Journal of Thermal Analysis and Calorimetry, Vol. 85 (2006) 3, 725–730

NON-DEBYE NATURE IN THERMAL RELAXATION AND THERMAL PROPERTIES OF LITHIUM BORATE GLASSES STUDIED BY MODULATED DSC

Y. Matsuda[1*], *C. Matsui*[2], *Y. Ike*[1], *M. Kodama*[3] *and S. Kojima*[1, 2]

[1]Graduate School of Pure and Applied Sciences, University of Tsukuba, Tsukuba, Ibaraki 305-8571, Japan
[2]College of Engineering Sciences, University of Tsukuba, Tsukuba, Ibaraki 305-8573, Japan
[3]Department of Applied Chemistry, Sojo University, Kumamoto 860-0082, Japan

Complex heat capacity, $C_p^*=C_p'-iC_p''$, of lithium borate glasses $x\mathrm{Li_2O}\cdot(1-x)\mathrm{B_2O_3}$ (molar fraction x=0.00–0.30) has been investigated by Modulated DSC. We have analyzed the shape of C_p^* by the Cole-Cole plot, performed fitting by the Havriliak-Negami equation, and then determined the parameters related to the non-Debye nature of thermal relaxation. Moreover, the concentration dependence of the thermal properties has been investigated. Glass transition temperatures become higher with the increase of molar fraction of $\mathrm{Li_2O}$ and shows the board peak around x=0.26. Temperature ranges of glass transitions become narrower with the increase of $\mathrm{Li_2O}$ concentration.

Keywords: *complex heat capacity, lithium borate glass, modulated DSC, non-Debye, relaxation, TMDSC*

Introduction

Glass is the one of the most technologically important materials. We can find the products made by glass everywhere. Despite the applied technology of glass has been improving, there are still lacks of the fundamental understandings of its physical properties and dynamics of glass transitions.

Glass has the random structures and undergoes a liquid–glass transition from supercooled liquid to glass states at a transition temperature (T_g). In the vicinity of T_g, the motion of atoms or molecules in the liquid becomes quite slowly. At last, the liquid is ‘frozen’ in practical time scale. Therefore, in general, glassy state is in non-equilibrium and the glass transition is regarded as one kind of relaxation phenomenon [1]. As dynamics of glass transitions, several kinds of relaxation phenomena can be observed such as α, β, γ relaxation and boson peak [2] etc.

In the system related to relaxation processes such as glass transition, physical quantities show the time or frequency dependent actuations and it related to dynamical or complex susceptibility $\chi(\omega)$. The change in an external ‘force’ induces a change in a conjugated variable. Under the assumption of linear approximation, $\chi(\omega)$ is related to a relaxation function, ψ(t), of the system by the linear response theory [3] (Eq. (1)). Therefore, $\psi(t)$ represents the characteristic feature of the relaxations in a glass transition. If we can determine the behavior of $\psi(t)$ by observing $\chi(\omega)$, we give new insights into the dynamics in glass transitions [4]. For the case where the external ‘force’ is an electric field and the response is the polarization, $\chi(\omega)$ is complex dielectric constant. Although this case has been well studied, the dielectric relaxation is connected only to polarization fluctuations. Complex elastic constant also has been studied, while the elastic relaxation is connected only to density fluctuations.

In the case that the perturbation applied to a system is temperature, the complex specific heat capacity (C_p*) is defined. This C_p* plays the important role in the study of relaxation process through a glass transition, because the thermal relaxation is related to total degree of freedom. Therefore, it provides us more general understanding of the relaxation process.

