Study of Molten Lanthanum, Praseodymium, and Neodymium by Electrostatic Levitation

Paul-François PARADIS,1 Takehiko ISHIKAWA,1 Noriyuki KOIKE,2 and Yuki WATANABE3

1Japan Aerospace Exploration Agency, Institute of Space and Astronautical Science, ISS Science Project Office, Tsukuba, Japan, paradis.paulfrancois@jaxa.jp.
2Chiba Institute of Technology, Narashino, Japan
3Advanced Engineering Services Co. Ltd., Tsukuba, Japan

Abstract

The understanding of the nature and behavior of rare earth metals in their liquid phases requires accurate values of their physical properties. However, keeping samples in their liquid phases free from contamination for time scales long enough to carry out measurements represents a formidable challenge. This is due to high reactivity and melt contamination of lanthanum, praseodymium, and neodymium with a crucible or gaseous environment. The use of a vacuum electrostatic levitator and laser heating circumvented these difficulties and permitted the determination of the density, the surface tension, and the viscosity of several rare earth metals above and below their melting temperature. In this paper, the levitator and the non-contact measurement methods are introduced and preliminary experimental data of several thermophysical properties of La, Pr, and Nd are reported over large temperature ranges.

1. Introduction

Lanthanum, praseodymium, neodymium and their compounds are currently used to improve the resistance of certain glasses, to fabricate hydrogen sponges and strong magnets, and as dopants in optical amplifiers [1]. To assist further material development, the knowledge of the physical properties of rare earth metals and their temperature dependences is therefore paramount. However, La, Pr, and Nd are very reactive, oxidizing rapidly when exposed to air and reacting directly with nitrogen and other elements [1]. This explains why accurate physical properties are difficult to measure above their melting points when traditional methods are used (e.g., crucible, support) and why there are no data reported in the undercooled region. Here, levitation of a sample by means of electrostatic forces in vacuum prevented contamination from walls and surrounding gases [2-5]. This circumvented the problems related to high temperature processing and allowed an accurate non-contact determination of the density, the surface tension, and the viscosity of liquid La, Pr, and Nd. This paper shortly introduces the facility, describes the processing and property determination methods, and then presents preliminary experimental results. It also addresses the necessity of performing experiments under microgravity conditions.

2. Experimental

2.1 Levitation Furnace

The facility consisted of a vacuum chamber (~10^-5 Pa pressure before processing) (Fig. 1a) that housed an electrostatic levitator (Fig. 1b). A sample, charged by electronic emission, was levitated between two disk electrodes, separated by 10 mm. These electrodes were used to control the sample in the vertical position whereas four spherical electrodes distributed around the bottom electrode were used for horizontal control. The positioning of the sample relied on a feedback loop that consisted of two sets of He-Ne lasers and position sensors located at right angles of each other [6]. The sample position information obtained by the position sensors was fed to a computer that instructed high voltage amplifiers to output voltages such that the sample could keep a selected position. The lower electrode was also surrounded by four coils that generated a rotating magnetic field that was used for rotation control [7]. In addition, oscillations of the molten sample could be triggered by superimposing an ac electric field on the levitation voltage from the bottom electrode (Fig. 1b)[8]. For these experiments, samples were prepared by cutting rods (La, Pr, Nd: 99.9 mass % purity) into pieces and then laser melting them into spheroids of about 2 mm in diameter.

The focused radiation of three CO2 laser beams (10.6 µm emission, total 200 W) was used for sample heating (Fig. 1a). The separation of the beams by 120 degrees and the sample rotation (< 5 Hz)[7,9] conferred temperature homogeneity. Temperature measurements were done by pyrometry (0.90 µm and 0.96 µm).

The sample was observed by three charged-coupled-device cameras (Fig. 1b). Two black and white high-resolution cameras equipped with telephoto objectives provided magnified views of the sample whereas one color camera offered an overview of the inside of the chamber. The rotation rate was measured by detecting the intensity of the reflected He-Ne laser
beam from the sample surface by adding an interference filter and a sensor to one of the telephoto objectives. Another sensor was attached to the other telephoto objective to measure the sample oscillation.

