*Thermochimica Acta*, 82 (1984) 345–355
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

# SOME PHYSICAL PROPERTIES CONCERNING THE THERMAL CONDUCTIVITY DATA OF BaO-CONTAINING SILICATE GLASSES IN RELATION TO STRUCTURE

S.M. SALMAN
*Glass Research Laboratory, National Research Centre, Cairo (Egypt)*

S. GHARIB
*National Institute for Standards, Cairo (Egypt)*

(Received 18 July 1984)

## ABSTRACT

The thermal conductivity, density, refractive index and viscosity of glasses with base composition (wt%): $Na_2O$, 20; CaO, 15; $SiO_2$ 65, in which CaO is partially replaced by BaO, have been investigated.

Both the thermal conductivity and the viscosity–temperature values progressively decreased by introducing BaO to replace CaO in the glasses. Meanwhile, this replacement caused an increase in other properties, i.e., density and refractive index. The experimental measurements and calculated values of either thermal conductivity or viscosity agree fairly well. The observed effects were correlated to factors such as polarization, field strength and ionic radii of the incorporated divalent cations, and their effect on the geometrical arrangement of the building units of the glassy network.

## INTRODUCTION

One of the aims of natural science is to find a relationship between the structural and physical properties of materials [1]. An explanation of the characteristic physical properties of such an important material as glass may be of special interest as it may give rise not only to theoretical advances, but also to practical measures leading to still further improvements in the properties of glass.

Many of the practical applications of materials and glasses in glass solders and glass coating requires an accurate knowledge of their thermal conductivity. Heat transfer and viscous properties are also of great importance in glass melting, annealing and forming.

It may be pointed out that the physical properties of the glass are essentially determined by its composition including the nature and arrangement of the constituent atoms as well as the role of the incorporated cations as building units in the glass structure [2–4].

0040-6031/84/$03.00

The purpose of this paper is to report the thermal conductivity, density, refractive index and viscosity–temperature characteristics of the glass in the system soda–lime–silica as affected by the modification introduced by BaO/CaO substitution on the structure of the glass. This system has been chosen as it is one of the most attractive from the point of view of the cheapness of the raw materials and as it forms the basis of most commercial glasses.

## EXPERIMENTAL

### *Glass preparation*

The starting materials used were high purity $SiO_2$ and reagent grade $Na_2CO_3$, $CaCO_3$ and $BaCO_3$. The glass compositions are given in Table 1. The batch materials were well mixed in the desired proportions and melted in Pt–Rh crucibles at 1450°C for 3 h, using an SiC electric furnace. The melts were stirred several times during melting to ensure homogeneity. The melts were cast into discs which were annealed, ground and polished to smooth flat parallel surfaces. The discs were 18 mm in diameter and 5 mm thick.

### *Thermal conductivity measurements*

The thermal conductivity of the glasses was measured at room temperature (25°C) by the steady-state method using the apparatus described by Haacke and Spitzer [5]. Heat flows through the glass sample to a sink, which transfers it by thermal radiation to the surrounding evacuated chamber which is kept at a uniform temperature. After thermal equilibrium is reached the temperature of the heater, heat sink and outer chamber are measured by means of attached thermocouples, details of which are given elsewhere [2,6].

TABLE 1

Chemical composition of the investigated glasses

| Glass No. | Oxides (wt%) | | | |
|---|---|---|---|---|
| | $SiO_2$ | $Na_2O$ | CaO | Ba = CaO [a] |
| 1 | 65 | 20 | 15 | 0 |
| 2 | 65 | 20 | 14 | 1 |
| 3 | 65 | 20 | 12 | 3 |
| 4 | 65 | 20 | 10 | 5 |
| 5 | 65 | 20 | 8 | 7 |
| 6 | 65 | 20 | 6 | 9 |

[a] The replacement was made on cation per cation basis.

The accuracy of the data is limited by the accuracy (5%) claimed for the thermal conductivity of the standard borosilicate glass samples used to calibrate the apparatus.

The experimental thermal conductivity is determined using the equation

$$\lambda = \epsilon \sigma S \frac{d}{A} \left( \frac{T_x^4 - T_0^4}{T_1 - T_x} \right)$$

where $\lambda$ is the thermal conductivity of the sample (W cm$^{-1}$ K$^{-1}$), $\epsilon$ the net emissivity, $\sigma$ the Boltzmann constant (equal to $5.67 \times 10^{-12}$ W cm$^{-1}$ K$^{-4}$), $S$ the surface area of the heat sink (cm$^2$), $d$ the sample thickness (cm), $A$ the sample cross-section (cm$^2$), $T_x$ the temperature of the heat sink, $T_1$ the temperature of the sample, and $T_0$ the temperature of the evacuated chamber.

