Densities of liquid lanthanoid sesquioxides measured with the electrostatic levitation furnace in the ISS

Chihiro Koyama1 | Takehiko Ishikawa2,3 | Hirohisa Oda1 | Hideki Saruwatari1 | Saeko Ueno1 | Masato Oshio1 | Yuki Watanabe4 | Yui Nakata4

1Human Spaceflight Technology Directorate, Japan Aerospace Exploration Agency (JAXA), Tsukuba, Japan
2Institute of Space and Astronautical Science, JAXA, Tsukuba, Japan
3SOKEN-DAI (The Graduate University for Advanced Studies), Sagamihara, Japan
4Advanced Engineering Services. Co. Ltd, Tsukuba, Ibaraki, Japan

Abstract
The densities of several liquid lanthanoid sesquioxides (Ln2O3, Ln = Er, Ho, Tb, Gd) were measured over the temperature range from 2700 K (the approximate melting point of these materials) to 3200 K. These measurements were performed using the Electrostatic Levitation Furnace onboard the International Space Station (ISS-ELF). Based on the Coulomb force between the charged samples and surrounding electrodes and employing a rapid feedback control process, specimens were stably levitated and subsequently melted by high power lasers. The molten oxides exhibited spherical morphologies and their volumes were readily calculated from magnified images. Subsequent weighing of the samples on Earth allowed the densities of the oxides to be determined. The densities of Er2O3, Ho2O3, Tb2O3, and Gd2O3 at their melting temperatures (T_m) were found to be 8170, 8035, 7451, and 7268 kg/m³, respectively, and these density values were shown to exhibit a linear correlation with temperature. The molar volumes of these oxides at their T_m values were calculated and compared with those of other sesquioxides (Al2O3, Ga2O3, and B2O3). The molar volumes of the nonglass-forming sesquioxides (Er2O3, Ho2O3, Tb2O3, Gd2O3, Al2O3, and Ga2O3) showed linear correlations with the cubes of their cation radii, whereas those of the glass-forming oxide (B2O3, As2O3, and Sb2O3) showed different correlations.

1 | INTRODUCTION

It can be very challenging to assess the thermophysical properties of melts at temperatures higher than 2000°C, due to chemical reactions between the molten samples and their containers. To overcome this problem, containerless techniques based on electromagnetic,1,2 aerodynamic,3,4 or electrostatic5 levitation have been developed. In the case of electrostatic levitation, the Coulomb force between a charged sample and surrounding electrodes is used to control the sample position. Following the development of several key technologies necessary for stable sample positioning and scientific observations,6-9 the Electrostatic Levitation Furnace (ELF) was installed in the International Space Station (ISS)10 to allow the analysis of containerless materials under microgravity conditions. Because it is difficult to provide a sufficient charge to the majority of oxides such that these materials will levitate under the standard gravitational force, a microgravity environment provides an ideal opportunity to perform experiments. Thus, a combination of laser heating and thermophysical property measurements has been employed in conjunction with the ISS-ELF to determine the...
density, surface tension, and viscosity of molten oxides at high temperatures.

Among the various oxides, lanthanoid sesquioxides (Ln$_2$O$_3$) have extremely high melting temperatures on the order of 2700 K. Ln$_2$O$_3$ compounds are representative of nonglass-forming oxides, and thus are commonly used as refractory materials and dopants for luminescent materials. Due to their high melting temperatures, the thermophysical properties of these compounds have rarely been assessed, and so these oxides were considered suitably challenging materials to demonstrate the capability of the ISS-ELF to permit the high-temperature analysis of various substances.

Density is one of the most fundamental properties of a material and is used in the calculation of other thermophysical characteristics, such as surface tension and viscosity, and is also an important aspect of structural analysis. Specifically, density data are necessary to calculate the total pair-distribution function, G(r), from the total structure factor, S(Q), determined experimentally by X-ray or neutron scattering techniques. In our previous work, the structure of liquid Er$_2$O$_3$ was investigated by analyzing synchrotron X-ray diffraction data together with a density value obtained using the ISS-ELF. The goal of the present work was to obtain the densities of other Ln$_2$O$_3$ oxides so as to assess the structures of these compounds. This report presents the results of density measurements of molten Ln$_2$O$_3$ oxides (Ln = Er, Ho, Tb, Gd) using the ISS-ELF, as well as a comparison of the molar volumes of these materials with those of other liquid sesquioxides and dioxides.

