

PACS 61.43.Dq, 71.55.Jv, 78.40.Fy

Role of Sb additive in the dielectric properties of $\text{Se}_{90}\text{In}_{10}$ and $\text{Se}_{75}\text{In}_{25}$ glassy alloys

J. Sharma, S. Kumar¹

Department of Physics, Christ Church College, Kanpur-208001, India

¹Corresponding author phone: +91-512-2573069, e-mail: dr_santosh_kr@yahoo.com

Abstract. In this paper, we report the effect of Sb additive on dielectric properties of two binary Se–In glassy systems, comparing the properties of a- $\text{Se}_{90}\text{In}_{10}$, a- $\text{Se}_{75}\text{In}_{25}$ and a- $\text{Se}_{75}\text{In}_{10}\text{Sb}_{15}$ glassy alloys. The temperature and frequency dependence of ϵ' and ϵ'' in glassy $\text{Se}_{90}\text{In}_{10}$, $\text{Se}_{75}\text{In}_{25}$, and $\text{Se}_{75}\text{In}_{10}\text{Sb}_{15}$ alloys are studied by measuring the capacitance and dissipation factor within the frequency 1 kHz–5 MHz and temperature 300–350 K ranges. Debye like relaxation of dielectric behavior has been observed, which is in agreement with the Guintini theory of dielectric dispersion based on two electron hopping over a potential barrier and is applicable in the present case. ϵ' , ϵ'' and loss tangent ($\text{Tan } \delta$) are found highly frequency and temperature dependent. Dependence of these dielectric parameters on the Sb metallic impurity has also been found in the present glassy system. The peculiar role of the third element Sb, as an impurity in the pure binary $\text{Se}_{90}\text{In}_{10}$ and $\text{Se}_{75}\text{In}_{25}$ glassy alloys, is also discussed in terms of electronegativity difference and covalent character between the elements used in making the aforesaid glassy system..

Keywords: chalcogenide glasses, dielectric measurement, defect state.

Manuscript received 26.01.11; accepted for publication 16.03.11; published online 30.06.11.

1. Introduction

The study of dielectric behavior of chalcogenide glasses is expected to reveal structural information which, in effect, can be useful for understanding the conduction mechanism as well. In addition, a study of temperature dependence of dielectric permittivity, particularly in the range of frequencies where dielectric dispersion occurs, can be of great importance to understand the nature and origin of losses occurring in these materials. Recently [1, 2] it has been reported that in chalcogenide glasses the dielectric dispersion does exist at low frequencies even though these materials are covalently bonded semiconductors. Glassy Se – In alloys have attracted great attention because of their potential application in solar cells [3-5]. The effect of incorporation of a third element into binary chalcogenide glassy alloys has always been an interesting problem in getting relatively stable glassy alloys as well as to change the conduction type from *p* to *n* as most of these glasses show *p*-type conduction only. In Ge – Se and Se – In systems, some metallic additives have been found to change conduction

from *p*- to *n*-type and hence these binary systems are of great importance. However, in these glasses limited reversibility and low crystallization temperatures are serious problems. These problems can be overcome by addition of a third element as a chemical modifier. The addition of dopant can modify the lattice perfection. Thus, there is need to predict the suitability of various glass compositions, with the dielectric relaxation being a key parameter.

From the above viewpoint, the effect of incorporation of some metallic impurities into glassy Se – In alloys has been reported by many workers in a series of papers. Electrical conductivity and relaxation of Se – S – In glasses has been studied by [6]. Electrical conduction mechanism in Se – In – Pb has been studied by [7]. Thermoelectric power measurements in the glassy Se – In system have been made by [7]. Optical band gap of amorphous thin films Se – In has been determined by [8]. Enthalpy recovery during relaxation and crystallization kinetics before and after slow neutron radiation has also been reported in glassy $\text{Se}_{96}\text{In}_4$ alloy by [9, 10].

Work was supported by University Grants Commission (UGC), New Delhi.

