Low-temperature excess heat capacity in fresnoite glass and crystal

Kensaku Nakamura, Yoshihiro Takahashi & Takumi Fujiwara

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

The effect of thermal annealing on low-temperature excess heat capacity was investigated in fresnoite (Ba$_2$TiSi$_2$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.

A morphous materials have an excess vibrational density of states (VDOS), $g(\nu)$, 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). The boson peak also appears as a broad band in the low-energy region of Raman/inelastic-neutron scattering spectra, and is a universal feature in amorphous matter because the boson peak is obtained regardless of the components, e.g., inorganic, organic, and metal substances. Although the boson peak is closely related to transverse acoustic phonons, 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. 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.

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. 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 phonon dispersion. 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. 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 conditions. 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 materials.

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. 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 phonon dispersion. 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. 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 conditions. 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 materials. In terms of the oxide glass, although the crystal counterpart is often obtained through thermal crystallization in the parent glass, 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 (Ba$_2$TiSi$_2$O$_8$) glass for this study because the isochemical Ba$_2$TiSi$_2$O$_8$ phase is crystallizable through homogenous nucleation, and there is adequate knowledge concerning structural and physical properties of fresnoite-type Ba$_2$TiSi$_2$O$_8$ crystal. Thus, fresnoite glass/crystal is a suitable system in this study.

Results

Figure 1 shows the volume fraction of the Ba$_2$TiSi$_2$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
1023 K were estimated to be ~1–2% and ~35%, respectively. The sample annealed at 1073 K consisted of an almost crystalline phase, i.e., ~95% of Ba₂TiSi₂O₈ crystal.

In Fig. 2, we show the heat capacities (Cₚ) as a function of temperature (T) in the studied samples. Although the obtained data seem to be ordinary curves [Fig. 2(a)], the decrease in Cₚ between the glassy and annealed samples, i.e., ΔCₚ, exhibited a positive value in the region below ~30 K [Fig. 2(b)]. The positive ΔCₚ indicates that the excess Cₚ 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 T³ law. However, above ~30 K, the ΔCₚ 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, Cₚ 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 Cₚ by annealing at 1003 K, which gives the positive value of ΔCₚ, 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 ΔCₚ strongly suggest that above ~30 K, Cₚ 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 crystalline crystal possess positive ΔCₚ values above ~30 K, whereas the CaAl₂Si₂O₈ system has negative values²⁵. Therefore, the ΔCₚ < 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 ΔCₚ²⁵.

In Fig. 3, we show the Cₚ/T³ and ΔCₚ/T³ curves as functions of temperature in the studied samples. In all measured samples, broad peaks could be observed in the Cₚ/T³–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, ΔCₚ/T³ 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 contributions²⁹,³⁰. Therefore, the difference in ΔCₚ/T³ below 4 K by the annealing temperature might be related to the disappearance of the tunneling contribution in the glassy phases²⁹.

**Discussion**

We noticed that Cₚ/T³ of the sample obtained at 1003 K was smaller than that of the as-prepared glass [Fig. 3(a)], indicating that Cₚ/T³ 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 temperature and with a smaller intensity than the as-prepared glass. Cₚ is known to be expressed as

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

where N is the number of atoms, ħ is Planck’s constant, k₉ is Boltzmann’s constant, and vD is the Debye frequency²⁷. Taking Eq. (1) into account, one can see that the decrease in Cₚ/T³ is due to the reduction of excess g(ω) by annealing at 1003 K, in accordance with the prediction obtained by the simulation¹¹. The annealing (or thermal relaxation) effect on Cₚ/T³ is also confirmed in metallic and organic materials³¹,³².

In terms of Cₚ/T³, 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 measured...
Figure 3 | Heat capacity measurements in studied samples: (a) $C_p/T$ 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 $C_p/T$ between as-prepared glass and samples annealed at different temperatures, i.e., $\Delta C_p/T$ as a function of temperature.

