

Contactless density and volumetric thermal expansion coefficient measurement of undercooled liquid (Ba,Sr)TiO₃ using aerodynamic levitator

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Almost-spherical (Ba,Sr)TiO₃, approximately 2.0 mm in diameter, was synthesized using an aerodynamic levitator. The densities and volumetric thermal expansion coefficient of the undercooled liquid (Ba,Sr)TiO₃ were measured from high speed video images of a molten droplet. The densities and volumetric thermal expansion coefficient of the undercooled liquid phase at temperatures ranging from 1678 K to 1948 K were 4.1~3.5 g/cm³ and 5.7×10^{-4} K⁻¹, respectively.

Key words: Aerodynamic levitation, (Ba,Sr)TiO₃, Density, Thermophysical properties.

Introduction

Barium strontium titanate, (Ba,Sr)TiO₃ is a representative perovskite (ABO₃ type) material applied widely in an electronics on account of its high dielectric constant and good ferroelectric properties [1]. The Curie temperature of (Ba,Sr)TiO₃ decreased linearly with increasing amounts of Sr in the BaTiO₃ lattice [2]. Donor-doped BaTiO₃ exhibits an anomalous increase in electrical resistivity near the Curie temperature (120 °C), which is known as positive temperature coefficient of resistivity (PTCR) behavior [3-5]. PTC ceramics have been applied extensively in many electronic parts including over-current limiters, motor starters and self-regulating heaters. Many studies focused on doping or microstructural control to enhance the PTCR characteristics of (Ba,Sr)TiO₃ [6-8].

On the other hand, there are no detailed reports on the thermophysical properties of (Ba,Sr)TiO₃ in the liquid state. 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 growth, iron- and steel-making industry, etc. [9].

Nevertheless, there is little data on the density of molten ceramics due to the experimental difficulties in classical density measurements at high temperatures due to the unavoidable chemical reactions with the

containers [10]. A containerless levitation technique offers a unique approach to determine the liquid material density [9-17]. Although an electrostatic levitator is a suitable apparatus for measuring the thermophysical properties of materials, it is expensive and requires considerable skill to establish stable levitation conditions for ceramic materials. In contrast, an aerodynamic levitator is economical and simple [12, 13].

This study reports the density and volumetric thermal expansion coefficient of molten (Ba,Sr)TiO₃ ceramics measured by aerodynamic levitation.

Experimental Procedure

Commercial Y-doped (Ba,Sr)TiO₃ (Toho Titanium Co. Ltd., Japan) containing SrTiO₃ (19.2 mol%) and Y₂O₃ (0.2 mol%) was used as the starting powder. The mean particle size and ferroelectric Curie temperature of the Y-doped (Ba,Sr)TiO₃ powder were 0.18 μm and 334 K, respectively. The powder was pressed uniaxially at 100 MPa and the rod-type green bodies were sintered at 1473 K for 2 hrs in air. Cylindrical pellets, 2.5 mm in diameter, were obtained from the rods.

Fig. 1 shows a schematic diagram of the levitation setup. The flow rate of the floating gas was controlled using a mass flow controller (MFC). The laser was aligned on the sample position using a diode pointer (emits a visible red laser beam) collinear with the main laser. The laser beam was focused on the sample using Au coated spherical mirrors. An anti-reflection (AR) coated ZnSe lens (reflection: < 0.25%, transmission: > 99.5%) was used to reduce the laser beam reflection

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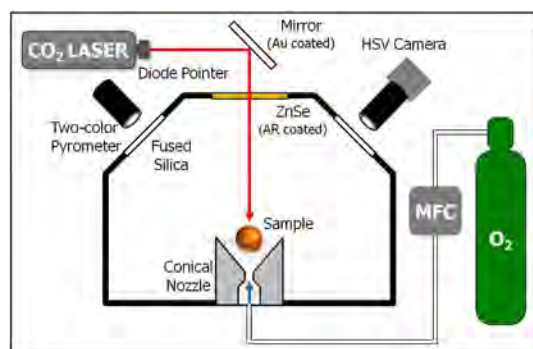


Fig. 1. Experimental setup for the density measurement of a sample using an aerodynamic levitator. An anti-reflection (AR) coated ZnSe lens was used to reduce the laser beam reflection from the surface. A high-speed video (HSV) camera was used to monitor the solidification behavior on the surface of the droplet during levitation and cooling.

from the surface. The samples were heated and melted completely using a 100 W CO₂ laser (Firestar t100, Synrad Inc., USA) directed from above. The surface temperature of the levitated droplet was monitored using a two-color pyrometer (Chino IRFBWWSP, 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 the measurement error of the as-measured temperature were 2.0 ms and ~0.5%, respectively. The droplet was cooled by turning off the CO₂ 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 of the droplet surface during levitation and cooling. A HSV camera can record 8,736 frames (256 × 240 pixels) at a speed of 1,000 frames per second.

