

## Solidification behavior and microstructure of (Ba,Sr)TiO<sub>3</sub> ceramics prepared by aerodynamic levitation

Ki-Ju Lee, Chi-Hoon Lee, Sang-Kyo Jung, Gye-Hyeok Lee, Won-Seung Cho and Woon-Suk Hwang\*

School of Materials Science and Engineering, Inha University, 253 Yonghyun-Dong, Nam-Gu, Incheon 402-751, Korea

Semiconducting (Ba,Sr)TiO<sub>3</sub> ceramics were solidified using an aerodynamic levitator and the solidification behaviors during recalescence and microstructure of the levitated (Ba,Sr)TiO<sub>3</sub> ceramic were investigated. A spheroid (Ba,Sr)TiO<sub>3</sub> was synthesized from a homogeneous melt using an aerodynamic levitator. The recalescence was observed, indicating that the undercooled melt solidified into a polycrystalline (Ba,Sr)TiO<sub>3</sub> phase. The levitated sample exhibited a radial dendrite structure originating from a surface nucleation point. Secondary dendrites on primary dendrites were formed due to temperature variations at the solid-liquid interface. The as-levitated sample was oxygen-deficient compared to the sintered sample. The as-levitated (Ba,Sr)TiO<sub>3</sub> sample had a cubic structure, and the positive temperature coefficient of resistivity (PTCR) characteristics were not observed. To analyze the transformation kinetics during recalescence, the growth velocity of the solid phase was estimated from the snap shot images of the molten droplet during recalescence.

**Key words:** Aerodynamic levitation, (Ba,Sr)TiO<sub>3</sub> ceramics, Recalescence, Solidification.

### Introduction

The containerless levitation technique is of interest field because it enables the melting and solidification of a sample without a container [1]. Containerless levitation techniques can prevent sample contamination due to the use of a container. This can also minimize the number of heterogeneous nucleation sites. In particular, it enables the liquid to be supercooled deeply at a relatively low cooling rate, allowing it to be used to study metastable phase formation and to develop new functional materials.

Containerless levitation techniques are classified in terms of the levitation source that counteracts the gravitational force on the samples. Typical levitation techniques include aerodynamic, electrostatic, acoustic, and electromagnetic levitation. Among these techniques, aerodynamic levitation is an economical method [2]. In aerodynamic levitation, the samples are floated on a gas stream that flows through the particularly designed conical nozzle.

Donor-doped BaTiO<sub>3</sub> ceramics are used widely in the fabrication of thermistors with a positive temperature coefficient of resistivity (PTCR) [3-6]. The resistivity can increase by several orders of magnitude near the phase transition temperature ( $T_c$ ) for the ferroelectric tetragonal to the paraelectric cubic phase transformation.

On the other hand, the growth behavior of the solid phase is an important event during a liquid-solid phase transformation, which influences subsequent solidification, the final structures and properties of the material [7].

Nevertheless, there was no detailed analysis of the transformation kinetics of (Ba,Sr)TiO<sub>3</sub> during recalescence in the literature.

In this study, semiconducting (Ba,Sr)TiO<sub>3</sub> ceramics were solidified using an aerodynamic levitator and the solidification behaviors during recalescence and microstructure of the levitated (Ba,Sr)TiO<sub>3</sub> ceramic were investigated.