Birge and Negal firstly observed the frequency-dependent specific heat capacity in the experiment [5, 6]. This method has been called ‘specific heat spectroscopy’. As was discussed by Birge, the dynamical specific heat C_p* is related to the $\psi(t)$ of the enthalpy by Eq. (1),

$$C_p^*(\omega)=C_p^{\infty}+(C_p^{0}-C_p^{\infty})\int_0^{\infty}\left\{-\dot{\psi}(t)\right\}\cdot e^{i\omega t}\,\mathrm{d}t \qquad (1)$$

where C_p^{∞} is the contribution of total degree of freedom that equilibrates very quickly, and C_p^{0} is the static specific heat in the equilibrium. Moreover, in the non-equilibrium statistical mechanics, the C_p^* is based

---

[*] Author for correspondence: s-matsuda@ims.tsukuba.ac.jp

1388–6150/$20.00

Akadémiai Kiadó, Budapest, Hungary
Springer, Dordrecht, The Netherlands

on the fluctuation-dissipation theory and defined by the correlation function of enthalpy fluctuation [7].

In the early 1990s, a new type of DSC, Modulated Temperature DSC (MDSC) was developed by Reading [8, 9] and has been applied to study the glass transition dynamics [10, 11]. MDSC is basically the extension of a conventional DSC. However, the different point is the applied temperature profile in which a small sinusoidal perturbation is superimposed on the underlying linear temperature ramp used in the conventional DSC. From the modulated component in the resultant heat flow signals, the frequency-dependent complex specific heat capacity, $C^*_p(\omega,\tau(T))=C'_p-iC''_p$, can be obtained. This method to analyze has been proposed by Schawe on the basis of the linear response theory [12, 13]. The method developed by Birge, called an alternating current calorimetry technique, is not general in use in laboratories and requires expert skill to detect weak third harmonic signals. On the contrary, MDSC is commercially available and a measurement can be performed in the course of usual and routine DSC scan. Within our knowledge, there is no publication for the time being to study the frequency-dependent C^*_p of lithium borate binary glasses by MDSC, while the frequency dependence of a few organic materials has been successfully observed [10, 11]. In the present study, we measure $C^*_p(\omega,\tau(T))$ of lithium borate glasses and study the thermal relaxation in order to make clear dynamical properties of glass transition phenomena.

Non-Debye relaxation

The relaxation process of a glass transition is reviewed in [1, 4]. As we described in the previous section, analytical expressions of the relaxation function $\psi(t)$ are important to understand the dynamics of glassy systems.

The simplest model is well-known the Debye's single relaxation process [4]. However, this exponential response is very rare in a glass transition, and most of glass-forming materials show non-Debye behavior. Therefore, the relaxation process has to be characterized by some other functions which include the distribution of relaxation time. Non-Debye nature is usually expressed by Kohlrausch-Williams-Watts (KWW) [14, 15] function by Eq. (2)

$$\psi(t)=\psi(0)\cdot\exp\left(-\frac{t}{\tau}\right)^{\beta} \tag{2}$$

where $\psi(0)$ is initial value of $\psi(t)$, τ is the characteristic relaxation time and β is a stretch exponential parameter with $0<\beta\leq 1$. The smaller value of the β is the less exponential function and show that the τ has distributed in its nature. Fourier transformation is necessary to analyze the KWW function in the frequency domain. However, there is no analytical expression for the Fourier transformation of the KWW function. Therefore, in the frequency domain, other empirical expressions have been used. There are main three ways of describe the exponentiality: Cole-Cole (CC) [16], Davidson-Cole (DC) [17] and Havriliak-Negami (HN) [18] equations. HN equation is given by Eq. (3) and includes the case of CC and DC as a special case,

$$C^*_p(\omega)=C^\infty_p+\frac{C^0_p-C^\infty_p}{[1+(i\omega\tau)^\alpha]^\gamma}, \tag{3}$$

where α and γ are parameters with $0\leq a$, $\gamma\leq 1$, respectively. The case $\alpha=1$ is equivalent to the DC equation and $\gamma=1$, the CC.

Experimentally, the Cole-Cole plot is widely used in the study of dielectric relaxation. This method is the plot of imaginary part of observed $\chi(\omega)$ *vs.* real part, and very useful because we can directly find the behaviors of the relaxation by our eyes. In the present study, we have used the Cole-Cole plot to analyzed the shape of observed C^*_p and try to determined the empirical parameters.

