Density of jadeite melts under high pressure and high temperature conditions

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The density of the jadeite (NaAlSi2O6) melt has been measured up to 6.5 GPa and 2273 K using the X-ray absorption technique at beamline 13-BM-D of the Advanced Photon Source. A fit of the pressure-density-temperature data to the high temperature Birch-Murnaghan equation of state yielded the following thermoelastic parameters: density, $\rho_0 = 2.36$ g/cm$^3$, isothermal bulk modulus, $K_T^0 = 21.5 \pm 0.8$ GPa, its pressure derivative, $K_T^0 = 8.9 \pm 1.2$, and the temperature derivative $(\partial K_T/\partial T)_P = -0.0021 \pm 0.0011$ GPa/K at a reference temperature $T_0 = 1473$ K. The densification of jadeite melt at low pressures is primarily dominated by topological changes in the structure, including a decrease in T-O-T angle and breaking and reforming of the T-O bond (T = Si$^{4+}$, Al$^{3+}$). Compressibilities of jadeite, albite, diopside, phonolite and peridotite melts display a systematic trend: the $K_0$-$K_0$ plot of these silicate melts exhibits an inverse linear relation.

Keywords: X-ray absorption method, Jadeite glass, Silicate melt, Density, High pressure, Equation of state

INTRODUCTION

The density of silicate melts is an important property for discussions of volcanic activities and differentiation of the terrestrial planets. Measurements on density of silicate melts have been carried out using several methods, including shock compression at very high pressures and sink-float in a large-volume press such as the multi-anvil press and piston cylinder apparatus (e.g., Rigden et al., 1984; Agee and Walker, 1988; Sakamaki et al., 2006). However, it is difficult to measure melt density precisely using these methods. Detailed characteristics of pressure and temperature dependences on the density of silicate melts are therefore difficult to clarify. An advanced technique becomes popular for melt density measurements. This technique combines synchrotron X-ray absorption measurement with a large volume press and has been conducted successfully on a number of melts by several authors (Katayama et al., 1993; Sanloup et al., 2000; Sakamaki et al., 2009, 2010a, 2010b, 2011; Nishida et al., 2011; van Kan Parker et al., 2012; Sakamaki et al., 2013; Seifert et al., 2013; Malfait et al., 2014a, 2014b). This well-established technique allows us to measure density of liquid under desired pressure and temperature conditions with much improved precision and accuracy. The technique is also applied to diamond anvil cell for density measurement of silicate glasses at much higher pressures (Sato and Funamori, 2008; Petitgirard et al., 2015).

Jadeite (NaAlSi2O6) is a basic sodium aluminosilicate and one of the important mantle minerals. Due to its importance, several properties of jadeite have been investigated (e.g., melting relationship: Bell and Roseboom, 1969; thermoelastic equation of state: Zhao et al., 1997; heat capacity: Hemingway et al., 1998). Recent studies also provide new insights associated with jadeite: wet jadeite solidus (Harlow et al., 2015); stability and changes of jadeite components in clinopyroxene in the upper mantle condition (Green et al., 2014). The melting curve of jadeite increases more rapidly with pressure than most known melting curves of other mantle materials and exceeds the melting temperatures of enstatite around 13 GPa (Litvin and Gasparik, 1993). A marked decrease in viscosity of jadeite melt with increasing has been observed by Kushiro (1976). For understanding this anomalous behavior, researchers have made efforts for obtaining insights by studying jadeite glass which is quenched from the melt (e.g., Velde and Kushiro, 1978). Moreover, structure of jadeite melt at high pressures has been observed using energy-dispersive X-ray diffraction and it

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concluded that the viscosity anomaly can be caused by a rapid shrinkage of intermediate-range order structure (Sakamaki et al., 2012). However, there has been no report on in-situ density measurements of jadeite melt under high pressure and high temperature. In this study, the density of jadeite melt has been measured using X-ray absorption method at high pressures and temperatures, and extracted equation of state information from our data. By combining these high temperature compression data with structure information, I discuss compression mechanisms of the jadeite melt.