## *Density and refractive index measurements*

Determination of the density ($d$) of the glasses was made by the displacement method of Archimedes using xylene as the immersion liquid. The measurements were made in duplicate with a maximum error of $\pm 0.0005$ g cm$^{-3}$.

The refractive index ($n_D$) was measured with an Abbe refractometer which permits measurements up to 1.7000, with a measuring accuracy of 0.0002. Monobromonaphthalene was used as the contact liquid between the surface of the apparatus prism and the test piece.

## *Viscosity measurements*

Glass fibres were drawn from the molten mass for the viscosity measurement. A fibre of the required diameter (0.5–0.6 mm) and 15 cm long could be obtained.

Viscosity was measured versus temperature for the glasses in the range $\log_{10} \eta = 7.6$ to about $\log_{10} \eta = 13.5$ using the fibre elongation method [7]. The apparatus was similar to that used by other investigators [8,9]. The fibres were vertically suspended in a furnace and a certain load was attached to the lower end of the fibre. After attachment of the load the elongation rate of the fibre was measured using a cathetometer. In this way several elongation rates at different temperatures can be obtained. Details of the equipment and method used can be found in several publications [7,9].

The following equation was used to calculate the experimental viscosity as it was verified by Lillie [10] and successfully adopted in our results

$$\eta = \frac{80 gFL}{\pi D^2 V}$$

where $\eta$ is the viscosity (P), $g$ gravity constant, $F$ the load on one end of the fibres (g), $L$ the length of the fibre (cm), $D$ the diameter of the fibre (cm), and $V$ the elongation rate (cm min$^{-1}$).

## RESULTS

The data obtained, including the thermal conductivity ($\lambda$), density ($d$), refractive index ($n_D$) and viscosity–temperature values, are listed in Tables 2–4 and illustrated graphically in Figs. 1–6.

The experimental thermal conductivity ($\lambda_{exp}$) values (Table 2) were used to calculate the factors representing the specific contribution of BaO (introduced in the studied glasses) to the thermal conductivity by the least-squares method. However, the factors representing the specific contribution of $Na_2O$, CaO and $SiO_2$ (Table 3) were taken from the literature [3,11,12].

The factors obtained were used to calculate the thermal conductivity of the investigated glasses using the following equation

$$10^3\lambda_{calc}(\mathrm{W\ m^{-1}\ K^{-1}}) = \sum_{n=1}^{i} F_i X_i$$

TABLE 2

Thermal conductivity, density and refractive indices of the glasses studied

| Glass No. | BaO wt% | $\lambda_{exp}$ (W m$^{-1}$ K$^{-1}$) | $\lambda_{calc}$ [a] (W m$^{-1}$ K$^{-1}$) | $\frac{\Delta\lambda}{\lambda} \times 100$ [b] | $\lambda_{calc}$ [c] (W m$^{-1}$ K$^{-1}$) | Density, $d$ | Refractive index, $n_D$ |
|---|---|---|---|---|---|---|---|
| 1 | 0 | 0.9746 | 0.9579 | −1.74 | 0.9796 | 2.58 | 1.540 |
| 2 | 1 | 0.9653 | 0.9477 | −1.86 | 0.9622 | 2.62 | 1.541 |
| 3 | 3 | 0.9415 | 0.9273 | −1.53 | 0.9391 | 2.69 | 1.544 |
| 4 | 5 | 0.9198 | 0.9069 | −0.87 | 0.9171 | 2.76 | 1.547 |
| 5 | 7 | 0.8960 | 0.8864 | −1.08 | 0.8961 | 2.83 | 1.550 |
| 6 | 9 | 0.8760 | 0.8660 | −1.15 | 0.8790 | 2.89 | 1.553 |

[a] Thermal conductivity calculated using the least-squares method.
[b] Discrepancy between experimental and calculated $\lambda$ values.
[c] Thermal conductivity calculated using the density values.