### Experimental Procedures

Commercial Y-doped (Ba,Sr)TiO<sub>3</sub> (Toho Titanium Co. Ltd., Japan) was used as the starting powders. The Y-doped (Ba,Sr)TiO<sub>3</sub> powders contained SrTiO<sub>3</sub> (19.2 mol.%) and Y<sub>2</sub>O<sub>3</sub> (0.2 mol.%). The mean particle size of the Y-doped (Ba,Sr)TiO<sub>3</sub> powder was 0.18  $\mu$ m. The powder was pressed uniaxially at 100 MPa and rod-type green bodies were then sintered at 1473K for 2 hrs in air. Cylindrical pellets with a diameter of 2.5 mm were obtained from the rod. A spherical sample was levitated by an aerodynamic levitator using O<sub>2</sub> gas at a flow rate of 560 ml/min. The flow rate of the floating gas was controlled by a mass flow controller (CR-300, Kofloc, Kyoto, Japan). The spherical sample was heated and melted using a CO<sub>2</sub> laser (Firestar-t series, Synrad Inc., USA) with an output power of 100 W. 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 spot size with a diameter of 1 mm. The response time of the pyrometer was 2.0 ms and the measurement error of the as-measured temperatures was ~ 0.5%. The droplet was subsequently cooled by turning off the

\*Corresponding author:  
Tel : +82-32-860-7540  
Fax: +82-32-862-5546  
E-mail: wnshwang@inha.ac.kr

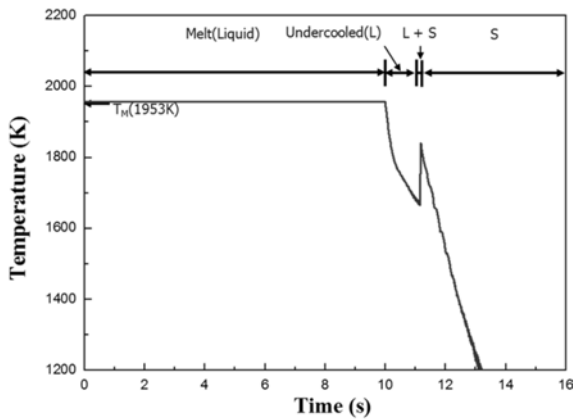
CO<sub>2</sub> laser. A high-speed video (HSV) camera (Photron FASTCAM R2 Inc., San Diego, CA) was used to observe the solidification of the droplet surface during recalescence with an acquisition rate of 1000 Hz.

The surface morphologies and cross-sectional microstructures of the samples were analyzed by scanning electron microscopy (SEM: JSM-5500, Jeol). An electron probe microanalyzer (EPMA: JXA-8900R, Jeol, Japan) was used to analyze the chemical compositions of the samples. The crystalline structure of the samples was analyzed by X-ray diffraction (XRD: PW-1710, Philips).

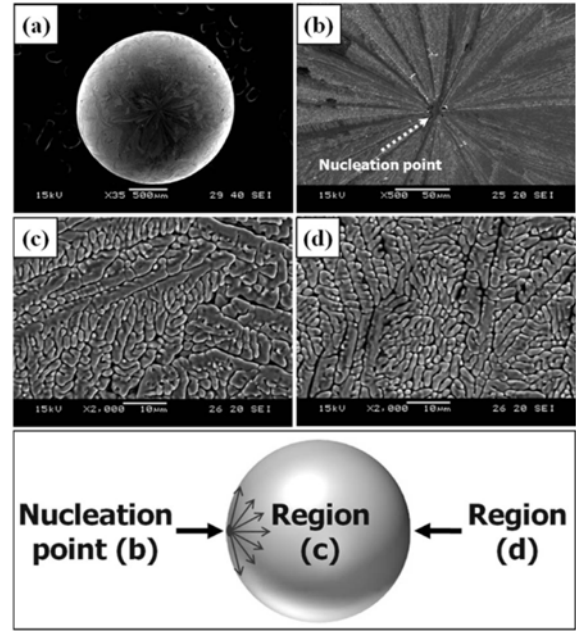
## Results and Discussion

Fig. 1 shows the temperature-time profile of (Ba,Sr)TiO<sub>3</sub> during aerodynamic levitation. (Ba,Sr)TiO<sub>3</sub> ( $T_L = 1953\text{K}$ ) was superheated and then undercooled by turning off the laser. The average cooling rate in the undercooled melt was approximately 250 K/s. Recalescence began at time  $t = 1.15\text{ s}$  after the laser was turned off. The recalescence was observed at 1665 K, indicating that the undercooled melt solidified into a polycrystalline (Ba,Sr)TiO<sub>3</sub> phase. The degree of recalescence was inferred directly from the temperature-time profile; it was found to be 175 K. The measured recalescence time interval ( $t_R$ ) was  $\sim 20\text{ ms}$ . After recalescence, the droplet was cooled to ambient temperature at a cooling rate of  $\sim 200\text{ K/s}$ .

