Melting curve of NaCl to 20 GPa from electrical measurements of capacitive current

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ABSTRACT

Using an in situ electrical method and the multi-anvil apparatus, we determined the melting curve of sodium chloride (NaCl) up to ~20 GPa, with an estimated uncertainty of ±40 K. Our results agree well with the existing data up to 6.5 GPa. At higher pressures, the melting temperatures from this study are as much as 200 K higher than those from an experimental study using the diamond anvil cell (DAC), and are up to 500 K lower than those from theoretical studies using molecular dynamics (MD). The discrepancies may originate from surface melting in the DAC measurements, which underestimate the melting temperature, and from superheating in MD calculations, which over-predict the melting temperature. Fitting our results to the Simon equation yield \( T/T_0 = (P/P_0)^{4.5} + 1 \), where \( T \) and \( T_0 \) are the melting temperatures at \( P \) and \( P_0 \), respectively. The Simon equation fits the experimental data within uncertainties and therefore can be used to interpolate the melting curve. Using the equation of state (EoS) of NaCl at 300 K, the results are fitted to the Kraut-Kennedy equation in the form of \( T/T_0 = (V_0 - V)/V_0 \cdot 2.52 + 1 \), where \( T \) and \( T_0 \) are the melting temperatures at \( V \) and \( V_0 \), respectively. At pressures above 14 GPa, the experimental data deviate from the Kraut-Kennedy equation fit towards lower temperatures, probably because the volume dependence of the Grüneisen parameter was ignored in the equation. The Gilvarry-Lindemann equation \( T_m \sim 0.00321 \cdot M^{2/3} \cdot \Theta^{2/3} \cdot (V_0/V)^2 (\gamma - 1/3) \) provides a satisfactory fit to the melting curve of NaCl between 0 GPa and 19 GPa if the
exponent $q$ in the volume dependence of the Grüneisen parameter $\gamma = \gamma_0 (V/V_0)^q$ is allowed to deviate from one. Given that the melting curve of NaCl up to 6.5 GPa is well established, monitoring the melting of NaCl offers an efficient alternative for pressure calibration of large-volume high-pressure apparatus for Earth science applications.

Keywords: Melting curve, high pressure, capacitive current, in situ electrical method, sodium chloride, Simon equation, Kraut-Kennedy equation, Lindemann's law
INTRODUCTION

Melting plays a critical role in planetary differentiation and dynamics. Knowledge of the pressure-dependent melting temperatures of Earth materials is of fundamental importance for constraining the Earth's thermal structure, understanding geochemical cycles, and interpreting seismic observations (Boehler 1996). Many experimental methods have been developed to investigate melting at high pressure. As a first order phase transition, melting is characterized by the loss of long-range atomic order, which manifests as the disappearance of reflections from lattice planes and appearance of diffuse scattering signal in X-ray diffraction patterns (Anzellini et al. 2013). Melting is associated with significant changes in lattice dynamics, which lead to vanishing Lamb-Mossbauer factor (Jackson et al. 2013). The latent heat of melting gives rise to enhanced absorption of heating power (Boehler et al. 1997; Lord et al. 2010) and may be detected through differential thermal analysis (DTA) (Akella et al. 1969). Furthermore, melting results in loss of shear strength and precipitous reduction in viscosity, which can be detected through textural change (Boehler 1997, Chen et al. 2008), from the sinking of a dense sphere marker (Dobson et al. 1996), or from discontinuous change in electrical resistivity (Brand et al. 2006). Measuring the melting temperatures of materials at the pressure conditions of deep Earth poses considerable technical challenges and consequently experimental data are limited and often uncertain (e.g., Anzellini et al. 2013; Boehler 1996; Shen and Lazor 1995).

