International Journal of Thermophysics, Vol. 27, No. 4, July 2006 (© 2006)
DOI: 10.1007/s10765-006-0087-5

Density Measurement of Molten CaF_2 by an Electrostatic Levitator[1]

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High-quality single crystalline calcium fluoride (CaF_2) has been of considerable practical concern as an optical lens to an excimer laser stepper in the deep-ultraviolet region due to its excellent transparency. Highly accurate thermophysical properties of molten CaF_2 are essential as input data for a numerical simulation of the crystal growth process. The density of molten CaF_2 has been successfully determined in the stable and undercooled liquid states (1600–1820 K) with an electrostatic levitator. The temperature dependence of the density of molten CaF_2 is given by

$$\rho/\mathrm{kg\cdot m^{-3}} = 3580 - 0.63T\,(\pm 1.6\%).$$

The coefficient of cubical expansion of molten CaF_2 has been determined to be

$$\beta/\mathrm{K^{-1}} = \frac{1}{5683 - T}.$$

KEY WORDS: CaF_2; density; electrostatic levitator; undercooled liquid.

[1] Paper presented at the Seventeenth European Conference on Thermophysical Properties, September 5–8, 2005, Bratislava, Slovak Republic.

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1. INTRODUCTION

For further development of semiconductor lithography techniques, optical lenses with higher transparency have been required. High-quality single crystalline calcium fluoride (CaF_2) has been of considerable practical concern as an optical lens to an ArF laser stepper in the deep-ultraviolet region due to its excellent transparency. The Bridgman-Stockbarger method [1, 2] has been mostly employed to fabricate a single crystalline CaF_2. Recently, a growth of a large size of CaF_2 crystal (diameter > 300 mm) has been attempted by means of the Czochralski method [3] to meet the demands in the stepper industry.

A global numerical simulation of heat transfer and fluid flow analysis in the crystal growth processes of CaF_2 is very important to understand and improve the processes. Thus, highly accurate thermophysical properties of molten CaF_2 are essential as input data to the simulation. However, it is difficult to measure the thermophysical properties of chemically reactive high-temperature melts such as molten CaF_2 because of contamination from containers.

To avoid any contamination, a non-contact method by means of an electrostatic levitator (ESL) is used for the thermophysical property measurements. An electrostatic levitator is a device that levitates a positively charged sample by the Coulomb force in an electrostatic field between top and bottom electrodes [4]. Therefore, various materials such as metals, semiconductors, ceramics, and glasses can be levitated when these materials are positively charged. A levitation of CaF_2 has not been reported previously. Thus, from both practical and scientific points of view, the purpose of the present study is first to levitate a molten CaF_2 droplet, and second, to measure the density of molten CaF_2 as a function of temperature.

2. EXPERIMENTAL

Figure 1 shows a top view of an experimental arrangement of the electrostatic levitator used for the density measurements of molten CaF_2 [5]. Figure 2 shows an electrode assembly consisting of a set of parallel electrodes and four side electrodes. A positively charged sample can be levitated by an electrostatic field applied between the disc electrodes. The vertical position of the sample was stabilized by controlling the voltage between the disc electrodes with an active feedback loop. In addition, the four side electrodes distributed around the bottom electrode were used for horizontal position control. The apparatus has an optical sensor for monitoring the sample vertical position by imaging the shadow of the sample