TABLE 3

Factors for calculating thermal conductivity at 25°C from amounts (wt%) of the constituent oxides in glass

| Oxides | Factors ($F$) (W m$^{-1}$ K$^{-1}$ × 10$^3$) | Ref. |
|---|---|---|
| $Na_2O$ | −4.75 | 3 |
| CaO | 12.43 | 3 |
| BaO | 2.23 | Present work |
| $SiO_2$ | 13.33 | 3, 11, 12 |

where $\lambda$ is the thermal conductivity of the glass. $X_i$ is the percentage weight composition of component oxide $i$, and $F_i$ is the factor representing the specific contribution of the individual oxide $i$ to thermal conductivity. The maximum discrepancy between the $\lambda_{\text{exp}}$ and $\lambda_{\text{calc}}$ values is around 2%.

The experimental density values (Table 2, column 7) were also used to calculate other thermal conductivity data applying the following empirical equation

$$\lambda = \frac{B}{d} + A$$

where $A$ and $B$ are constants calculated by the least-squares method (0.071687 and 2.333216, respectively).

TABLE 4

The viscosity-temperature characteristics and predicted activation energy of the glasses studied

| Glass No. | BaO wt% | Softening point (°C) | Annealing point (°C) | Strain point (°C) | Activation energy (kcal mol$^{-1}$) |
|---|---|---|---|---|---|
| 1 | 0 | 695.5 | 438.5 | 403.5 | 71.25 |
| 2 | 1 | 689.8 | 429.9 | 395.5 | 69.12 |
| 3 | 3 | 681.6 | 416.3 | 381.7 | 65.56 |
| 4 | 5 | 679.1 | 404.9 | 369.8 | 62.52 |
| 5 | 7 | 653.0 | 381.1 | 346.5 | 59.15 |
| 6 | 9 | 650.4 | 369.9 | 334.9 | 56.23 |

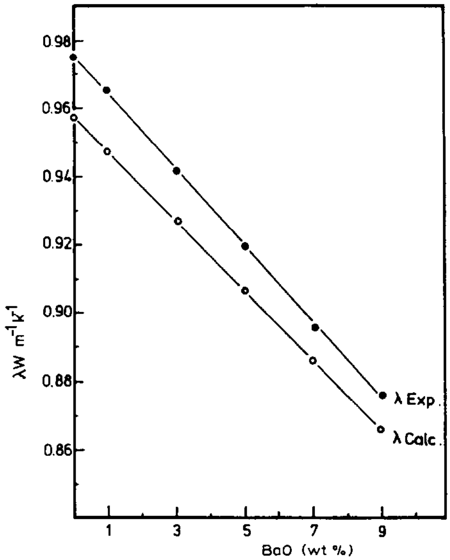

Fig. 1. The effect of BaO/CaO replacement on the thermal conductivity of $Na_2O$–CaO–$SiO_2$ glasses.

The thermal conductivity data and their correlation with the density values revealed the following:

(1) the experimental λ values progressively decreased by introducing BaO to replace CaO in the glasses (Fig. 1);

(2) the correlation between the glass composition and the calculated λ values gave similar results. Both the experimental and calculated λ values of the glasses (Fig. 1 and Table 2, columns 3 and 4) agree fairly well;

(3) the values of density progressively increased with increasing BaO content in replacement of CaO in the glasses (Fig. 2);

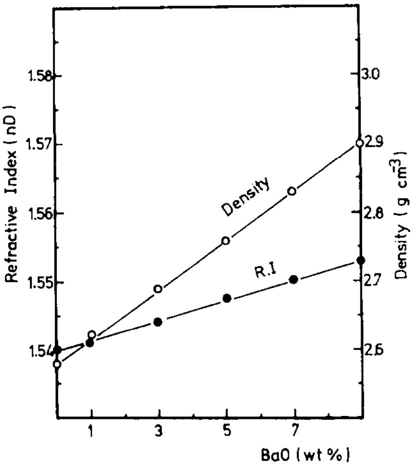

Fig. 2. The effect of BaO/CaO replacement on the density and refractive index of $Na_2O$–CaO–$SiO_2$ glasses.

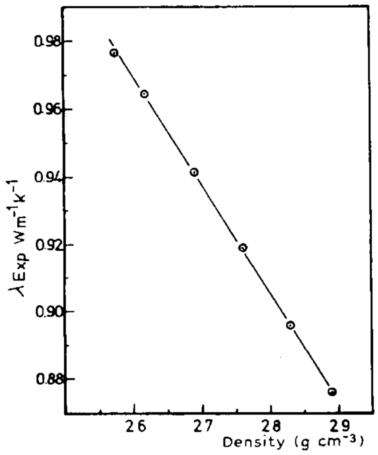

Fig. 3. Thermal conductivity–density relationship of $Na_2O$–CaO–BaO–$SiO_2$ glasses.