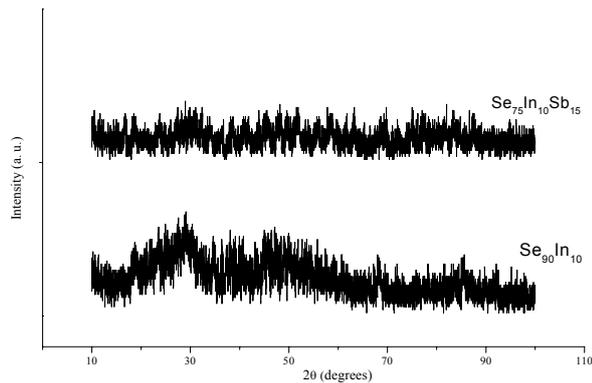


Fig. 1. X-ray diffraction pattern of $\text{Se}_{90}\text{In}_{10}$ and $\text{Se}_{75}\text{In}_{10}\text{Sb}_{15}$ glassy alloys.

In view of the above, we have decided to study the effect of Sb impurity on dielectric properties of two well-known binary $\text{Se}_{90}\text{In}_{10}$ and $\text{Se}_{75}\text{In}_{25}$ glassy systems. The next section describes the experimental details of the measurements. The results are presented and discussed in the third section. The final section deals with the conclusions drawn from this work.

2. Experimental details

2.1. Preparation of glassy alloys

Glassy alloys of $\text{Se}_{90}\text{In}_{10}$, $\text{Se}_{75}\text{In}_{25}$ and $\text{Se}_{75}\text{In}_{10}\text{Sb}_{15}$ systems were prepared by quenching technique. High purity (99.999 %) materials were weighed according to their atomic percentages and were sealed in silica ampoules (length ~ 5 cm and internal diameter ~ 8 mm) with vacuum $\sim 10^{-5}$ Torr. The ampoules containing the materials were heated up to 900 °C and held at that temperature for 10-12 hours. The temperature of the furnace was raised slowly at a rate ~ 3 - 4 °C/min. During heating, all the ampoules were constantly rocked, by rotating a ceramic rod to which the ampoules were tucked in the furnace. This was done to obtain homogenous glassy alloys.

After rocking for about 10 hours, the obtained melts were cooled rapidly by removing the ampoules from the furnace and dropping to ice-cooled water. The quenched samples were taken out by breaking the silica ampoules. The amorphous nature has been checked by XRD. Fig. 1 shows XRD plots of $\text{Se}_{90}\text{In}_{10}$ and $\text{Se}_{75}\text{In}_{10}\text{Sb}_{15}$ glassy alloys. Compositional analysis was performed using electron probe microanalysis (EPMA) technique.

Pellets of diameter ~ 10 mm and thickness $\sim (1-2)$ mm were prepared by compressing the finely grounded powder in a die in a hydraulic press under a load of ~ 3 - 4 tons. Measurements were performed after coating the pellets with indium film deposited by vacuum evaporation technique.

2.2. Dielectric relaxation measurements

A specially designed metallic sample holder was used for the measurements of dielectric parameters in vacuum $\sim 10^{-3}$ Torr. The pellets were mounted in between two steel electrodes of the sample holder. The temperature was measured using a calibrated copper-constantan thermocouple mounted very near to the sample, which could provide measurements of temperature with an accuracy of 1 °C. The temperature dependence of the dielectric constant (ϵ') and dielectric losses (ϵ'') were studied in a heating run at a heating rate of 1 K/min. The frequency dependences of ϵ' and ϵ'' were also measured by maintaining constant temperature inside the sample holder.

Dielectric measurements were made using a “Hioki 3532-50 LCR Hi TESTER”. The parallel capacitance and dissipation factor were measured, and then ϵ' and ϵ'' were calculated using it. Three-terminal measurements were performed to avoid the stray capacitances.

We preferred to measure dielectric behavior of the pellet rather than of the bulk samples, as macroscopic effects (gas bubbles, etc.) may appear in the bulk during preparation. It has been shown by (Goyal et al., 1981), both theoretically and experimentally, that bulk ingots and compressed pellets exhibit similar dielectric behavior in chalcogenide glasses for the suspected inhomogeneities in case of compressed pellets in these materials. The number of localized sites induced by grain boundary effects can be neglected as compared to charged defect states which are quite large ($\sim 10^{18}$ to 10^{19} $\text{eV}^{-1}\text{cm}^{-3}$) in these glasses. Microsoft Excel programming has been used for more accurate calculations in this study.