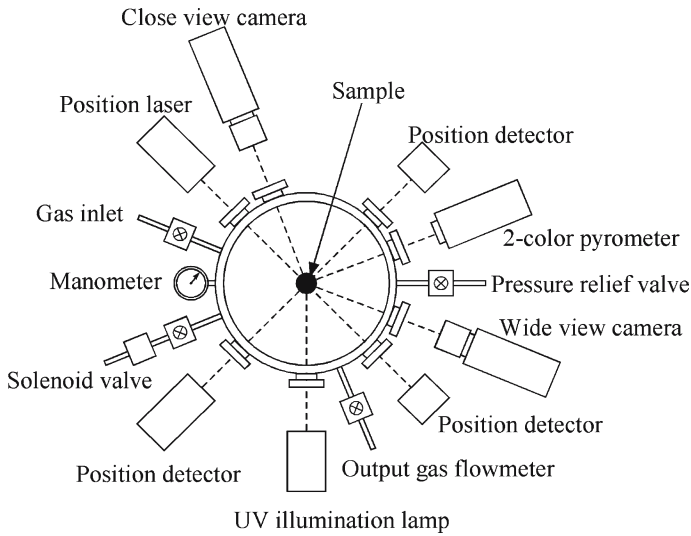

Fig. 1. Schematic diagram of top view of apparatus for measuring density of molten CaF_2.

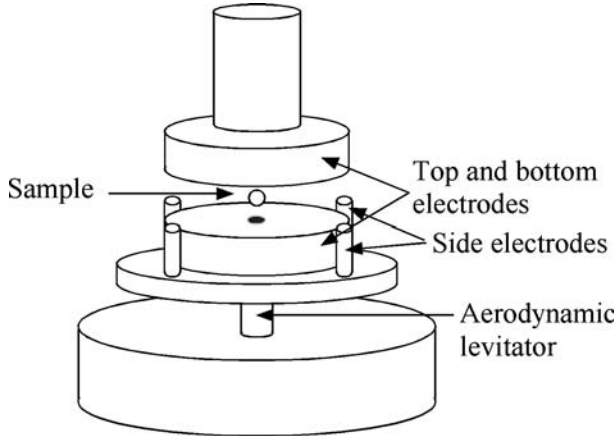

Fig. 2. Schematic diagram of electrode assembly of the electrostatic levitator.

illuminated with a He–Ne laser. More details can be found elsewhere on the setup [5] and on the position control system [4].

Single crystalline CaF_2 (99.99 mass%) was used as an initial sample. A piece of the sample with a diameter of about 2 mm (5–7 mg) was placed in the chamber and heated by a CO_2 laser to make a spherical sample. An aerodynamic force was initially used so that the sample was free from

the bottom electrode during heating. The sample was sufficiently charged by thermoelectronic emission prior to launch [6]. After that, the sample was electrostatically levitated by applying a voltage of 7 kV between the disc electrodes. Once a sample was levitated, the laser power was gradually increased until the sample was completely melted. The density measurements were conducted under a high purity nitrogen atmosphere at 4.5 bar. The sample temperature was monitored using a two-color pyrometer (IR-CAQ, Chino Corp., Tokyo, Japan). The pyrometer was calibrated at the melting point of CaF_2 as determined by a recalescence peak (rapid release of the latent heat of fusion of CaF_2).

The density of the molten CaF_2 was measured using an imaging technique described in detail elsewhere [7]. A high-resolution, black and white charged-coupled-device video camera (resolution of 640×480 pixels, shutter speed of 1/1000) was equipped with a telephoto objective and a high-pass filter at 450 nm in conjunction with an UV lamp. This optical system yielded a large and clear image of the sample, allowing sample perimeter and surface features to be analyzed even at high temperatures. A rim of the sample droplet was extracted from each image, and the radius was estimated by fitting the rim to a harmonic function using the program developed by the Japan Aerospace Exploration Agency (JAXA). The recorded images were calibrated by levitating a sphere with a precisely known radius under identical experimental conditions. The sample mass was measured after the experiment to minimize the effect of vaporization of molten CaF_2 during the course of the experiment.

3. RESULTS

3.1. Levitation of Molten CaF_2

Figure 3 shows a molten CaF_2 droplet levitated in the electrostatic levitator, which exhibits a spherical shape and good position stability. However, in most cases a levitated CaF_2 sample became unstable when the sample was melted by laser heating.

Figure 4 shows a typical temperature variation of the CaF_2 droplet with time. The abrupt temperature rise at 5.2 s indicates occurrence of a recalescence. The calibration of the pyrometer was conducted at the plateau region after the recalescence corresponding to the melting point of CaF_2. The density measurements were conducted along the cooling curve from 1820 to 1600 K. After the laser heating was turned off at around 4 s, the electric charge on the sample surface was abruptly decreased, and the sample drastically moved down. The sample levitation was still maintained and stabilized within a second with an active feedback operated at

Fig. 3. Molten CaF_2 droplet levitated in the electrostatic levitator.

