Heat capacity, entropy, configurational entropy, and viscosity of magnesium silicate glasses and liquids

Juraj Majzlan1 · Jean A. Tangeman2 · Edgar Dachs3

Received: 22 March 2021 / Accepted: 3 July 2021 / Published online: 19 July 2021 © The Author(s) 2021

Abstract

In this work, five Mg-silicate glasses with compositions between MgSiO3 and Mg2SiO4 were synthesized by aerodynamic levitation combined with laser melting. Low-temperature heat capacity (Cp) was measured (by relaxation calorimetry in the range 2–310 K) for all of them, with the resulting vibrational entropies at T = 298.15 K: sample MG50 with composition Mg0.996SiO2.996 and entropy 72.88 J mol⁻¹K⁻¹; MG54 Mg1.174SiO3.174 78.54; MG58 Mg1.364SiO3.364 85.05; MG62 Mg1.611SiO3.611 91.40; and MG67 Mg1.907SiO3.907 102.75. Heat capacity of the glasses is higher than that of the corresponding crystal mixtures below 200 K but plunges below the Cp,crystal at higher temperatures. High-temperature Cp was measured (by differential scanning calorimetry in the range 300–970 K) for MG50 and MG67 up to ≈1000 K. Using our Cp data, selected data for entropies of fusion, Cp of crystals, and fictive temperatures, the configurational entropy (Sconf) at glass transition temperature (Tg) were calculated. For the near-forsterite glass MG67, the Sconf is 1.9 J mol⁻¹K⁻¹ at Tg = 1040 K. As this small value is a difference of several large numbers, its uncertainty is relatively high; we consider a conservative estimate of 15 J mol⁻¹K⁻¹. Using the expression logη = A + B/[TSconf(T)], the available experimental viscosities (η) and the temperature-dependent configurational entropy from our work, we refined the parameters A = −2.34 and B = 76,500 for this equation, with Sconf(T) = 1.90 + (83.7 ln(T/1040)). The configurational entropy for the enstatitic MG50 glass is 16.8 J mol⁻¹K⁻¹ at Tg = 1063 K. The presented data can be combined with enthalpies of formation and thermophysical properties of Mg-silicate glasses for models that could elucidate geological and geophysical observations in the crust and mantle of the Earth.

Keywords Silicate glasses · Melts · Heat capacity · Configurational entropy · Viscosity

Introduction

Silicate glasses are important materials in geology, mineralogy, geochemistry, and geophysics (Mysen and Richet 2005). Their importance relates not particularly to their occurrence in nature but lies mostly in the fact that they open a window for the experimental investigation and understanding of the properties of silicate melts. Melting of the material in the crust and mantle of the Earth is one of the principal processes of this geologically active planet. The two most common rock types of continental and oceanic crust—granite and basalt—both originate from molten silicate liquid generated at depth. A significant amount of data exists on glasses and melts which correspond to the composition of individual minerals (e.g., Robie et al. 1978) or mixed compositions (e.g., Tangeman and Lange 1998). Naturally, the quantity of our knowledge is skewed to the glasses which can be prepared relatively easily and in large quantities in the laboratory and the available data do not cover the geologically important systems in a representative way. In particular, until recently, data were lacking for the intermediate or Mg-dominated compositions of the MgO–SiO2 system, simply because the preparation of such glasses was difficult or impossible. Tangeman et al. (2001) synthesized a larger amount of Mg2SiO4 glass using aerodynamic levitation coupled with laser melting (Weber et al. 1994) and opened the possibility to study the Mg-silicate glasses in detail (e.g., Wilding et al. 2004a; Benmore et al. 2011). Such
glasses were studied by nuclear magnetic resonance (NMR) spectroscopy (e.g., Kroecker and Stebbins 2000), Raman spectroscopy (e.g., Kalampounias et al. 2009), X-ray and neutron scattering (e.g., Wilding et al. 2008), and Brillouin spectroscopy (Speziale et al. 2009). Vibrational properties of these glasses were also studied by molecular dynamics (Belonoshko and Dubrovinsky 1996) and ab initio simulations (Spiekermann et al. 2013).

In this work, we measured the heat capacity \( \left( C_p \right) \) of the Mg-silicate glasses along the \( \text{MgSiO}_3-\text{Mg}_2\text{SiO}_4 \) join, corresponding to the compositions of the minerals, enstatite-forsterite, respectively. Most of the data were acquired at low (sub-ambient) temperatures and allow the calculation of entropy at \( T = 298.15 \text{ K} \). Additional high-temperature data were measured for selected compositions. These data were used, in conjunction with previously published \( C_p \) for crystalline substances and estimates of \( C_p \) for supercooled liquids, to calculate configurational entropies of these compositions.

Methods and materials

The magnesium silicate glasses were synthesized by a technique using aerodynamic levitation combined with laser melting, described previously by Tangeman et al. (2001). Briefly, the precursors for the glass synthesis were prepared by mixing high-purity MgO and SiO\(_2\) powders, laser hearth melting the mixture, and then crushing the centimeter-sized fused granules into millimeter-sized pieces. The pieces were aerodynamically levitated using pure oxygen in a conical nozzle and melted by a continuous-wave CO\(_2\) laser. The molten, levitating droplets were then cooled to glass spheroids by blocking the laser beam. The size of the pieces used for the production of glass was dictated by the ability of the material to vitrify; larger pieces could be used for the enstatite compositions that vitrify more easily, the smallest pieces had to be used for the forsterite composition which is the most difficult to vitrify.

Powder X-ray diffraction (XRD) data were measured with a Bruker D8 DαVinci diffractometer with Cu Kα radiation (\( \lambda = 1.54056 \) Å). The chemical composition of the samples was determined with a Cameca SX100 electron microprobe under these conditions and with these standards: current 15 nA, accelerating voltage 20 kV, beam spot 2 μm, periclase (MgO) for Mg and hypersthene (hy-19) ((Mg,Fe)SiO\(_4\)) for Si.

