left(\frac{\Delta E}{E_{MN}}\right), \tag{2}$$

where Z_{00} and E_{MN} are positive constants. E_{MN} is known as the Meyer–Neldel energy for the process under consideration. This empirical relation is known as the MN relation or compensation effect [1]. The compensation effect was observed in a wide variety of materials for a number of phenomena [2–8]. In the class of amorphous semiconductors, the effect was found in a-Si:H films in which ΔE was varied by doping, surface absorption, lighting, or by producing films under different conditions [9–11].

In the case of chalcogenide glasses, the activation energy ΔE of d. c. conduction was changed , fulfilling the MN rule, by varying either the composition of certain glassy alloys [12–16] or intensity of lighting [17, 18].

Though the results of investigation into the MN effect have been reported for a number of activated phenomena such as solid state diffusion in crystals and polymers, dielectric relaxation and conduction in polymers, thermally stimulated processes in polymers, and electronic conduction in amorphous semiconductors [2–8], less effort has been made to study the MN effect in the kinetic phenomena such as crystallization.

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In this paper, we discuss the results of investigation into applicability of the MN rule to isothermal crystallization in glassy $Se_{80-x}Ge_{20}In_x$ ($0 \le x \le 20$) and $Se_{78-x}Ge_{22}Bi_x$ ($0 \le x \le 10$) alloys. A strong correlation between the pre-exponential factor K_0 and activation energy of crystallization E_c is revealed.

2. EXPERIMENTAL

Glassy alloys of $Se_{80-x}Ge_{20}In_x$ ($0 \le x \le 20$) and $Se_{78-x}Ge_{22}Bi_x$ ($0 \le x \le 10$) were produced by means of quenching. Exact proportions of high purity (99.999%) Se, Ge, In, and Bi elements, in accordance with their atomic percentage, were weighed using an electronic balance (LIBROR, AEG-120) accurate to 10^{-4}gm. The material was then sealed in evacuated (~ 10^{-5} Torr) quartz ampoules (length ~5 cm and internal diameter ~8 mm). The ampoules containing material were heated to 1000°C and held at that temperature for 12 hours. The temperature of the furnace was slowly increased at a rate of 3–4°C/minute. During heating, the ampoules were constantly rocked, by rotating a ceramic rod to which the ampoules were fixed. This was done to produce homogeneous glassy alloys.

After rocking for about 12 hours, the obtained melts were rapidly cooled by removing the ampoules from the furnace and putting them into ice-cool water. The quenched samples were then taken out by breaking the quartz ampoules. The glasses, thus prepared, were ground to make fine powder and the pellets (diameter ~6 mm and thickness ~ 0.5–1 mm) were obtained after compressing the powder in a die at a load of $3\text{–}4 \times 10^4$ N.

The isothermal amorphous to crystalline (a-c) phase transformation was studied by measuring the d.c. conductivity σ as a function of time (1–2 min intervals) at various annealing temperatures between the glass transition and crystallization temperatures. The annealing temperature T was kept constant during the a-c phase transformation period. The pronounced increase in σ suggests that at any time t, σ is the result of two conductivities σ_a and σ_c , which corresponds to a double phase system, amorphous and crystalline.

The conductivity was measured in vacuum ~10^{-2} Torr by mounting the samples in a specially designed sample holder. The resistance was measured using a Kiethely Electrometer (model 614). The temperature was measured using a calibrated constantan thermocouple. Different pellets were taken for each value of T. The annealing temperature T was attained at a fast heating rate and then maintained constant until saturation in resistance was obtained.