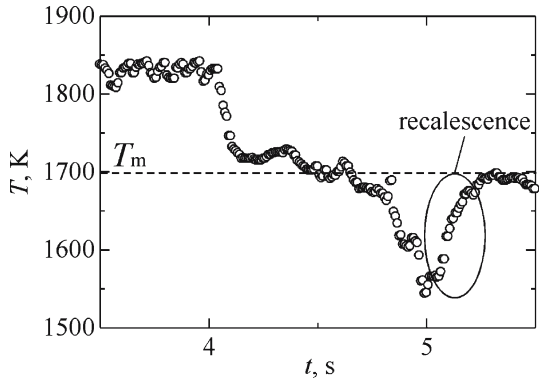

Fig. 4. Temperature variation of the CaF_2 droplet with time (T_m = melting point of CaF_2).

720 Hz during this period. Thus, this position fluctuation caused the temperature fluctuation, but after the stabilization, no significant instability was observed until recording the plateau region after the recalescence. As explained above, during the period corresponding to the sudden moving down of the sample, a part of the sample image was beyond the observation area in a monitor, and, therefore, an accurate volume of the sample was not evaluated from 1730 to 1800 K.

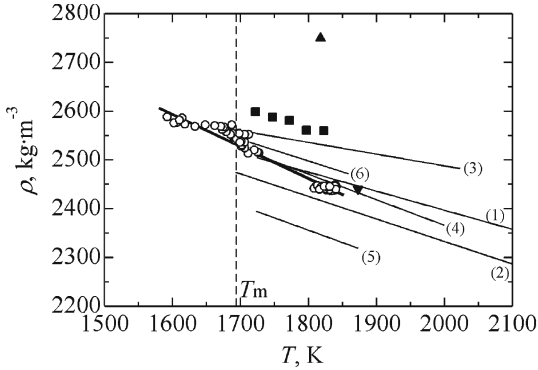

Fig. 5. Densities of molten CaF_2 as a function of temperature together with values reported by several investigators (T_m = melting point of CaF_2). -○- Present study; ▲ Baak [10]; ■ Winterhager et al. [13]; ▼ Povolotskii et al. [14]; (1) Kirshenbaum et al. [11]; (2) Kulifeev et al. [12]; (3) Mitchell and Joshi [15]; (4) Zhmoidin [9]; (5) Ogino and Hara [16]; Hara and Ogino [8].

3.2. Density of Molten CaF_2

Figure 5 shows the results of the density measurements. The density (ρ) of molten CaF_2 has been successfully measured in the temperature range from 1600 to 1820 K including the undercooled liquid region. The temperature dependence of the density is given by

$$\rho/\mathrm{kg \cdot m^{-3}} = 3580 - 0.63T\,(\pm 1.6\%) \tag{1}$$

using a least-squares method. On the basis of the above results, the coefficient of cubical expansion (β) is determined to be

$$\beta/\mathrm{K^{-1}} = \rho \frac{\partial {}^{1}\!/_{\rho}}{\partial T} = \frac{1}{5683 - T} \tag{2}$$

The values reported by several investigators [8–16] were also plotted in the figure for a comparison and listed in Table I. These investigators mostly used a buoyancy method or a maximum bubble pressure method. The details on the methods are given in Section 4.2.

4. DISCUSSION

4.1. Experimental Uncertainty

The experiment uncertainty in the density measurements was primarily caused by the accuracy of the analysis of the video images of the