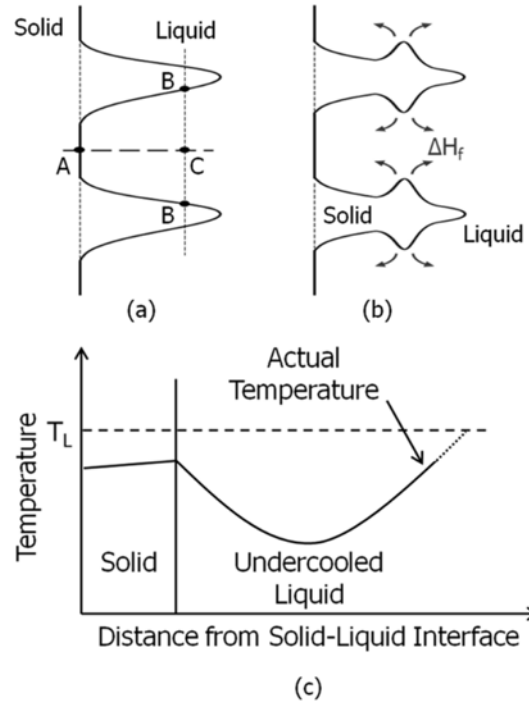
Fig. 2 shows SEM images on the surface of the (Ba,Sr)TiO<sub>3</sub> after aerodynamic levitation. As shown in Fig. 2(a), a spheroidal sample approximately (1.7 ~ 2.2 mm) in diameter was prepared. Fig. 2(b) shows clear evidence that solidification began at the nucleation point, and propagated radially. Fig. 2(c) reveals a typical dendritic structure, which is observed frequently in the solidification of metals [8]. The interfacial instability at the solid-liquid interface resulted in a dendritic microstructure. Fig. 2(d) shows an enlarged dendrite, revealing dendrites



**Fig. 1.** Temperature-time profile of (Ba,Sr)TiO<sub>3</sub> during aerodynamic levitation. L and S denote the solid and liquid phase, respectively.

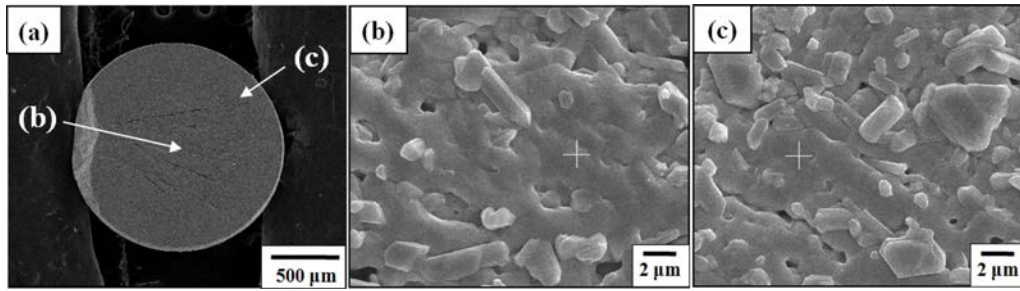


**Fig. 2.** SEM images of the surface of the (Ba,Sr)TiO<sub>3</sub> after aerodynamic levitation; (a) spheroidal shape, (b) nucleation point, (c) intermediate region, and (d) opposite region to nucleation point. A schematic (bottom image) indicates the region with observing direction.