An almost-spherical sample (approximately 2 mm in diameter) with a mass of ~25 mg was levitated on an O₂ gas stream at a flow rate of ~420 ml · minute⁻¹. The spherical sample was heated and melted by the continuous wave radiation of the CO₂ laser with a power of 60 W. The high temperature density and volumetric thermal expansion coefficients were estimated from the snap shot images recorded on the HSV camera.

Results and Discussion

Fig. 2 shows the change in temperature of a levitated (Ba,Sr)TiO₃ droplet as a function of time. (Ba,Sr)TiO₃ was superheated above the liquidus temperature ($T_L = 1953$ K [18]) and held at that temperature for 30 sec. to achieve a homogeneous melt. Subsequently, the levitated droplet was undercooled to ~1676 K (~0.86 T_L) by turning off the laser. Recalescence was observed at ~1676 K, suggesting that the undercooled melt had solidified into a single/polycrystalline (Ba,Sr)TiO₃ phase. The degree of recalescence and the recalescence time interval (t_R) were ~147 K and ~20 ms, respectively.

The density measurements of levitating liquids in

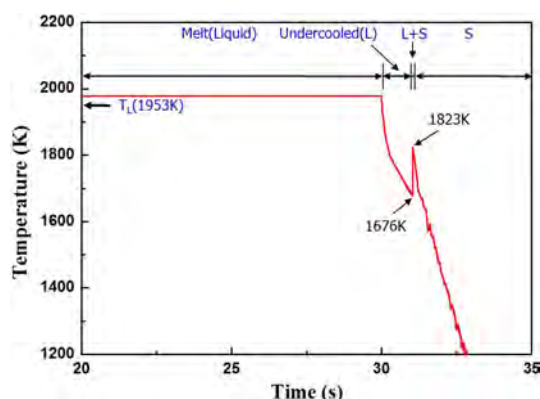


Fig. 2. Temperature-time profile of (Ba,Sr)TiO₃ during aerodynamic levitation. L and S denote the solid and liquid, respectively.

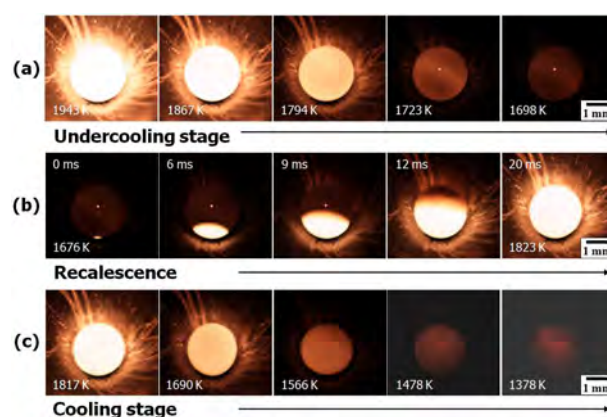


Fig. 3. Snap shot images of a molten droplet (a) undercooled liquid, (b) recalescence and (c) cooled solid after recalescence. The arrow denotes the elapsed time.

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 temperatures can be calculated using the following equation: $\rho = 3m/4\pi r^3$. The sample radius, r was measured from the snap shot images.

Fig. 3 shows snap shot images, which were recorded on a color HSV camera, for the undercooling stage, recalescence and cooling stages of the molten droplet. Most images were clear enough to determine the radius. On the other hand, the radius was difficult to determine in some images due to the samples glowing (at high temperature) and darkening (at low temperatures). Fortunately, the tiny contour of droplet was observed by adjusting the contrast and brightness of the images. Fig. 3(b) shows snap shot images during recalescence, crystallization (nucleation and growth) occurs from the undercooled liquid and propagates rapidly through the melt volume.

Snap shot images of a spherical ZrO₂ reference sample (diameter: 2.018 mm) was taken under identical conditions in an attempt to eliminate the uncertainty in the measurements of the sample radius. The measured sample radius of levitated (Ba,Sr)TiO₃ was calibrated using reference sample images with a known diameter.