The heat capacity data were measured by a commercial Physical Properties Measurement System (PPMS) manufactured by Quantum Design®. For each experiment, 20.2–25.7 mg of crushed sample was loaded into an aluminum pan and sealed in air. Cooling in the calorimeter was achieved by liquid nitrogen or helium, as needed. The temperature is measured by two thermocouples; each of them operates in a separate temperature range. The PPMS calorimeter uses the heat-pulse technique, whereby the instrument inputs a known amount of heat into the sample and monitors the temperature change of the sample. Heat capacity was measured in the range of 2–310 K. Calculation of the heat capacity from raw data, the precision, and the accuracy for geological samples has been reviewed by Dachs and Bertoldi (2005). The performance of this instrument was also critically evaluated by Lashley et al. (2003).

The low-temperature \( C_p \) data measured in this study and those previously published for crystalline enstatite and forsterite were fitted by orthogonal polynomials. A polynomial with odd powers of \( T \) \( C_p = a_3T^3 + a_5T^5 + a_7T^7 \) was used for the extrapolation to \( T = 0 \text{ K} \). The polynomials were merged at the points where the fitted \( C_p \) had equal values although usually the slopes of the polynomials were slightly different in these points.

High-temperature \( C_p \) data were measured with a differential scanning calorimeter (DSC) Setaram DSC-111. The Setaram DSC-111 is a true Calvet microcalorimeter used in scanning mode. Samples were packed into platinum crucibles and measured in the temperature range 300–970 K. Corundum (powdered, 99.997% metals basis) was used as the heat capacity standard. Quartz and hematite were used to judge the accuracy of the data; the data collected for quartz and hematite deviated less than 2% from the \( C_p \) of Robie and Hemingway (1995).

Results

The chemical composition of the glass spherules does not deviate significantly from the target composition (Table 1). With the exception of MG54, all glasses are slightly depleted in MgO in comparison to the target composition. This depletion could be caused by a preferential loss of MgO during the fusion of the starting MgO and SiO\(_2\) powders. No elements other than Mg and Si were detected in the electron microprobe analyses. The X-ray diffraction (XRD) patterns of all samples showed only diffuse background with no Bragg peaks. The MG50 and MG67 samples were analyzed by XRD prior to and after the calorimetric measurements and no changes were observed. Previous \(^{29}\text{Si}\) nuclear magnetic resonance (NMR) study of the MG67 material Tangeman et al. (2001) showed that approximately 1% of crystalline forsterite is present in this sample. Such a small amount of crystalline phase could be easily missed by powder XRD.

The thermodynamic functions at \( T = 298.15 \text{ K} \) for all glasses and crystalline enstatite and forsterite are listed in Table 2. The measured data and the thermodynamic functions in the whole measurement range (0–300 K) are available as electronic supplementary material.
The numbers in parentheses are 2 standard deviations. The target Mg/(Mg + Si) value is given as the value in the sample name.

*Analysis from Tangeman et al. (2001)*

The entropies of the glasses at $T = 298.15$ K, as expected, are larger than those of their crystalline counterparts (Table 2). The entropies of vitrification are relatively small and the driving force for devitrification at room temperature, as expected, is the enthalpy (Fig. 3), not entropy. Both enthalpies and entropies of vitrification vary linearly in the region between Mg/(Mg + Si) of 0.5 to $\approx 0.65$. Above this range, toward the composition of forsterite, the linear trends no longer hold (Fig. 4). The deviation from linearity indicates structural changes in the glasses. Indeed, Wilding et al. (2004b) reported discontinuities in the coordination of Mg in the range of Mg/(Mg + Si) of 0.62–0.67. These structural changes are related to the fractions of MgO$_4$ and MgO$_5$ polyhedra in the glasses.

An interesting observation is that the $C_p$ of the glasses plunges below the $C_p$ of the corresponding mechanical

### Discussion

**Comparison of heat capacities of glasses and crystalline mixtures**

The entropies of the glasses at $T = 298.15$ K, as expected, are larger than those of their crystalline counterparts (Table 2). The entropies of vitrification are relatively small and the driving force for devitrification at room temperature, as expected, is the enthalpy (Fig. 3), not entropy. Both enthalpies and entropies of vitrification vary linearly in the region between Mg/(Mg + Si) of 0.5 to $\approx 0.65$. Above this range, toward the composition of forsterite, the linear trends no longer hold (Fig. 4). The deviation from linearity indicates structural changes in the glasses. Indeed, Wilding et al. (2004b) reported discontinuities in the coordination of Mg in the range of Mg/(Mg + Si) of 0.62–0.67. These structural changes are related to the fractions of MgO$_4$ and MgO$_5$ polyhedra in the glasses.

An interesting observation is that the $C_p$ of the glasses plunges below the $C_p$ of the corresponding mechanical

![Fig. 1](image-url) Low-temperature $C_p$ data for the glasses from this study: a Data for MG67 and MG50, compared to those of their crystalline counterparts. Data for enstatite from Krupka et al. (1985b), for forsterite from Robie et al. (1982). b Data for the glasses MG54, MG58, and MG62

---

**Table 1 Chemical analyses of the studied glasses by electron microprobe**

| Sample | MgO (wt.%) | SiO$_2$ (wt.%) | $\Sigma$ (wt.%) | 100Mg/(Mg + Si) (molar ratio) | Formula | Formula weight (g mol$^{-1}$) |
|--------|------------|----------------|----------------|-----------------------------|---------|-----------------------------|
| MG50   | 40.6 (0.3) | 60.9 (0.9)     | 101.5 (1.0)    | 49.9                        | Mg$_{0.996}$SiO$_{2.996}$         | 100.2278 |
| MG54   | 44.6 (0.3) | 56.7 (0.5)     | 101.4 (0.4)    | 54.0                        | Mg$_{1.174}$SiO$_{3.174}$         | 107.3982 |
| MG58   | 48.6 (0.4) | 53.1 (0.7)     | 101.7 (0.6)    | 57.7                        | Mg$_{1.364}$SiO$_{3.364}$         | 115.0622 |
| MG62   | 52.6 (0.3) | 48.7 (0.8)     | 101.3 (0.8)    | 61.7                        | Mg$_{1.611}$SiO$_{3.611}$         | 125.013  |
| MG67*  | 56.7 (1.0) | 44.3 (0.6)     | 101.1 (0.5)    | 65.6                        | Mg$_{1.907}$SiO$_{3.907}$         | 136.944  |

The numbers in parentheses are 2 standard deviations. The target Mg/(Mg + Si) value is given as the value in the sample name.

