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Density measurement of undercooled liquid $BaTiO_3$ by aerodynamic levitation

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An almost-spherical $BaTiO_3$ approximately 2.0 mm in diameter was synthesized using an aerodynamic levitator. The densities of the undercooled liquid $BaTiO_3$ were measured from high speed video images of a molten droplet. The densities of the undercooled liquid phase were 4.2~4.0 g/cm^3 at temperatures ranging from 1622 K to 1693 K. The aerodynamic levitation technique provided an effective method for determining the thermophysical properties, such as the density and volumetric thermal expansion coefficient of the material.

Key words: Aerodynamic levitation, $BaTiO_3$ ceramics, Density, Thermophysical properties.

Introduction

Studies of the liquid state are important for technological applications because the molten state is an essential stage in many industrial processes, such as glass making, single-crystal growing, iron- and steel-making, etc. [1].

The density of materials at high temperatures is important for examining the basic thermophysical properties. On the other hand, there is little data available on the density of molten ceramics due to the experimental difficulties in density measurements at high temperatures. Measurements of the molten material density at high temperature are difficult using classical density measurements because chemical reactions with the containers are unavoidable [2]. The containerless levitation technique offers a unique approach for determining the liquid material density [1-6]. Although electrostatic levitation is suitable for measuring the thermophysical properties of materials, it is difficult to establish stable levitation conditions for ceramic materials. Moreover, it is expensive and requires skill to manipulate, and contamination of the vacuum chamber is inevitable due to vaporization from molten materials. In contrast, aerodynamic levitation is simple and economical, and can solve the above-mentioned problems [4, 5]. In preliminary experiments, a levitated sample with a diameter of approximately 2.0 mm showed an almost-spherical shape.

Therefore, this study reports the results of density measurements performed on molten $BaTiO_3$ ceramics.

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Experimental Procedure

Commercial $BaTiO_3$ (99.96%, tetragonal, Toho Titanium Co., Japan) was used as the starting powder. The mean particle size of the $BaTiO_3$ powder was 0.48 μm. The powder was pressed uniaxially at 100 MPa, and rod-type green bodies were then sintered at 1473 K for 2 h in air. Cylindrical pellets, 2.5 mm in diameter, were obtained from the rods.

Fig. 1 shows a schematic levitation setup. The flow rate of the floating gas was controlled with a mass flow controller (MFC). The laser was aligned onto the sample position using a diode pointer (which emits a visible red laser beam) collinear with the main laser. The samples were heated and completely melted using a 100 W CO_2 laser (Firestar-t100 series, Synrad Inc., USA) directed from above. The laser beam was

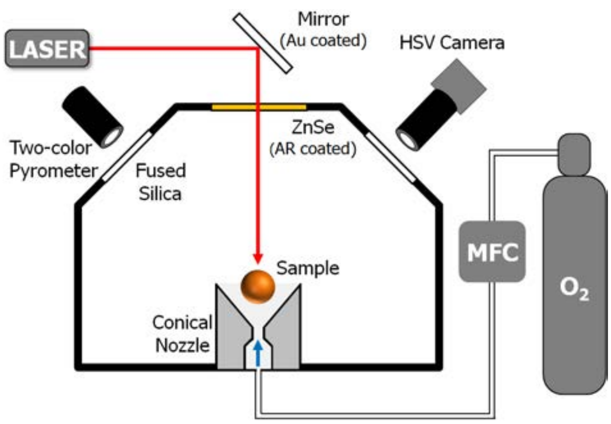

Fig. 1. Experimental setup for the density measurement of a sample using an aerodynamic levitator. An anti-reflection (AR) coated ZnSe lens was used to reduce the laser beam reflection from the surface.

focused on the sample by Au coated spherical mirrors. An anti-reflection (AR) coated ZnSe lens was used to reduce the laser beam reflection from the surface. The surface temperature of the levitated droplet was monitored using a two-color pyrometer (Chino IRFBWWHSP, Chino Corp., Tokyo, Japan) at a sampling rate of 100 Hz and a 1 mm diameter spot size. The response time of the pyrometer and measurement error of the as-measured temperature was 2.0 ms and ~0.5%, respectively. The droplet was then cooled by turning off the CO_2 laser. A high-speed video (HSV) camera (FASTCAM R2, Photron Inc., USA) at a sampling rate of 1000 Hz was used to monitor the solidification behavior on the surface of the droplet during levitation and cooling. A HSV camera can record 8,736 frames at a speed of 1,000 frames per second.