As a simple ionic compound, sodium chloride (NaCl) has been investigated extensively in an attempt to gain insights into its melting mechanism and melt structure (e.g., Clark 1959; Boehler et al. 1997; An et al., 2006). In high-pressure research, NaCl is widely used as a thermal insulating material and pressure marker in diamond-anvil cell (DAC) experiments, and therefore knowledge of its melting curve helps to assess its applicable ranges of pressure and temperature.
Furthermore, monitoring the melting of NaCl offers an appealing alternative for pressure calibration of large-volume apparatus such as the piston-cylinder apparatus and multi-anvil press (e.g., Leinenweber et al. 2012), with several advantages including 1) melting occurs much more rapidly than solid-state phase transition; 2) melting can be readily recognized using a sinking marker such as a Pt sphere; 3) high-purity NaCl is readily available and less expensive than gold, the melting curve of which has been used for pressure calibration.

Earlier studies have determined the melting curve of NaCl to 6.5 GPa using the piston-cylinder apparatus and DTA method (Clark 1959; Pistorius 1966; Akella et al. 1969). The pressure coverage was subsequently extended to 100 GPa using the diamond anvil cell technique (Boehler et al. 1997). On the other hand, molecular dynamics (MD) calculations have been performed to constrain the high-pressure melting curve of NaCl (e.g., Belonoshko and Dubrovinsky 1996; Vočadlo and Price 1996; Chen et al. 2004; Cheng et al. 2003; An et al. 2006). At 20 GPa the calculated melting temperatures from MD simulations exceed the measured values by as much as 25% and the discrepancies were attributed to superheating and surface melting effects (An et al. 2006; Vočadlo and Price 1996).

Melting of an ionic compound is accompanied by an abrupt and large increase in conductivity, when ions locked in the crystal lattice are freed and become capable of carrying charges. If an alternating voltage is applied through two electrodes and the voltage stays below the thresholds of oxidizing or reducing the ions at the electrodes, an ionic melt can support capacitive current, with ions move back and forth between the two electrodes, resembling the charging and discharging of a capacitor (Rieger 1994). At sufficiently high voltage, ionic conduction and redox reactions at the electrode would produce Faradic current instead. In this
study, we developed an in situ electrical method to determine the melting temperature of compressed NaCl by monitoring sudden rise in the capacitive current. We aimed to establish the melting curve of NaCl up to ~ 20 GPa using the multi-anvil apparatus and to examine if the Simon equation (Simon 1929), the Kraut-Kennedy equation (Kraut and Kennedy 1966), and the Gilvarry-Lindemann equation (Gilvarry 1956, 1966; Poirier 2000) can adequately describe the melting behavior of ionic compounds at high pressures.

**METHODS**

High-pressure experiments were conducted using the 1000-ton Walker-style multi-anvil apparatus at the University of Michigan. For experiments at pressures up to 10 GPa, we used Fansteel tungsten carbide cubes with 8-mm truncation edge length (TEL) and octahedron-shaped pressure medium casted from Aremco 584 old-style material (Walker 1991). For experiments at pressures up to 21 GPa, we used Toshiba-Tungaloy F-grade tungsten carbide cubes with 5-mm TEL and the COMPRES 10/5 assembly (Leinenweber et al. 2012), which was modified for the electrical measurements (Fig. 1a). The relation between the sample pressure and applied ram pressure was established using the Bi I-II, II-III and III-V transitions at room temperature (Decker et al. 1972) and the known phase boundaries at 1473 K including quartz-coesite-stishovite (Bohlen and Boettcher 1982; Zhang et al. 1996), CaGeO₃ garnet-perovskite (Susaki et al. 1985) and forsterite-wadsleyite-ringwoodite transitions (Katsura and Ito 1989). The sample pressure \( P \) is calculated from the ram force \( p \) according to the following formulae:

\[
P \text{ (GPa)} = -0.03 + 3.21 \times 10^{-2} \cdot p \text{ (US ton)} - 1.40 \times 10^{-5} \cdot p^2 \text{ for 8-mm TEL}
\]

\[
P \text{ (GPa)} = 5.65 \times 10^{-2} \cdot p \text{ (US ton)} - 3.80 \times 10^{-5} \cdot p^2 \text{ for 5-mm TEL.}
\]