*Analysis from Tangeman et al. (2001)*
mixture of the crystals at $\approx 200$ K, with the exception of the MG67 glass (Figs. 1a and 5). The $C_p$ of the MG67 glass is above that of the corresponding forsterite+enstatite mixture ($\approx 94$ mol.% forsterite, $\approx 6$ mol.% enstatite) at all temperatures between 0 and 300 K.

Initially, the observation of lower $C_p$ of glass than the $C_p$ of the mechanical mixture of forsterite+enstatite was perceived skeptically as an experimental error. This observation, however, was confirmed by the later DSC measurements (Fig. 2) and the negative $\Delta C_p (= C_{p,glass} - \Sigma m_i C_{p,i}$, where $m_i$ is the molar fraction of the crystalline phase $i$) values are therefore intrinsic to the samples.

For most of the glasses and their crystalline counterparts, $\Delta C_p$ is positive in the region below 400 K (Robie et al. 1978), i.e., glasses have a higher $C_p$ than the crystals.

An exception is our MG50–MG62 glasses and the anorthite glass (Robie et al. 1978) (Fig. 5). All glasses, however, show a peak in the $\Delta C_p$ function, where the difference is at its maximum. For our Mg-silicate glasses, the peak occurs at $\approx 80$ K, while for the glasses with compositions near NaAlSi$_3$O$_8$, KAlSi$_3$O$_8$, CaAl$_2$Si$_2$O$_8$ (the compositions of feldspar end-members), the peak was found at 30–50 K (Robie et al. 1978).

### Boson peak in the heat capacity of the glasses

Heat capacity of glasses has been shown to deviate significantly from the Debye law $C_p = A_3 T^3$ at low temperatures (< 50 K) (e.g., Pohl 1981; Zotov 2002; Richet 2009). This anomaly can be approximately described by Bose-Einstein statistics and is therefore called the boson peak.

Heat capacity of alkaline earth silicate glasses was investigated in detail by Richet et al. (2009). They showed that the intensity of the boson peak scales with the mass of the alkaline earth cations, being the highest for Ba$^{2+}$ and the smallest for Mg$^{2+}$ (Fig. 6a). Their Mg silicate glass had composition Mg$_{1.12}$Si$_{0.88}$O$_{2.88}$. In the terminology used in this paper, such composition corresponds to MG56. The data for MG56 of Richet et al. (2009) overlap closely with the data for our sample MG58 (Fig. 6b). The data for MG54 and MG50 lie above and the data for MG62 and MG67 below. Overall, these observations agree with the conclusion of Buchenau et al. (1986) that the intensity of the boson peak should decrease with decreasing degree of tetrahedral polymerization in the silicate glasses. At the top of the boson peak, however, the data for MG67 are slightly higher than those for MG62, suggesting that the polymerization degree is not the only

### Table 2

Thermodynamic functions of the studied glasses and crystalline forsterite and enstatite at $T = 298.15$ K

| Sample   | $C_p^{298.15}$ J mol$^{-1}$ K$^{-1}$ | $S_298.15$ J mol$^{-1}$ K$^{-1}$ | $H_{298.15} - H_0$ kJ mol$^{-1}$ |
|----------|------------------------------------|---------------------------------|----------------------------------|
| MG50     | 80.08                              | 72.9± 0.9                       | 12.43± 0.15                     |
| MG54     | 87.31                              | 78.5± 0.9                       | 13.46± 0.16                     |
| MG58     | 94.36                              | 85.1± 1.0                       | 14.62± 0.18                     |
| MG62     | 101.89                             | 91.4± 1.1                       | 15.76± 0.19                     |
| MG67     | 115.68                             | 102.8± 1.2                      | 17.78± 0.21                     |
| enstatite|                                     |                                 |                                 |
| forsterite|                                   |                                 |                                 |

$H_{298.15} - H_0$ is the heat content (difference in enthalpies) between $T = 298.15$ K and $T = 0$ K. Data for enstatite from Krupka et al. (1985b), for forsterite from Robie et al. (1982). These functions, tabulated at selected temperatures between 0 and 298.15 K are available as an electronic supporting information to this publication.

---

**Fig. 2** Low-temperature (large circles) and high-temperature (small circles, only selected data points shown) $C_p$ data for the glasses MG50 and MG67. The solid thin lines show the Richet–Fiquet fits to the high-temperature $C_p$ data.
variable that controls the intensity and shape of the boson peak. Coordination changes of Mg (Wilding et al. 2004b) may play also a role although the quantification of such effects is very difficult.

| Sample        | $k_0$   | $k_1$   | $k_2 \times 10^{-6}$ | $k_3 \times 10^{-8}$ | $T$ range |
|---------------|---------|---------|----------------------|----------------------|-----------|
| Forsterite    | 271.3   | -3379   | 13.26                | -28.72               | 298–1850  |
| Orthoenstatite| 177.0   | -1586   | 0.2388               | -1.574               | 298–1300  |
| MG67 glass    | 230.7   | -1637   | -4.108               | 6.165                | 298–980   |
| MG50 glass    | 160.7   | -1011   | -4.321               | 6.661                | 298–980   |

| $a$           | $b$     | $c \times 10^{-4}$ | $d \times 10^{-7}$ | $e \times 10^{-9}$ |
|---------------|---------|---------------------|---------------------|---------------------|
| Forsterite    | -403.2  | 74.34               | 8.773               | -2.597              | 2.546     | 298–1850  |
| Orthoenstatite| 102.4   | 6.626               | -2.455              | 0.3839              | -0.5085   | 298–1300  |
| Protoenstatite| 41.95   | 12.24               | -0.4960             | 0                   | 0         | 1300–1810 |
| MG67 glass    | -790.4  | 123.7               | 15.00               | -4.136              | 4.233     | 298–980   |
| MG50 glass    | -437.7  | 71.93               | 9.230               | -2.922              | 3.335     | 298–980   |