An almost-spherical sample (approximately 2 mm in diameter) was levitated on an O_2 gas stream at a flow rate of 420 mlminute^{-1}. The spherical sample was heated and melted under continuous wave radiation of the CO_2 laser with a power of 60 W. The high temperature densities and volumetric thermal expansion coefficients were estimated from the snap shot images recorded using HSV camera.

Results and discussion

Fig. 2 shows the temperature change of a levitated $BaTiO_3$ (T_m = 1893 K) droplet as a function of time. $BaTiO_3$ was superheated by ~55 K above the melting temperature (T_m = 1893 K) and held for 30 s to get a homogeneous melt. Then, the levitated droplet was undercooled to ~1621 K (~ 0.86 T_m) by turning off the laser. Recalescence was observed at ~1621 K, indicating that the undercooled melt had solidified into a polycrystalline $BaTiO_3$ phase. The degree of recalescence and the recalescence time interval (t_R) were ~190 K and ~20 ms, respectively.

Fig. 3 shows snap shot images, which were recorded using a color HSV camera, for the undercooling stage,

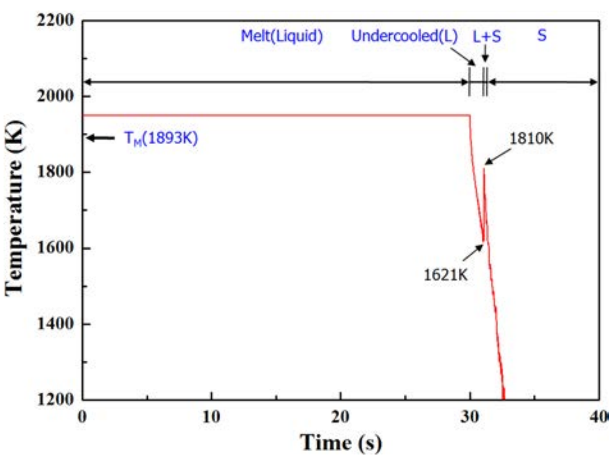

Fig. 2. Temperature-time profile of $BaTiO_3$ during aerodynamic leviation. L and S denote the solid and liquid, respectively.

recalescence and cooling stages of the molten droplet. From snap shot images during recalescence, it is clear that nucleation and crystallization occur from the undercooled liquid, and propagate rapidly through the volume of the melt.

Density measurements of levitating liquids in aerodynamic devices are based on an approximation of perfect sphericity of a liquid drop; as the sample mass, m, is known, the density, ρ, at high temperature can be calculated using the following equation: $\rho = 3m/4\pi r^3$. In this study, the sample radius, r was measured from the snap shot images.

Snap shot images of a spherical ZrO_2 reference sample (diameter: 2.01 mm) were taken under identical conditions to eliminate the uncertainty in the measurement of the sample radius. The measured sample radius of the levitated $BaTiO_3$ was calibrated using reference sample images with a known diameter.

Fig. 4 shows a photograph of a levitated sample. The levitated sample with a diameter of approximately 2.0 mm (approximately 21 mg) showed an almost-spherical shape. The shape of the levitated sample

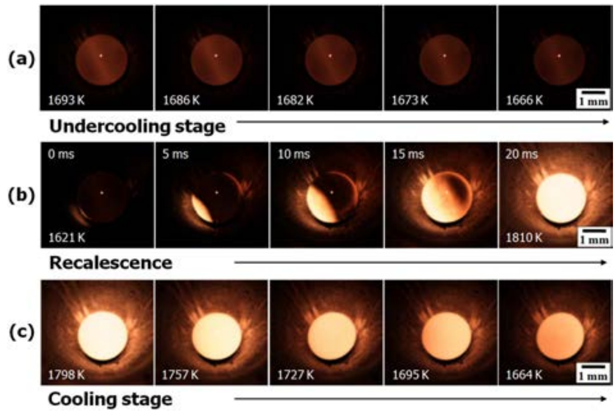

Fig. 3. Snap shot images of a molten droplet (a) undercooled liquid, (b) recalescence and (c) cooled solid after recalescence. The arrow denotes the elapsed time.