2.2 Physical Property Determination

For properties measurements, the samples were levitated either using the pre-heating technique [4] or directly from room temperature by simultaneously UV irradiating and slowly laser heating the sample. Once levitated, the sample was slightly rotated, melted, and re-solidified to confirm pyrometer calibration and alignment. The radiance temperature was measured by the pyrometers and was calibrated to the true temperature using the known melting temperatures $T_m$ (La: 1191 K; Pr: 1204 K; Nd: 1294 K). Calibration to the true temperature was performed from Planck’s law using an in-house developed software. The lack of data for liquid rare earth metals led us to assume that the emissivity remained constant over the whole temperature range, although there are studies that indicate emissivity variations in the liquid phase for several metals [10].

The density was determined by simultaneously recording the temperature and the magnified images of a sample illuminated from behind with an ultraviolet source [4]. As shown in Fig. 2, Upon closing the shutters of all heating lasers, each La, Pr, and Nd samples (La: mass: 14.15 mg; dia.: 1.69 mm; Pr: mass: 11.20 mg; dia.: 1.49 mm; Nd: mass: 11.67 mg; dia.: 1.50 mm) exhibited undercooling, liquid-solid transition (La: 1191 K; Pr: 1204 K; Nd: 1294 K) as well as the allotropic transitions (La: fcc to bcc, 1134 K; Nd: cph to bcc, 1128 K)[11]. The sample area was extracted from each digitized video images and matched to the temperatures corresponding to the liquid phase. These images were calibrated by levitating a sphere of precisely known diameter under identical conditions. Since the sample was axi-symmetric and because its mass was known, the density could be found for each temperature by dividing the mass by the volume. When in their liquid states, the surface of the processed La samples was shiny (specular reflection of He-Ne lasers) but impurities appears upon cooling. For Pr and Nd samples, even while molten, a few impurity islands were seen floating on the surface. Once recovered, all samples rapidly oxidized and became grey.

Fig. 1 Experimental set-up (a) and levitator (b).

Fig. 2 Radiative cooling curves exhibiting undercooling, liquid-solid transitions, and allotropic transitions for La (a), Pr (b), and Nd (c).
The surface tension and viscosity were obtained by inducing an oscillation \( (P_2 \cos(\theta) \text{-mode}) \) to a liquid sample by superimposing a small sinusoidal electric field on the levitation field \([8, 12, 13]\). The sample was slightly rotated (< 10 Hz) to prevent oscillations other than mode-2 from happening. The transient signal that followed the termination of the excitation field was detected and analyzed using a custom-built software. This was performed a few times at a given temperature and repeated for several temperatures. Using the characteristic oscillation frequency \( \omega \) of this signal after correcting for non-uniform surface charge distribution \([14]\), the surface tension \( \sigma \) was determined from \([8]\):

\[
\omega^2 = \frac{8\sigma}{ro^3 \rho} W
\]

where \( W \) is a function of surface tension \( \sigma \), drop charge \( Q \), radius \( ro \) of the sample when it assumed a spherical shape, permittivity of vacuum \( \varepsilon_o \), and applied electric field \( E \). Similarly, the viscosity \( \eta \) was found by extracting the decay time \( \tau \) given by the same signal:

\[
\eta = \frac{pr_o^2}{5\tau}.
\]

Real-time values of the radius and density data obtained by the image analysis were substituted in equations (1) and (2) to avoid any detrimental effects of sample evaporation on the surface tension and viscosity data.

3. Results
3.1 Density
The density measurements of liquid La, Pr, and Nd taken over wide temperature ranges are presented in Fig. 3 together with the values appearing in the literature for comparison. The density of La, Pr, and Nd, like that of other pure liquid metals, exhibited a linear behavior as a function of temperature and can be fitted by the relationship:

\[
\rho(T) = \rho(T_m) - C(T - T_m)
\]

where \( \rho(T_m) \) is the density at the melting temperature \( T_m \) and \( C \) is the temperature coefficient (Table 1). In these measurements, the uncertainty was estimated to be less than 2 % from the resolution of the video grabbing capability (640 x 480 pixels) and from the uncertainty in mass measurements (± 0.0001 g).