Table 3 Heat capacity polynomial coefficients for the polynomials proposed by Berman and Brown (1985, eq. 1) and Richet and Fiquet (1991, eq. 2)

Data for the crystalline substances from Gillet et al. (1991), Krupka et al. (1985a), Thiéblot et al. (1999). For details, see text

Fig. 3 Enthalpies of vitrification ($\Delta_{\text{vitr}}H$, Nasikas and Navrotsky 2014) and $-T\Delta_{\text{vitr}}S$ values from this work, both at $T = 298.15$ K. Note that the values from Nasikas and Navrotsky (2014) were recalculated to the formulae Mg$_x$SiO$_{2x+1}$ used in this work (they normalized the compositions to 2 O atoms, not 1 Si atom as in this work)

Fig. 4 Entropies of the magnesium silicate glasses and the corresponding mechanical mixtures of enstatite and forsterite, all at $T = 298.15$ K. The dashed line is a fit through the data for MG50, MG54, MG58, and MG62, and shows the deviation of the sample MG67 from this linear trend

**Configurational entropy of forsteritic glass**

The configurational entropy of a glass at the fictive temperature $T$ (defined below) can be calculated from an equation (Richet 1984) (corrected because entropy is obtained by integrating $C_p/T$ d$T$ (or $C_p$ d$\ln T$) and not $C_p$ d$T$)
where \( S_{cc} \) is the zero-point entropy of the crystal, \( \Delta_{fusion}S \) is the entropy of fusion which occurs at temperature \( T_{fusion} \), and \( T \) is the fictive temperature. The fictive temperature, \( T \), of a glass is the “temperature at which the actual configurational state of a glass would be the equilibrium configuration of the liquid; operationally, is the glass transition temperature on cooling” (Richet 1984).

For the compositions considered in this study, the \( S_{cc} \) values are 0 because neither enstatite nor forsterite structures are disordered. Parts of the integrals were already evaluated by calculation of the entropy at \( T = 298.15 \) K (as \( S_{298.15}^o = S^o \) in Table 2). The expression can be re-written as

\[
S_{conf}(T) = S_{cc} + \int_0^{T_{fusion}} C_p,crystal d\ln T + \Delta_{fusion}S + \int_{T_{fusion}}^T C_p,liquid d\ln T + \int_0^T C_p,glass d\ln T
\]
It would be interesting and desirable to calculate the configurational entropies of the studied glasses. When reviewing the available literature and data, however, we found that some important data are missing or are rather scattered. For example, the fusion enthalpy of forsterite was measured by Navrotsky et al. (1989) and Richet et al. (1993). The two fusion enthalpies differ but overlap within their uncertainties: (Navrotsky et al. 1989) 114.0 ± 20.0 kJ mol\(^{-1}\) (at 2163 K), (Richet et al. 1993) 142.0 ± 14.0 kJ mol\(^{-1}\) (at 2174 K). Kojitani and Akaogi (1997) used these two values to evaluate the non-ideal nature of mixing in the melts of the CaO–MgO–Al\(_2\)O\(_3\)–SiO\(_2\) system. They concluded that if the value of Richet et al. (1993) is used, the mixing within this system is ideal. On the other hand, the value of Navrotsky et al. (1989) suggests a positive mixing enthalpy. Additional scattered estimates of \(\Delta_{\text{fusion}} h\) for forsterite were provided in the earlier literature (Bottinga and Richet 1978; Ghiorso and Carmichael 1980; Stebbins et al. 1984) but were made obsolete by the above-mentioned measurements of Navrotsky et al. (1989) and Richet et al. (1993).

Using the simple expression \(\Delta_{\text{f}} S = \Delta_{\text{fusion}} h / T_{\text{fusion}}\), we get an entropy of fusion of 52.7±9.2 J mol\(^{-1}\) K\(^{-1}\) from Navrotsky et al. (1989) and of 65.3±6.4 J mol\(^{-1}\) K\(^{-1}\) from Richet et al. (1993).

The fictive temperature \(T_f\) of the Mg67 glass is unknown because this glass crystallizes before it enters the glass-transition region. However, Tangeman et al. (2001) assumed that crystallization is initiated just before the glass transition and estimated \(T_f\) as 1040 K. Richet et al. (1993) estimated \(T_f\) of the forsteritic glass at a temperature of 990±10 K when the configuration entropy of such glass would vanish. Our data (Fig. 2) show no sign of glass transition or crystallization up to 970 K and Tangeman et al. (2001) showed that the glass transition region is not entered at temperatures even slightly higher than 1000 K. Therefore, we assume that the fictive temperature is equal to 1040 K, in line with the earlier estimate of Tangeman et al. (2001).

A greater difficulty is encountered when seeking the \(C_p\) of the supercooled liquids. The temperatures at which they exist exceed the normal temperature range of operation of many calorimeters. The Mg-silicate glasses tend to crystallize upon or soon after the glass transition, thus precluding the \(C_p\) measurement at very high temperatures. Tangeman et al. (2001) estimated the average \(C_p\) of Mg\(_2\)SiO\(_4\) supercooled liquid as 225 J mol\(^{-1}\) K\(^{-1}\) for the temperature range 1040–1773 K, based on solution calorimetry work of Navrotsky et al. (1989). Stebbins et al. (1984) and Lange and Navrotsky (1992) calculated the \(C_p\) of supercooled Mg\(_2\)SiO\(_4\) liquid as 285–295 J mol\(^{-1}\) K\(^{-1}\) from partial molar heat capacities in the range 1200–1850 K. Using first principles molecular dynamics simulations, de Koker et al. (2008) derived \(C_p\) for Mg\(_2\)SiO\(_4\) liquid at \(T = 2163\) K as 265 J mol\(^{-1}\) K\(^{-1}\). Navrotsky et al. (1990) listed the average difference between the \(C_p\) of forsterite crystal and \(C_p\) of Mg\(_2\)SiO\(_4\) liquid, \(\Delta C_p\), as 35 J mol\(^{-1}\) K\(^{-1}\). This value would lead to \(C_p,\text{liquid}(T = 1100\,\text{K})\) of 214 J mol\(^{-1}\) K\(^{-1}\), taking the \(C_p\) data for forsterite crystal from Gillet et al. (1991). Navrotsky et al. (1990) also used earlier data of Ghiorso and Carmichael (1980) and Ghiorso and Carmichael (1987) to arrive at a \(\Delta C_p\) value of 64 J mol\(^{-1}\) K\(^{-1}\), leading to \(C_p,\text{liquid}(T = 1100\,\text{K})\) of 243 J mol\(^{-1}\) K\(^{-1}\).