3. Results and discussion

3.1. Dielectric behavior of various glassy alloys

Temperature dependences of ϵ' and ϵ'' were measured at various frequencies (1 kHz to 5 MHz) for various glassy alloys studied in our case. The measurements have been performed within the temperature range 300 to 350 K. ϵ' and ϵ'' were found to be temperature dependent in the above frequency range in all the glassy samples studied here. (See Figs 2 and 3 for aforesaid glassy alloys.) ϵ' and ϵ'' increase with the increase of temperature, the increase being different for various frequencies. This type of behavior has been reported by various workers [11, 12] in chalcogenide glasses. Since in chalcogenide glasses, the dielectric properties can be interpreted by considering a set of dipoles as long as the temperature is increased high. Each dipole has a relaxation time depending on its activation energy, which is attributed to the existence of a potential barrier over which the carrier can hop. Because of containing

dipoles, the contribution due to dipolar or orientational polarization dominates at low frequencies.

As the frequency increases high, dipolar or orientational polarization normally removes due to inertia of molecules and the electronic polarization contributes. Thus, the dispersion is low at high frequencies. Since the orientational or dipolar polarization is associated with the thermal motion of pair of charges. The orientation of the dipoles increases as the temperature increases, leading to the increase of dielectric constant.

It has been also found that ϵ' decreases with increasing the frequency. In dielectric spectroscopy, large frequency dependent contributions to the dielectric response, especially at low frequencies, may come from build-ups of charge. This, the so-called Maxwell-Wagner polarization occurs either at inner dielectric boundary layers on a microscopic scale, or at the external electrode-sample interface on a macroscopic scale. In both cases, this leads to a separation of charges. The charges are often separated over a considerable distance, and the contribution to dielectric response can therefore be orders of magnitude larger than the dielectric response due to molecular vibration that occurs at high frequencies, because at high frequencies the energy is too high to cause rotation, yet too low to effect electrons directly, and is absorbed in the form of molecular vibrations. Thus, ϵ' decreases with increasing the frequency. This type of behavior at low and high frequencies comes under interfacial polarization.

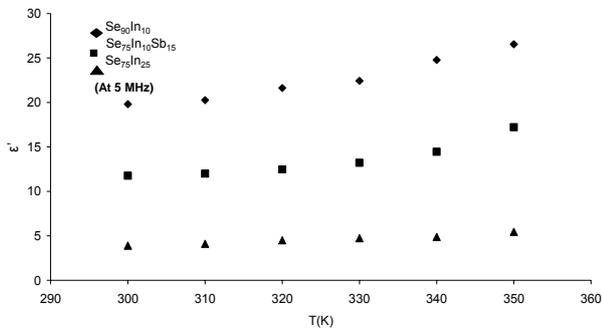


Fig. 2. Temperature dependences of the dielectric constant (ϵ') in all the glassy alloys at 5 MHz.

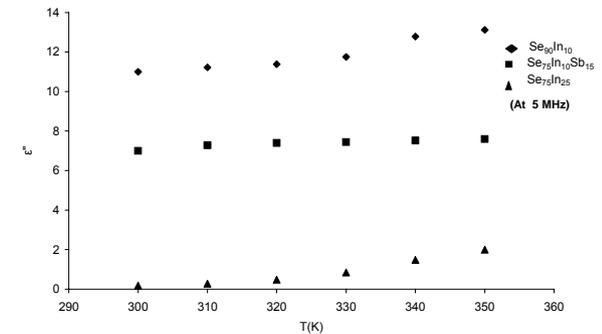


Fig. 3. Temperature dependences of the dielectric losses (ϵ'') in all the glassy alloys at 5 MHz.

In the above glassy alloys, ϵ'' is found to follow a power law with frequency, i.e. $\epsilon'' = A\omega^m$. Fig. 4 (for a- $\text{Se}_{75}\text{In}_{10}\text{Sb}_{15}$) confirms this behavior, where $\ln \epsilon''$ versus $\ln \omega$ dependences are found to be straight lines at various temperatures. The power m is calculated from the slopes of these curves and found that the values of m are negative at all temperatures of measurements. The magnitude of m increases with the increase of temperature in all the samples studied here. Guintini [13] had proposed a dipolar model for dielectric dispersion in chalcogenide glasses. This model is based on Elliott [14] hopping of charge carriers over a potential barrier between charged defect states (D^+ and D^-). These defects are responsible not only for the position of the Fermi level, but also for the transport properties of this material. In addition, they act as traps and recombination centers for carriers and (D^+ / D^-) is assumed to form a dipole that has a relaxation time depending on its activation energy; the latter can be attributed to the existence of a potential barrier over which the carriers hop. This potential barrier, as proposed by Elliot, is due to the Coulombic interaction between neighboring sites forming a dipole.