The precision in pressure calibration is estimated at ±5% on the basis of duplication experiments and does not include the effect of temperature, which will be discussed later.
High temperature was generated using cylindrical-shaped foil of rhenium, with a thickness of 0.0015 inch or 0.038 mm for 8-mm experiments and 0.0025 inch or 0.064 mm for 5-mm experiments. A standard type-C thermocouple (W26%Re and W5%Re, 0.005 inch or 0.127 mm in diameter) was used to monitor the temperature. The uncertainty in the measured temperature is estimated at ±1% for experiments up to 15 GPa and 2600 K, which includes the precisions in the thermocouple calibration and the positioning of the thermocouple junction relative to the sample (Li et al. 2003) and does not include the effect of pressure on the electromotive force (emf), which will be discussed later.

For the electrical measurements, a pair of 200 μm-thick Pt wires were inserted into a four-bore alumina holder and used as the electrodes (Fig. 1b). The electrode tips and thermocouple junction were placed along the rotational axis of the cylindrical-shaped heater and at the same distance to the equator of the heater, in order that the thermocouple measured the same temperature where the electrode tips sit, and they were kept within the middle third of the heater length, where the temperature variation was expected to be less than 100 K (Leinenweber et al. 2012). The measurement circuit consisted of a Mastech variac power supply, which converted 110 V, 60 Hz AC voltage from the wall outlet to 0.1 to 1 V, 60 Hz AC voltage, and a Fluke 289 multi-meter, which recorded the current through the sample. For most measurements, the AC voltage was set to 0.1 V to prevent electrolysis reactions and irreversible changes in sample composition. In order to avoid the electromagnetic perturbation from the heating current and the motor for pressure control, the voltage was occasionally raised to 1 V, which was found to be still below the threshold for electrolysis reactions.

Powder of NaCl from Aldrich (99.99%, #38,886-0) was dried in a vacuum oven at ~ 400 K for more than one week before being packed inside a Pt tubing, which served as the sample
container and helped to reduce the temperature gradient. The complete assembly was dried in the vacuum oven at 400 K for at least 24 hours before loading into the multi-anvil apparatus. In a typical high-pressure experiment, the ram pressure was increased at the rate of 100 US ton per hour during compression, and decreased at the rate of 35 US ton per hour during decompression. Data were acquired at several target pressures along the compression path. At each target pressure the assembly was heated at the rate of 60 K per minute until melting was detected, and then cooled rapidly to 1000 K and heated again at the same rate of 60 K per minute to replicate melting detection at least once. At the highest pressure and temperature of each run, we quenched the sample by turning off the power. The run products were recovered and inspected for the positioning of the electrode tips and thermocouple junctions with a Zeiss microscope with the reflected light and 10x magnification objective lens. A number of run products were examined for chemical contamination through semi-quantitative energy-dispersive spectroscopy analyses using the Cameca SX100 electron microprobe at the University of Michigan.

To test the validity of the in situ electrical measurements, we performed two experiments using Pt sphere markers, one quench experiment at the University of Michigan and another synchrotron radiography experiment at GSECARS, the Advanced Photon Source at the Argonne National Laboratory. The quench experiment used the 8-mm configuration and was run at 6 GPa and 1923 K, following similar pressure and temperature paths as described above. The synchrotron experiment used the COMPRES 10/5 on-line design with graphite-filled linear slots in the lanthanum chromite sleeve as windows for X-ray diffraction and radiography measurement (Chen et al. 2008; Leinenweber et al. 2012). The experiment was compressed at room temperature to the target oil load and then heated to 750 K at the rate of 60 K per minute, where an X-ray diffraction pattern was collected on crystalline NaCl sample for in situ pressure
8
determination. During further heating at the rate of 60 K per min, we monitored the X-ray
radiograph until the Pt marker sank and then quenched the experiment by turning off the power.

