

Aerodynamic Levitation: Thermophysical Property Measurements of Liquid Oxides

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Abstract

We report on a compact laser-heated aerodynamic levitation facility which can be used for studies of thermophysical properties like density, surface tension and viscosity of liquid oxides at high temperatures. The facility is characterized by employing an acoustic excitation system for controlled excitation of droplet oscillations which is key for measurements of surface tension and viscosity. Results of measurements of density and viscosity of pure liquid Al_2O_3 as well as CaAl_2O_4 are presented. The data are discussed in the context of available literature data. It is shown that with the present setup the experimentally accessible temperature ranges could be enlarged. For viscosity high precision data for high melting point and highly reactive oxide melts can now be obtained using aerodynamic levitation.

Keyword(s): aerodynamic levitation, thermophysical properties, oxide melts

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1. Introduction

Thermophysical properties of liquids are important parameters for characterizing the behavior of materials upon cooling from the melt. This is in particular true for metal alloys where thermophysical properties play a crucial role in casting applications. Density, surface tension, and viscosity are key parameters for not only understanding the casting process for a particular material from a technological point of view but also to understand and to model microstructure formation in a material. Thermophysical properties of high temperature liquid metal alloys or oxides are relatively scarce due to their typically high reactivity with container materials used in conventional measurements. With the advent of suitable levitation techniques an important step forward towards thermophysical property investigations was made in particular for metals and their alloys [cf. Ref. 1,2) and references therein for an overview]. For oxides the situation on the other hand is slightly different. Up to now density, viscosity and surface tension data, whereby a clear focus is on the former two, have been presented in literature. Mostly the data were obtained using conventional techniques. For instance for the $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$ system, molar volumes have been reported by Courtial and Dingwell³⁾. For Al_2O_3 and some Al_2O_3 -based systems also data determined in levitation experiments exist⁴⁻⁶⁾. If we take Al_2O_3 as an example, it can be recognized, that the available data vary quite substantially from measurement to measurement regarding e.g. not only their absolute values but also their temperature dependencies.

Whereas in conventional measurements again melt-container reactions play an important role, in levitation experiments, sample evaporation, uncontrolled shape changes, and the difficulty in determining absolute temperatures pose a challenge.

In depth knowledge about oxide systems is, however, required from various points of view. In geosciences, detailed knowledge of the temperature and composition dependence of density and viscosity is required in order to understand e. g. magma flow. In steel industry oxide slags are important for material refinement as well as flow properties of the molten steel.

In the present paper we describe a laser-heated aerodynamic levitation (ADL) technique, which has been developed to allow for accurate measurements of density and viscosity in liquid oxide melts. The technique makes use of the oscillating drop method to determine viscosity from a liquid droplet. The advantage of the present setup is the ability for controlled droplet oscillation excitation.

2. Aerodynamic Levitation

2.1 Setup

The original setup of the laser-heated aerodynamic levitation furnace has been presented by Langstaff et al.⁷⁾. Here we describe a further developed version that enables thermophysical property measurements also for lower melting point materials than pure Al_2O_3 ⁸⁾. With this setup measurements are possible also towards low temperatures (<1500K) in a very

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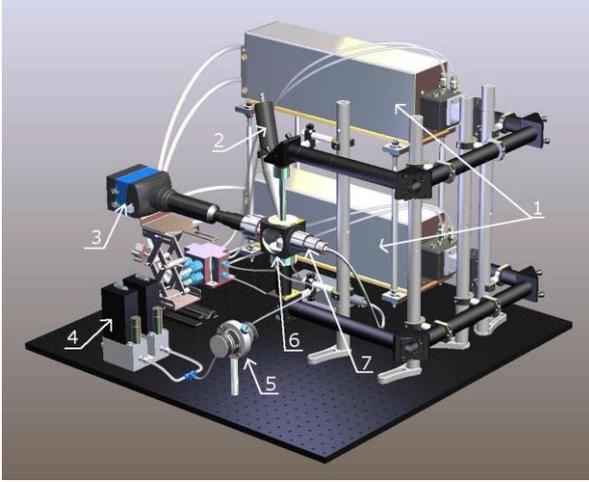