The relaxation time connected with a hop is given by:

$$T = \tau_0 \exp(W/kT). \quad (1)$$

Combining the imaginary part of the permittivity with the circular frequency ω of the applied electric field, we can write:

$$\epsilon''(\omega) = (\epsilon_0 - \epsilon_\infty) 4\pi N \epsilon_0 kT / n \times \int_0^\infty e^{-2} R^4 \left[\frac{\omega}{1 + \omega^2 \tau^2} \right] d\tau. \quad (2)$$

Where R (a function of τ) is the distance between the localized sites. This integral has already been evaluated [14, 15]. According to Guintini et al., assuming $\omega\tau \ll 1$, ϵ'' , at a particular frequency in the temperature range where dielectric dispersion occurs, is given by:

$$\epsilon''(\omega) = (\epsilon_0 - \epsilon_\infty) 2\pi^2 N (ne^2 / \epsilon_0)^3 kT \tau_0^m W_m^{-4} \omega^m. \quad (3)$$

Here, m is a power of the angular frequency, which is negative in this case and given by:

$$m = -4kT/W_m, \quad (4)$$

where n is the number of electrons that hop, N – concentration of localized sites, ϵ_0 and ϵ_∞ are the static and optical dielectric constants, respectively, W_m – energy required to move the electron from a site to infinity.

According to (3), ϵ'' should follow a power law with frequency, i.e., $\epsilon'' = A\omega^m$ where m should be negative and linear with T as given by (4). This equation is consistent with the expression of $\epsilon''(\omega)$ obtained from

the Kramers-Kronig relations. In our samples, we found also that ϵ'' follows a power law with frequency at higher temperatures where dielectric dispersion occurs. The values of m at various temperatures are negative and follow a linear relation with temperature (see Fig. 5 for $\text{Se}_{75}\text{In}_{10}\text{Sb}_{15}$ glassy alloy). Similar results have been also found for other glasses. Using the values of m , W_m is calculated and plotted in Fig. 6 (for a- $\text{Se}_{75}\text{In}_{10}\text{Sb}_{15}$). The values of loss tangent ($\text{Tan } \delta = \epsilon''/\epsilon'$) are also calculated, and the results obtained are given in Table 1. It is clear from this table that the value of W_m increases, while $\text{Tan } \delta$ decreases with impurity incorporation. The values of ϵ' and ϵ'' in aforesaid glassy alloys are given in Table 2.

From the above discussion, it seems that the paired defect states (D^+ and D^-) behave as dipoles in the aforesaid glasses studied here. These results are in agreement with the theory of hopping of charge carriers over a potential barrier as suggested by Elliott in case of chalcogenide glasses.

Table 1. Values of W_m and $\text{Tan } \delta$ for various glassy alloys.

Glassy alloys	W_m (eV)	$\text{Tan } \delta$ (1 kHz, 300 K)
$\text{Se}_{90}\text{In}_{10}$	0.35	0.67
$\text{Se}_{75}\text{In}_{10}\text{Sb}_{15}$	0.38	0.62
$\text{Se}_{75}\text{In}_{25}$	0.49	0.40

Table 2. Dielectric parameters of various glassy alloys.

Glassy alloys	ϵ' (1 kHz, 300 K)	ϵ'' (1 kHz, 300 K)
$\text{Se}_{90}\text{In}_{10}$	21.42	14.44
$\text{Se}_{75}\text{In}_{10}\text{Sb}_{15}$	14.92	9.28
$\text{Se}_{75}\text{In}_{25}$	8.71	3.53

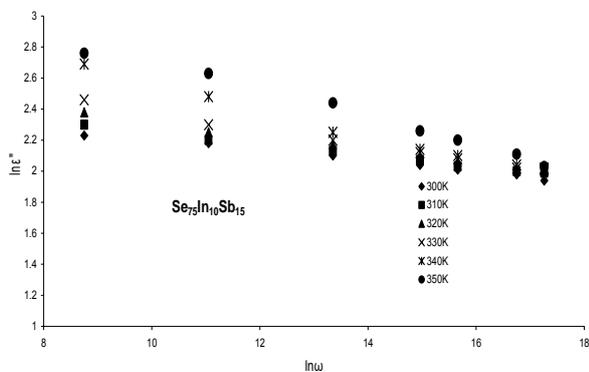


Fig. 4. $\ln \epsilon''$ versus $\ln \omega$ dependences in glassy $\text{Se}_{75}\text{In}_{10}\text{Sb}_{15}$ alloy at certain fixed temperatures.