Using the data derived in this work and discussed above, we attempted to calculate the configurational entropy of the Mg67 glass, close to the forsterite composition. The \(S_{\text{cc}}\) value was taken as 0 J mol\(^{-1}\) K\(^{-1}\); the entropy of fusion as a mean of the two values above, 59 J mol\(^{-1}\) K\(^{-1}\). The entropies of crystal and glass at \(T = 298.15\) K are listed in Table 2. The coefficients for \(C_p\) polynomials used are listed in Table 3. Both types of polynomials (Berman–Brown and Richet–Fiquet) performed in a similar way, the differences in the integrals being negligible (< 0.05 %). The least certain value is the \(C_p\) of the liquid. We adopted a mean of the estimates above (Stebbins et al. 1984; Lange and Navrotsky 1992; Tangeman et al. 2001; de Koker et al. 2008), 260 J mol\(^{-1}\) K\(^{-1}\). Using these data, the configurational entropy of Mg67 glass at \(T_g\) was estimated as 1.9 J mol\(^{-1}\) K\(^{-1}\) (for the composition Mg\(_{50.66}\)Si\(_{3.97}\)O\(_{1.34}\)) or 0.7 J gfw\(^{-1}\) K\(^{-1}\) (for the composition normalized to 1 cation, Mg\(_{0.656}\)Si\(_{0.34}\)O\(_{1.34}\)). This small configurational entropy agrees with the prediction of Richet et al. (1993) that it would be essentially zero at \(T_g\). This conclusion was derived by extrapolation of viscosity data for Mg aluminosilicate melts. The validity of \(S_{\text{conf}}\) derived in our study could be strengthened, however, if a more precise determination of \(C_p,\text{liquid}\) was available.

The \(S_{\text{conf}}\) calculated according to equation (6) is a composite value whose uncertainty is difficult to judge. The uncertainties on \(S_{\text{conf}}\) are relatively small, on the order of 1 J mol\(^{-1}\) K\(^{-1}\) or less (see Table 2). The uncertainty of \(\Delta_{\text{f}} S\) is much higher, almost 10 J mol\(^{-1}\) K\(^{-1}\). The superambient heat capacities of crystals and glasses, both experimentally measured, are also well constrained. In the absence of \(C_p\) anomalies, one can count with overall precision of 3%. Finally, the \(C_p\) of the liquid, derived by a mathematical regression on several liquid compositions
(Courtial and Richet 1993) introduces another potential error. Hence, it seems that a conservative estimate of the overall uncertainty on the $S_{\text{conf}}$ could be 15 J mol$^{-1}$ K$^{-1}$, much more than the value of this variable itself. Such state of affairs is, however, typical for small numbers determined as a difference of several large numbers. Despite of the large ratio of the error and the value of $S_{\text{conf}}$, we still consider this value to be a fairly accurate estimate and proceed to calculate further associated quantities from it.

The configurational entropy at a higher temperature $T$ can be calculated as

$$S_{\text{conf}}(T) = S_{\text{conf}}(T_g) + \int \frac{C_{p,\text{conf}}}{T} dT$$

(5)

where

$$C_{p,\text{conf}}(T) = C_{p,\text{liquid}}(T) - C_{p,\text{glass}}(T_g)$$

(6)

The results of such a calculation for MG67 glass are shown in Fig. 7. In this case, $C_{p,\text{conf}}$ is a constant, because $C_{p,\text{liquid}}$ is considered to be a constant.

**Viscosity of forsteritic liquids**

The consequence of the rapid increase of the configurational entropy is flattening of the viscosity-temperature curve at high temperatures, a typical feature of ‘fragile’, non-Arrhenian liquids (cf. Lange and Navrotsky 1993). Hence, initial rapid drop in viscosity just above $T_g$ will be replaced by a nearly constant viscosity of such melts at high temperatures. The relationship between configurational entropy and viscosity, $\eta$, is Adam and Gibbs (1965):

$$\log \eta = A + B \frac{TS_{\text{conf}}}{T_g}$$

(7)

Because of experimental difficulties, the viscosities were measured at elevated temperatures and pressures preferentially for fayalitic, not for forsteritic liquids (e.g., Shiraishi et al. 1978; Spice et al. 2015). Viscosities of peridotitic, forsterite-similar liquid were measured over a broad $P$-$T$ range by Liebske et al. (2005) and calculated at high temperatures by Lacks et al. (2007) and Adjaoud et al. (2008). All these data are shown in Fig. 8 and were used to fit the parameters $A$ and $B$ in eq. 7. The resulting parameters are $A = -2.34$ and $B = 76,500$, with $S_{\text{conf}}(T) = 1.90 + (83.7 \ln (T/1040))$. The predicted variation of viscosity with temperature is shown in Fig. 8. The data of Urbain et al. (1982) are also shown in Fig. 8 but were not used for fitting because they appear somewhat lower than the other available values.
Partial molar heat capacities in magnesium silicate liquids

The least certain parameter in the calculation above appears to be $C_{p, \text{liquid}}$. The easiest method to tabulate heat capacities of silicate liquids is the determination of partial molar heat capacities ($\overline{C}_{p,i}$) of the oxide components. Stebbins et al. (1984) and Courtial and Richet (1993) derived a set of $\overline{C}_{p,i}$ values. It could be expected that one of the most accurate values is that for SiO$_2$. Many silicate compositions were measured and direct measurements on SiO$_2$ glasses and liquids are also possible. The $\overline{C}_{p,\text{SiO}_2}$ value in Courtial and Richet (1993) is 81.37 J g$^{-1}$ K$^{-1}$, that in Stebbins et al. (1984) 80.0±0.9 J g$^{-1}$ K$^{-1}$. The $\overline{C}_{p,\text{MgO}}$ of 85.78 J g$^{-1}$ K$^{-1}$ in Courtial and Richet (1993) superseded the older and higher estimate in Stebbins et al. (1984) (99.7 J g$^{-1}$ K$^{-1}$) that was less certain and based only on a few experimental points.