**EXPERIMENTAL PROCEDURE**

Starting material is jadeite glass, which was prepared. By mixing reagent-grade oxides (SiO₂, Al₂O₃) and crystalline powder of Na₂Si₂O₅, which was previously synthesized from Na₂CO₃ and SiO₂, in an agate mortar with acetone for 2 h. The mixed powder was melted at 1673 K for 5 min. The recovered materials was repeatedly crushed and fused again three times in order to homogenize the glass starting materials. The composition of synthesized glass was analyzed by electron microprobe analyzer, and the ratio of SiO₂, Al₂O₃ and Na₂O are 60, 25, and 15 wt%, respectively, corresponding to a Na₀.₉₇Al₀.₉₈Si₂O₆ composition.

Density measurements were carried out using a DIA-type cubic press at the 13-BM-D beamline at APS, USA using 0.10 (vertical) × 0.05 (horizontal) mm monochromatic beam tuned to the desired energy (20 keV) using a Si (111) double-crystal monochromator. Details of the experimental setup are given in Figure 1. The intensities of the incident and transmitted X-rays were measured by two ion chambers placed in the front and rear of the press, respectively, for X-ray absorption measurements.

The cell assembly used is shown in Figure 2. The pressure medium was made of a boron–epoxy resin mixture and heater was graphite. Each sample was contained in a single-crystal diamond cylinder with an inner diameter of 0.5 mm and an outer diameter of 1.0 mm, to minimize changes in sample shape at high pressure and temperature conditions. A diamond piston was inserted into the top of the cylinder and the bottom and top of the cylinder were sealed with Re lids. The sample within the capsule was pressurized by the advancement of the diamond piston into the cylinder during loading of the entire assembly. The pressure marker was a mixture of MgO and h–BN (2:3 by volume) placed just above the sample container. The temperature was measured using a W₉₅Re₅–W₇₄Re₂₆ thermocouple and the pressure was calculated based on the energy-dispersive X-ray diffraction patterns of the MgO pressure marker using the equation of state (EOS) of Speziale et al. (2001). The energy-dispersive X-ray diffraction data were collected with a Ge solid-state detector (SSD). When switching between polychromatic (for pressure measurement) and monochromatic radiation (for density measurement), the ion chambers were removed or reinserted accordingly. Errors in temperature were estimated based on thermocouple fluctuation during absorption measurement and errors in pressure were based on the uncertainties of measured unit.
Figure 3. Typical experimental observations. (a) X-ray radiography image of the sample and diamond capsule at 1.97 GPa and 1573 K using the monochromatic X-ray tuned to 20 keV. Light grey region is jadeite melt and white part is diamond. (b) X-ray absorption of a jadeite melt and diamond at 1.97 GPa and 1573 K as a function of the sample position.

The density of jadeite melts 3
cally 1–2% based on the errors in the parameters and fitting errors.

Assuming that the mass absorption coefficient depends only on the energy of the X-rays and the atomic number, and it is independent of pressure and temperature. This assumption means that the mass absorption coefficient of glass under ambient conditions is equal to that of melt at high pressures and high temperatures. The absorption profiles of the starting material and diamond were measured under ambient conditions, where the density and thickness of the sample were already known, to determine the mass absorption coefficient of the sample ($\mu_{\text{sample}}$) and that of diamond ($\mu_{\text{diamond}}$), respectively. The density of diamond ($\rho_{\text{diamond}}$) at elevated pressure and temperature was calculated using the EOS of diamond (McSkimin and Andreatch, 1972; Zouboulis et al., 1998).