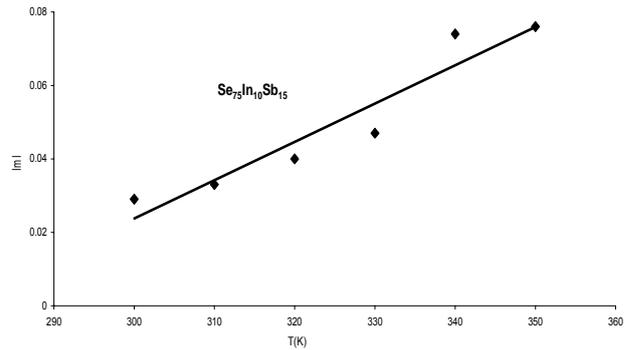


Fig. 5. $|m|$ vs T dependence in glassy $\text{Se}_{75}\text{In}_{10}\text{Sb}_{15}$ alloy.

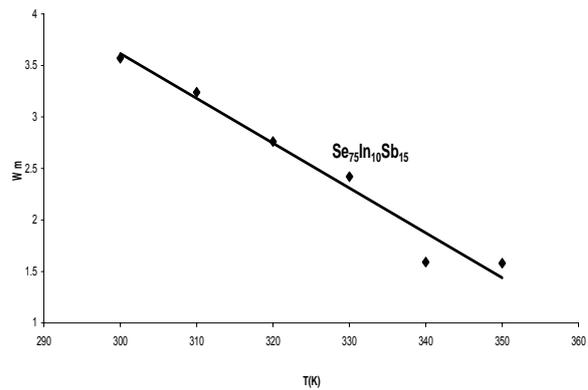


Fig. 6. W_m vs T dependence in glassy $\text{Se}_{75}\text{In}_{10}\text{Sb}_{15}$ alloy.

3.2. Impurity dependence of ϵ' and ϵ''

The degree of covalency of the studied compositions can be estimated according to the following relation [17]:

$$\text{The proportion of covalent character} = 100\% \exp [-0.25(\chi_A - \chi_B)^2]. \quad (5)$$

Where χ_A and χ_B are the electronegativities of atoms A and B, respectively. The values of covalent characters are listed in Table 3.

Incorporation of Sb in both $\text{Se}_{90}\text{In}_{10}$ glassy system leads to decreasing the value of the dielectric constant as given in Table 2. This decrease can be understood in terms of the nature of bonding in the system. It may be assumed that incorporation of Sb in the binary alloy leads to increasing density of stronger bonds Sb-Sb, In-In and Se-Se than other bonds in the network

Table 3. Calculated covalent character of bonds for considered compositions.

Bonds for bond type	% covalent character
Se-Se	100
In-In	100
Sb-Sb	100
Se-In	88.47
Se-Sb	91.39
Sb-In	99.75

structure, i.e, decreases the weaker bond density in the investigated compositions, which are more responsive to electric field than the stronger bonds. Thus, the value ϵ' decreases with Sb incorporation in $\text{Se}_{90}\text{In}_{10}$ system. The decrease in the dielectric losses may be caused by the decrease in the density of defect states, when the third element Sb as an impurity is incorporated in pure binary $\text{Se}_{90}\text{In}_{10}$ glassy alloy. Similarly, when Sb is incorporated in both $\text{Se}_{75}\text{In}_{25}$ glassy system at the cost of In leads to increasing the value of the dielectric constant as given in Table 2. This increase can be understood in terms of the nature of bonding in the system. It may be assumed that the incorporation of Sb in the binary alloy leads to decreasing the density of stronger bonds Sb–In, In–In and Sb–Sb than other bonds in the network structure, i.e, increases the weaker bond density in the investigated compositions, which are more responsive to electric field than the stronger bonds. Thus, the value ϵ' increases with Sb incorporation in $\text{Se}_{75}\text{In}_{25}$ system.

When iso-electronic atom Te is added to amorphous selenium, the density of defect states is increased, and hence the residual potential increases in xerographic experiment. Onozuka et al. [16] have therefore observed that, when introducing Cl to Se–Te system, the residual potential is decreased again. This result was interpreted on the basis of a structural defect model where Te was assumed to form positively charged impurities due to small electronegativity of Te as compared to Se, while Cl atoms having higher electronegativity than selenium [17] form negatively charged impurities, thereby compensating the effect of Te.