RESULTS and DISCUSSION

The melting temperatures of NaCl were determined between 1.8 and 21 GPa (Table 1). In a
typical experiment, we saw a rise in the current during heating from a few µA at temperatures
below 1000 K to a few hundred µA upon melting (Fig. 2). Assuming that melting leads to the
sharpest rise in the measured current, we took the starting point of the steepest segment of the
current-temperature curve as the melting point. As the heating cycle was repeated multiple times
in the same experiment, melting was detected within ±5 K. The measured melting temperatures
from duplicate experiments at the same condition agree within ±30 K. At pressures below 4 GPa,
the measured melting temperature sometimes shifted up by 10 to 40 K during the first two or
three heating cycles, which may result from thermal relaxation of internal stress in the assembly.
In these cases heating cycles were repeated until the melting temperature reached a stable value,
except at 1.8 GPa where the electrodes failed shortly after melting during the first heating cycle
(Fig. 2). The current-temperature relation was reversed upon cooling at up to 20 K lower in
temperature (Fig. 2). The hysteresis between the heating and cooling cycle can be attributed to
super-cooling, which is caused by kinetic barrier in nucleation, but there is not a counterpart
effect upon melting (Galiński et al. 2006), so the melting temperatures in the study were all
picked up from heating ramps.

Electron microprobe analyses of several recovered samples showed no contamination from
the four-bore alumina, which was in direct contact with the sample, or from any other
components in the assembly, which might diffuse into the sample. Optical inspection of the
experimental products revealed that in Experiment 071614 the thermocouple junction was
positioned further away from the center of the heater than the electrode tips (Fig. 1c). As a result, the measured temperatures from this experiment shifted systematically to lower values (Table 1). These data were not included in the fitting of melting equations.

The melting temperature of NaCl was found to increase continuously with pressure from ~1100 K at 1.8 GPa to ~2300 K at 19 GPa (Table 1, Fig. 3a). In the synchrotron radiography experiment (Experiment T1103), melting was detected between 1643 and 1648 K at 4.2 GPa, whereas the quench sinking sphere experiment (Experiment 012411) indicated that melting occurred below 1923 K at 6.0 GPa. These results are consistent with the in situ electrical measurements.

As mentioned earlier, our measurements are subject to uncertainties arising from the effect of pressure on the emf of thermocouple, which is poorly known and hence not corrected. Limited data suggest that the type C thermocouple underestimates the temperature with a systematic error that generally increases with pressure and temperature and could amount to tens of degrees or even more than 100 K at 15 GPa and above 2000 K (Li et al. 2003). Consequently, our melting temperatures may need to be corrected upwards by tens to 100 K, especially at high pressures.