Fig. 1 Schematic drawing of the levitation setup. 1) CO₂ lasers, 2) pyrometer, 3) high-speed camera, 4) mass-flow controller, 5) acoustic excitation system, 6) levitation chamber, and 7) diode laser for backlighting.

stable way. **Figure 1** shows an overview of this novel setup. The setup consists of two 30W SynRAD Firestar v40 CO₂-lasers instead of the earlier used SynRAD Evolution Series 125W lasers. These lasers are mounted on top of each other. Laser beams are redirected towards the levitation chamber using a set of flat and focusing gold-coated Cu mirrors. The focusing mirrors are used only as final mirrors. The focal spot size of the laser is about 1mm in diameter at the sample position. Typical sample sizes are about 2 mm diameter. A top and bottom configuration is chosen to enable to increase temperature homogeneity across the sample directing the bottom laser beam directly onto the sample through the levitation nozzle. Temperature measurements are carried out using a single-color pyrometer calibrating the temperature to known temperatures of the processed materials. Typically the melting point, the liquidus or recalescence temperatures of the crystallizing undercooled melt are used. The assumption is in all these calibrations that emissivity stays constant in the investigated temperature range. This is an assumption that was shown to be valid to a good approximation for Al₂O₃ for the pyrometer wavelength used⁷⁾.

2.2 Shape-determination

For measuring density, surface tension and viscosity of molten droplets time-resolved determinations of the sample shape are prerequisite. This is achieved by using a high-speed camera (Mikrotron EOSense MotionBlitz Cube 6) in combination with a telecentric optics (SILL) achieving sample magnification of up to a factor five and an effective per pixel resolution of about 2.6 μm. The telecentric optics ensures that sample size is independent of small motions of the sample towards or away from the camera. In order to achieve good contrast and to render measurements independent of sample

brightness variations with temperature, a shadow-casting technique is used. Hereby, the levitated droplet is illuminated by a laser beam and its shadow is projected onto the camera. To cover a wide-range of temperatures – essentially from the boiling point of Al₂O₃ at roughly 3300 K down to very low temperatures of less than 1500 K – a sufficiently powerful diode laser (200mW) combined with a beam expander generating a near parallel-beam is used. In order to avoid other wavelengths from reaching the camera a narrow (10nm FWHM) band-pass filter centered on the wavelength of the diode laser is employed. To determine the sample shape a LabView program is used. A region of interest covering the sample surface at all recording times is set to all images of the video file. Points on the sample surface are determined by using image processing routines available in LabView. A proper description of the sample surface is normally given by fitting Legendre polynomials to the points on the sample surface. However, in the current setup the sample is observed horizontally from the side. Due to this fact the sample is always partially (1/4 to 1/3) hidden by the nozzle. Therefore, the points on the surface are fitted with an ellipse, which turns out to be a good approximation of the sample shape. This also indicates that viewing the sample vertically would lead to erroneous results. For density determinations rotational symmetry of the ellipse around the vertical axis is assumed and the volume of the ellipsoid is determined. The temperature dependent sample density can be calculated using the known sample mass recorded after quenching of the sample from high temperature. For surface tension and viscosity measurements also the sample shape is determined following the previously described procedure⁷⁾. However, not the volume of the ellipsoid but rather its time-dependent minor and major axis are of interest. Those can be equally derived from the determined sample shape.

2.3 Oscillating Drop Method

In order to determine surface tension and viscosity droplet oscillations are analyzed. The analysis is based on equations by Lamb⁹⁾ and Rayleigh¹⁰⁾. In these equations surface tension σ is related to the resonance frequency of the oscillating droplet and viscosity η to the damping constant of the oscillation reading:

$$\sigma = \frac{3\pi M v_l^2}{l(l-1)(l+2)} \quad (1)$$

$$\eta = \frac{1}{(l-1)(2l+1)} \frac{3M\Gamma_l}{4\pi a} \quad (2)$$

In the equations M is the sample mass, a is its radius, l is the number of the mode, and Γ_l is the damping constant of the l^{th} mode. Typically, the $l=2$ mode is observed being the dominant mode for not too large excitation amplitudes. The equation for surface tension is valid for a non-rotating spherical droplet. In