3. THEORETICAL BASIS

Crystallization kinetics in chalcogenide glasses can be investigated using isothermal and non-isothermal methods [19–26]. In isothermal methods, the sample is heated close to crystallization temperature very quickly and then any physical, drastically changing quantity is measured as a function of time. In non-isothermal methods, the sample is heated at a fixed rate and the physical parameters are recorded as a function of temperature. Any physical, drastically changing parameter can be taken as a measure of extent of crystallization depending on time. It was found in [19–26] that the values of activation energy of crystallization determined by isothermal methods are in good agreement with those calculated using a non-isothermal DSC technique. This proves the applicability of Avrami's equation to description of changes in conductivity in amorphous to crystalline phase transition (a-c phase transformation) as suggested in [19].

During the isothermal transformation, the extent of crystallization (α) of a certain material is represented by Avrami's equation [27] as

$$\alpha(t) = 1 - \exp(-Kt^n) \tag{3}$$

where K is the rate constant and n is the order parameter which depends upon the mechanism of crystal growth.

In general, the crystallization rate constant K increases exponentially with temperature, indicating that crystallization is a thermally activated process. Mathematically, it can be expressed as

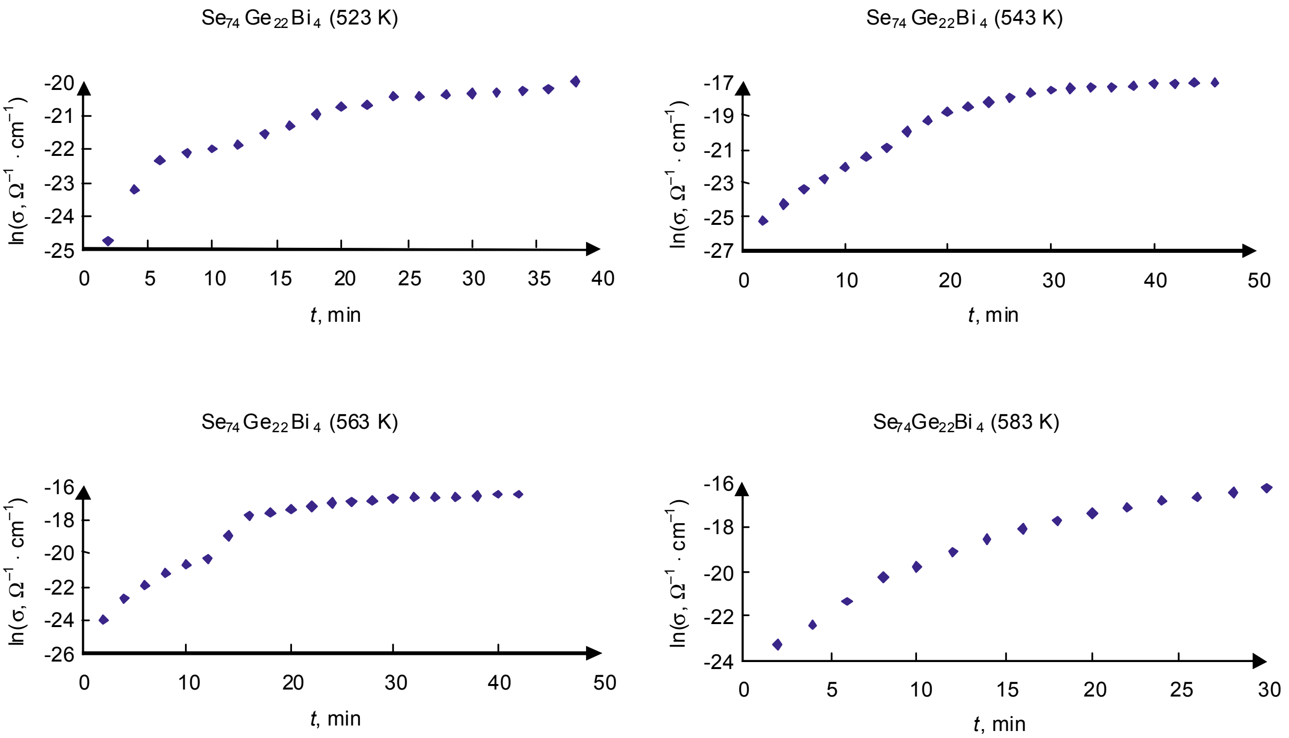

Fig. 1. Annealing time dependence of d.c. conductivity for a glassy $Se_{74}Ge_{22}Bi_4$ alloy at different annealing temperatures.