**Fig. 3.** Formation of secondary dendrites (or spikes) on primary dendrites: (a) primary dendrites and (b) secondary dendrites on primary ones. (c) Temperature variations in the solid and the liquid with distance from solid-liquid interface in molten droplet.

with an arm spacing of  $\sim 2\text{ }\mu\text{m}$ . In contrast, the regime near the nucleation point (Fig. 2(b)) revealed fine dendrites. The degree of undercooling is an important factor in determining microstructural development. If the

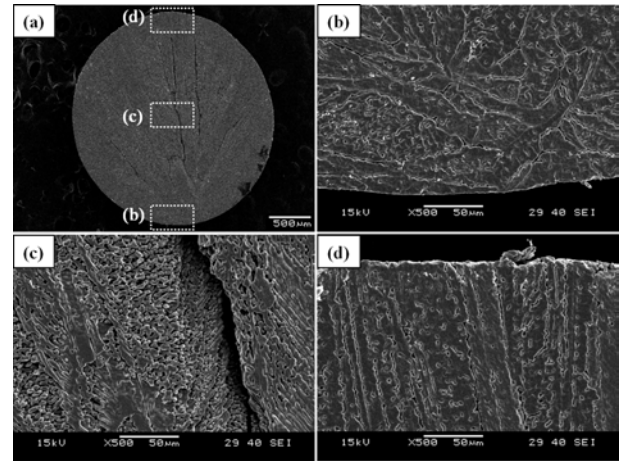


**Fig. 4.** SEM images of levitated (Ba,Sr)TiO<sub>3</sub>: (a) a polished cross section of the levitated sample, (b) center region, and (c) periphery region.

degree of undercooling is large, the nucleation rate may increase, but the growth rate may decrease due to the slow diffusion rate at the low temperature. As solidification proceeds, the degree of undercooling of the remaining liquid is decreased gradually due to the release of latent heat at the front of the solid-liquid interface. Therefore, the last solidified regime (Fig. 2(d)) would reveal a coarse dendrite compared to preceding solidified regime (Fig. 2(b)) due to diminished undercooling.

On the other hand, secondary dendrites (or spikes) on primary dendrites were formed as shown in Fig. 2(c) and 2(d). The reason is discussed briefly below. Consider the interface shown in Fig. 3(a). The interface contains a few primary dendrites. The temperature at location C, which is in between the two dendrites, is lower than that on the surface at A and the liquid at location C is in a supercooled state. On the other hand, the temperature at point B on the surface of the dendrite is higher than that at location C because of the evolution of heat of solidification at B. Therefore, there is supercooled liquid in between the primary dendrites. Such a situation is suitable for the formation of secondary dendrites on the surface of the primary dendrites. Therefore, secondary dendrites, may also form on primary dendrites (Fig. 3(b)). Fig. 3(c) presents the schematic temperature variations with distance from the solid-liquid interface.

Fig. 4 shows the cross-sectional microstructure of the center and the periphery region in the levitated (Ba,Sr)TiO<sub>3</sub>. The sample in Fig. 4(a) was etched thermally at 1573 K for 0.5 hrs in air. Fig. 4(b) and 4(c) show the morphologies in the center and periphery, respectively. The morphology was similar in the center and periphery region. Unlike the microstructure on the