Experimental

Composition formula of lithium borate glasses is denoted by $x\mathrm{Li_2O}\cdot(1-x)\mathrm{B_2O_3}$, where x is the molar fraction of $\mathrm{Li_2O}$. A series of the glasses was prepared at regular intervals 0.02 molar fractions in the composition range $0\leq x\leq 0.30$. All of the glasses were prepared with high homogeneity in order to investigate the inherent nature of binary system. To achieve high homogeneity, we chemically synthesized the powder of the lithium borate glasses by reacting in aqueous solution. Analytical reagent grade $\mathrm{LiOH\cdot H_2O}$ (whose purity is greater than 99.0%) and $\mathrm{H_3BO_3}$ (greater than 99.7%) were used as the starting materials. The preparation method of the glasses is described elsewhere [19].

The MDSC (DSC2920, TA Instruments) has been used for all of the experiments. Before the measurements, we performed the calibrations to measure accurate data. Temperature calibration has been done to examine the heat of fusion of In, Sn and Zn metals. Baseline calibration also has been done through the entire temperature range used in the experiments, and heat capacity calibration has been performed by using a sapphire disk as a standard, same modulation frequency applied to temperature program.

The powdered sample was put into an aluminum pan, and the mass of each sample was about 10.0 mg. Then, the sample pan and the reference empty pan in the sample chamber were heated through dynamical T_g with the temperature profile; underlying heating rate is 1ºC min^{-1}, modulation amplitude ±1ºC and modulation period 100 s. Dry nitrogen was flowed in the sample chamber as purge gas with the flow rate of 20m L min^{-1} during the experiments.

Results and discussion

The complex specific heat capacity observed by MDSC

Resultant heat flow contains a linear and modulation parts. From the latter, we can obtain the amplitude of modulation in heat flow A_{MHF} and the phase angle φ between modulation in the heat flow and heating rate. The absolute value of C_p^* is defined as the ratio of A_{MHF} and the amplitude of modulation in the heating rate (A_{Mq}), by Eq. (4)

$$\left|C_p^*\right| = \frac{A_{HF}}{mA_q}, \tag{4}$$

where m is mass of the sample. Figure 1 shows the absolute value of C_p^* and phase angle.

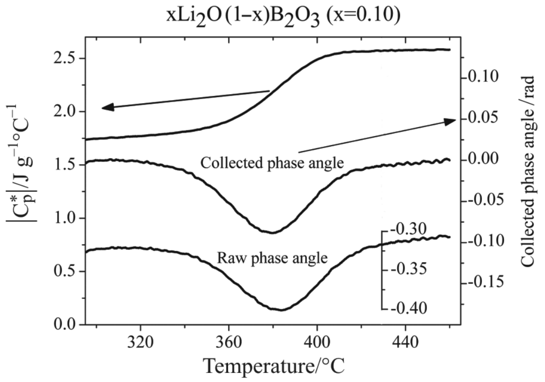

Fig. 1 The absolute value of complex heat capacity, raw phase angle without any data processing and collected phase angle are shown

Moreover, we can separate C_p^* into the real (C_P') and imaginary (C_p'') part using the phase angle φ by Eqs (5) and (6) [12],

$$C_p' = \left|C_p^*\right| \cos\varphi, \tag{5}$$

$$C_p'' = \left|C_p^*\right| \sin\varphi. \tag{6}$$

In order to obtain C_P' and C_P'', the evaluation of phase angle is important. In theory, the phase angle before and after glass transition should be zero. However, experimental result shows non-zero phase angle (see law phase angle in Fig. 1). The main reasons are the effect of heat transfer among a sample, cell and heater, and the effect of heat conductance of the sample itself. Therefore, we must separate the instrumental phase angle φ_{inst} and the phase angle φ_{relax} caused by relaxation process in a sample.