$$K = K_0 \exp\left(\frac{-E_c}{kT}\right), \tag{4}$$

where E_c is the activation energy of crystallization and K_0 is the pre-exponential factor. The foregoing equation is referred to as the Arrhenius law and is used to determine the activation energy of crystallization.

The extent of crystallization (α) was calculated using the following relation [28, 29]:

$$\alpha = \frac{(\ln\sigma - \ln\sigma_a)}{(\ln\sigma_c - \ln\sigma_a)}. \tag{5}$$

4. RESULTS AND DISCUSSION

Figure 1 shows the time dependence of ln σ during the a-c phase transformation of glassy $Se_{74}Ge_{22}Bi_4$ alloys at different annealing temperatures in the temperature range 520–590 K. The results for other glassy alloys were similar. During the phase transformation process, there appears to be three regimes in ln σ vs annealing time t curves. The first regime in Fig. 1 is linear and represents a gradual increase in σ as a result of normal heating of the glassy alloys. Somewhat less pronounced increase in σ during the second regime is mostly accompanied by nucleation and nucleus growth due to the parent amorphous phase. The third regime, which covers a relatively large increase in σ, indicates further crystal growth of a new phase until maximum crystallization of the sample volume. Once the values of σ_a and σ_c are known at different isothermal annealing temperatures, the value of α as a function of time can be calculated using Eq. (5).

Equation (3) can be rewritten as

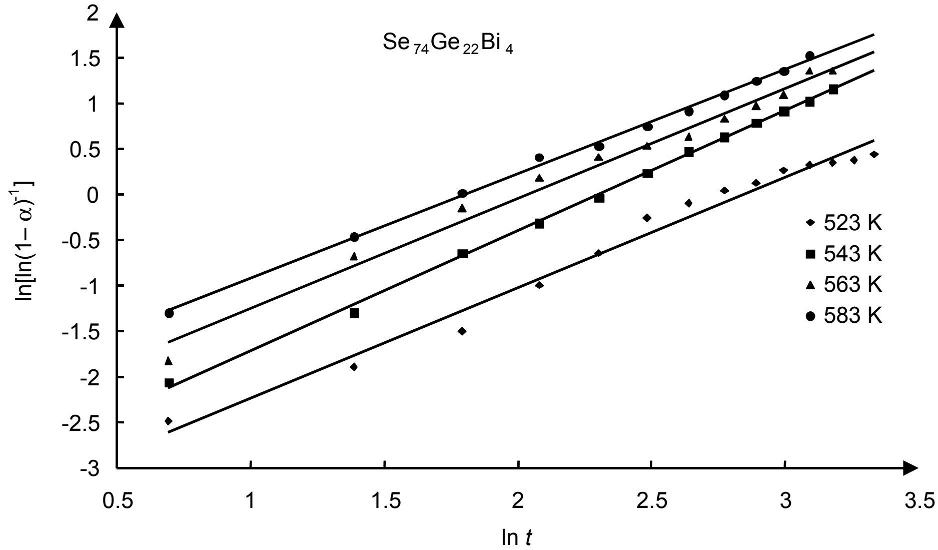

Fig. 2. ln [ln (1 – α)$^{-1}$] vs ln *t* for a glassy $Se_{74}Ge_{22}Bi_4$ alloy.