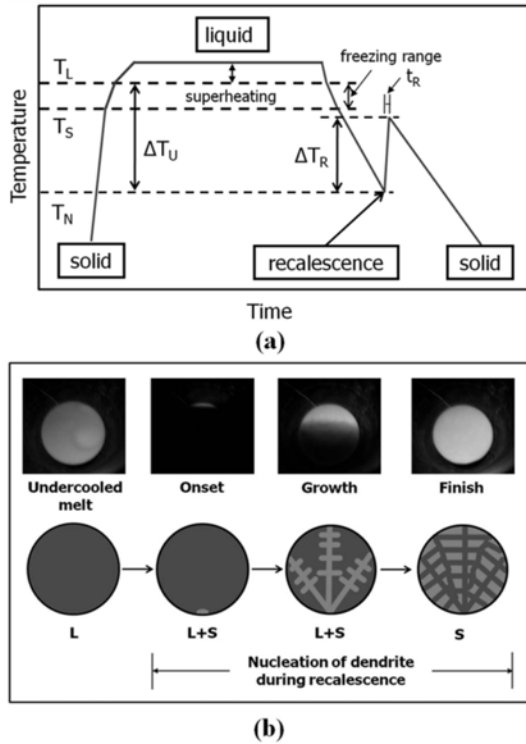
**Fig. 5.** SEM images of levitated (Ba,Sr)TiO<sub>3</sub>: (a) a polished cross section of levitated sample, (b) nucleation point, (c) center region and (d) periphery region.

surface, the dendritic structure was not observed clearly both in the center and periphery. As the radial dendrite grew three dimensionally throughout the volume of the melt, the apparent morphology of the dendrite will be changed, depending on the orientation of observed cross-section. Therefore, the microstructure on the polished surface of the sample was re-examined along the growth direction of the dendrite, as shown in Fig. 5. The sample in Fig. 5(a) was polished parallel to the growth direction of the dendrite, then etched thermally. Like the regime on the surface, Fig. 5(b) ~ (d) shows clear evidence that solidification began at the nucleation point, and dendrites were propagated radially. The crack in Fig. 5(c) was formed along the growth of the dendrite,

**Table 1.** Ba, Ti and O contents in the as-levitated (Ba,Sr)TiO<sub>3</sub> sample and sintered (Ba,Sr)TiO<sub>3</sub> sample (EPMA analyses).

|                     |              |              |              |              |                 | wt% (at%)               |
|---------------------|--------------|--------------|--------------|--------------|-----------------|-------------------------|
| As-levitated sample |              |              |              |              | Sintered sample | Theoretical composition |
| Parallel            |              | Vertical     |              |              |                 |                         |
| Center              | Periphery    | Center       | Periphery    |              |                 |                         |
| Ba                  | 63.57(26.51) | 63.12(26.03) | 62.44(25.81) | 62.68(25.99) | 61.67(25.00)    | 49.62(16.16)            |
| Sr                  | 5.75(3.76)   | 5.43(3.51)   | 6.27(4.08)   | 6.21(4.05)   | 6.43(4.08)      | 7.52(3.84)              |
| Ti                  | 16.81(20.10) | 17.31(20.46) | 17.30(20.49) | 17.16(20.40) | 17.30(20.11)    | 21.40(20.00)            |
| O                   | 13.87(49.63) | 14.15(50.01) | 14.00(49.62) | 13.94(50.00) | 14.60(50.80)    | 21.46(60.00)            |

wt% (at%)

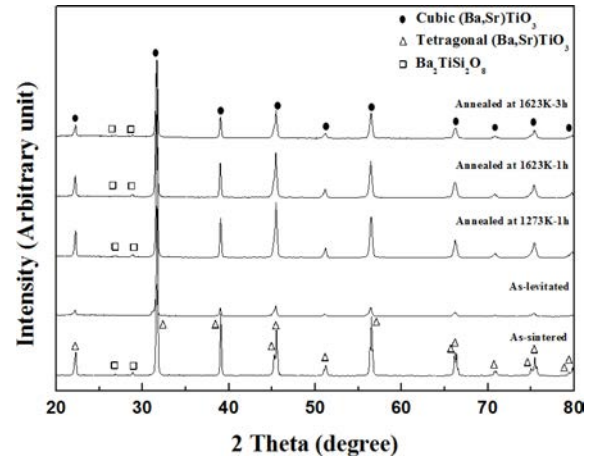


**Fig. 6.** (a) Schematic temperature-time profile for (Ba,Sr)TiO<sub>3</sub> during aerodynamic levitation.  $T_L$ ,  $T_S$ ,  $T_N$ ,  $\Delta T_U$ ,  $\Delta T_R$ , and  $t_R$  denote the liquidus temperature, solidus temperature, onset temperature of nucleation, undercooling level, degree of recalescence, and recalescence time, respectively. (b) Images and schematic of the nucleation growth of a dendrite in (Ba,Sr)TiO<sub>3</sub> during recalescence. L and S denote the liquid phase and solid phase, respectively.

and is believed to have formed by solidification shrinkage.

