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Low-temperature excess heat capacity in fresnoite glass and crystal

SUBJECT AREAS:

PHASE TRANSITIONS
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Kensaku Nakamura, Yoshihiro Takahashi & Takumi Fujiwara

Department of Applied Physics, Tohoku University, 6-6-05 Aoba-ku, Sendai 980-8579, Japan.

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requests for materials
should be addressed to
K.N. (k-nakamura@
laser.apph.tohoku.ac.
jp)

The effect of thermal annealing on low-temperature excess heat capacity was investigated in fresnoite ($\text{Ba}_2\text{TiSi}_2\text{O}_8$) glass. The amplitudes of the excess heat capacity decreased, and their positions shifted to a higher temperature by relaxation or crystallization. In particular, we revealed that the change in the excess heat capacity during transition from the glassy state to the crystalline state is relatively small compared with that of other oxides. Therefore, it is suggested that distribution of the excess vibrational density of states of the glass is similar to that of the corresponding crystal.

Amorphous materials have an excess vibrational density of states (VDOS), $g(\omega)$, over that predicted by the Debye theory in the terahertz frequency range. This excess VDOS manifests as a larger heat capacity (C_p) than the Debye T^3 law in the low-temperature region, and a hump, a so-called “boson peak,” appears in the C_p/T^3 - T plot (T : temperature in Kelvin)¹. The boson peak also appears as a broad band in the low-energy region of Raman/inelastic-neutron scattering spectra^{2,3}, and is a universal feature in amorphous matter because the boson peak is obtained regardless of the components, e.g., inorganic, organic, and metal substances⁴⁻⁶. Although the boson peak is closely related to transverse acoustic phonons⁷⁻⁹, its origin is still debated and many theoretical and experimental studies have been conducted in order to elucidate the mechanism of the boson peak. Theoretical simulations have indicated that thermal history governs the boson-peak feature, e.g., the height and position^{10,11}. In addition, it has been experimentally found that thermal annealing decreases the boson-peak intensity in the low-temperature heat capacity of oxide, organic and metallic glasses^{5,12,13}.

It is known that some crystals also show excess C_p in the low-temperature range similar to that of the boson peak in the C_p/T^3 - T plot^{4,14}. The excess C_p of a crystal is associated with an increase in VDOS at the critical points, i.e., the so-called “van-Hove singularity,” at which the Brillouin-zone boundary is situated in phonon dispersion^{4,14}. In addition, the position of the excess VDOS at the van-Hove singularity shifts to a lower frequency when the force constant gets into a disorder^{8,9}. According to Chumakov, the excess-DOS distribution of sodium iron silicate glass approaches that of the corresponding crystal phase as the glass is subjected to high-pressure conditions¹⁵. These studies encouraged us to consider the anomalous C_p behavior due to excess VDOS of the glassy state originating through a similar mechanism as that observed in the crystal state. Therefore, comparison between the boson peak in the glassy state, and the excess modes of its crystal-state counterpart, is a direct and decisive method of understanding the nature of the boson peak. Some studies have experimentally shown the comparison of the excess heat capacities between glass and its counterpart, and crystallization effect on the excess heat capacity in oxide, inorganic and metallic materials¹⁴⁻²⁰. In terms of the oxide glass, although the crystal counterpart is often obtained through thermal crystallization in the parent glass¹⁵⁻¹⁷, the effect of annealing conditions on the excess C_p and/or VDOS have not been dealt with. Therefore, it is significant to employ an oxide glass, in which the crystal fraction is controllable, to elucidate the effect of crystallization on the excess heat capacity (VDOS). In this paper, we examine the effects of structural relaxation and subsequent crystallization processes, on low-temperature excess heat capacity by thermal annealing of a glass and discuss the relation of the excess C_p between the glass and its crystal counterpart. We chose fresnoite ($\text{Ba}_2\text{TiSi}_2\text{O}_8$) glass for this study because the isochemical $\text{Ba}_2\text{TiSi}_2\text{O}_8$ phase is crystallizable through homogenous nucleation²¹, and there is adequate knowledge concerning structural and physical properties of fresnoite-type $\text{Ba}_2\text{TiSi}_2\text{O}_8$ crystal^{22,23}. Thus, fresnoite glass/crystal is a suitable system in this study.