Fig. 4. Photograph of the levitated (Ba,Sr)TiO₃ sample with a diameter and mass of ~2.0 mm and 25.14 mg, respectively.

Table 1. EPMA analysis of the Ba, Sr, Ti and O contents in the as-levitated (Ba,Sr)TiO₃. wt% (at%)

	As-levitated sample	
	Center	Periphery
Ba	52.43 (15.46)	51.02 (14.54)
Sr	5.08 (2.35)	4.73 (2.11)
Ti	15.04 (12.71)	15.08 (12.28)
O	27.45 (69.48)	29.17 (71.07)

Fig. 4 shows a photograph of the levitated sample. The levitated sample with a diameter of approximately 2.0 mm (25.14 mg) had an almost-spherical shape. The shape of the levitated sample will depend on the mass and surface tension of the droplet, as well as the velocity of flowing gas, etc. In preliminary experiments, the levitated sample, approximately 2.0 mm in diameter, showed an almost-spherical shape. Glorieux et al. [14] measured the density of liquid alumina drops by aerodynamic levitation, and reported that an almost-spherical shape could be obtained for droplets weighing < 78 mg. On the other hand, the shape of the undercooled liquid was oblate spheroid, rather than spherical due to the upward stream of flowing gas and droplet rotation (~60 rpm). The deviation to an oblate spheroid is more prominent in a solid than liquid. If solidification begins simultaneously from the periphery of the droplet and finishes at the center region, there will be no shape difference between the liquid and solid. This is not true in the present study because solidification began at a certain nucleation point, and propagated radially, as shown in Fig. 3(b). Therefore, a density difference between the solid and liquid will tend to cause the droplet to deviate from a spherical shape due to a change in the center of mass. Hence, ρ of an oblate spheroid can be calculated using $\rho = 3m/4\pi a^2b$ (a is the horizontal radius at the equator and b is the vertical radius). The percentage error was estimated to be < 3% by assuming a sphere in the density calculation instead of a spheroid.

Table 1 lists the results of EPMA analyses of the center and periphery region after mirror-like polishing

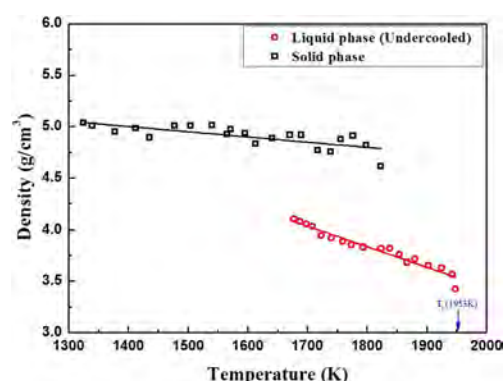


Fig. 5. High-temperature densities of liquid and solid (Ba,Sr)TiO₃. The densities of the liquid and solid phase were estimated at temperatures ranging from 1678 K to 1948 K (undercooling stage) and from 1325 K to 1823 K (cooling stage to ambient temperature immediately after recalescence), respectively.

of the as-levitated (Ba,Sr)TiO₃ sample. The periphery region of the as-levitated sample was oxygen-deficient compared to the center region. With the levitated sample, the periphery region exposed to flowing O₂ gas showed a higher oxygen content than the center region. The Ba and Sr contents in the periphery region were slightly lower than those in the center region, suggesting evaporation. Therefore, the masses of the levitated sample before and after levitation were measured carefully using a high precision microbalance (UMX2, Mettler Toledo, readability; 0.1 μ g). The percentage weight loss was approximately 5.4%. The experiment for high vapor pressure materials should be performed rapidly enough to limit the significant loss of mass [17]. In this study, the density was calculated based on the mass after levitation assuming that the mass loss was negligible after laser shutdown. This assumption is reasonable because the mass loss rate due to evaporation will be significantly higher in the superheating stage.

Fig. 5 shows the densities of the liquid and solid (Ba,Sr)TiO₃ at high-temperatures. The densities of the liquid and solid phase increased linearly with decreasing temperature. The densities of the undercooled liquid phase and solid phase were estimated at temperatures ranging from 1678 K to 1948 K (undercooling stage) and from 1325 K to 1823 K (cooling stage to ambient temperature immediately after recalescence), respectively. The densities of the liquid and solid were approximately 3.5 ~ 4.1 g/cm³ and 4.8 ~ 5.0 g/cm³, respectively.