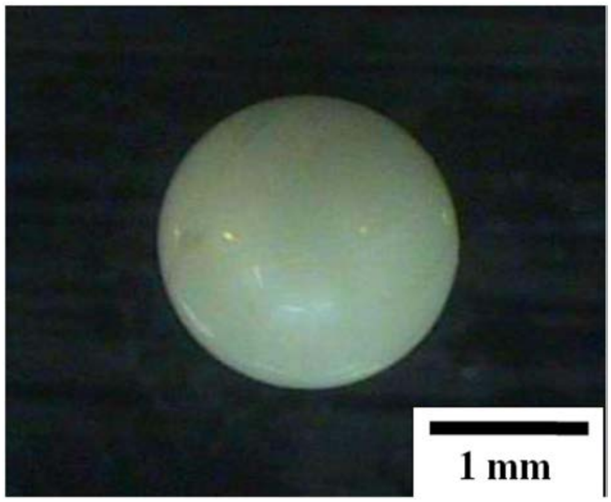

Fig. 4. Photograph of a levitated $BaTiO_3$ sample with a diameter of ~2.0 mm and mass of 21 mg.

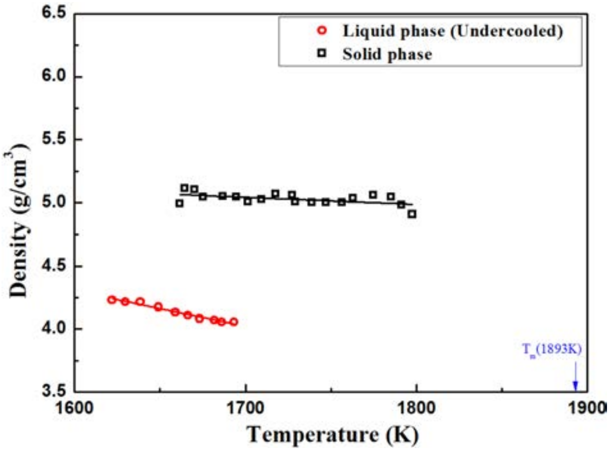

Fig. 5. High-temperature densities of liquid and solid $BaTiO_3$. The densities of the liquid and solid phase were estimated at temperatures from 1622 K to 1693 K (undercooling stage) and from 1662 K to 1798 K (cooling stage to ambient temperature just after recalescence), respectively.

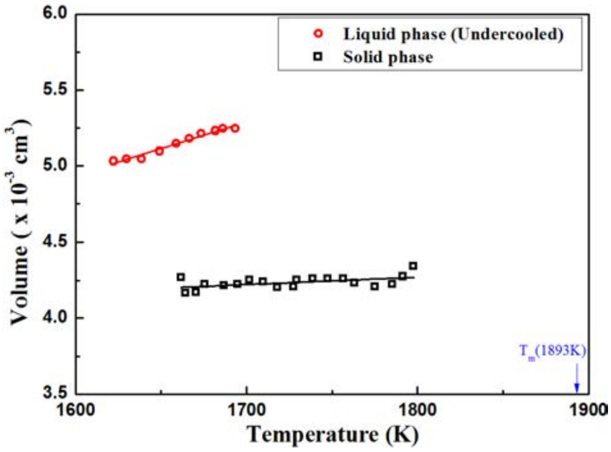

Fig. 6. Volumes of liquid and solid $BaTiO_3$ as a function of temperature. The volumes of the liquid and solid phase were estimated at temperatures from 1622 K to 1693 K (undercooling stage) and from 1662 K to 1798 K (cooling stage to ambient temperature just after recalescence), respectively.