Results

Figure 1 shows the volume fraction of the $\text{Ba}_2\text{TiSi}_2\text{O}_8$ crystal as a function of annealing temperature, which is obtained on the basis of TEM observation in the test samples. The fractions in the test samples at 1003 K and

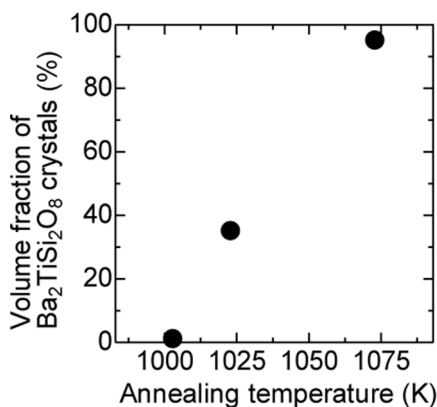


Figure 1 | Relation between volume fraction of fresnoite phase and annealing temperature (annealing period of 1 h). The fraction was estimated via TEM observation in samples.

1023 K were estimated to be ~ 1 – 2% and $\sim 35\%$, respectively. The sample annealed at 1073 K consisted of an almost crystalline phase, i.e., $\sim 95\%$ of Ba₂TiSi₂O₈ crystal.

In Fig. 2, we show the heat capacities (C_p) as a function of temperature (T) in the studied samples. Although the obtained data seem to be ordinary curves [Fig. 2(a)], the difference in C_p between the glassy and annealed samples, i.e., ΔC_p , exhibited a positive value in the region below ~ 30 K [Fig. 2(b)]. The positive ΔC_p indicates that the excess C_p of the glassy sample is larger than that of the annealed samples in this temperature range because this region is affected by the excess heat capacity beyond that corresponding the Debye T^3 law. However, above ~ 30 K, the ΔC_p of the sample at 1003 K is positive, while that of samples at 1023 K and 1073 K are negative. It is known that over a few tens of K, C_p of as-prepared glass tends to be larger than that of the annealed (relaxed) glasses²⁴. Since the sample annealed at 1003 K was almost in the glassy state, as seen in Fig. 1, the decrease in C_p by annealing at 1003 K, which gives the positive value of ΔC_p , is due to relaxation of the glassy phase. On the other hand, the samples at 1023 K and 1073 K involve the crystalline phase, and therefore the negative values of ΔC_p strongly suggest that above ~ 30 K, C_p of the Ba₂TiSi₂O₈ crystal is larger than that of the parent glass. According to Richet, in many silicate systems, the heat capacity difference between the glass and the corresponding crystal possess positive ΔC_p values above ~ 30 K, whereas the CaAl₂Si₂O₈ system has negative values²⁵. Therefore, the $\Delta C_p < 0$ in Ba₂TiSi₂O₈ is a rare case, similar to that in the CaAl₂Si₂O₈ composition. Richet has

also described that the degree of structural ordering of the crystalline phase is related to the value of ΔC_p ²⁵.

In Fig. 3, we show the C_p/T^3 and $\Delta C_p/T^3$ curves as functions of temperature in the studied samples. In all measured samples, broad peaks could be observed in the C_p/T^3 – T plot around 10 K–20 K [Fig. 3(a)], and the intensity of these peaks decreased with the increase in the annealing temperature. In addition, below 4 K, $\Delta C_p/T^3$ increased as the temperature decreased [Fig. 3(b)]. Generally, the heat capacity of glass is attributed to by the two-level tunneling states, which appear at lower temperatures than boson-peak contributions^{19,26}. Therefore, the difference in $\Delta C_p/T^3$ below 4 K by the annealing temperature might be related to the disappearance of the tunneling contribution in the glassy phases¹⁹.