(4) the correlation between the thermal conductivity and density of the glasses studied showed that as the density increased the thermal conductivity of the glasses decreased (Fig. 3).

For the refractive index measurements the data obtained revealed that the BaO/CaO substitution increased the refractive index of the glass progressively (Fig. 2).

For the viscosity measurements, the empirical formula describing the viscosity of a glass as a function of the temperature is that suggested by

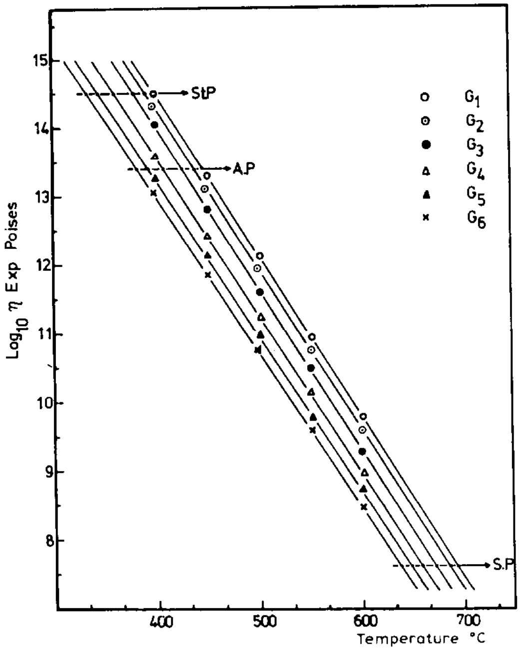

Fig. 4. Viscosity–temperature relationship of BaO-containing glasses.

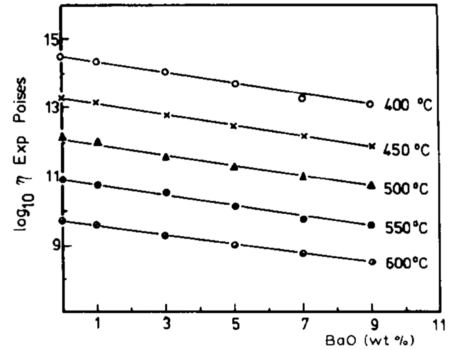

Fig. 5. Viscosity isotherms of $Na_2O$–CaO–BaO–$SiO_2$ glasses.

Flucher [13]

$$\log_{10} \eta = A + \frac{B}{T_a}$$

where $T_a$ is the absolute temperature at which the viscosity is measured, $A$ and $B$ are constants. The experimental data fitted the formula within 0.5%. In the present work the constants $A$ and $B$ were obtained using the constant derived from each value of $\log_{10}$ $\eta$ (viscosity) and were calculated for nominal values of temperature. The discrepancy between the calculated $\log_{10}$ $\eta$ value and experimental data ranges from −5.69 to 1.02%.

The experimental viscosity–temperature relationships are recorded in Fig. 4, meanwhile, the viscosity isotherms of the glasses investigated are presented in Fig. 5, from which it can be seen that the viscosity values progressively decrease with increasing temperature. They also decreased with BaO/CaO replacement in the glasses. They decrease more pronouncedly with increasing BaO in the glasses.

The viscosity dependence of the temperature measured were used to calculate certain characteristic temperatures at which the glass attains particular values of viscosity. Therefore, the reference points, namely softening, annealing and strain points, of the glasses studied were calculated by applying the parameters of the Flucher [13] equation. The data obtained are given in Table 4 and graphically presented in Fig. 6. It can be seen from this figure that the BaO/CaO replacement caused a progressive decrease in the values of these reference points.

For calculating the activation energy of the molecule movements, the following equation [14] was used

$$\log_{10} \eta = A + \frac{E_n}{4.57T}$$

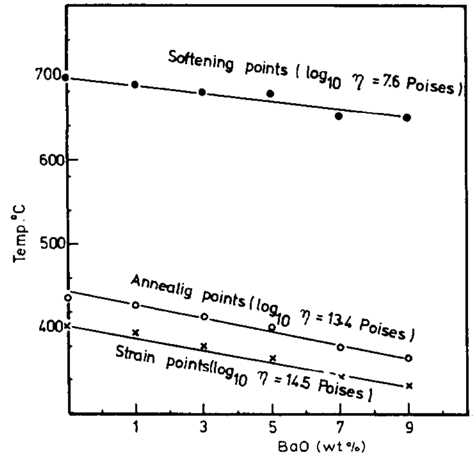

Fig. 6. The variation of the fixed points with the BaO content in the glasses.