Using the $\overline{C}_{p,i}$ from Courtial and Richet (1993), the $C_{p,\text{liquid}}$ (Mg$_2$SiO$_4$) is 253 J mol$^{-1}$ K$^{-1}$ but the earlier data from Stebbins et al. (1984) give 279.4 J mol$^{-1}$ K$^{-1}$. The latter datum, however, would lead to negative configurational entropies for forsteritic glasses at $T_g$. If $\overline{C}_{p,\text{MgO}}$ is set to 90 J g$^{-1}$ K$^{-1}$, then $C_{p,\text{liquid}}$ (Mg$_2$SiO$_4$) is 260 J mol$^{-1}$ K$^{-1}$, the value obtained above as a mean of available estimates and applied in the calculations. The adjusted $\overline{C}_{p,\text{MgO}}$ value is between the values proposed by Stebbins et al. (1984) and Courtial and Richet (1993). The parameters proposed by Courtial and Richet (1993) appear to be more accurate but it is not clear to what extent do they apply to Mg$_2$SiO$_4$ composition. As shown above (e.g., Figs. 3, 4), the properties of the Mg$_2$SiO$_4$ glass deviate from linear trends defined by Mg-silicate glasses with higher SiO$_2$ proportions. For consistency, we will use the $\overline{C}_{p,\text{MgO}}$ of 90 J g$^{-1}$ K$^{-1}$ also for enstatitic melts below, with $C_{p,\text{liquid}}$ (MgSiO$_3$) = 170 J mol$^{-1}$ K$^{-1}$. The $C_{p,\text{liquid}}$ (MgSiO$_3$) derived from Courtial and Richet (1993) is 167 J mol$^{-1}$ K$^{-1}$, only marginally different from this value.

Configurational entropy of enstatitic glass

For enstatite, the enthalpy of fusion is 75.3±6.0 kJ mol$^{-1}$ (cf. Stebbins et al. 1984; Richet and Bottinga 1986) at $T_{\text{fusion}} = 1834$ K, although Stebbins et al. (1984) discussed additional scattered values for $\Delta_{\text{fusion}}H$. The resulting entropy of fusion is 41.1 J mol$^{-1}$ K$^{-1}$. The glass transition temperature was determined by Briggs (1975) as 1063 K. The fits to the $C_p$ data for the MG50 glass are presented in Table 3.

A challenge in the case of enstatite is the integration of its heat capacity up to the melting temperature of 1834 K. Upon heating, orthoenstatite transforms to clino- and protoenstatite and shows significant pre-melting phenomena (Thièblot et al. 1999). Measurements on orthoenstatite extend well into the stability field of clinoenstatite but generally agree well with each other (White 1991; Krupka et al. 1985a; Thiéblot et al. 1999). At $T = 1300$ K, orthoenstatite transforms to protoenstatite, with an associated $C_p$ drop. The available $C_p$ data were therefore re-fitted (orthoenstatite) or adopted (protoenstatite) and the resulting polynomials are summarized in Table 3.

Another question is the entropy of the ortho- to protoenstatite transition. Thiéblot et al. (1999) measured the enthalpy of transformation as 2 kJ mol$^{-1}$ but they were not certain if the results can be interpreted in terms of a complete transformation. Gasparik (1990) estimated 9–11 kJ mol$^{-1}$ for this transformation. These differences account for transformation entropies of 1.5–8.5 J mol$^{-1}$ K$^{-1}$ and introduce an additional large uncertainty in the calculation of the configurational entropy. The $\Delta H$ values of 9–11 kJ mol$^{-1}$ seem to be too large for a displacive transformation, however. For comparison, the enthalpy of α–β quartz transformation is 0.5 kJ mol$^{-1}$ (average of values found in the literature, see Sheffield 1994). Even for reconstructive transformations of polymorphs of simple composition and structure, the enthalpies are small, e.g., for andalusite-sillimanite transformation, $\Delta H$ is 2 kJ mol$^{-1}$ or less (Salje and Werneke 1982). Therefore, we adopt the $\Delta H$ value from Thiéblot et al. (1999) with the corresponding $\Delta S$ of 1.5 J mol$^{-1}$ K$^{-1}$.

The configurational entropy at $T_g$ for enstatitic glass is calculated as 16.8 J mol$^{-1}$ K$^{-1}$, including the contribution of $\Delta_{\text{ortho}}S_{\text{proto}}$ of 1.5 J mol$^{-1}$ K$^{-1}$ (Fig. 7). The comparison of the magnitude of the $\Delta_{\text{ortho}}S_{\text{proto}}$ values [1.5 J mol$^{-1}$ K$^{-1}$ from Thiéblot et al. (1999) versus 8.5 J mol$^{-1}$ K$^{-1}$ from Gasparik (1990)] makes it clear that the ortho- to protoenstatite transformation is potentially a source of large error. Stebbins et al. (1984) report $S_{\text{conf}}(T/T_g = 1.5) = 3.4$ J g-atom$^{-1}$ K$^{-1}$, equal to 17 J mol$^{-1}$ K$^{-1}$. Our results are higher than this datum; calculation at higher temperatures with our data and assumptions give $S_{\text{conf}}(T/T_g = 1.5) = 32$ J mol$^{-1}$ K$^{-1}$. Obviously, the difficulties related to the thermodynamics of the MgSiO$_3$ polymorphs must be resolved before the thermodynamic assessment of the configurational entropy of enstatitic glass can continue.