Table I. Reported Values of the Density of Molten CaF_2

Investigator	Method	Density ($kg \cdot m^{-3}$)	Temperature (K)
Hara and Ogino [8]	Archimedes	$3299–0.445T$	1714–1859
Zhmoidin [9]	maximum bubble pressure	$3416–0.525T$	1700–2000
Bååk [10]	not stated	2750	1818
Kirshenbaum et al. [11]	Archimedes	$3179–0.391T$	1700–2100
Kulifeev et al. [12]	maximum bubble pressure	$3257–0.462T$	1693–2100
Winterhager et al. [13]	maximum bubble pressure	$3206–0.420T$	1748–1823
Povolotskii et al. [14]	not stated	2440	1873
Mitchell and Joshi [15]	Archimedes	$2970–0.241T$	1673–2023
Ogino and Hara [16]	Archimedes	$3267–0.506T$	1723–1873

sample. The CCD camera used in the present study is characterized by the following specifications: a resolution of 640×480 pixels and a shutter speed of 1/1000. From the resolution of the video images of the samples, the relative uncertainty in a sample volume is less than $\pm 0.9\%$. The uncertainty in determining the mass of the sample is ± 0.1 mg corresponding to a relative uncertainty of $\pm 1.3\%$. As a consequence, the uncertainty in the density value is less than $\pm 1.6\%$.

4.2. Comparisons with Previous Results

In previous studies, the densities of molten CaF_2 were mostly measured by the buoyancy method (the so called Archimedes method) [8, 11, 15, 16] and the maximum bubble-pressure method [9, 12, 13], as listed in Table I. These values are widely scattered. The present results agree with the results obtained by Zhmoidin [9] and Hara and Ogino [8] within a reasonable experimental uncertainty. Zhmoidin measured the density of molten CaF_2 by the maximum bubble method using a molybdenum capillary. On the other hand, Hara and Ogino [8] employed the buoyancy method using two different size platinum bobs to remove the effect of surface tension on a suspension wire.

5. CONCLUSION

The density of molten CaF_2 in the stable and undercooled liquid states (1600–1820 K) has been successfully determined with the electrostatic levitator. The coefficient of cubical expansion of molten CaF_2 has been derived based on the temperature dependence of the density.

REFERENCES

1. D. C. Stockbarger, *J. Opt. Soc.Am*. **39**:731 (1945).
2. P. W. Bridgman, *Proc. Amer. Acad. Arts. Sci.* **60**:305 (1925).
3. H. Yanagi, T. Nawata, Y. Inui, Y. Hatanaka, E. Nishijima, and T. Fukuda, *Opt. Microlithography XVIII* (Proc. of SPIE, No. 5377, 2004), p. 1886.
4. W-K Rhim, S-K Chung, D. Barber, K. F. Man, G. Gutt, A. A. Rulison, and R. E. Spjut, *Rev. Sci. Instrum.* **64**:2961 (1993).
5. P-F Paradis, T. Ishikawa, J. Yu, and S. Yoda, *Rev. Sci. Instrum.* **72**:2811 (2001).
6. P-F Paradis, F. Babin, and J-M Gagn′e, *Rev. Sci. Instrum.* **67**:262 (1996).
7. T. Ishikawa, P-F Paradis, and S. Yoda, *Rev. Sci. Instrum.* **72**:2490 (2001).
8. S. Hara and K. Ogino, *J. Japan Inst. Metals* **52**:1098 (1988).
9. G. I. Zhmoidin, *Russ. J. Phys. Chem*. **49**:1486 (1975).
10. T. Bååk, *Acta chemica scandinavia* **9**:1406 (1955).
11. A. D. Kirshenbaum, J. A. Cahill, and C. S. Stokes, *J. Inorg. Nucl. Chem.* **15**:297 (1960).
12. V. F. Kulifeev, V. I. Panchishni, and G. P. Stanolevich, *Iz. Vuz. Tsvetn. Metall*. **2**:116 (1968).
13. H. Winterhager, R. Kammel, and A. Gad, *Forschungsber des Landes Nordrhein-Westfalen No.* 2115 (Westeutscher verlag koln und opladen, Germany, 1970), pp. 1–42.
14. D. Y. Povolotskii, V. A. Voronov, and B. M. Nikitin, *Steel in the USSR* **1**:952 (1971).
15. A. Mitchell and S. Joshi, *Metall. Trans.* **3**:2306 (1972).
16. K. Ogino and S. Hara, *J. Jpn.Inst. Metals* **63**:2141 (1977).