RESULTS AND DISCUSSION

Thermoelastic equation of state of jadeite melts

Our density measurements of the jadeite melt were carried out at pressures from 0.4 to 6.4 GPa and temperatures from 1473 to 2273 K. The experimental $P$–$T$ conditions are plotted in Figure 4, comparing with melting curve of jadeite (Litvin and Gasparik, 1993). The results of density measurements are summarized in Table 1 and pressure–density diagram is shown in Figure 5. The pressure–density temperature data are fitted using the high temperature Birch–Murnaghan equation of state (EOS). The third-order Birch–Murnaghan EOS is given by the following expression:

$$
\frac{\rho}{\rho_0} = 1 - \frac{1}{2} \frac{K_0}{K_0'} P + \frac{1}{2} \left( \frac{K_0}{K_0'} \right)^2 \frac{P}{\rho_0} - \frac{1}{2} \left( \frac{K_0}{K_0'} \right)^3 \frac{P^2}{\rho_0^2} + \frac{1}{2} \left( \frac{K_0}{K_0'} \right)^4 \frac{P^3}{\rho_0^3} - \frac{1}{2} \left( \frac{K_0}{K_0'} \right)^5 \frac{P^4}{\rho_0^4} + \cdots
$$

The uncertainties in density are 1–2%.

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<tr>
<th>T (K)</th>
<th>P (GPa)</th>
<th>Density (g/cm³)*</th>
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* The uncertainties in density are 1–2%.
where $\rho$ is the density under high pressure, $\rho_0$ is the density at an ambient pressure and $K_T$ is the isothermal bulk modulus. The value of $\rho_0$ at high temperature was calculated using the partial molar volume of each oxide and their thermal expansions reported by Lange and Carmichael (1987) and Lange (1997). $K_T$ is expressed as follows:

$$K_T = K_{T0} + \left( \frac{\partial K_T}{\partial T} \right)_P (T - T_0)$$  \hspace{1cm} \text{(Eq. 7)},$$

where $\left( \frac{\partial K_T}{\partial T} \right)_P$ is the temperature derivative of the bulk modulus and $T_0$ is the reference temperature. Although the reference temperature is usually 300 K in the case of the EOS for solid materials, it is not suitable for this study. Here I use a reference temperature at 1473 K, which is the lowest experimental temperature in this study. $K'_T$ is assumed to be constant. A least-squares fitting of the present $P$-$\rho$-$T$ data to the high-temperature Birch–Murnaghan EOS conduces to the following thermoelastic parameters: $K_{T0} = 21.5 \pm 0.8$ GPa, $K'_T = 8.9 \pm 1.2$ and $\left( \frac{\partial K_T}{\partial T} \right)_P = -0.0021 \pm 0.0011$ GPa/K (with $T_0 = 1473$ K). These uncertainties are come from the Levenberg-Marquard method for nonlinear least squares curve-fitting.

**Compression mechanism of jadeite melts**

With increasing pressure, silicate melts undergo continuous and gradual structural changes, by shrinkage of the intermediate-range network and decreasing the $T$–$O$–$T$ bond angles (e.g., Sakamaki et al., 2012). The dynamic responses of silicate melts to pressure are very different from those of solids. A comparison of compressibility between jadeite melt and crystalline jadeite may be informative in examining the differences in compression mechanisms. The compressibility ($\beta_T$) is by definition the inverse of bulk modulus:

$$\beta_T(P) = \frac{1}{K_T(P)}$$  \hspace{1cm} \text{(Eq. 8)},$$

The compressibility of crystalline jadeite has been reported by Zhao et al. (1997). Figure 6 demonstrates that melt and solid of the same composition have striking different compressibilities. The enhanced compressibility of jadeite melt at low pressures (<2 GPa) relative to the crystalline form reflects the shrinkage of the $\ldots$–$T$–$O$–$T$–$\ldots$ intermediate-range order structure of jadeite melt, which is topological changes in the distribution of $TO_4$ tetrahedra ($T = Si^{4+}, Al^{3+}$). The structure of jadeite melt was studied using energy-dispersive X-ray diffraction technique up to 4.9 GPa, and reported that the intermediate–range order structure shrink with pressure (Sakamaki et al., 2012). In that paper, the large shrinkage of intermediate–range order structure and decrease in $T$–$O$–$T$ angle between 1 atm and 2 GPa were observed. The decrease in $T$–$O$–$T$ angle and intermediate–range ordering distances suggests that the topology of tetrahedral connectivity changes toward a more compact network structure. The topological changes include the breaking and re-bonding of $T$–$O$–$T$ connection to make smaller member rings. This structural change in turn influences properties of the melt, for example viscosity, because the connectivity of $T$–$O$–$T$ networks is a controlling factor of the viscosity of a melt (Mysen et al., 1985). A large decrease in viscosity of jadeite melt with pressure was reported (Suzuki et al., 2011), and their results also support that $T$–$O$–$T$ angle decreased and the bond were broken and reformed. These results showed that the viscosity decreases rapidly to 2.2 GPa, after which the changes are minimal up to 5.5 GPa. In the diffraction data, the shrinkage of intermediate–range network correlates with the viscosity change up to 4.9 GPa. This correlation may be explained by two competing factors. First, the breakage of $T$–$O$–$T$ bonds in the network may result in a negative dependence of viscosity on pressure (Suzuki et al., 2011). Second, closer packing of atoms in general ex-

![Figure 6. The isothermal compressibility of jadeite melt and crystalline jadeite as a function of pressure at 1473 K.](image-url)
erts a positive effect in pressure dependence of viscosity (Taniguchi, 1993). For jadeite melt, the breakage of T–O–T bonds may be dominant at low pressures (below ~2 GPa), and thus may have caused a strong negative pressure effect on viscosity. As packing efficiency increases with pressure, the positive pressure effect due to void space reduction may play a more important role above 2 GPa, leading to a weak pressure dependence of viscosity above 2 GPa and even a positive pressure dependence above 4 GPa. These structure and viscosity studies of jadeite melts are consistent with our results of density measurements. A densification of jadeite melt at low pressure is likely to be dominated by the topological rearrangements.

**Compositional dependence of the isothermal compressibility for silicate melts**

The compressibility for jadeite melt is compared to that for four other silicate melts (albite: NaAlSi3O8 and diopside: CaMgSi2O6) in Figure 7. The compressibility for albite melt is calculated by fusion-curve analysis (Tenner et al., 2007), whereas the equation of state for diopside melt were measured by acoustic velocity measurement (Ai and Lange, 2008). The isothermal bulk modulus $K_0$ of albite melt is 17.3 (3) GPa and its pressure derivative ($K_0'$) is 10.8 (15) at 1773 K, respectively. On the other hand, $K_0$ of diopside melt is 22.5 (4) GPa and $K_0'$ is 6.8 (2) at 1773 K. These parameters are summarized in Table 2. One of the most striking features of the $\beta_T(P)$ curves in Figure 7 is that the order of which liquid is less compressible changes with increasing pressure. Diopside melt shows low compressibility at ambient pressure and a small decrease with pressure. The compressibility crossover occurs between 1.0 and 1.5 GPa, and diopside becomes high compressible melt above around 1.5 GPa. The compressibility of the jadeite melt shows intermediate feature between albite and diopside melts. Jadeite melt exhibits the lowest compressibility between 1.0 and 1.5 GPa. The crossover in $\beta_T$ between jadeite and diopside occurs at around 1 GPa and is caused by the higher $K_0'$ value (8.9) for jadeite melt than that (6.8) for diopside melt. Similarly, although albite melt has a much higher compressibility at ambient pressure than jadeite melt, its higher $K_0'$ value (10.8) causes its compressibility to become smaller than that for jadeite melt around 2.0 GPa. Thus, the albite melt is the least compressible above 2 GPa although it shows the most compressible of the three silicate melts at ambient pressure. In Figure 8, $K_0'$ is plotted as a function of $K_0$ for jadeite, albite, diopside melts. For comparison, $K_0$–$K_0'$ plot of phonolite (Seifert et al., 2013) and pyrolytic peridotite (Sakamaki et al., 2010a) melts, which have complex composition, are also plotted in the figure. This figure indicates that $K_0'$ and $K_0$ are inversely related in these silicate melts. The ratio between the number of non-bridging oxygen anions (NBO) and that of tetrahedrally coordinat-ed cations (T), commonly referred as NBO/T, is an important indicator for structures of silicate glasses and melts (NBO/T = 4: a monomer, 3: a dimer, 2: a chain, 1: a sheet). If NBO/T equals zero, such is the case for jadeite melt, all tetrahedra are interconnected via four oxygen anions and a three-dimensional network structure is formed (Seifert et al., 1982). The NBO/T of albite and phonolite melts are 0 and 0.13, respectively. Thus, they are polymerized melts.