depends on the mass of the droplet. Glorieux et al. [6] measured the density of liquid alumina drops using aerodynamic levitation, and reported that an almost-spherical shape could be obtained for droplets weighing < 78 mg. On the other hand, it should be noted that the shape of the levitated sample was an oblate spheroid, rather than spherical. Therefore, ρ was calculated using $\rho = 3m/4\pi a^2 b$ (a is the horizontal radius at the equator and b is the vertical radius). Assuming a sphere in the density calculation, instead of a spheroid the percentage error involved was estimated to be < 3%. In this study, the $BaTiO_3$ droplet was kept at 1948 K for 30 s, weight losses can occur due to evaporation during laser ablation. Therefore, the mass of the levitated sample was measured carefully using a high precision microbalance (UMX2, Mettler Toledo, Max. Cap. : 2,100 mg, readability; 0.1 μg), and the density was calculated based on the mass after levitation.

Fig. 5 shows densities of the liquid and solid $BaTiO_3$ at high-temperatures. The densities of the undercooled liquid phase were estimated at temperatures ranging from 1622 K to 1693 K (undercooling stage). Those of the solid phase were estimated at temperatures ranging from 1662 K to 1798 K (cooling stage to ambient temperature immediately after recalescence). The densities of the liquid and solid phase increased linearly with decreasing temperature. The densities of the liquid and solid were approximately 4.0 ~ 4.2 g/cm^3 and 5.0 ~ 5.1 g/cm^3, respectively. The data were fitted by least-squares regression, and is expressed by the following equations:

$$\rho_L(T)\ (g/cm^3) = 8.83 - (2.83 \times 10^{-3})T,\ (1622\text{-}1693\ K) \quad (1)$$

$$\rho_S(T)\ (g/cm^3) = 6.01 - (5.68 \times 10^{-4})T,\ (1662\text{-}1798\ K) \quad (2)$$

where ρ_L is the density of the liquid, ρ_S is the density of solid and T is the temperature in Kelvin. From these equations, the density of the liquid at the melting point was estimated. The value (3.48 g/cm^3) extrapolated to the melting point (1893 K) is in poor agreement with the value proposed by Paradis et al. (4.04 g/cm^3) [7]. This discrepancy might be due to differences in the temperature interval investigated.

The volumetric thermal expansion coefficients were also estimated using the same snap shot images used for the density measurements. In the case of a liquid, the volumetric coefficient of thermal expansion was given by the formula, $\beta = (1/V)(dV/dT)_P$. The subscript P indicates that the pressure is held constant during the expansion. For a solid, the effects of pressure on the material can be ignored. Fig. 6 shows volumes of liquid and solid $BaTiO_3$ at high-temperature. The slopes in the figure correspond to the rates of volume change with temperature, $(dV/dT)_P$. It was found that the volumetric thermal expansion coefficient of the liquid at 1622 ~ 1693 K was approximately $7.00 \times 10^{-4}\ K^{-1}$. It can be easily surmised that the molten droplet exhibits isotropic behavior. For isotropic materials, the linear thermal expansion coefficient (α) is almost exactly one-third of the volumetric coefficient; $\alpha = \beta/3$. Therefore, the linear thermal expansion coefficient of the liquid was assumed to be $2.33 \times 10^{-4}\ K^{-1}$. The volumetric thermal expansion coefficient of the solid at 1662~1798 K was approximately $1.14 \times 10^{-4}\ K^{-1}$.

Conclusions

The densities of liquid $BaTiO_3$ at high temperatures were measured from high speed video snap shot images taken during aerodynamic levitation. The densities of the undercooled liquid phase were 4.2 ~ 4.0 g/cm^3 at temperatures ranging from 1622 K to 1693 K. The aerodynamic levitation technique provided an effective method for determining the thermophysical properties, such as the density and volumetric thermal expansion coefficient of materials.

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