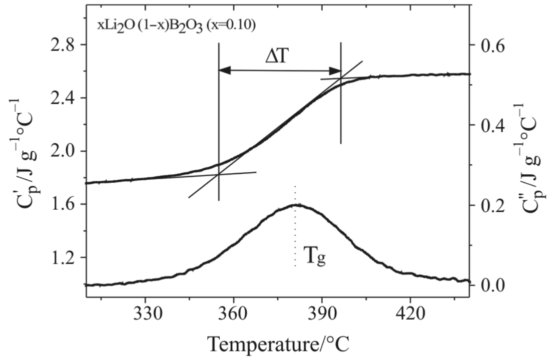

Fig. 2 Real C_p' and imaginary parts C_p'' of the complex heat capacity of 0.1 Li_2O·0.9 B_2O_3 as a function of temperature

The simple way to collect phase angle is to subtract a straight line interpolated between the start and end points of the raw phase angle curve. The more advanced collection method in glass transition region has been proposed by Weyer *et al*. [20], and the reliability of this method has been confirmed experimentally by Jiang *et al*. [21]. In the present study, we performed the phase collection by both the simple and Weyer's method ([20] for the detail calculating method for φ_{inst}). The collected phase angles show the no difference between the two methods for the composition range $0 \le x \le 0.10$. However, as for $0.14 \le x \le 0.30$, the raw phase angles before and after glass transition shows the small sigmoidal step change, as was discussed in [20 and 21]. Therefore, we have performed the phase collection by the Weyer's method in $0.14 \le x \le 0.30$. Figure 1 shows the collected phase angle φ. Then, we have obtained the C_p' and C_p'' through Eqs (5) and (6) by using the collected phase angle. Figure 2 shows the C_p' and C_p'' of

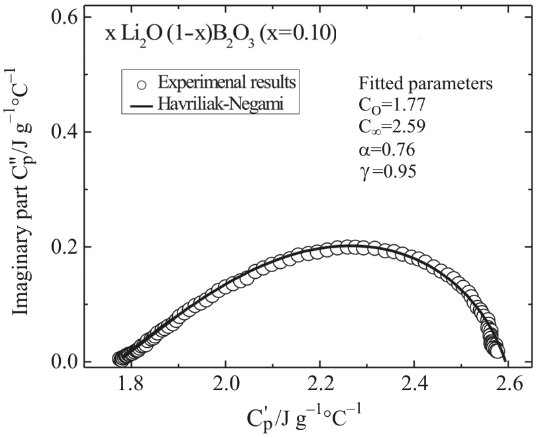

Fig. 3 Cole-Cole plot of 0.10 Li_2O·0.90 B_2O_3. Circles denote the experimental results. Total number of data deceases by 1/22 from the original data in Fig. 2. Solid line denotes the fitted values by HN equation

the lithium borate glass (x=0.10) near T_g. As you can see from Fig. 2, the curve of C_p' shows step-like and C_p'' has a broad peak around T_g. Both of them are the characteristic features of the dynamic susceptibility of a relaxation process.

Non-Debye parameters determined by Cole-Cole plot

We analyzed C_p' and C_p'' by the Cole-Cole plot representation in which the sets of (C_p', C_p'') are plotted as (x, y). Here, we show two results of the Cole-Cole plot. Figure 3 shows the Cole-Cole plot of the lithium borate glass with the composition x=0.10. Figure 4 is the case of x=0.22. It is noted that the shape of the curves seems to be a distorted semi-circle and have asymmetry. These are the typical features of the shape of the Davidson-Cole (DC) or Havriliak-Negami (HN) equation. The solid line in Fig. 3 is the result of the fitting by Havriliak-Negami (HN) equation for $\omega=2\pi/100$. As we can see Fig. 3, HN equation is well fitted by the parameters; C_p^{∞}=1.77, C_p^{0}=2.59, α=0.76 and γ=0.48. In Fig. 4, the HN curve of the distribution parameter α=0.95 and γ=0.56 also well expresses the experimental data.