Table 1 shows EPMA analyses of the center and periphery region after mirror-like polishing of the as-levitated (Ba,Sr)TiO<sub>3</sub> sample. For comparison, a (Ba,Sr)TiO<sub>3</sub> sample prepared by sintering at 1623 K for 1 hr in air was also analyzed. No substantial difference in the Ba and Ti contents was observed between the levitated sample and sintered sample. The as-levitated sample was oxygen-deficient compared to the sintered sample. With the levitated sample, the periphery region, which was exposed to flowing O<sub>2</sub> gas, showed a higher oxygen content than the center region. The levitated sample appeared light blue, whereas the sintered sample appeared beige in color. The apparent color may depend on the oxygen content. The blue color of BaTiO<sub>3</sub> has been attributed to an oxygen deficiency [9, 10]. Levitation techniques provide the opportunity for solidification under a non-equilibrium condition, which significantly affects the resulting microstructure, composition distribution and properties of the materials [1].

For a better understanding of the solidification behavior during the levitation process, Fig. 6(a) shows the schematic temperature-time profile during levitation melting. In this figure,  $T_L$ ,  $T_S$ ,  $T_N$ ,  $\Delta T_U$ ,  $\Delta T_R$ , and  $t_R$  denote the liquidus temperature, solidus temperature, onset temperature of