Another source of uncertainty in the data may result from pressure drift during heating. Recent synchrotron experiments showed that the sample pressure at constant applied ram pressure drifted upwards or downwards as temperature increased from 1473 to 2273 K (Fei et al. 2004a, 2004b; Leinenweber et al. 2012). The direction and magnitude of the pressure drift varied with the TEL, configuration, temperature, pressure and heating history in a complicated manner, making it difficult to correct for the effect of temperature on pressure calibration. For the COMPRES 10/5 assembly, on which our experiments were based, available data showed that upon heating from 1473 K to 1800 K the sample pressure drifted downwards by 0.2 GPa at 20
GPa, and by 1 GPa at 15 and 17 GPa. On the other hand, the sample pressure was found to drift upwards by 2 GPa when heated from 1473 K to 2273 K at 23 GPa after experiencing a previous heating cycle (Fei et al. 2004a). Synchrotron experiments may be more susceptible to pressure drifts because the cell configurations were modified to allow X-ray access to the sample, which introduced additional heat sinks and mechanical weakness. In this study, the melting temperature at 3.6 GPa was found 30 K higher in the second heating cycle, probably because the sample pressure shifted up by about 0.3 GPa. On the other hand, experiments above 4 GPa yielded consistent melting temperatures (within ±5 K) among multiple heating cycles, indicating little pressure drift. For these reasons, we expect that the sample pressures in this study deviate from the calibration curve at 1473 K by less than 1 GPa at 15 GPa and by less than 2 GPa at ~20 GPa, no greater than synchrotron experiments mentioned above. At low pressures where the melting temperature increases rapidly with pressure at a rate of ~200 K per GPa, any pressure drift would lead to large errors in the measured melting temperature. Fortunately, pressure drift generally scales with temperature (e.g., Fei et al. 2004b), and therefore smaller pressure drifts are expected at lower pressures where the melting temperatures are lower. At high pressures where the rate drops to 20 K per GPa at ~15 GPa and 10 K per GPa at ~20 GPa, a pressure drift of ±1 GPa at 15 GPa or ±2 GPa at 20 GPa would introduce an additional error of ±20 K. The combined uncertainties in the measured melting temperature, including the precision of the type C thermocouple, the reproducibility within a single experiment and among duplicate experiments, and the pressure drift at high temperature, are estimated at ±40 K, assuming that the sources of uncertainties are random and independent.

Comparison with existing data
The melting curve of NaCl determined in this study agrees well with the existing experimental results at pressures up to 6.5 GPa and is marginally consistent with those at higher pressures (Fig. 3a). The results reproduced the existing data from piston-cylinder experiments (Akella et al. 1969) within ±20 K, suggesting that emf correction and melting temperature change caused by pressure drift are smaller than ±20 K within the relevant pressure and temperature ranges, unless the two effects cancel out. At pressures above 12 GPa, the melting temperatures determined in this study exceed the DAC results (Boehler et al. 1997) by 100 K to 200 K. The discrepancies between the two sets of data, however, generally fall within the estimated uncertainty of ±40 K in this study and the reported uncertainties of ±50 K up to 15 GPa and ±100 K up to 20 GPa in the DAC study. Heating-induced pressure drifts in the positive direction would bring our results into better agreements with the DAC data, whereas emf corrections and pressure drifts in the negative direction are expected to do the opposite. Further studies are necessary to quantify the effect of pressure on emf and to reduce the uncertainties in sample pressure, for example, by using an internal pressure marker. Vočadlo and Price (1996) suggested that DAC measurements tend to underestimate the melting temperature because of observational biases under extreme conditions. If corrected upwards by about 10% to account for surface melting effect (Cheng et al. 2003), the DAC data would agree well with the results of this study.

Compared with the latest theoretical results (An et al. 2006), the melting temperatures reported here are in agreement at 5 GPa, 100 K lower at 10 GPa, and 150 K lower at 20 GPa (Fig. 3a). Earlier results from MD simulations exceed that from DAC experiments by as much as 500 K at 20 GPa, well beyond the estimated uncertainty of ±100 K using the supercell methodology (Vočadlo and Price, 1996). Cheng et al. (2003) proposed that the melting
Temperature from simulation should be corrected downward by about 20% to account for superheating effect resulting from small system size and short time scale. More recent MD simulation (An et al. 2006) yielded substantially lower melting temperatures for NaCl, which requires no more than 5% correction for superheating to match the melting temperature at 20 GPa determined in this study.

Fitted melting equations

The empirical Simon equation has been widely used to fit pressure-dependent melting temperature in the form of \((T/T_0)^c = (P-P_0)/A + 1\), where A and c are constants with values \(\geq 1\), \(T_0\) and \(T\) are the melting temperatures at the reference pressure \(P_0\) and \(P\), respectively. The Simon equation stands out in its simplicity and has the advantage of not requiring any knowledge of the equation-of-state (EoS) of the solid phase. It has the drawbacks that the fitting parameters A and c have no clear meanings and that they correlate with each other. Consequently, the equation works well for interpolation but cannot be used for extrapolating melting temperatures beyond the experimental pressure range. Indeed, the parameters that fitted data up to 6.5 GPa (Akella et al. 1969) differ considerably with that of this study (Table 2) and the melting curve extrapolated from the low-pressure fitting over-predicts the data by nearly 100 K at 20 GPa (Fig. 3a).