Figure 5 shows the concentration dependence of the distribution parameters (α and γ) of the HN equation. In the study of dynamics in a glass transition, KWW function in the time domain has been widely used. Alvarez *et. al*. has found the empirical relationship among the parameters of HN equation and that of KWW function [22] by Eq. (7)

$$\alpha\gamma=\beta^{1.23} \qquad (7)$$

where β is called stretched exponential parameter. This relationship gives us the direct way of transformation from the parameters of HN equation into that of KWW function. Figure 6 shows the concentration dependence of the stretched exponential parameter β obtained by Eq. (9), and indicates that β has remarkable concentration dependence. The smaller value of the β means that the relaxation time τ has distribution in its nature.

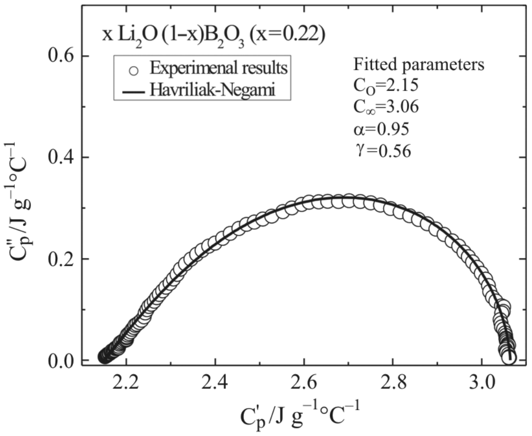

Fig. 4 Cole-Cole plot of $0.22Li_2O\cdot 0.88B_2O_3$. Circles denote the experimental results. Total number of data decreases by 1/10. Solid line denotes the fitted values by HN equation

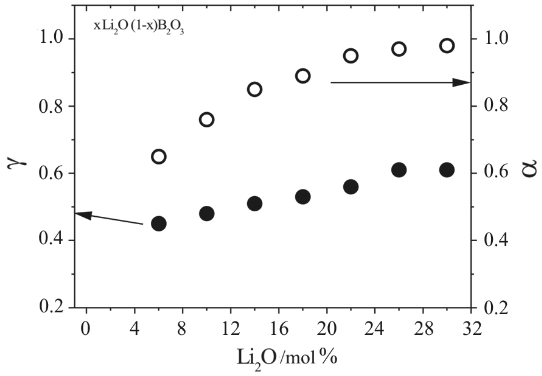

Fig. 5 Concentration dependence of the distribution parameters (α and γ) of the HN equation

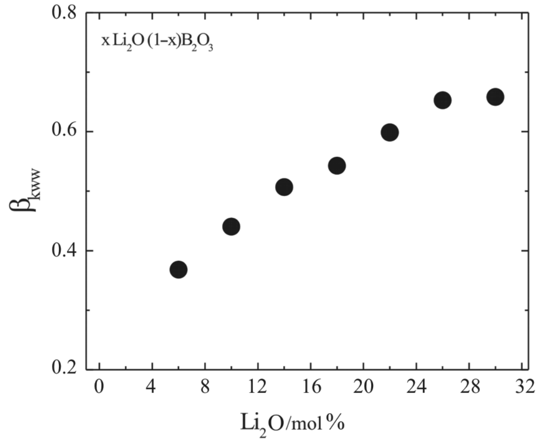

Fig. 6 Concentration dependence of the stretched exponential parameter (β) of the KWW function