To our knowledge, the La, Pr, and Nd measurements are the first to cover the undercooled domain. When the respective experimental uncertainties are taken into account, our values at the melting temperature are identical to those reported in the literature \([15-20]\). Moreover, our temperature coefficients lie exactly between the values reported in the literature using either the pycnometric or the sessile drop method \([15,16,19-21]\).

3.2 Surface Tension
The data for the surface tension of La, Pr, and Nd exhibited a linear relationship as a function of
Table 1  
Comparison with literature values of the density of La, Pr, and Nd.

<table>
<thead>
<tr>
<th></th>
<th>$\rho$</th>
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<th>Temp. range</th>
<th>Ref.</th>
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<td></td>
<td>(Tm)</td>
<td>(kg·m$^{-3}$)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>La</td>
<td></td>
<td>$C$</td>
<td>(kg·m$^{-3}·K^{-1}$)</td>
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<tr>
<td>5950</td>
<td>-</td>
<td>Tm [17] Calc.</td>
<td></td>
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<tr>
<td>5930</td>
<td>-</td>
<td>Tm [18] Ses.drop</td>
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<td>Pr</td>
<td></td>
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<td></td>
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<tr>
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</table>

The surface tension (Fig. 4) measured over large temperature ranges can be expressed by

$$\sigma(T) = \sigma(T_m) - Z(T - T_m)$$

(4)

where $\sigma(T_m)$ is the surface tension at the melting temperature $T_m$ and $Z$ is the temperature coefficient (Table 2). The data listed on Table 2 are also superimposed on the figures for comparison.

When considering the experimental uncertainties, our results at the melting temperature, although higher, compare well with most literature values [16, 18, 22-27]. In particular, they show excellent agreement with the works of Chentsov [22] and Bezukladnikova et al. [23](La) and those of Bezukladnikova et al. [23](Pr). Our temperature coefficients also exhibit a trend similar to those reported in earlier publication [16, 18-24].

The lower surface tension data reported elsewhere [16, 18, 22-24, 27] could be explained by the fact that the measurements were done with techniques for which a contact between a molten sample and a surface (e.g., sessile drop technique) occurred, which is not the case with our technique. The contact could have further contaminated the surface of the sample and therefore lowered the surface tension [28]. Additional surface contamination could have occurred for samples that were processed under non-high vacuum conditions because of the oxygen and nitrogen affinity of La, Pr, and Nd [1].
The experimental data of the viscosity $\eta(T)$ of La, Pr, and Nd are shown in Fig. 5. The data can be fitted by the following Arrhenius function:

$$\eta(T) = A \exp\left[\frac{B}{RT}\right]$$

(5)

where $R$ is the gas constant (8.31 J·mol⁻¹·K⁻¹) and $A$ and $B$ are listed in Table 3. The estimated uncertainty of the measurement is around 20%.

At the melting point, our values agree well with the published data for La and Pr when the experimental
uncertainties are considered. However, our value for Nd is much larger than that calculated by Mills [31]. Additional experiments are planned to confirm and explain this large discrepancy.

4. Conclusions

Preliminary data of La, Pr, and Nd in their liquid phases were successfully obtained by containerless processing in vacuum and non-contact diagnostic techniques. For the first time, the density, the surface tension, and the viscosity were reported over large temperature intervals that covers the undercooled regions. Further analysis of the data will be reported elsewhere.

Although the density and surface tension data show excellent agreement with the values published in the literature and could be taken down into the undercooled region, the viscosity data should be improved. On the ground, the high strength of the electrical field as well as the feedback control frequency needed to levitate a sample could have some effects on the damping constant and hence could alter the viscosity measurements. Therefore, microgravity conditions would allow easier and quieter non-contact positioning. In addition, a quieter environment for undercooled samples would offer an attractive platform to perform solidification studies from deep undercooled phases. Parallel efforts should also be devoted to find ways to clean the surface of the levitated sample to obtain more accurate physical property values.

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References