The Kraut-Kennedy melting equation describes how the melting temperature scales with volume and it can be written in the form of \(T/T_0 = C \cdot \Delta V/V_0 + 1\), where \(\Delta V = V_0 - V\) is the volume reduction of the solid resulting from compression, \(T\) and \(T_0\) are the melting temperatures at \(V\) and \(V_0\) respectively, \(C\) is a constant that relates to the vibrational Grüneisen parameter \(\gamma_0\) at \(V_0\) and it equals to \(2 \cdot (\gamma_0 - 1/3)\). In this equation \(V\) and \(V_0\) refer to the 300 K volumes of the solid phase at a given pressure and 0 GPa, respectively. For NaCl, we used the EoS parameters from Birch.
(1986) to calculate $V$ from $V_0$ and found that $\gamma_0$ is $2.52\pm0.05$. These values are in general agreement with existing results (Table 2). For example, by using the EoS parameters from Bridgman (1940), Akella (1969) reported a $\gamma_0$ value of 2.78, which is similar to the fitted value of $2.62\pm0.02$ using the EoS parameters from Birch (1986).

Lindemann's law (1910) provides a semi-empirical scaling relation to fit discrete measurements of melting temperatures for interpolation, and in the absence of data it is often used together with an equation of state to predict $T_m$ at high pressures (Poirier, 2000). Given that Lindemann (1910) only used the equation to calculate the vibrational frequency of a solid from its melting point, and that Gilvarry (1956, 1966) developed the theory of melting from Lindemann's law, we will call it Gilvarry-Lindemann melting equation. The equation takes the form $T_m \sim 0.00321 \times M/2^2 \times \Theta_0^2 \times V^{2/3}$, where $M$ (the molar mass in grams) and $f$ (the critical Gilvarry-Lindemann factor) are independent of pressure, and $\Theta_0$ (the Debye temperature) varies with $V$ (the molar volume in cubic centimeter). The volume dependence of $\Theta_0$ can be described by the vibrational Grüneisen parameter $\gamma = -\partial \ln \Theta_0 / \partial \ln V$. It is commonly assumed that $\gamma$ itself scales with volume in the form $\gamma \gamma_0 = (V/V_0)^q$, where $\gamma$ and $\gamma_0$ are the Grüneisen parameters at $V$ and $V_0$, respectively, and $q$ is a constant that is usually assumed to be one in shock wave data reduction (Fei et al. 2004b). The equation can then be expressed as $T_m \sim 1.689 \times f^2 \times \Theta_0^2 \times (V_0/V)(2 \gamma_0 (V_0/V)^q - 1/3)$, where $\Theta_0$ is the Debye temperature at $V_0$. In this form, the equation has four fitting parameters ($f$, $\Theta_0$, $\gamma_0$, $q$), all of which may be obtained from or compared with independent measurements, and an isothermal EoS at 300 K is used to calculate the volume at a given pressure.