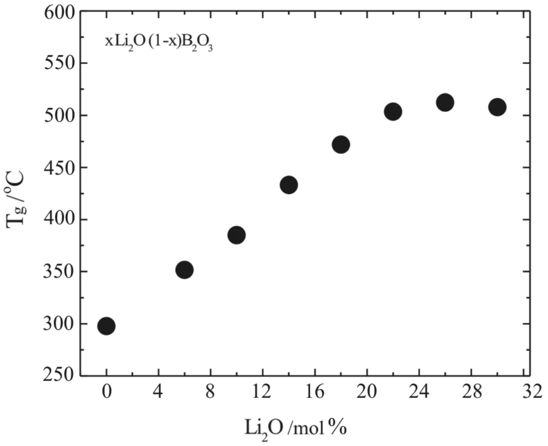

Fig. 7 Concentration dependence of dynamical glass transition temperature T_g (underlying heating rate is 1°C min^{-1}, and modulation period is 100 s)

The physical properties of alkali metal borate glasses often exhibit maxima or minima *vs.* their concentration, known as ‘borate anomalies’. One of the causalities is that the coordination number of boron atoms constituting the framework of the system changes from 3 to 4. The network of B_2O_3 (x=0) is mostly constructed by planar triangle BO_3 units. The addition of Li_2O causes the structural change of the system and leads to the formation of the 3-dimensional tetrahedral BO_4 units [23–26]. There are marked variations of the structural units in the intermediate range [27]. The non-Debye nature may directly reflects the heterogeneity of intermediate structures in the lithium borate system. Namely, the distribution of intermediate structures causes the distribution of relaxation time, which is directly connected with the non-Debye parameters.

Thermal properties of lithium borate glasses

In the present study, we have determined the dynamical T_g as the peak temperature in the C_p'' curves under the concentration range $0 \leq x \leq 0.30$. Figure 7 shows the dynamical T_g as a function of molar concentration of Li_2O. This figure clearly shows the concentration dependences of T_g. These glass transition temperatures increase linearly with the increase of Li_2O in the systems, and show the very broad peak around composition of Li_2O, x=0.26. Moreover, we have also analyzed the temperature range (ΔT) of the glass transition region from the C_p' curves of different concentration in such a way described in Fig. 2. Figure 8 shows the concentration dependence of ΔT. The width of glass transition regions have a tendency to be narrower with the increase of the Li_2O in the glass system.

In the present results, some amounts of borate units change from the planar triangle BO_3 unit to the 3-dimensional tetrahedral BO_4 with the increase of the Li_2O, as was discussed in the previous sub-section, and this leads the glass network to more and more ‘rigid’. This result is consistent with Brillouin scattering results by which an elastic constant has been observed [28]. The additive effect of Li_2O in borate system has been also discussed in relation with the change in fragility [2]. Concentration dependence of the ΔT is related to the change of fragility. In Fig. 8, as the molar concentration Li_2O increases, lithium borate glass systems tend to change from ‘strong’ into ‘fragile’ comparatively. This interpretation has been consistent with and supported by the result of the previous sub-section, where non-Debye parameters have been analyzed.

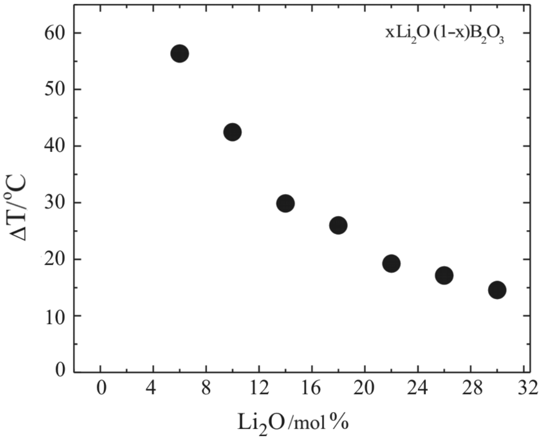

Fig. 8 Concentration dependence of the width of glass transitions, ΔT

Conclusions

MDSC is the powerful tool to investigate both the thermal properties and dynamics of a glass transition. In the present study, the complex specific heat capacity of lithium borate glasses (x=0.00–0.30) has been investigated by Modulated DSC. In the vicinity of T_g, the remarkable temperature dependence is clearly observed in the real and imaginary parts of complex heat capacity. Moreover, we have determined the distribution parameters of relaxation time in the Havriliak-Negami equation and the stretched exponential parameter in the Kohlrausch-Williams-Watts function. The composition dependence indicates the non-Debye nature is suppressed with the increase of Li_2O concentration. Dynamical T_g and the temperature range of the glass transition also have been determined as a function of Li_2O. These results showed remarkable changes with the increase of Li_2O. The additive effect of Li_2O causes the change of intermediate structures of the borate glass system, and induces the change of the fragility markedly.