Discussion

We noticed that C_p/T^3 of the sample obtained at 1003 K was smaller than that of the as-prepared glass [Fig. 3(a)], indicating that C_p/T^3 decreased via relaxation of the glassy phase by annealing at 1003 K. Singh et al. have simulated the VDOS of glass based on the potential energy landscape theory and have suggested that the boson peak shifts to a higher frequency and decreases in height when the cooling rate is slower (from the liquid state)¹¹. In other words, the boson peak of glass, in which the energy state is trapped at a deeper minimum in the landscape, shows a higher frequency and lower intensity. In this study, the as-prepared glass could have a higher energy than the sample annealed at 1003 K because the sample is adequately relaxed. Therefore, it is reasonable that the boson peak in the sample at 1003 K appears at a higher frequency and with a smaller intensity than the as-prepared glass. C_p is known to be expressed as

$$C_p(T) = 3Nk_B \int_0^{\nu_D} g(\omega) \left(\frac{\hbar\omega}{k_B T} \right)^2 \frac{\exp\left(\frac{\hbar\omega}{k_B T}\right)}{[\exp\left(\frac{\hbar\omega}{k_B T}\right) - 1]^2} d\omega, \quad (1)$$

where N is the number of atoms, \hbar is Planck's constant, k_B is Boltzmann's constant, and ν_D is the Debye frequency²⁷. Taking Eq. (1) into account, one can see that the decrease in C_p/T^3 is due to the reduction of excess $g(\omega)$ by annealing at 1003 K, in accordance with the prediction obtained by the simulation¹¹. The annealing (or thermal relaxation) effect on C_p/T^3 is also confirmed in metallic and organic materials^{5,13}.

In terms of C_p/T^3 , the values of the samples annealed at 1023 K and 1073 K, in which crystalline Ba₂TiSi₂O₈ is main the phase, were lower than those of the as-prepared precursor and sample annealed at 1003 K, in which the glass is in the total/main phase [Fig. 3(a)]. According to Crupi et al., the low-temperature heat capacity mea-

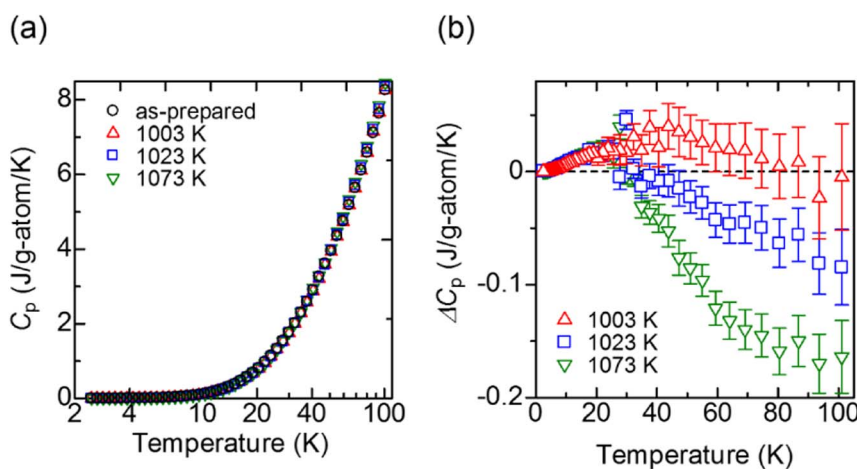


Figure 2 | Heat capacity (C_p) measurements in as-prepared and annealed glasses: (a) Measured C_p as a function of temperature (as-obtained data). (b) Difference in C_p between as-prepared and annealed samples, i.e., ΔC_p .