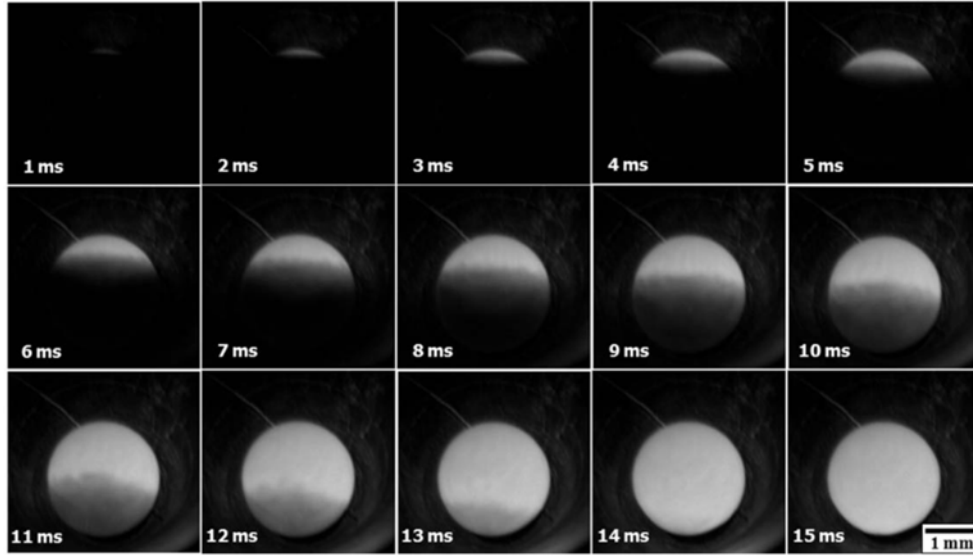


**Fig. 7.** XRD patterns of the as-levitated (Ba,Sr)TiO<sub>3</sub> sample.

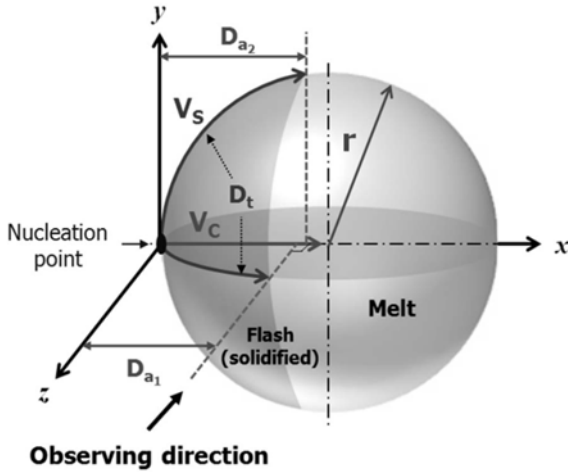
nucleation, undercooling level, degree of recalescence, and recalescence time, respectively. Fig. 6(b) shows several images and a corresponding schematic of the growth of the dendrite during recalescence. After superheating, the sample was undercooled immediately to  $T_N$ , at which point nucleation was triggered. Solidification then took place under quasiadiabatic conditions, leading to a rapid increase in temperature due to the release of the latent heat [11]. After recalescence, the sample was cooled to ambient temperature.

Fig. 7 shows XRD patterns of the levitated (Ba,Sr)TiO<sub>3</sub> ceramics under annealing conditions. For comparison, the sample, sintered at 1623 K for 1 hr in air, was also analyzed. The as-levitated sample had a cubic structure, while the sintered sample showed a tetragonal structure. The secondary Ba<sub>2</sub>TiSi<sub>2</sub>O<sub>8</sub> phase appeared in the sample annealed at 1273 K for 1 hr in air, in addition to the cubic phase. This phase was also observed in the XRD patterns of (Ba,Sr)TiO<sub>3</sub> sintered at 1623 K for 1 hr in air. In the powder preparation, SiO<sub>2</sub> was added as a sintering aid. Therefore, during calcination of mixture, the secondary phase may be formed by a reaction between BaTiO<sub>3</sub> and SiO<sub>2</sub>. A small hump in the levitated sample was detected at between 20° ~ 30° 2θ. This suggests that a small amount of amorphous Ba<sub>2</sub>TiSi<sub>2</sub>O<sub>8</sub> phase might be formed by rapid cooling, and, the Ba<sub>2</sub>TiSi<sub>2</sub>O<sub>8</sub> phase had precipitated on the (Ba,Sr)TiO<sub>3</sub> phase by subsequent annealing.

On the other hand, the electrical resistivity of the as-levitated (Ba,Sr)TiO<sub>3</sub> ceramics was investigated as a function of temperature. The resistivity of the as-levitated sample at room temperature was  $6.5 \times 10^3 \Omega\text{cm}$ , indicating semiconducting characteristics, and there was no substantial change with increasing temperature. As mentioned in the EPMA results, the low resistivity of the as-levitated sample can be explained by ionic conduction due to oxygen vacancies. This supposition is in accordance with study in the literature. Generally, it was reported that the BaTiO<sub>3</sub>-based ceramics prepared under reducing atmosphere, such as vacuum and H<sub>2</sub>, showed lower



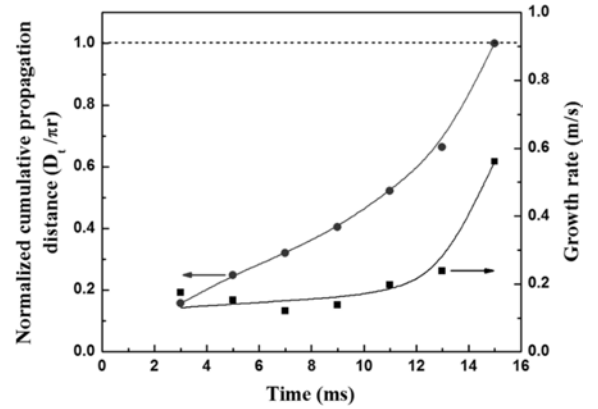
**Fig. 8.** Snap shots showing the nucleation and growth of polycrystalline perovskite (Ba,Sr)TiO<sub>3</sub> phases during recalescence. The pictures were taken at 1,000 frames per second.