Conclusions

Using new thermodynamic data for magnesium silicate glasses, we derived configurational entropies of forsteritic and enstatitic supercooled liquids and point at discrepancies that may introduce substantial errors in these calculations. These data allow the prediction of viscosities of such liquids at temperatures which are not accessible experimentally. Such data can be used in modeling and supporting of algorithms to define thermodynamic properties of a range of vitreous substances and melts (e.g., Jacobs et al. 2017).
They can be combined with enthalpies of formation (Nasikas and Navrotsky 2014) and thermophysical properties (Jacobs and de Jong 2007) for models that could elucidate geological and geophysical observations in the crust and mantle of the Earth.

Supplementary Information The online version contains supplementary material available at https://doi.org/10.1007/s00269-021-01153-7.

Acknowledgements We are very thankful to Pascal Richet and an anonymous reviewer for their constructive criticism that helped to improve this manuscript. We thank Rebecca Stevens for help and guidance with the $C_p$ data fitting and Hiltrud Müller-Sigmund for the help with the microprobe measurements.

Funding Open Access funding enabled and organized by Projekt DEAL.

Data availability The measured low-temperature (PPMS) and high-temperature (DSC) $C_p$ data for all glasses, the fit polynomials used to derive the entropy at $T = 298.15 \, \text{K}$, and the thermodynamic functions calculated from these polynomials at regularly spaced temperature intervals are available as supporting electronic information (MS Excel spreadsheets) to this publication.

Declarations

Conflict of interest The authors declare that they have no conflict of interest.

Open Access This article is licensed under a Creative Commons Attribution 4.0 International License, which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons licence, and indicate if changes were made. The images or other third party material in this article are included in the article’s Creative Commons licence, unless indicated otherwise in a credit line to the material. If material is not included in the article’s Creative Commons licence and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder. To view a copy of this licence, visit http://creativecommons.org/licenses/by/4.0/.

References

Adam G, Gibbs JH (1965) On the temperature dependence of cooperative relaxation properties in glass-forming liquids. J Chem Phys 43:139–146

Adjaoud O, Steinle-Neumann G, Jahn S (2008) Mg$_2$SiO$_4$ liquid under high pressure from molecular dynamics. Chem Geol 256:184–191

Belonoshko AB, Dubrovinsky LS (1996) Molecular and lattice dynam-ics study of the MgO–SiO$_2$ system using a transferable interatomic potential. Geochim Cosmochim Acta 60:1645–1656

Benmore CJ, Saignard E, Guthrie M, Amin SA, Weber JKR, McKie-ernan K, Wilding MC, Yarger JL (2011) High pressure X-ray diffraction measurements on Mg$_2$SiO$_4$ glass. J Non-Cryst Solids 357:2632–2636

Berman RG, Brown TH (1985) Heat capacity of minerals in the system Na$_2$O–K$_2$O–CaO–MgO–FeO–Fe$_2$O$_3$–Al$_2$O$_3$–SiO$_2$–TiO$_2$–H$_2$O–CO$_2$: representation, estimation, and high-temperature extrapolation. Contrib Mineral Petrol 89:168–183

Bottina Y, Richet P (1978) Thermodynamics of liquids silicates, a preliminary report. Earth Planet Sci Lett 40:382–400

Briggs J (1975) Thermodynamics of the glass transition temperature in the system CaO–MgO–Al$_2$O$_3$–SiO$_2$. Cent Glass Ceram Res Inst Bull 22:73–82

Buchenau U, Prager M, Nücker N, Dianoux AJ, Ahmad N, Phillips WA (1986) Low-frequency modes in vitreous silica. Phys Rev B 34:5665–5673

Courtiot P, Richet P (1993) Heat capacity of magnesia aluminosili-cate melts. Geochim Cosmochim Acta 57:1267–1275

Dachs E, Bertoldi C (2005) Precision and accuracy of the heat-pulse calorimetric technique: low-temperature heat capacities of milligram-sized synthetic mineral samples. Eur J Mineral 17:251–261

de Koker NP, Stixrude L, Karki BB (2008) Thermodynamics, structure, dynamics, and freezing of Mg$_2$SiO$_4$ liquid at high pressure. Geochim Cosmochim Acta 72:1427–1441

Gasparik T (1990) A thermodynamic model for the enstatite-diopside join. Am Mineral 75:1080–1091

Ghiorso MS, Carmichael ISE (1980) A regular solution model for met-aluminous silicate liquids: applications to geothermometry, immiscibility, and the source regions of basic magmas. Contrib Mineral Petrol 71:323–342

Ghiorso MS, Carmichael ISE (1987) Modeling magmatic systems: petrologic applications. Rev Mineral 17:467–499

Gillet P, Richet P, Guyot F, Fiquet G (1991) High-temperature thermodynamic properties of forsterite. J Geophys Res 96(B7):11805–11816

Jacobs MHG, de Jong BHWS (2007) Placing constraints on phase equilibria and thermophysical properties in the system MgO–SiO$_2$ by a thermodynamically consistent vibrational method. Geochim Cosmochim Acta 71:3630–3655

Jacobs MHG, Schmid-Fetzer R, van den Berg AP (2017) Phase dia-grams, thermodynamic properties and sound velocities derived from a multiple Einstein method using vibrational densities of states: an application to MgO–SiO$_2$. Phys Chem Miner 44:43–62

Kalampounias A, Nasikas N, Papanastasopoulou G (2009) Glass formation and structure in the Mg$_2$Si$_2$O$_7$–Mg$_2$SiO$_4$ pseudobinary system: from degraded networks to ioniclike glasses. J Chem Phys 131:114513. https://doi.org/10.1063/1.3225431

Kojitani H, Akagi M (1997) Melt enthalpies of mantle peridote: calorimetric determinations in the system CaO–MgO–Al$_2$O$_3$– SiO$_2$ and application to magma generation. Earth Planet Sci Lett 153:209–222

Kroeker S, Stubbins JF (2000) Magnesium coordination environments in glasses and minerals: new insight from high-field magne-sium-25 MAS NMR. Am Mineral 85:1459–1464

Krupka KM, Hemingway BS, Robie RA, Kerrick DM (1985a) High-temperature heat capacities and derived thermodynamic properties of anthophyllite, diopside, dolomite, enstatite, bronzite, talc, tremolite and wollastonite. Am Mineral 70:261–271