2 | METHODS

2.1 | Sample preparation

Ln$_2$O$_3$ powders (Ln = Er, Ho, Tb, Gd) with a purity of 99.99% (Koujundo Chemical Laboratory Co., Ltd.) were employed in this work. Prior to the ISS trials, each powder was sintered, melted, and solidified in ambient air, using an aerodynamic levitator in conjunction with a 100 W CO$_2$ laser. The resulting polycrystalline samples, typically 2 mm in diameter, were subsequently weighed, transferred into special sample holders and launched to the ISS.

2.2 | Experimental levitation procedure

Figure 1 shows a photographic image of a levitated sample in the ISS-ELF. Each specimen had an accumulated positive charge in the range of 10$^{-11}$–10$^{-12}$ C$^{10}$ and was levitated using six electrodes in dry air under a pressure of 2 atm. The specimen remained stable while levitated and its position was determined using a high-speed feedback control process. Each sample was heated to its melting point using four 980 nm diode lasers (each with a power of 40 W) arranged in a tetrahedral formation so as to heat the sample evenly$^{13}$ The oxide temperature was determined by measuring the intensity of the radiation emitted using a pyrometer over the wavelength range of 1.45-1.8 μm. The actual sample temperature was determined by adjusting the emissivity value so that the temperature plateau matched with its the melting temperature. After each oxide transitioned to a molten state, it adopted a perfectly spherical shape as a result of the surface tension of the compound and the microgravity environment. The specimen was subsequently cooled by shutting off the heating lasers. During cooling, magnified sample images were acquired with ultraviolet back lighting (Figure 2). Following these trials, the processed samples were returned to the sample holder and brought back to Earth.

FIGURE 1 A levitated sample and the surrounding electrodes in the ISS-ELF [Color figure can be viewed at wileyonlinelibrary.com]

FIGURE 2 A close-up photographic image of a molten Ln$_2$O$_3$ specimen acquired with ultraviolet backlighting
2.3 Calculation of density and thermal expansion

The density values ($\rho$) of the molten samples were calculated from the volumes obtained based on analysis of the images together with the sample masses. The details of the image analysis technique are described in Ref. [14]. Briefly, 400 edge points were detected and converted to polar coordinates ($R, \theta$) that were fit with spherical harmonic functions up to sixth order, as

$$R(\theta) = \sum_{n=0}^{6} c_n P_n(\cos\theta),$$  \hspace{1cm} (1)

where $P_n(\cos\theta)$ are $n$-th order Legendre polynomials and $c_n$ are coefficients that minimize the value calculated as

$$F = \sum_{j=1}^{400} \left( R_j - R_j(\theta) \right)^2,$$  \hspace{1cm} (2)

The volume was subsequently calculated using the equation

$$V = \frac{2\pi}{3} \int_0^{\pi} R^3(\theta) \sin\theta d\theta.$$  \hspace{1cm} (3)

Pixels in the images were converted to actual sample sizes (in units of mm) based on images acquired of a 2.0 mm diameter stainless steel ball levitated in the ISS-ELF.

The mass, $m$, of each specimen was determined by weighing after the samples were returned to Earth, and densities were obtained from the formula

![Figure 3](image)

**FIGURE 3** The densities of liquid Ln$_2$O$_3$ samples as functions of temperature: (A) Er$_2$O$_3$, (B) Ho$_2$O$_3$, (C) Tb$_2$O$_3$, and (D) Gd$_2$O$_3$. The error bars in the ISS-ELF (data 1 and 2) represent 2%, whereas those for the Ref. [16] data indicate 5%. [Color figure can be viewed at wileyonlinelibrary.com]
3 | RESULTS AND DISCUSSION