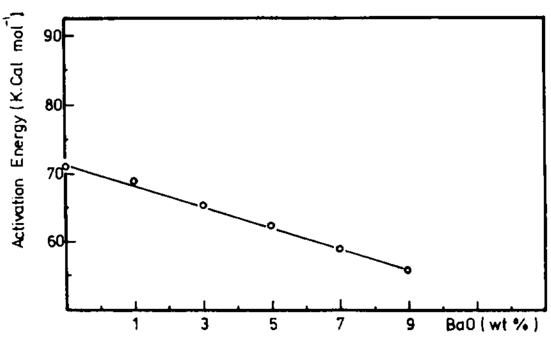

Fig. 7. The effect of BaO/CaO replacement on the activation energy of $Na_2O$–CaO–$SiO_2$ glasses.

where $E_n$ is the activation energy (kcal $mol^{-1}$).

The data obtained (Table 4 and Fig. 7) show that a gradual decrease of the activation energy occurred on introducing BaO instead of CaO in the glasses studied.

## DISCUSSION

To understand and interpret the effect of BaO/CaO replacement on the physical properties of the glasses studied, certain factors such as polarization, field strength, ionic radii of the incorporated divalent cations and their effect on the geometrical arrangement of the building units of the glassy network must be considered.

When modifying oxides, such as alkali or alkaline earth oxides, react with silica to form a glass, the silica–oxygen network is broken up by the ions of these oxides as evidenced by the much lower viscosity of these glasses as compared with fused silica [15]. So long as the number of $A_2O$ or AO units (A is the metallic ion) is in a less than one-to-one ratio to the number of $SiO_2$ units, the Si–O tetrahedron is linked to at least three other tetrahedra and the glass-forming tendency of the mixture is retained. As more such modifying oxide is added beyond the one-to-two ratio, the network becomes more disrupted, as more tetrahedra are bonded to only two other tetrahedra. Therefore, glass formation becomes progressively more difficult because the rates of nucleation and crystallization in the glass are greatly increased.

The conduction of heat in a non-metallic solid is assumed to be due to the propagation of mechanical waves through the material [1]. Heat is considered as being transmitted by phonons, which are the quanta of energy in each vibration and the mean free path is a measure of the rate at which energy is exchanged between different phonon modes [1].

The thermal conductivity is not influenced by the chemical nature of the solid as much as it is by its structure, and is therefore considered to be a structure sensitive property that responds strongly to defects and hetorogeneities [16]. Non-crystalline solids or glasses can be regarded as highly disordered crystals. Therefore, the phonon mean free path is short because of the random structure, and the thermal conductivity is very low and increases only slightly when the temperature is raised [17–19]. Accordingly, the thermal conductivity of glass is a function of the short-range order of its network structure; the thermal conductivity will decrease with the increasing disorder of the network [20]. In general, a simple structure will have a high lattice thermal conductivity. For a similar molecular structure, the material having the lowest molecular weight will generally have the highest thermal conductivity [2].

It is logical to assume that the introduction of non-bridging oxygen ions decreases the coherency of the network in the glass structure and consequently lowers its viscosity. Therefore, an increase in the relative number of non-bridging oxygen ions in the glass will lead to lower annealing and softening temperatures [14].

As the flow of glass is controlled by the Si–O–Si bonds [10], the addition of divalent oxides would eventually decrease the viscosity of the glass [21]. With respect to the type of divalent cation, the loosening of the Si–O structure is more apparent with the larger Ba [1] ions (1.35 Å) than Ca ions (0.99 Å). The former will acquire a lower field strength than the latter, it is therefore expected that the BaO/CaO replacement will result in a decrease in the thermal conductivity and viscosity values of the glass.

The same basis can be considered in explaining the calculated activation energy data. The introduction of such large $Ba^{2+}$ ions instead of the smaller $Ca^{2+}$ ions in the glass is expected to weaken the structure of the glass and cause it to be increased in size by their occupation in the modifier ion positions. Accordingly, the movement of the ions is therefore easier [17], i.e., activation energy will be low.