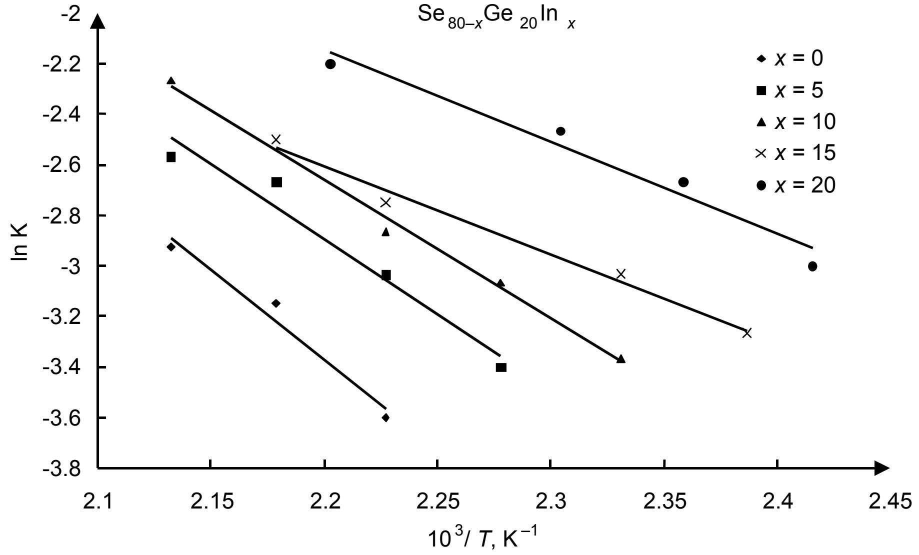

Fig. 3. ln K vs 1000 / *T* for a glassy $Se_{80-x}Ge_{20}In_x$ alloy.

$$\ln[\ln(1-\alpha)^{-1}] = \ln K + n \ln t \,. \tag{6}$$

According to Eq. (6), the plot of ln [ln (1 – α)$^{-1}$] vs ln *t* leads to a straight line of intercept ln K. This was verified for the glassy $Se_{74}Ge_{22}Bi_4$ alloy in Fig. 2. Similar plots were obtained for other glassy alloys.

The values of the temperature dependent crystallization rate constant K, calculated from the intercepts of ln [ln (1 – α)$^{-1}$] vs ln *t* curves are plotted as a function of temperature. Such plots are shown in Fig. 3 for glassy $Se_{80-x}Ge_{20}In_x$ ($0 \le x \le 20$) alloys. The straight line, thus obtained, confirms the validity of Eq. (4). Similar plots were constructed for glassy $Se_{78-x}Ge_{22}Bi_x$ ($0 \le x \le 10$) alloys. The values of E_c and ln K_0 for various alloys obtained from the slopes of ln K vs $10^3 / T$ curves are given in Tables 1 and 2.

TABLE 1. Values of E_c and ln K_0 for glassy $Se_{80-x}Ge_{20}In_x$ alloys

Composition	E_c (e V)	ln K_0	ln K_0 = ln K_{00} + [E_c / k T_0]
$Se_{80}Ge_{20}$	0.61	12.29	12.42
$Se_{75}Ge_{20}In_5$	0.51	10.14	10.09
$Se_{70}Ge_{20}In_{10}$	0.47	9.37	9.21
$Se_{65}Ge_{20}In_{15}$	0.30	5.07	5.36
$Se_{60}Ge_{20}In_{20}$	0.31	5.88	5.67

TABLE 2. Values of E_c and ln K_0 for glassy $Se_{78-x}Ge_{22}Bi_x$ alloys

Composition	E_c (e V)	ln K_0	ln K_0 = ln K_{00} + [E_c / k T_0]
$Se_{78}Ge_{22}$	0.63	11.40	11.14
$Se_{76}Ge_{22}Bi_2$	0.53	9.32	9.12
$Se_{74}Ge_{22}Bi_4$	0.48	7.77	8.26
$Se_{70}Ge_{22}Bi_8$	0.36	5.58	5.89
$Se_{68}Ge_{22}Bi_{10}$	0.25	4.02	3.65