Acknowledgements

This research was partially supported by the Ministry of Education, Culture, Sports, Science and Technology, Grant-in-Aid for Scientific Research (A), Japan, 2005, No.15654057.

References

1 C. A. Angell, K. L Ngai, G. B. Mckenna, P. F. McMillan and S. W. Martin, J. Appl. Phys., 88 (2000) 3113.
2 S. Kojima, V. N. Novikov and M. Kodama, J. Chem. Phys., 113 (2000) 6344.
3 R. Kubo, Rep. Prog. Phys., 29 (1966) 255.
4 A. Hunt, J. Non-Cryst. Solids, 160 (1993) 183.

5 N. O. Birge and S. R. Nagel, Phys. Rev. Lett., 54 (1985) 2674.
6 N. O. Birge, Phys. Rev. B, 34 (1986) 1631.
7 R. Kubo, J. Phys. Soc. Jpn., 12 (1957) 570.
8 M. Reading, Trends Polymer Sci., 1 (1993) 248.
9 M. Reading, D. Elliott and V. L. Hill, J. Thermal Anal., 40 (1993) 949.
10 I. Park and S. Kojima, Thermochim. Acta, 352 (2000) 147.
11 L. Carpentier, O. Bustin and M. Decamps, J. Phys. D, 35 (2002) 402.
12 J. E. K. Schawe, Thermochim. Acta, 261 (1995) 183.
13 J. E. K. Schawe and G. W. H. Höhne, Thermochim. Acta., 287 (1996) 213.
14 F. Kohlrausch, Prog. Ann. Phys., 119 (1863) 352.
15 G. Williams and D. C. Watts, Trans. Faraday Soc., 66 (1970) 80.
16 K. S. Cole and R. H. Cole, J. Chem. Phys., 9 (1941) 341.
17 D. W. Davidson and R. H. Cole, J. Chem. Phys., 19 (1951) 1484.
18 S. Haviliak and S. Negami, Polymer, 8 (1967) 161.
19 M. Kodama, T. Matsushita and S. Kojima, Jpn. J. Appl. Phys., 34 (1994) 2570.
20 S. Weyer, A. Hensel and C. Schick, Thermochim. Acta, 304 (1997) 267.
21 Z. Jiang, C. T. Imrie and J. M. Hutchinson, Thermochim. Acta, 315 (1998) 1.
22 F. Alvarez, A. Algeria and J. Colmenero, Phys. Rev. B, 44 (1991) 7306.
23 G. Carini, M. Cutroni, A. Fontana, G. Mariotto and F. Rocca, Phys. Rev. B, 29 (1984) 3567.
24 J. Zhong and P. J. Bray, J. Non-Cryst. Solids, 111 (1989) 67.
25 P. J. Bray and J. G. O'Keefe, Phys. Chem. Glasses, 4 (1963) 37.
26 S. K. Lee, M. Tatsumisago and T. Minami, J. Ceram. Soc. Jpn., 103 (1995) 398.
27 G. D. Charyssikos and E. I. Mamitsos, Proc. 2nd Int. Conf. on Borate Glasses, Crystals and Melts, p. 128.
28 Y. Ike, Y. Matsuda, C. Matsui, M. Kodama and S. Kojima, Proc. 5th Int. Conf. on Borate Glasses, Crystals and Melt, 2005 to be published.

DOI: 10.1007/s10973-006-7652-9