Complex Heat Capacity of Lithium Borate Glasses

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A glassy state is in non-equilibrium and the glass transition is regarded as one kind of relaxation phenomenon [1]. In the system containing relaxation processes, the heat capacity is time or frequency dependent in its nature, called dynamic heat capacity or complex heat capacity. The "specific-heat spectroscopy [2]" is the important method to investigate relaxation process through the glass transition region, because the enthalpy relaxation process observed by heat capacity spectroscopy includes total degree of freedom.

Although Modulated-Temperature Differential Scanning Calorimetry (MDSC or MTDSC) is the powerful tool to investigate glass transition phenomena, there are few papers to study frequency dependences of the complex heat capacity of inorganic materials, especially alkali borate glasses by MDSC.

In the present study, we have investigated the composition dependences of the thermal properties of lithium borate glasses around the glass transition temperature (T_g) by MDSC and also investigated the frequency-dependence of the complex heat capacity.

Composition formula of lithium borate glasses is $xLi_2O \cdot (1-x)B_2O_3$, where x is the molar fraction of Li_2O. A series of the glasses was prepared at regular intervals of 0.02 molar fractions ($0 \leqq x \leqq 0.28$). All of the glasses were prepared with high homogeneity [3].

In MDSC (DSC2920, TA Instruments), a small sinusoidal perturbation is superimposed on an underlying linear temperature ramp used in conventional DSC. The sample was heated through T_g at a constant underlying heating rate of 5 ºC/min with the modulation amplitude of ±1 ºC every 100, 60 or 40 sec. From the modulated heat flow signals, complex heat capacity ($C_p^* = C_p' - i\, C_p''$) can be obtained. The real part (C_p') is related to in-phase components with temperature modulation and technically called reversing heat capacity. Imaginary part (C_p'') is related to out-of-phase and called kinetic heat capacity [4].

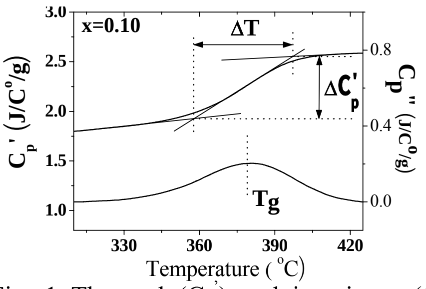

Fig. 1 The real (C_p') and imaginary (C_p'') parts of heat capacity of $0.1Li_2O \cdot 0.9B_2O_3$ as a function. of temperature.

Figure 1 shows the C_p' and C_p'' of the lithium borate glass (x = 0.10) near T_g. The C_p' shows step-like and C_p'' has a broad peak around T_g. These are the characteristic features of the dynamic susceptibility of a relaxation process. We have analyzed the width (ΔT) and height ($\Delta C_p'$) as shown in Fig. 1.Then, we have determined the calorimetric T_g defined as the center of peak temperature in Cp" curve.

Figure 2 shows T_g as a function of Li_2O. This figure clearly shows the composition dependence of T_g.

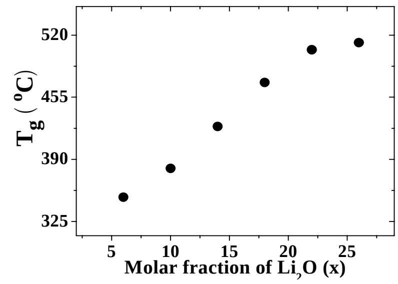

Fig.2 Glass transition temperatures T_g as a function of molar fraction of Li_2O for the frequency 10 mHz

This may be related to the change of structural units in borate system and result in the change of fragility [5].

Figure 3 shows the imaginary part (C_p'') normalized by the maximum value of C_p'' as a function of temperature for various frequencies (x = 0.10). The frequency dependence of complex heat capacity is clearly observed in the vicinity of T_g. The center of peak temperature in C_p''/C_{pMax}'' curve shifts toward higher temperature with increasing the measuring frequency. We can investigate the temperature dependence of relaxation time and such analysis is in progress.

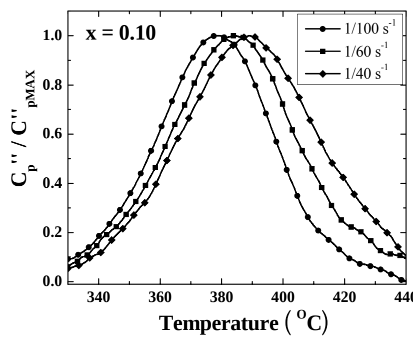

Fig. 3 Frequency dependence of the C_p'' normalized by the max. of C_p'' of $0.1Li_2O \cdot 0.9B_2O_3$ as a function of temperature.

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