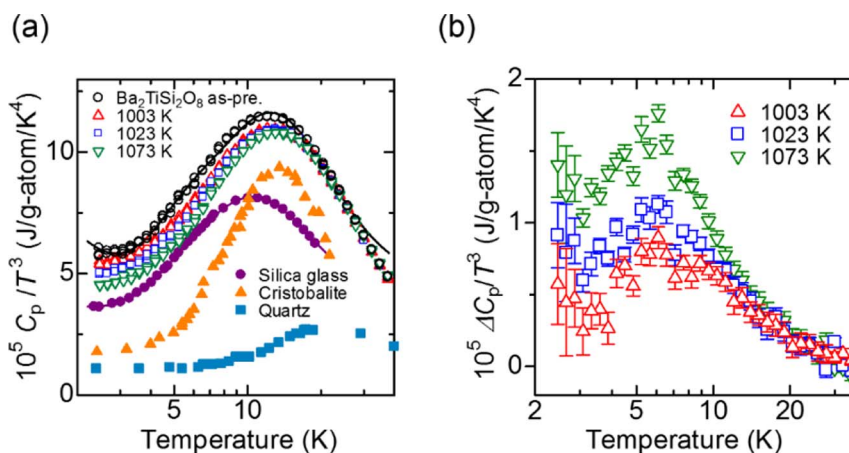


Figure 3 | Heat capacity measurements in studied samples: (a) C_p/T^3 versus temperature in fresnoite glass and annealed samples (open symbols). The solid lines correspond to the fitting curves (see text). Data for quartz, cristobalite, and silica glass are also included (closed symbols). (b) Difference in C_p/T^3 between as-prepared glass and samples annealed at different temperatures, i.e., $\Delta C_p/T^3$ as a function of temperature.

surement revealed that the boson-peak intensity in CsB_3O_5 glass is higher than the excess heat capacity in the CsB_3O_5 crystal¹⁶. In addition, Chumakov also demonstrated that the boson peak of the $\text{Na}_2\text{FeSi}_3\text{O}_{8.5}$ glass has higher amplitude than the excess VDOS of its $\text{NaFeSi}_2\text{O}_6$ crystal counterpart¹⁵. Therefore, taking their reports into account, the results in this study are reasonable.

In Fig. 3(a), we include the data from SiO_2 with different states, i.e., quartz and cristobalite (polymorphs) and silica glass to compare the C_p/T^3 values between SiO_2 and fresnoite samples. In Fig. 4, we show the relation between $(C_p/T^3)_{\text{max}}$ and T_{max} in these samples. The data from the SiO_2 samples were cited from references^{18,28,29}. Figs. 3(a) and 4 brings to our notice that the values of C_p/T^3 in the SiO_2 samples satisfy cristobalite > glass > quartz. Richet found that the difference in the C_p/T^3 values between SiO_2 glass and the cristobalite is considerably small compared with the difference between other glass-forming oxides (B_2O_3 and GeO_2) and their corresponding crystals¹⁸. In addition, it was found that when the difference in density between them is small, C_p/T^3 of the glass approaches that of the crystal. Relative-density differences between the SiO_2 glass and quartz were determined to be $\sim 20\%$, while the cristobalite was determined to be $\sim 6\%$ ¹⁸. In stoichiometric $\text{Ba}_2\text{TiSi}_2\text{O}_8$, the difference between the glass and crystal is $\sim 3.5\%$ ³⁰ and its value is smaller than those mentioned above. Chumakov et al. suggested that the excess VDOS of the $\text{Na}_2\text{FeSi}_3\text{O}_{8.5}$ glass (density: 2.714 g/cm^3) approached that of the $\text{NaFeSi}_2\text{O}_6$ crystal counterpart (density 3.631 g/cm^3) via high-pressure densification, suggesting that the boson peak also appears in other similar phenomena, which is seen in the crystal state, i.e., piling up of the acoustic states at the Brillouin-zone boundary¹⁵. Taking the

descriptions into account, the results in this study strongly suggest that if the difference in density between the glass and crystal is small, the difference in the excess C_p (or VDOS) is also small. Furthermore, we found considerable similarity in not only C_p/T^3 but also T_{max} between the glass and crystal in fresnoite composition (Fig. 4). Since C_p is expressed as an integration of $g(\omega)$, according to Eq. (1), the similarity of excess C_p between the glass and crystal does not necessarily mean that the same is true for distribution of $g(\omega)$. However, Safarik experimentally reveals that the T_{max} values are associated with the Brillouin-zone boundary frequency in metallic systems¹⁴. In oxide systems, the compositional dependence of $(C_p/T^3)_{\text{max}}$ and T_{max} is consistent with the dependence of the intensity and position for the excess VDOS³¹. Furthermore, very recently, it is demonstrated that the SiO_2 glass and a SiO_2 polymorph, which has a similar density to the glass, have the same number of the excess state in VDOS and show the same heat capacity³². These studies indicate that the analysis of excess C_p is helpful for understanding excess VDOS. Since the comparison between the glassy fresnoite and its corresponding crystal indicated that the minimum change in C_p/T^3 and T_{max} is due to glass–crystal transformation, it is reasonable to conclude that the excess-VDOS distribution of the glass closely resembles that of the crystal.