Along the same lines, one can expect that when Sb, having lower electronegativity than Se, is introduced in $\text{Se}_{90}\text{In}_{10}$ at the cost of Se, positive charged defects will be created, but the extent of their creation will be smaller since the amount of In is the same in both. On the other hand, when the same Sb is incorporated in $\text{Se}_{75}\text{In}_{25}$ at the cost of In, the density of defect states increases.

As the dielectric losses in these glasses depend on the total number of localized sites, the change in dielectric losses with Sb incorporation can be understood in terms of the change in the density of defects on addition of Sb to Se–In glassy system. Due to the change in number of dipoles (D^+ and D^-), the dielectric constant is also expected to change as found by us in the present study.

4. Conclusions

The temperature and frequency dependence of the dielectric constants and the dielectric losses in a- $\text{Se}_{90}\text{In}_{10}$, a- $\text{Se}_{75}\text{In}_{25}$, and a- $\text{Se}_{75}\text{In}_{10}\text{Sb}_{15}$ glassy systems within the frequency range 1 kHz–5 MHz and temperature range 300–350 K have been measured. It has been found that both the dielectric constant and dielectric losses are highly dependent on frequency and temperature as well as found to be dependent on the impurity incorporated in Se–In glassy system. The frequency dependence of the

dielectric losses in the above temperature range could be interpreted in terms of the hopping of charge carriers over a potential barrier between charged defect states (D^+ and D^-). It is clear from the results obtained that the addition of Sb affects the charged defect states in the pure Se–In glassy network, which also affects the dielectric properties. The difference in the order of changing the defect states in two $\text{Se}_{90}\text{In}_{10}$ and $\text{Se}_{75}\text{In}_{25}$ binary glassy systems could be explained on the basis of the electro-negativity difference and covalent character between the constituent elements used in making the above glassy alloys.

Acknowledgements

We are very much grateful to UGC, New Delhi for providing us financial support as a major research project during the span of this work.

References

1. R. Arora and A. Kumar // *Phys. status solidi (a)*, **115**, p. 307-314 (1989).
2. M. Ohta // *Phys. status solidi (a)*, **15**, p. 461-468 (1997).
3. T.T. Nang, T. Matsushita, M. Okuda, and A. Suzuki // *Jpn. J. Appl. Phys.* **16**, p. 253-257 (1977).
4. T. Matsushita, A. Suzuki, M. Okuda and T. Sakai // *Jpn. J. Appl. Phys.* **S19**, p. 123 (1980).
5. N. Musahwar, M.A. Majeed Khan, M. Husain, and M. Zulfequar // *J. Phys. D*, **40**, p. 7787-7793 (2007).
6. M. Khan, M. Zulfequar, and M. Husain // *Current Appl. Phys.* **2**, p. 401-406 (2002).
7. Z.H. Khan, M. Zulfequar, A. Kumar and M. Husain // *Canadian J. Phys.* **80**, p. 19-27 (2002).
8. A.S. Maan, D.R. Goyal, S.K. Sharma, and T.P. Sharma // *J. Phys. III (France)*, **4**, p. 493-501 (1994).
9. M.M.A. Imran, D. Bhandari and N.S. Saxena // *Physica B*, **293**, p. 394-401 (2001).
10. M.M.A. Imran, N.S. Saxena, Y.K. Vijay and N.B. Maharjan // *J. Non-Cryst. Solids*, **298**, p. 53-59 (2002).
11. D.K. Goel, C.P. Singh, R.K. Shukla, and A. Kumar // *J. Mater. Sci.*, **35**, p. 1017-1021 (2000).
12. D.R. Goyal, S. Walker and K.K. Srivastava // *Phys. status solidi (a)*, **64**, p. 351-357 (1981).
13. J.C. Guintini, J.V. Zanchetta, D. Jullien, R. Eholie, and P. Houenou // *J. Non-Cryst. Solids*, **45**, p. 57 (1981).
14. S.R. Elliott // *Phil. Mag.* **36**, p. 1291-1304 (1977).
15. M. Pollak // *Phil. Mag.* **23**, p. 519 (1971).
16. A. Onozuka, O. Oda, I. Tsuboya // *Thin Solid Films*, **149**, p. 9-15 (1987).
17. L. Pauling, *The Nature of the Chemical Bond*. Oxford and IBH, Calcutta, 1969, p. 93.