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

Measurements revealed that the boson-peak intensity in CsB$_3$O$_5$ glass is higher than the excess heat capacity in the CsB$_3$O$_5$ crystal\textsuperscript{16}. In addition, Chumakov also demonstrated that the boson peak of the Na$_2$FeSi$_3$O$_8$.5 glass has higher amplitude than the excess VDOS of its NaFeSi$_3$O$_8$ crystal counterpart\textsuperscript{15}. 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 $C_p/T$ values between SiO$_2$ and fresnoite samples. In Fig. 4, we show the relation between $(C_p/T)_\text{max}$ and $T_\text{max}$ in these samples. The data from the SiO$_2$ samples were cited from references\textsuperscript{16,28,29}. Figs. 3(a) and 4 brings to our notice that the values of $C_p/T$ in the SiO$_2$ samples satisfy cristobalite $>$ glass $>$ quartz. Richet found that the difference in the $C_p/T$ values between SiO$_2$ glass and the cristobalite is considerably small compared with the difference between other glass-forming oxides (B$_2$O$_3$ and GeO$_2$) and their corresponding crystals\textsuperscript{16}. In addition, it was found that when the difference in density between them is small, $C_p/T$ 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$6%\textsuperscript{30}. In stoichiometric Ba$_2$TiSi$_2$O$_8$, the difference between the glass and crystal is $\sim$3.5%\textsuperscript{30} and its value is smaller than those mentioned above. Chumakov et al. suggested that the excess VDOS of the Na$_2$FeSi$_3$O$_8$.5 glass (density: 2.714 g/cm$^3$) approached that of the NaFeSi$_3$O$_8$ 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 boundary\textsuperscript{31}. 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 $C_p/T$ but also $T_\text{max}$ between the glass and crystal in fresnoite composition (Fig. 4). Since $C_p$ is expressed as an integration of $\rho(\omega)$, 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 $\rho(\omega)$. However, Safarik experimentally reveals that the $T_\text{max}$ values are associated with the Brillouin-zone boundary frequency in metallic systems\textsuperscript{14}. In oxide systems, the compositional dependence of $(C_p/T)_\text{max}$ and $T_\text{max}$ is consistent with the dependence of the intensity and position for the excess VDOS\textsuperscript{15}. 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 capacity\textsuperscript{32}. 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 $C_p/T$ and $T_\text{max}$ 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 (Ba$_2$TiSi$_2$O$_8$) composition. The $C_p/T$–$T$ 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 $C_p/T$ 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, $C_p/T$ 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 Ba$_2$TiSi$_2$O$_8$. Therefore, comparison of excess heat capacity (or VDOS) in freshnoite glass and crystal, which have same composition (stoichiometry), can be useful to understand the origin of boson peak.

Methods

Test sample preparation. Ba$_2$TiSi$_2$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 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
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 Ba,Ti,Si, 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 $C_p(T)/T^3$–$T$ plot and then were analyzed by the sum of a Debye contribution and Einstein modes to evaluate the maximum ($C_p(T)/T^3$)max and its position $T_{\text{max}}$. For evaluation of the measured samples, we additionally took a quantum tunneling term into account.