In summary, we measured the low-temperature heat capacity of the as-prepared, relaxed, and fresnoite-crystallized glasses, which have a stoichiometric fresnoite ($\text{Ba}_2\text{TiSi}_2\text{O}_8$) composition. The C_p/T^3 – T plot revealed a broad peak around 10 K–20 K, corresponding to excess heat capacity. Particularly, the relaxed/crystallized samples possessed a lower value of C_p/T^3 and higher maximum position situated at a high temperature, compared with the as-prepared sample. Furthermore, although the as-prepared glass undergoes a drastic structural transformation after crystallization, i.e., a glass–crystal transition, C_p/T^3 of the crystallized sample was almost identical to that of the relaxed sample. This strongly suggests that the distribution of excess VDOS of the glassy fresnoite is considerably similar to that of the crystalline $\text{Ba}_2\text{TiSi}_2\text{O}_8$. Therefore, comparison of excess heat capacity (or VDOS) in fresnoite glass and crystal, which have same composition (stoichiometry), can be useful to understand the origin of boson peak.

Methods

Test sample preparation. $\text{Ba}_2\text{TiSi}_2\text{O}_8$ glass, i.e., the glassy state of stoichiometric fresnoite phase, was synthesized by a conventional melt-quenching method. The synthesis was processed at 1723 K using a platinum crucible, and finally we acquired the transparent and colorless glassy sample having a glass-transition temperature $T_g \sim 990 \text{ K}$, which is estimated through differential thermal analysis (heating rate: 10 K/min). Test samples were obtained via annealing the glass at 1003 K, 1023 K, and

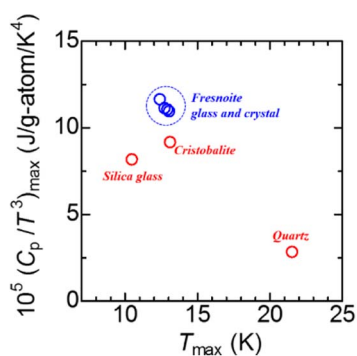


Figure 4 | Relation between $(C_p/T^3)_{\text{max}}$ and T_{max} in glassy and crystalline states for fresnoite ($\text{Ba}_2\text{TiSi}_2\text{O}_8$) and silica (SiO_2).



1073 K for 1 h. The x-ray diffraction analysis in the as-prepared glass and sample annealed at 1003 K showed a halo pattern, indicating the amorphous state. On the other hand, sharp diffraction peaks due to the formation of $\text{Ba}_2\text{TiSi}_2\text{O}_8$ crystals were confirmed in the samples at 1023 K and 1073 K.

Characterizations. We also conducted transmission electron microscopy (TEM) to evaluate crystal fractions for each sample. Low-temperature heat capacity measurements were performed via a relaxation method using a physical properties measurement system (Quantum Design Inc.). The obtained data were plotted as a function of temperature, i.e., a C_p/T^3 - T plot and then were analyzed by the sum of a Debye contribution and Einstein modes to evaluate the maximum $(C_p/T^3)_{\text{max}}$ and its position $T_{\text{max}}^{16,33,34}$. For evaluation of the measured samples, we additionally took a quantum tunneling term into account^{16,19,26}.

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Author contributions

Y.T. and T.F. designed the study. K.N. performed experiments to characterize the test samples, and performed the analyses. K.N., Y.T. and T.F. wrote the paper.

Additional information

Competing financial interests: The authors declare no competing financial interests.

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