By using the EoS parameters from Birch (1986), two sets of fitting parameters were obtained: one for a fixed $q$ at 1, and the other allowing $q$ to be fitted by the data (Table 2). The
parameters $f$ and $\Theta_0$ correlate with each other and cannot be uniquely fitted. With $\Theta_0$ fixed at 302 K (Poirier, 2000), the fitted Gilvarry-Lindemann factor $f \sim 0.08$ is lower than the known value of 0.11 for alkali halides (Martin and O'Connor, 1977). If $f$ is fixed at 0.11, the fitted $\Theta_0$ value is 228 K, which is closer to 279±11 K, which is cited in Decker (1971). We found that holding $q$ at 1 failed to reproduce the curvature of the melting curve between 0 and 20 GPa, whereas a good fit is obtained when $q$ is allowed to vary. Recent experimental and theoretical studies on MgO demonstrated that variable $q$ is required to satisfy the high $P$-$T$ static and shock wave data (Fei et al. 2004b). For NaCl, a volume-dependent $q$ value may be needed to describe the thermoelastic behavior, or it may indicate that extending the Gilvarry-Lindemann melting equation to ionic crystals does not work well because the Debye-Waller theory is limited to monoatomic solids (Gilvarry, 1956).

As widely recognized the Kraut-Kennedy melting equation can be derived from the Lindemann equation by assuming that the volume dependence of melting temperature is constant and equals to the value at $V_0$ (e.g. Akella et al. 1969). This approximation does not apply at higher pressures, where the measured melting temperatures deviated from the fitted curve towards lower temperatures due to the volume dependence of gamma (Akella et al. 1969). In our study, the measured melting temperature began to deviate from a linear trend at pressures above 14 GPa, where the Grüneisen parameter is expected to be higher because of the reduced volume.

**IMPLICATIONS**

The melting temperatures of NaCl between 0 and ~20 GPa, determined using a newly developed in situ capacitive current method and the multi-anvil apparatus and, reproduce existing data up to 6.5 GPa but show considerable discrepancies with both diamond-anvil-cell and theoretical results at higher pressures. The discrepancies suggest that superheating effect in
molecular dynamic calculations may be as much as 150 K at about 20 GPa. Alternatively, the
discrepancies may originate from pressure effect on the emf of type C thermocouple, which was
expected to underestimate the melting temperatures and are uncertain at pressures above 4 GPa
(e.g., Li et al. 2003; Fei et al. 2004b). In high-pressure experiments, temperatures are commonly
measured with a thermocouple or spectral radiometry. While the thermocouple method is subject
to poorly constrained pressure effect on emf, the spectral radiometry also suffers from limited
knowledge of wavelength dependent emissivity and optical aberration (Shen et al., 2001),
leading to errors that are more than 100 K (Campbell, 2008). An independent evaluation of the
pressure effect on emf remains a challenge.

The capacitive current method can be applied to determine the melting temperatures of ionic
compounds at high pressures. This method uses Pt as the electrodes and sample container and is
applicable below the melting point of Pt, which increases from 2042 K at 0 GPa to 2600 to 2900
K at 20 GPa (Belonoshko and Rosengren 2012). Compared with the existing methods (e.g.,
Anzellini et al. 2013; Jackson et al. 2013; Boehler et al. 1997; Chen et al., 2008; Akella et al.
1969), the capacitive current approach is characterized by its high signal/noise ratio and high
efficiency. The experimental procedure has been optimized to generate non-destructive
capacitive current through the sample so that it can be melted more than 20 times before failure
because of electrodes shorting in a single experiment to yield results that are reproducible within
±5 K at a given pressure. By using this approach, we can repeat measurements at each pressure
and collect data at multiple pressures in each experiment. The melting curve of NaCl may be
used for hot pressure calibration of piston cylinder and multi-anvil apparatus up to about 7 GPa.
At higher pressures, the melting slope becomes rather shallow, increasing by only 20 K per GPa
at 15 GPa. Considering the weak dependence of melting temperature on pressure and significant
uncertainties the melting temperature of NaCl, the melting curve of NaCl does not appear to be a good candidate for pressure calibration above 10 GPa.