1. Pohl, R. O. [Low Temperature Specific Heat of Glasses]. Amorphous Solids: Low-Temperature Properties [Phillips, W. A. (ed.)] [27–52], (Springer Verlag, New York, 1981).
2. Malinovsky, V. K. & Sokolov, A. P. The nature of boson peak in Raman scattering in Glasses. Solid State Comm. 57, 757–761 (1986).
3. Sokolov, A. P., Buchenau, U., Steffen, W., Frick, B. & Wischnewski, A. Comparison of Raman- and neutron-scattering data for glass-forming systems. Phys. Rev. B 52, 9815–9818 (1995).
4. Liu, X. & Löhneysen, H. V. Specific-heat anomaly of amorphous solids at intermediate temperature (1 to 30 K). Europhys. Lett. 33, 617–622 (1996).
5. Li, Y. Yu, P. & Bai, H. Y. Study on the boson peak in bulk metallic glasses. J. Appl. Phys. 104, 033520–113526 (2008).
6. Hassaine, M. et al. Low-temperature thermal and elastoooustic properties of butanol glasses: Study of position isomerism effects around the boson peak. Phys. Rev. B 85, 104206–104216 (2012).
7. Shintani, H. & Tanaka, H. Universal link between the boson peak and transverse phonons in glass. Nature Mater. 7, 870–877 (2008).
8. Schirmacher, W., Diezemann, G. & Ganter, C. Harmonic vibrational excitations in disordered solids and the ‘boson peak’ Phys. Rev. Lett. 81, 136–139 (1998).
9. Taraskin, S. N., Loh, Y. L., Natarajan, G. & Elliott, S. R. Origin of the boson peak in system with lattice disorder. Phys. Rev. Lett. 86, 1255–1258 (2001).
10. Grigera, T. S., Mayor, V. M., Parisi, G. & Verrucchio, P. Phonon interpretation of the ‘boson peak’ in supercooled liquids. Nature 422, 289–292 (2003).
11. Singh, S., Ediger, M. D. & Pablos, J. J. Ultrastable glasses from in silico vapor deposition. Nature Mater. 12, 139–144 (2013).
12. Champagnon, B., Chemarin, C. & Richet, P. Fictive temperature and medium range order in silicate glasses: a relationship between heat capacity and boson peak. Philos. Mag. B 77, 663–669 (1998).
13. Castañeda, T. P., Riibóo, R. J. J. & Ramos, M. A. Two-level systems and boson peak remain stable in 110-million-year-old amber glass. Phys. Rev. Lett. 112, 165901–165905 (2014).
14. Safari, D. J., Schwarz, R. B. & Hundley, M. F. Similarities in the $C_p(T)/T^3$ peaks in amorphous and crystalline metals. Phys. Rev. Lett. 96, 195902–195905 (2006).
15. Chumakov, A. I. et al. Equivalence of the boson peak in glasses to the transverse acoustic van Hove singularity in crystals. Phys. Rev. Lett. 106, 225501–225505 (2011).
16. Crupi, C., Angelo, G. D. & Vasi, C. Low-energy vibrational dynamics of cesium borate glasses. J. Phys. Chem. B 116, 6499–6505 (2012).
17. Carini, G. et al. Influence of packing on low energy vibrations of densified glasses. Phys. Rev. Lett. 111, 245502–245506 (2013).
18. Richet, P., Lingny, D. & Westrum Jr, E. F. Low-temperature heat capacity of GeO$_2$ and B$_2$O$_3$ glasses: thermophysical and structural implications. J. Non-Cryst. Solids 315, 20–30 (2003).
19. Talón, C., Ramos, M. A. & Vieira, S. Low-temperature specific heat of amorphous, orientational glass, and crystal, and crystal phases of ethanol. Phys. Rev. B 66, 012201–012204 (2002).
20. Vasilev, A. N. et al. Relationship between low-temperature boson heat capacity and high-temperature shear modulus relaxation in a metallic glass. Phys. Rev. B 80, 172102–172105 (2009).
21. Cabral, A. A., Fokin, V. M., Zanotto, E. D. & Chinaglia, C. R. Nanocrystallization of fresnoite glass. I. Nuclear growth and kinetic. J. Non-Cryst. Solids 330, 174–186 (2003).
22. Robert, M. G. & Tarte, P. Vibrational spectrum of fresnoite (Ba,Ti,Si, O, and isostructural compounds. Phys. Chem. Minerals 7, 26–30 (1981).
23. Markgraf, S. A., Halliday, A., Bhalla, A. S., Newnham, R. E. & Prewitt, C. T. X-ray structure refinement and pyroelectric investigation of fresnoite, Ba,Ti,Si, O,
24. Ferroelectrics 26, 17–26 (1985).
25. Richet, P., Robie, R. A. & Hemingway, B. A. Low-temperature heat capacity of diopside glass (Ca,Mg,Si, O,): A calorimetric test of the configurational-entropy theory applied to the viscosity of liquid silicates. Geochim. Cosmochim. Acta 50, 1521–1533 (1986).
26. Richet, P., Robie, R. A. & Hemingway, B. A. Entropy and structure of silicate glasses and melts. Geochim. Cosmochim. Acta 57, 2751–2766 (1993).
27. Phillips, W. A. Tunneling states in amorphous solids. J. Low Temp. Phys. 7, 351–360 (1972).
28. Sokolov, A. P., Kisluk, A., Quittmann, D. & Duval, E. Evaluation of density of vibrational states of glasses from low-frequency Raman spectra. Phys. Rev. B 48, 7692–7695 (1993).
29. Flubacher, P., Leadbetter, A. J., Morrison, J. A. & Stoicheff, B. P. The low-temperature heat capacity and the Raman and Brillouin spectra of vitreous silica. J. Phys. Chem. Solids 12, 53–65 (1959).
30. Bilir, N. & Phillips, W. A. Phonons in SiO, the low-temperature heat capacity of cristobalite. Philos. Mag. 32, 113–122 (1975).
31. Shinozaki, K., Honma, T. & Komast. T. Elastic properties and Vickers hardness of optically transparent glass-ceramics with fresnoite Ba,Ti,Si, O nanocrystals Mater. Res. Bull. 46, 922–928 (2011).
32. Chumakov, A. I. et al. Role of Disorder in the Thermodynamics and Atomic Dynamics of Glasses. Phys. Rev. Lett. 112, 025502–025507 (2014).
33. Zhou, Z. et al. On the existence of Einstein oscillators and thermal conductivity in bulk metallic glass. Appl. Phys. Lett. 89, 031924–031926 (2006).
34. Melot, B. C. et al. Large low-temperature specific heat in pyroclore B,$_2$O,$_7$. Phys. Rev. B 79, 224111–224115 (2009).

Acknowledgments
This work was supported by the Ministry of Education, Culture, Sports, Science and Technology (MEXT) of the Japanese government. The authors would like to thank Prof. Takamichi Miyazaki of Department of Instrumental Analysis, School of Engineering, Tokohuo University for significant contributions to this study.

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.

How to cite this article: Nakamura, K., Takahashi, Y. & Fujiwara, T. Low-temperature excess heat capacity in fresnoite glass and crystal. Sci. Rep. 4, 6523; DOI:10.1038/srep06523 (2014).

This work is licensed under a Creative Commons Attribution-NonCommercial-NoDerivs 4.0 International License. The images or other third party material in this article are included in this article's Creative Commons license, unless indicated otherwise in the credit line; if the material is not included under the Creative Commons license, users will need to obtain permission from the license holder in order to reproduce the material. To view a copy of this license, visit http://creativecommons.org/licenses/by-nc-nd/4.0/