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**Table 2.** Comparison of elastic parameters of each silicate melt at 1773 K

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<tbody>
<tr>
<td>$K_0$ 1773 K (GPa)</td>
<td>20.8 (8)</td>
<td>17.3 (3)</td>
<td>22.5 (4)</td>
<td>24.9 (13)</td>
<td>14.6 (32)</td>
</tr>
<tr>
<td>$K_0'$</td>
<td>8.9 (12)</td>
<td>10.8 (15)</td>
<td>6.8 (2)</td>
<td>7.3 (8)</td>
<td>8.9 (33)</td>
</tr>
<tr>
<td>$\beta_0$ 1073K (GPa⁻¹)</td>
<td>0.048 (2)</td>
<td>0.059 (1)</td>
<td>0.044 (1)</td>
<td>0.040 (2)</td>
<td>0.068 (20)</td>
</tr>
</tbody>
</table>


* The composition is pyrolite.

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**Figure 7.** The isothermal compressibility of jadeite, albite, diopside, peridotite, phonolite melts as a function of pressure at 1773 K. The uncertainties of the compressibility are shown in Table 2.
Density of jadeite melts

Figure 8. A plot of $K$ versus $K_0$ for five silicate melts. Data of jadeite, peridotite and phonolite melts are obtained using X-ray absorption density measurements.

On the other hand, diopside and peridotite melts have depolymerized structure because the NBO/T of these melts are 2 and 2.5, respectively. There are at least two interpretations for the pattern of data in Figure 8. One possibility is that polymerized melts (jadeite and albite composition: NBO/T = 0; phonolite composition: NBO/T = 0.13) show lower $K_T$ and higher $K'$ than depolymerized melts (diopside composition: NBO/T = 2; peridotite composition: NBO/T = 2.5). The other interpretation is that low-SiO$_2$ melts (jadeite: NaAlSi$_2$O$_6$, diopside: CaMgSi$_2$O$_6$, peridotite) is higher $K_T$ and lower $K'$ than high-SiO$_2$ ones (albite: NaAlSi$_2$O$_6$, phonolite). In this case, the SiO$_2$ content in the silicate melts may be an important parameter to constrain the elastic properties of the melt. The jadeite is known to be formed by breakdown of albite around 1.5 GPa (e.g., Newton and Smith, 1967; Holland, 1980). Assuming that NaAlSi$_2$O$_6$–NaAlSi$_2$O$_6$ + SiO$_2$ system, albite melt can be formed at lower pressure and its elastic properties control the magma migration. Under the pressure condition which jadeite can be stable, the jadeite melt is generated although there is a possibility that the melt composition could be albite due to a coexistence with quartz. Since the compressibility of jadeite at 1773 K is higher than that of albite above 1.5 GPa (Figure 7), the densification of the melt occurs efficiently with pressure.

ACKNOWLEDGMENTS

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