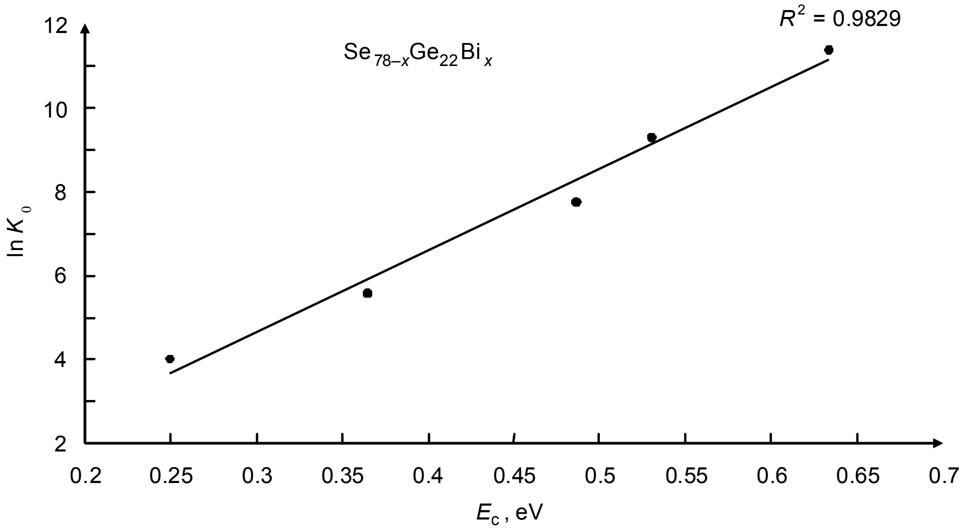

Fig. 4. ln σ_0 versus E_c for $Se_{80-x}Ge_{20}In_x$ alloys.

It is clear from these tables that E_c and K_0 are composition dependent and K_0 is not a constant but depends on E_c. Figures 4 and 5 show the plots of ln K_0 vs E_c for glassy $Se_{80-x}Ge_{20}In_x$ ($0 \le x \le 20$) and $Se_{78-x}Ge_{22}Bi_x$ ($0 \le x \le 10$) alloys. Curve fitting is done by the least squares method, and the square of coefficient of correlation (R^2) of the ln K_0 vs E_c plot is shown in Figs. 4 and 5. It is evident, that ln K_0 vs E_c plot is a straight line of good correlation coefficient indicating that K_0 varies exponentially with E_c following the relation

$$\ln K_0 = \ln K_{00} + \frac{E_c}{k\,T_0}. \tag{7}$$

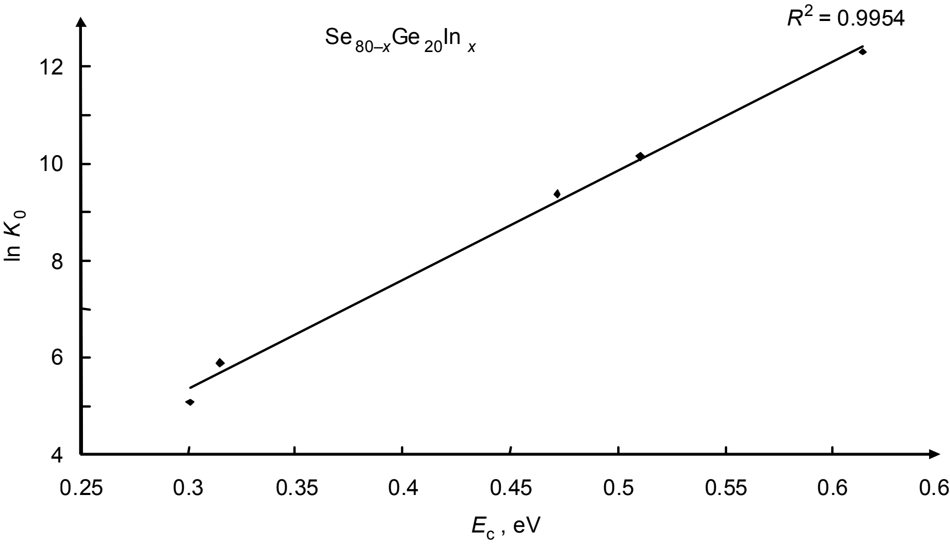

Fig. 5. ln σ_0 versus E_c for $Se_{78-x}Ge_{22}Bi_x$ alloys.