Figure 3 plots the densities of the liquid Ln$_2$O$_3$ compounds (Ln = Er, Ho, Tb, Gd) as a function of the temperature obtained in the ISS-ELF. To allow an evaluation of the repeatability of these experiments, two sets of data points are plotted for each sample. These plots include previously reported results for Er$_2$O$_3$ and Gd$_2$O$_3$ obtained from our earlier work together with literature data from Granier and Heurtault, who determined the densities of these oxides via aerodynamic levitation. Other than their work, no other literature data were found. The $T_m$ values for these oxides as indicated in the plots were obtained from a publication by Sarou-Kanian et al. The uncertainty in these measurements was estimated to be 2% based on the respective uncertainties in the mass and volume of each specimen. Specifically, each sample mass ($m$) of approximately 20 mg had an associated uncertainty ($\Delta m$) of 0.05 mg, such that the relative uncertainty ($\Delta m/m$) was estimated to be 0.3%. The uncertainty in the volume ($\Delta V/V$) was $3\Delta r/r$, where $\Delta r$ is the uncertainty in the radius of the sample and $r$ is the radius. As $\Delta r$ and $r$ in these experiments were approximately 1 and 160 pixels, respectively, $\Delta V/V$ was estimated to be 1.9%. Thus, the overall uncertainty in the density values ($\Delta \rho/\rho$) was 2.0%. The variation between datasets 1 and 2 is within this uncertainty.

The density data exhibited linear correlations with temperature and, using a least square regression with a confidence interval of 95%, could be fitted to the equation

$$\rho = \rho_m \left[ 1 - \alpha (T - T_m) \right] \text{ (kg/m}^3)$$

where $\rho_m$ is the liquid density at $T_m$ and $\alpha$ is the thermal expansion coefficient, which is assumed to be constant over the liquidus temperature range. Because the correlation coefficients for dataset 1 were larger than those for dataset 2, the fitting results for the former are included in Table 1 as the recommended values. It should be noted that the densities reported in Ref. [16] are lower than the present values, and this discrepancy is primarily attributed to the difference in the backlighting illumination used to acquire the sample images. In the experiments reported herein, ultraviolet backlighting was employed to remove the effect of the intense infrared radiation emitted by the high-temperature samples. On the other hand, no backlighting was used and images of the bright samples were analyzed in Ref. [16]. According to our earlier work, these types of measurements can potentially lead to overestimation of the sample volume such that the density is underestimated.

Courtial and Dingwell calculated molar volume of Ln$_2$O$_3$ (Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, and Yb) with indirect method. They measured the density of Na-disilicates which contained 0 to 6 mol % of lanthanide sesquioxide using the double bob Archimedean method. The partial molar volumes of Ln$_2$O$_3$ were determined using these density data. The measured partial molar volumes were linearly fitted as a function of the concentration of lanthanide sesquioxide, and this relation was extrapolated to 100% to get the molar volume of lanthanide sesquioxide.

Molar volumes calculated from our density measurements were compared with the ones by Courtial and Dingwell. As shown in Table 2, the volumes except Ho$_2$O$_3$ are significantly different with each other. The deviations are larger than the uncertainties in both works. They are assumed to be originated from the extrapolations form 0-6 mol% partial molar volume to 100%, as indicated in Ref. [18]. This result indicates that the excess volumes in the mixing of the silicate and Ln$_2$O$_3$ derived from the interaction between these two components should be taken into account for more accurate extrapolation.

As shown in Table 2 the Ln$_2$O$_3$ volumes evidently increased with decreasing radius of the Ln$^{3+}$ cation, $r$, in the case of sixfold coordination. These radii decrease in the order of Er$_2$O$_3$ (89.0 pm), Ho$_2$O$_3$ (90.1 pm), Tb$_2$O$_3$ (92.3 pm), and Gd$_2$O$_3$ (93.8 pm). Figure 4 summarizes the relationship between the molar volume at $T_m$, $V_m(r)$, and the cube of the cation radius, $r^3$, and confirms a linear correlation between the two variables. A least squares linear fit of these values with a confidence interval of 95% gave the equation

$$V_m(r) = (1.98 \pm 0.24) r^3 + (33.1 \pm 3.3) \text{ (cm}^3/\text{mol})$$

In order to compare $V_m(r)$ for the Ln$_2$O$_3$ series with those for other representative sesquioxides, the $V_m(r)$ values for

| Ln$_2$O$_3$ | $V_m$ [cm$^3$/mol] | Dingwell$^{18}$ | $\Delta$ [%] | $r$ [pm] |
|------------|-------------------|----------------|-------------|----------|
| Er$_2$O$_3$ | 46.8              | 42.5            | -9.2        | 89.0     |
| Ho$_2$O$_3$ | 47                | 46.9            | -0.2        | 90.1     |
| Tb$_2$O$_3$ | 49.1              | 40.3            | -17.9       | 92.3     |
| Gd$_2$O$_3$ | 49.9              | 54.4            | 9.0         | 93.8     |