Krupka KM, Robie RA, Hemingway BS, Kerrick DM, Ito J (1985b) Low-temperature heat capacities and derived thermodynamic properties of anthophyllite, diopside, enstatite, bronzite and wollastonite. Am Mineral 70:249–260

Lacks DJ, Rear DB, Van Orman JA (2007) Molecular dynamics investiga-tion of viscosity, chemical diffusivities and partial molar volumes of liquids along the MgO–SiO$_2$ join as functions of pressure. Geochim Cosmochim Acta 71:1312–1323

Lange RA, Navrotsky A (1992) Heat capacities of Fe$_2$O$_3$-bearing sili-cate liquids. Contrib Mineral Petrol 110:311–320

Lange RA, Navrotsky A (1993) Heat capacities of TiO$_2$-bearing sili-cate liquids: evidence for anomalous changes in configurational...
entropy with temperature. Geochem Cosmochim Acta 57:3001–3011

Lashley JC, Hundley MF, Migliori A, Sarrao JL, Pagliuso PG, Darling TW, Jaime M, Cooley JC, Hults WL, Morales L, Thoma DJ, Smith JL, Boerio-Goates J, Woodfield BF, Stewart GR, Fisher RA, Phillips NE (2003) Critical examination of heat capacity measurement made on a Quantum Design physical property measurement system. Cryogenics 43:369–378

Liebske C, Schmickler B, Terasaki H, Poe BT, Suzuki A, Funakoshi K, Ando R, Rubie DC (2005) Viscosity of peridotite liquid up to 13 GPa: implications for magma ocean viscosities. Earth Planet Sci Lett 240:589–604

Mysen B, Richet P (2005) Silicate glasses and melts: properties and structure. Elsevier, Amsterdam

Nasikas NK, Navrotsky A (2014) Energetics of silica-poor glasses in the systems MgO–SiO2 and Mg0.5Ca0.5O–SiO2. J Am Ceram Soc 97:451–456

Navrotsky A, Ziegler D, Ostrich R, Maniar P (1989) Calorimetry of silicate melts at 1773 K: measurement of enthalpies of fusion and of mixing in the systems diopside–anorthite–albite and anorthite–forsterite. Contrib Mineral Petrol 101:122–130

Navrotsky A, Maniar P, Oestrike R (1990) Energetics of glasses in the system diopside–anorthite–forsterite. Contrib Mineral Petrol 105:81–86

Pohl RO (1981) Low temperature specific heats of glasses. In: Phillips WA (ed) Amorphous solids. Topics in current physics, vol 24. Springer, Berlin. https://doi.org/10.1007/978-3-642-81534-8_3

Richet P (1984) Viscosity and configurational entropy of silicate melts. Geochim Cosmochim Acta 48:471–483

Richet NP (2009) Heat capacity and low-frequency vibrational density of states. Inferences for the boson peak of silica and alkali silicate glasses. Physica B 404:3799–3806

Richet P, Bottinga Y (1986) Thermochromic properties of silicate glasses and liquids: a review. Rev Geophys 24:1–25

Richet P, Fiquet G (1991) High-temperature heat capacity and premelting of minerals in the system CaO–MgO–Al2O3–SiO2. J Geophys Res 96:445–456

Richet P, Robie RA, Hemingway BS (1991) Thermodynamic properties of wollastonite, pseudowollastonite and CaSiO3 glass and liquid. Eur J Mineral 14:11655

Richet P, Bottinga Y, Richet P (1982) Viscosity of liquid fayalite up to 9 GPa. Geochim Cosmochim Acta 48:219–227

Shiraishi YK, Ikeda K, Tamura A, Saito T (1978) On the viscosity and density of the molten FeO–SiO2 system. Trans Jpn Inst Met 19:264–274

Spiekermann G, Steele-MacInnis M, Kowalski PM, Schmidt C, Jahn S (2013) Vibrational properties of silica species in MgO–SiO2 glasses obtained from ab initio molecular dynamics. Chem Geol 346:223–33

Spiegelman S, Cardinale B, de Grouchy C, Kono Y (2015) Viscosity of liquid fayalite up to 9 GPa. Geochim Cosmochim Acta 48:219–227

Stebbins JF, Carmichael ISE, Moret LK (1984) Heat capacities and entropies of silicate liquids and glasses. Contrib Mineral Petrol 86:131–148

Tangeman JA, Lange RA (1998) The effect of Al3+, Fe3+, and Ti4+ on the configurational heat capacities of sodium silicate liquids. Phys Chem Miner 26:83–99

Tangeman JA, Phillips BL, Navrotsky A, Weber JKR, Hixson AD, Key TS (2001) Vitreous forsterite (Mg2SiO4); synthesis, structure, and thermochemistry. Geophys Res Lett 28:2517–2520

Thiébaut L, Téqui C, Richet P (1999) High-temperature heat capacity of grossular (Ca3Al2Si3O12), enstatite (Mg2SiO4), and titanite (CaTiSiO5). Am Mineral 84:848–855

Urbain G, Bottinga Y, Richet P (1982) Viscosity of liquid silica, silicates and alumino-silicates. Geochim Cosmochim Acta 46:1061–1072

Weber JKR, Hampton DS, Morkel DR, Rey CA, Zatarski MM, Nordine PC (1994) Aero-acoustic levitation: a method for containerless liquid-phase processing at high temperatures. Rev Sci Instrum 65:456–465

Wilding MC, Benmore CJ, Tangeman JA, Sampath S (2004a) Coordination changes in magnesium silicate glasses. Europhys Lett 67:212–218

Wilding MC, Benmore CJ, Tangeman JA, Sampath S (2004b) Evidence of different structures in magnesium silicate liquids: coordination changes in forsterite- to enstatite-composition glasses. Chem Geol 213:281–291

Wilding MC, Benmore CJ, Weber JKR (2014) In situ diffusion studies of sodium silicate liquids. J Mater Sci 43:5707–5713

White WP (1919) Silicate specific heats. Am J Sci 47:1–44

Zotov N (2002) Heat capacity of sodium silicate glasses: comparison of experiments with computer simulations. J Phys Condens Matter 14:11655

Publisher’s Note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.