From the slope and intercept of the line, we have calculated the values of $(kT_0)^{-1}$ and K_{00} for the glassy Se–Ge–In and Se–Ge–Bi systems. Using these values, the expected ln K_0 values were calculated for the glassy $Se_{80-x}Ge_{20}In_x$ and $Se_{78-x}Ge_{22}Bi_x$ alloys and compared with the reported values (see Tables 1 and 2). General good agreement between these two values supports the validity of the MN relation for glassy $Se_{80-x}Ge_{20}In_x$ and $Se_{78-x}Ge_{22}Bi_x$ alloys.

Different models or assumptions to explain the MN rule for such kinetic phenomena were developed and discussed in [30–33]. The concluding remarks of the models or assumptions are given below:

The applicability of the MN rule for some chalcogenide glasses in the Se–Ge–Sb system was considered in [30, 31]. Annealing some Se–Ge–Sb glasses, the workers observed two crystalline phases: Sb_2Se_3 and $GeSe_2$. According to [30, 31], such a compensation effect may be attributed to primary crystallization of the Sb_2Se_3 phase. In glassy Se–Ge–In and Se–Ge–Bi systems, there are two well known crystalline phases: (1) In_2Se_3 and $GeSe_2$ for the glassy Se–Ge–In system [34, 35] and (2) Bi_2Se_3 and $GeSe_2$ for the glassy Se–Ge–Bi system [36], which are not crystallized simultaneously. This may be the reason for observation of the compensation effect in the foregoing glasses of the Se–Ge–In and Se–Ge–Bi systems as suggested by Bordas *et al.* In [32], a model for the MN rule in activated processes was developed. According to this model, the annealing time parameter obeys the MN rule. As the rate constant K also depends on annealing time, our results confirm the validity of the model proposed in [32]. In [33], it was shown that the kinetic compensation effect mathematically results from the exponential form of the rate constant. A change of activation energy is thus compensated by the same change in temperature or in the logarithm of the pre-exponential factor. Our results also show that an increase in E_c is compensated by an increase in the pre-exponential factor K_0. The activation energy and pre-exponential factor satisfies the MN rule for the glassy $Se_{80-x}Ge_{20}In_x$ and $Se_{78-x}Ge_{22}Bi_x$ alloys.

5. CONCLUSION

Glassy $Se_{80-x}Ge_{20}In_x$ ($0 \le x \le 20$) and $Se_{78-x}Ge_{22}Bi_x$ ($0 \le x \le 10$) alloys were produced by means of quenching. The temperature dependence of crystallization rate constant K(T) was studied at various annealing temperatures. We found that crystallization is a thermally activated process, with the activation energy, however, depending on the composition.

It was also found that the activation energy and pre-exponential factor satisfy the MN rule for the glassy $Se_{80-x}Ge_{20}In_x$ and $Se_{78-x}Ge_{22}Bi_x$ alloys. This testifies to the fact that the MN effect, which is generally observed for solid state diffusion in crystals and polymers, dielectric relaxation and conduction in polymers, thermally stimulated processes in polymers, and electronic conduction in amorphous semiconductors is also characteristic for isothermal crystallization in chalcogenide glasses.