$\Delta$ is the relative $V_m$ difference between present work and Ref. [18].
liquid Al$_2$O$_3$, Ga$_2$O$_3$, B$_2$O$_3$, and vitreous As$_2$O$_3$ and Sb$_2$O$_3$ calculated from their densities are plotted in Figure 4. The density of Al$_2$O$_3$ at its $T_m$ (2327 K) was obtained using the ISS-ELF under the same conditions as in the present study, whereas the values for Ga$_2$O$_3$ (at 2123 K) and B$_2$O$_3$ (at 723 K) were determined by the Archimedean method. No liquid As$_2$O$_3$ and Sb$_2$O$_3$ data were found, and data in glass phase were used. The molar volumes for Al$_2$O$_3$ and Ga$_2$O$_3$ are in good agreement with the trend predicted by Equation (6), whereas those of B$_2$O$_3$, As$_2$O$_3$, and Sb$_2$O$_3$ show another correlation. Al$_2$O$_3$, Ga$_2$O$_3$, and Ln$_2$O$_3$ are known to be nonglass-forming oxides and have not been reported to vitrify, whereas B$_2$O$_3$, SiO$_2$, GeO$_2$, and TeO$_2$ are strongly glass-forming oxide. The cation radii of sesquioxides and dioxides correspond to ones in the case of six- and four-fold coordination, respectively [Color figure can be viewed at wileyonlinelibrary.com]

CONCLUSION

The densities of a number of different liquid Ln$_2$O$_3$ compounds were ascertained with the ISS-ELF. This process prevented contamination of the samples such that precise density values could be obtained over a wide temperature range. The molar volumes at $T_m$ exhibited a linear relationship with the cubes of the Ln$^{3+}$ radii in these oxides, as was also the case for other nonglass-forming sesquioxides such as Al$_2$O$_3$ and Ga$_2$O$_3$. In contrast, the data for B$_2$O$_3$, a glass-forming oxide, as well as As$_2$O$_3$ and Sb$_2$O$_3$ glasses showed different correlations with the cubes. The molar volumes of nonglass-forming dioxide and glass-forming dioxides also exhibited that two different linear correlations, respectively.

ACKNOWLEDGMENT

The authors are grateful to the ISS crew members and the ground operation staff for their support during the onboard experiments. This work was supported by JSPS KAKENHI (Grant No. 20H05882 and 20H05878).

ORCID

Chihiro Koyama https://orcid.org/0000-0002-8320-4302

REFERENCES

1. Saito T, Shiraishi Y, Sakuma Y. Density measurement of molten metals by levitation technique at temperatures between 1800 and 2200°C. Trans ISIJ. 1969;9:118–26.
2. Fecht HJ, Wunderlich RK. Fundamentals of liquid processing in low earth orbit: from Thermophysical properties to microstructure formation in metallic alloys. JOM. 2017;69:1261–8.
3. Babin F, Gagné JM, Paradis PF, Coutures JP, Rifflet JC. High temperature containerless laser processing of dielectric samples in microgravity: study of aerodynamic trapping. Micrograv Sci Technol. 1995;7:283–9.
4. Langstaff D, Gunn M, Greaves GN, Marsing A, Kargl F. Aerodynamic levitator furnace for measuring thermophysical properties of refractory liquids. Rev Sci Instrum. 2013;84:124901.
5. Rhim WK, Chung SK, Barber D, Man KF, Gutt G, Spujt RA, et al. An electrostatic levitator for high-temperature containerless materials processing in 1-G. Rev Sci Instrum. 1993;64:2961–70.
6. Paradis PF, Ishikawa T, Yoda S. Position stability analysis of electrostatically levitated samples for thermophysical and structural properties measurements of materials. Space Technol. 2002;22:81–92.
7. Ishikawa T, Paradis PF, Yoda S. New sample levitation initiation and imaging techniques for the processing of refractory metals with an electrostatic levitator furnace. Rev Sci Instrum. 2001;72:2490–5.
8. Ishikawa T, Okada JT, Paradis PF, Watanabe Y. Thermophysical property measurements of high temperature melts using an electrostatic levitation method. J.J.A.P. 2011;50:11R03.
9. Ishikawa T, Okada JT, Paradis PF, Kumar MV. Towards Microgravity experiments using the electrostatic levitation furnace
(ELF) in the International Space Station (ISS). Trans JSASS Aerospace Tech Jpn. 2014;12(ists29):Th-15–18.