**Fig. 9.** Propagation of the solid phase (flash) on the surface of a molten droplet during recalescence.  $D_t$  and  $D_a$  ( $D_{a1}$ ,  $D_{a2}$ ) denote the actual propagated distance on the surface of the molten droplet and the apparent propagated distance as measured from a two-dimensional image, respectively.  $V_C$  and  $V_S$  denote the growth velocity throughout the center and surface, respectively.

resistivity, indicating semiconducting characteristics [12]. The PTCR phenomenon is related to a phase transition; this characteristic in BaTiO<sub>3</sub> based ceramics appears to be due to tetragonal to a cubic transition at the Curie point, leading to the extinction of spontaneous polarization [3, 4]. Because the as-levitated and annealed samples had a cubic structure at room temperature, the PTCR phenomenon was not observed in the levitated and annealed samples.

To analyze the transformation kinetics during recalescence, the solidification behavior of a molten droplet was recorded using a color HSV camera, and snap shot images of this are shown in Fig. 8. The frames were taken at 0.001s intervals. A sudden flash of light is produced when nucleation and growth occur



**Fig. 10.** Growth rate and cumulative distance ( $D_t$ ) of the solid phase propagated on the surface of a molten droplet. The growth rate was calculated at an interval of 2 ms and the cumulative propagation distance was normalized by one half of the circumference of a molten droplet.

from undercooled liquids. Nucleation occurs from the undercooled melt, and propagates rapidly through the volume of the melt. An attempt was made to estimate the growth rate of the solid phase, but it was difficult to measure the actual velocity of the solid phase because the sample was opaque. Fortunately, as a flash of light was observed by the release of latent heat due to the crystallization (nucleation and growth), it could be regarded as a solidified region, as shown in Fig. 9. For simplicity, the shape of the levitated sample was assumed to be spherical instead of an oblate spheroid.

To estimate the growth velocity of the solid phase, the apparent propagation distances ( $D_a$ ) of the solid phase were measured from two-dimensional snap shot images, after which the actual propagation distances ( $D_t$ ) were calculated using Eq. (1):

$$D_t = r \cos^{-1} \left( 1 - \frac{D_a}{r} \right) \quad (1)$$

where  $r$  is the radius of a molten droplet. To eliminate the uncertainty in the distance measurement, the distance was measured in the images taken at 3 ~ 15 ms. Fig. 10 presents the cumulative propagation distance and the growth rate of the solid phase. The cumulative propagation distance was normalized by one half of the circumference of a molten droplet. The growth velocity ( $V_s$ ) of the solid phase from the undercooled melt increased gradually from 0.15 m/s to 0.24 m/s, and increased rapidly up to 0.57 m/s after 13 ms. In the case of the Ni, Ni-B, and Cu-Ni melts, it was reported that the dendrite growth velocities from undercooled melts was in the range of 1-100 m/s at large undercoolings [13, 14]. Therefore, the dendrite growth velocity from undercooled (Ba,Sr)TiO<sub>3</sub> liquid was relatively low compared to the metal system.

### Conclusions

The solidification behavior and microstructure of the aerodynamic levitated BaTiO<sub>3</sub> ceramics were investigated carefully. The levitated sample revealed a radial dendrite structure originating from a surface nucleation point. The surface microstructure revealed a unique featherlike structure. The as-levitated sample revealed a cubic structure, and the PTCR jump was not observed. The growth velocity of the solid phase was estimated from snap shot images of the molten droplet during recalescence. The growth velocity of the solid phase from the undercooled melt was located in ranges from 0.15 m/s to 0.57 m/s.

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