REFERENCES

1. W. Meyer, H. Neldel, Zh. Tech. Phys., **18**, 588 (1937).
2. J. Deren, J. Haber, A. Podgorecka, J. Burzyk, J. Catalysis, **2**, 161 (1963).
3. L. D. Ahuja, A. S. Brar, J. Coll. Inter. Sci., **50**, 197 (1975).
4. T. Dosdale, R. J. Brook, Solid State Ionics, **8**, 297 (1983).
5. R. Metselaar, G. Oversluizen, J. Sol. Stat. Chem., **55**, 320 (1984).
6. J. W. Niemantsverdriet, K. Markert, K. Wandelt, Applied Surface Science, **31**, 211 (1988).
7. W. Bogusz, D. E. Kony, F. Krok, Mater. Sci. Eng. B, **15**, 169 (1992).
8. G. C. Bond, Catalysis Today, **49**, 41 (1999).
9. W. E. Spear, D. Allan, P. Lecomber, A. Gaith, Phil. Mag. B, **41**, 419 (1980).
10. M. Tanielian, Phil. Mag. B, **45**, 435 (1982).
11. R. S. Crandall, Phys. Rev. B, **43**, 4057 (1991).
12. R. Arora, A. Kumar, Phys. Stat. Sol. A, **1125**, 273 (1991).
13. S. K. Dwivedi, M. Dixit, A. Kumar, J. Mater. Sci. Lett., **17**, 233 (1998).
14. A. Abd-El Mongy, Egypt. J. Sol., **24**, 207 (2001).
15. Y. L. A. Ei-Kady, Physica B, **305**, 259 (2001).
16. D. Kumar, S. Kumar, Bull. Mater. Sci., **27**, 101 (2004).
17. D. Kumar, S. Kumar, Vacuum, **74**, 113 (2004).
18. D. Kumar, S. Kumar, J. Optoelectron. Adv. Mater., **6**, 777 (2004).
19. P. Agarwal, S. Goel, A. Kumar, J. Phys. III, **1**, 1429 (1991).
20. S. K. Agrahari, R. Arora, A. Kumar, Physica B, **191**, 203 (1993).
21. A. Singh, A. K. Nagpal, A. Kumar, Adv. Mater. Optics Electron., **9**, 95 (1999).
22. A. Singh, J. S. P. Rai, A. Kumar, Adv. Mater. Optics Electron., **9**, 107 (1999).
23. S. A. Khan, M. Zulfequar, M. Husain, J. Mater Sci., **21**, 1085 (2002).
24. S. A. Khan, M. Zulfequar, M. Husain, Curr. Appl. Phys., **3**, 337 (2003).
25. F. A. Abdel-Wahab, S. A. El-Hakim, M. F. Kotkata, Physica B, **366**, 38 (2005).
26. N. Mehta, A. Kumar, J. Therm. Anal. Calor., **83**, 669 (2006).
27. M. Avrami, J. Chem. Phys., **8**, 212 (1940).
28. V. I. Odelevsky, J. Tech. Phys., **21**, 673 (1951).
29. M. F. Kotkata, A. F. El-Dib and F. A. Gani, Mater. Sci. Eng., **72**, 163 (1985).
30. S. Bordas, M. T. Clavaguera-Mora, N. Clavaguera, Thermochimica Acta, **133**, 293 (1988).
31. S. Bordas, M. T. Clavaguera-Mora, N. Clavaguera, J. Non-Cryst. Sol., **119**, 232 (1990).
32. P. H. Fang, Phys. Lett. A, **30**, 217 (1969).
33. N. Koga, J. Sestak, Thermochimica Acta, **182**, 201 (1991).
34. M. K. Rabinal, K. S. Sangunni, E. S. R. Gopal, J. Non-Cryst. Sol., **188**, 98 (1995).
35. J. M. Saiter, J. Ledru, G. Saffarini, S. Benazeth, Mat. Lett., **28**, 451 (1996).
36. N. A. Bhat, K. S. Sangunni, Sol. Stat. Commun., **116**, 297 (2000).