10. Tamaru H, Koyama C, Saruwatari H, Nakamura Y, Ishikawa T, Takada T. Status of the electrostatic levitation furnace (ELF) in the ISS-KIBO. Microgravity Sci Technol. 2018;30:643–51.

11. Ushakov SV, Maram PS, Kapush D, Pavlik AJ III, Fyhrie M, Gallington LC, et al. Phase transformations in oxides above 2000°C: experimental technique development. Adv Appl Ceram. 2018;117:S82–S89.

12. Koyama C, Tahara S, Kohara S, Onodera Y, Småbråten DR, Selbach SM, et al. Very sharp diffraction peak in nonglass-forming liquid with the formation of distorted tetraclusters. NPG Asia Mater. 2020;12:43.

13. Schroers J, Bossuyt S, Rhim WK, Li J, Zhou Z, Johnson WL. Enhanced temperature uniformity by tetrahedral laser heating. Rev Sci Instrum. 2004;75:4523–5.

14. Chung SK, Thiessen DB, Rhim WK. A noncontact measurement technique for the density and thermal expansion coefficient of solid and liquid materials. Rev Sci Instrum. 1996;67:3175.

15. Ishikawa T, Koyama C, Saruwatari H, Tamaru H, Oda H, Oshio M, et al. Densities of molten gadolinium oxide measured with the electrostatic levitation furnace in the International Space Station. High Temp-High Press. 2020;49:5–15.

16. Granier B, Heurtault S. Density of liquid rare-earth sesquioxides. J Am Ceram Soc. 1988;71:C466.

17. Sarou-Kanian V, Rifflet JC, Millot F. UV-visible pyrometry of refractory oxides at high temperature. High Temp High Press. 2011;40:249–61.

18. Courtial P, Dingwell DB. High-temperature density of lanthanide-bearing Na-silicate melts: partial molar volumes for Ce2O3, Pr2O3, Nd2O3, Sm2O3, Eu2O3, Gd2O3, Tb2O3, Dy2O3, Ho2O3, Er2O3, Tm2O3, and Yb2O3. Am Miner. 2005;90:1597–605.

19. Dingwell DB. Density of Ga2O3 liquid. J Am Ceram Soc. 1992;75:1656–7.

20. Napolitano A, Macedo PB, Hawkins EG. Viscosity and density of boron trioxide. J Am Ceram Soc. 1965;48:613–6.

21. Clare AG, Wright AC, Sinclair RN, Galeener FL, Geissberger AE. A neutron diffraction investigation of the structure of vitreous As2O3. J Non-Cryst Solids. 1989;111:123–37.

22. Terashima K, Hashimoto T, Uchino T, Kim SH, Yoko T. Structure and nonlinear optical properties of Sb2O3-B2O3 binary glasses. J Ceram Soc Jpn. 1996;104:1008–14.

23. Dingwell DB. The density of Titanium(IV) oxide liquid. J Am Ceram Soc. 1991;74:2718–9.

24. Gallington L, Ghadar Y, Skinner L, Weber J, Ushakov S, Navrotsky A, et al. The structure of liquid and amorphous hafnia. Materials (Basel). 2017;10(11):E1290.

25. Kohara S, Akola J, Patrikeev L, Ropo M, Ohara K, Itou M, et al. Atomic and electronic structures of an extremely fragile liquid. Nat Commun. 2014;5:5892.

26. Aksay IA, Pask JA, Davis RF. Densities of SiO2-Al2O3 melts. J Am Ceram Soc. 1979;62:332–6.

27. Dingwell DB, Knoche R, Webb SL. A volume temperature relationship for liquid GeO2 and some geophysically relevant derived parameters for network liquids. Phys Chem Miner. 1993;19:445–53.

28. Haruki S, Tokunaga H, Sukenaga S, Saito N, Nakashima K. Density and surface tension of M2O-TeO2 (M = Li, Na and K) Melts. J Jpn Inst Metals. 2010;74(10):629–34. (in Japanese).

How to cite this article: Koyama C, Ishikawa T, Oda H, et al. Densities of liquid lanthanoid sesquioxides measured with the electrostatic levitation furnace in the ISS. J Am Ceram Soc. 2021;104:2913–2918. https://doi.org/10.1111/jace.17674