The solid density measurements showed more scatter than those of the liquid. The liquid droplet maintained the same axisymmetry but the solid droplet lost its axisymmetry slightly upon solidification (see Fig. 3(c)), resulting in some scatter of the density data. During recalescence, dendrites grew radially from the melt and solidified. Interdendrite shrinkage during solidification resulted in surface roughness (see Fig. 4) as well as a loss of axisymmetry [17].

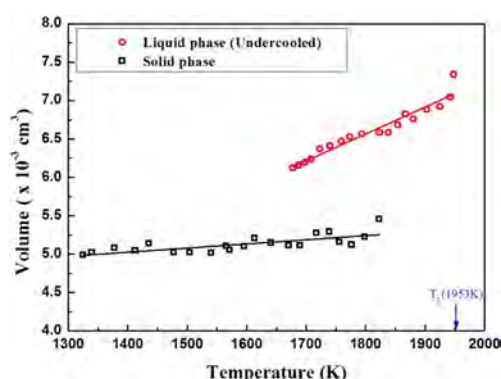


Fig. 6. Volumes of liquid and solid (Ba,Sr)TiO₃ as a function of temperature. The volumes of the liquid and solid phase were estimated at temperatures from 1678 K to 1948 K (undercooling stage) and from 1325 K to 1823 K (cooling stage to ambient temperature immediately after recalescence), respectively.

The data was fitted by least-squares regression, and is expressed by the following equations:

$$\rho_L(T) \text{ (g/cm}^3\text{)} = 7.45 - (2.01 \times 10^{-3})T, \text{ (1678 to 1948 K)} \quad (1)$$

$$\rho_S(T) \text{ (g/cm}^3\text{)} = 5.71 - (5.08 \times 10^{-4})T, \text{ (1325 to 1823 K)} \quad (2)$$

where ρ_L is the density of the liquid, ρ_S is the density of the solid and T is the temperature in Kelvin. The density of the solid at room temperature (293 K) was estimated using these equations. The value extrapolated to room temperature was 5.6 g/cm³, which is a lower value than the theoretical density (6.0 g/cm³). The density at room temperature was also measured using the Archimedeian method, and found to be approximately 5.3 g/cm³.

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 (β) can be given by the formula, $\beta = (1/V)(dV/dT)_P$. Subscript P indicates that the pressure is held constant during expansion. For a solid, the effects of pressure on the material can be ignored. Fig. 6 shows the volumes of liquid and solid (Ba,Sr)TiO₃ at high-temperature. Rather accurate values were obtained for the volumetric thermal expansion coefficient due to the disappearance of uncertainties in both the mass and reference sample radius when calculating β .

The slopes in the figure correspond to the rates of the volume change with temperature, $(dV/dT)_P$. The volumetric thermal expansion coefficient of the liquid at 1678 ~ 1948 K was approximately $5.7 \times 10^{-4} \text{ K}^{-1}$. The molten droplet would exhibit isotropic behavior. For isotropic materials, the linear thermal expansion coefficient (α) was approximately one-third of the volumetric coefficient, $\alpha = \beta/3$. Therefore, the linear thermal expansion coefficient of the liquid was assumed to be $1.9 \times 10^{-4} \text{ K}^{-1}$. On the other hand, the volumetric thermal expansion coefficient of the solid at 1325 ~ 1823 K was approximately

$1.1 \times 10^{-4} \text{ K}^{-1}$. The estimated volumetric thermal expansion coefficient of the solid and liquid (Ba,Sr)TiO₃ samples are considered reasonable despite the lack of values for the density and volumetric thermal expansion coefficient of (Ba,Sr)TiO₃ in the literature.

Conclusions

The densities and volumetric thermal expansion coefficient of liquid (Ba,Sr)TiO₃ at high temperatures were measured from high speed video snap shot images taken during aerodynamic levitation. The density and volumetric thermal expansion coefficient of the undercooled liquid phase at temperatures ranging from 1678 K to 1948 K were 4.1 ~ 3.5 g/cm³ and $5.7 \times 10^{-4} \text{ K}^{-1}$, respectively. The aerodynamic levitation technique provides an effective method for determining the thermophysical properties of materials, such as the density and volumetric thermal expansion coefficient.

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