As the $Ca^{2+}$ or $Ba^{2+}$ ions could either occupy interstices with the network or form bridges between the network-forming units the introduction of a cation having a relatively weak field potential with respect to $Ca^{2+}$ ion, like $Ba^{2+}$, leads to highly polarizable oxygen ligands [22]. As a result, the electromagnetic waves passing through the glass containing BaO suffered higher refraction due to the increased polarizability of the oxygen ions. It was also pointed out [16] that the $O^{2-}$ ions in the medium are exposed to the potential field of the network-modifying cations which will influence their state of polarization. Cations causing $O^{2-}$ ions to be more polarized will be expected to cause a contraction in volume and, consequently, an increase in density. Therefore, the factors affecting the density of the glass can be attributed to; the specific volume of the ions ($\frac{1}{d}$); the coordination number of the cations; and the ionic radii and polarizing effect of the cations. The increased density values of the glasses by BaO/CaO replacement may be attributed to the fact that the specific volume of $Ba^{2+}$ (0.265) is less than that of $Ca^{2+}$ (0.649).

The effects observed in the present work reveal that the replacement of CaO by BaO in the glasses causes their thermal conductivity and viscosity values to decrease considerably, while their density and refractive indices increase. This may be considered an advantage from the technical viewpoint, particularly in determining the physical properties of commercial glasses.

## REFERENCES

1 D.G. Holloway, The Physical Properties of Glasses, Wykeham Publications, London, 1973, pp. 41–48.
2 N.A. Ghoneim, A.A. Ahmed and S. Gharib, Thermochim. Acta, 71 (1983) 43.
3 E.H. Ratcliffe, Glass Technol., 4 (1963) 113.
4 A.F. Dingwall and H. Moore, Glass Technol., 37 (1953) 316.
5 G. Haacke and D.P. Spitzer, J. Sci. Instrum., 42 (1965) 702.
6 M.M. Ammar, Kh. El Badry, M.R. Moussa, S. Gharib and M.M. Halawa, Centr. Glass Ceram. Res. Inst. Bull., 22 (1975) 10.
7 A. Napolitano and N.C. Howkins, J. Natl. Bur. Stand., Sect. A, 68 (1964) 439.
8 N.W. Taylor and P.S. Dear, J. Am. Ceram. Soc., 20 (1937) 296.
9 Kh. El Badry and N.A. Ghoneim, Centr. Glass Ceram. Res. Inst. Bull., 29 (1982) 3.
10 H.R. Lillie, J. Am. Ceram. Soc., 22 (1939) 367.
11 M.M. Ammar, M.M. Halawa, N.A. Ghoneim, A.F. Abbas and H.A. El Batal, J. Am. Ceram. Soc., 65 (1982) C174.
12 M.M. Ammar, S.A. Gharib, M.M. Halawa, Kh. El Badry, N.A. Ghoneim and H.A. El Batal, J. Non-Cryst. Solids, 53 (1982) 165.
13 G.S. Flucher II, J. Am. Ceram. Soc., 24 (1941) 103.
14 W.L. Konijnendyk, The structure of borosilicate glasses, Thesis, Technological Uni-Eindhoven, Philips Res. Rep. Suppl. No. 1, 1975, pp. 170–181.
15 R.H. Doremus, Glass Science, Wiley, New York, 1973, pp. 23–43.
16 W.A. Weyl and E.C. Marboe, The Constitution of Glasses, a Dynamic Interpretation, Wiley, New York, 1962, Vol. 1.
17 C. Kittel, Introduction to Solid State Physics, 2nd edn., Wiley, London, 1962, Chap. 6, p. 138.
18 R. Berman, Thermal Conduction in Solids, Clarendon Press, Oxford, 1976.
19 P.C. Klemens, in J.A. Prins (Ed.), Physics of Non-crystalline Solids, North Holland, Amsterdam, 1965, p. 152.
20 A.V. Muratov and A.V. Chernyshov, Sov. J. Glass Phys. Chem. (English Trans., Consultants Bureau, New York), 5 (1979) 100.
21 Kh. El Badry, N.A. Ghoneim, H.A. El Batal, M.M. Ammar and S. Gharib, Sprechsaal, 114 (1981) 599.
22 H.A. El Batal, G.M. Ashour and A.H. Metwally, Centr. Glass Ceram. Res. Inst. Bull., 17 (1970) 117.