In this study the frequency of the test voltage is 60 Hz, which is readily available and adequate for detecting melting. In impedance spectroscopy studies, a wide range of frequencies from 1 Hz to 1 MHz have been used (e.g., Gaillard et al. 2008; Yoshino et al. 2010). The signal/noise ratio may improve at higher frequencies that match ionic relaxation more closely. In future development, a waveform generator may be used to optimize the frequency of the test voltage. The design of the pressure assembly can also be modified to further reduce the random errors in temperature by improving the positioning precision and minimizing the size of the thermocouple junction. Finally, this approach may be integrated with other high-pressure devices such as diamond anvil cells to extend the pressure coverage.

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FIGURE CAPTIONS

**Fig. 1** Experimental configurations for melting detection using capacitive current method.

a. Schematic configuration of the 5-mm assembly used in this study.

b. Illustrations of the platinum electrodes in four-bore alumina in opaque and translucent views.

c. Reflected light microscopic images of recovered charges of Experiment 021314 (left) showing symmetric placement of the electrode tips and thermocouple (TC) junction (circles) with respect to the equator of the heater (horizontal line) and the sample position (box), and Experiment 071614 (right) showing that the TC junction is located further away from the equator of the heater than the electrode tips.

**Fig. 2** Representative current-temperature curves at selected pressures. Melting is located the abrupt take-off point of each blue curve (Experiment 021314), or as the starting point of the steepest segment for each yellow curve (Experiment 100313). The black curve represents data collected along the cooling path at 15 GPa in Experiment 021314. The down-going part of the red curve (Experiment 092613) indicates instability of the electrodes before they failed by contacting each other or with adjacent Pt capsule.

**Fig. 3** Fittings of experimental data to melting equations. Results from this study (Table 1) are shown as narrow diamonds for 8-mm experiments 092613 (blue) and 100313 (Red), regular diamonds for 5-mm experiments 021314 (red) and 070114 (black), and solid triangles for the experiments using Pt sphere markers. Open triangles and circles represent experimental data from Akella et al. (1969) and Boehler et al. (1997), respectively. Bars and pounds represent theoretical results from Belonoshko and Dubrovinsky (1996) and An et al. (2006), respectively.

a. Simon’s equation fittings for data from this study (black thick solid curve) and for those of Akella et al. (1969) (gray thin solid curve).
b. Kraut-Kennedy equation fittings for data from this study (black thick solid line), for those of Akella et al. (1969) (gray thin solid curve), and those of Bohler et al. (1997) (gray thin dashed line).

c. Gilvarry-Lindemann equation fittings for data from this study with $q$ fitted by the data (black thick solid line) or $q$ fixed at 1 (gray thick solid line), for those of Akella et al. (1969) (gray thin solid curve), and those of Bohler et al. (1997) (gray thin dashed line).
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¹Data from this experiment were not used for fitting because the thermocouple junction was located at a significantly colder position than the electrode tips.
²At 3.6 GPa, the melting temperature is taken from the second heating cycle and it is higher than that from the first heating cycle by 40 K.
³The marker sank at this temperature.
<table>
<thead>
<tr>
<th>Equation Type</th>
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<th>Clark 1959</th>
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\(^1\) Fitted for the reported data.

\(^2\) Fitted for the reported data using Birch (1986) EoS parameters.

Numbers in parentheses are uncertainties on the last digits.
Simon Melting Equation

\[ \left( \frac{T}{T_0} \right)^c = \left( \frac{P}{P_0} \right)/A + 1 \]
Approximate Pressure, GPa

Kraut-Kennedy Melting Equation

\[ T/T_0 = 2(\gamma - 1/3)(V_0 - V)/V_0 + 1 \]

Temperature, K

(V_0-V)/V_0
Gilvarry-Lindemann Melting Equation

\[ T \sim 0.00321 \cdot M \cdot f^2 \cdot \Theta^2 \cdot V^{2/3} \]
\[ \sim 1.689 \cdot f^2 \cdot \Theta_0^2 \cdot (V_0/V)^{2(\gamma^{-1/3})} \]
\[ \gamma = \gamma_0 \cdot (V_0/V)^{-q} \]