case of deviations from a spherical shape and sample rotations the resonance frequency for the $l=2$ mode is split into five modes with the additional index $m=0,\pm 1,\pm 2$. For electromagnetic levitation correction terms have been calculated and a sum-rule has been derived¹¹. For aerodynamic levitation the proper correction terms are currently unknown. Nevertheless a splitting of the lines into five individual modes has been observed and the nature of the individual modes has been determined⁷. For the viscosity measurement the sample is excited at its ($l=2,m=0$) mode, whereby projected sample shape changes are not influenced by rotation. Different to previously reported measurements⁴, with the current setup sample excitation can be precisely set in terms of its frequency as well as its amplitude. For surface tension therefore a precise resonance frequency scan with a 1Hz resolution – mainly limited by the recording time – over several tens of Hertz can be carried out. A Fourier transform of the amplitude oscillation results in frequency dependent Fourier amplitudes from which the resonance peaks can be clearly distinguished. For viscosity measurements the bespoke frequency is selected. The sample is excited at its resonance frequency and after having switched off the excitation the decay of the oscillation amplitude with time is determined.

3. Experiments and Discussion

3.1 Density of Al_2O_3

Figure 2 shows the density of liquid Al_2O_3 using high precision ruby spheres (Oscar Moser) as starting material in comparison with literature data. Data taken from literature have both been obtained conventionally using container-based techniques¹² as well as using levitation^{4, 13}. With the current

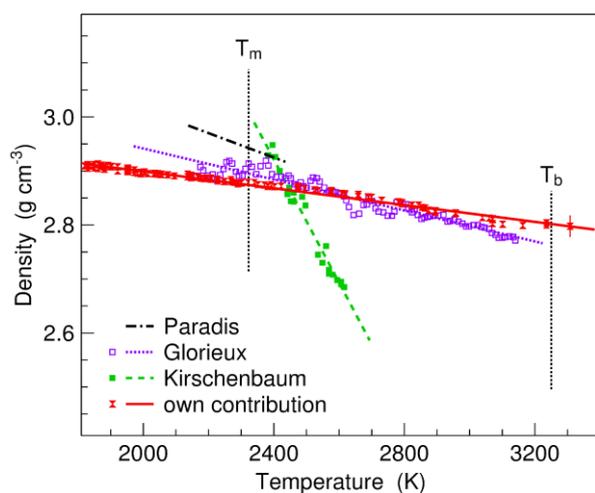


Fig. 2 Density of liquid Al_2O_3 compared with conventional data by Kirschenbau¹², with ADL data by Glorieux et al.⁴ and electrostatic levitation data by Paradis et al.¹³.

setup the temperature range is considerably larger compared with previous measurements. Deviations towards lower temperatures, comparing our results with data from Glorieux et al.⁴, can be explained by Glorieux et al. erroneously assuming spherical symmetry of their sample and using sample self-illumination. On the other hand the data of Paradis et al.¹³ using electrostatic levitation might have been influenced by sample evaporation. For the conventionally measured data by Kirshenbaum and Cahill¹² melt container interaction cannot be ruled out.

3.2 Density of $\text{CaO-Al}_2\text{O}_3$

Figure 3 shows the density of CaAl_2O_4 (CA) synthesized from a sintered pellet of CaO and Al_2O_3 in comparison to pressurized electrostatic levitation data by Kumar et al.⁵. Whereas Kumar et al. processed the CA samples in N_2 , O_2 , and air atmospheres the present work made use of Argon as levitation gas. Moreover, our sample was processed at ambient pressure conditions, whereas in the Kumar et al. experiments the samples were subjected to a pressure of several bar. Conventionally measured data by Courtial and Dingwell³ and Oliveira et al.¹⁴ as well as by molecular dynamics simulations by Drewitt et al.¹⁵ are also shown for comparison. Overall the temperature dependence of the CA samples processed in N_2 and air agree quite well with data reported here, though the present data are lower in their absolute values. The temperature dependence of the sample processed in O_2 atmosphere is stronger. Whereas the Courtial and Dingwell³ data show similar

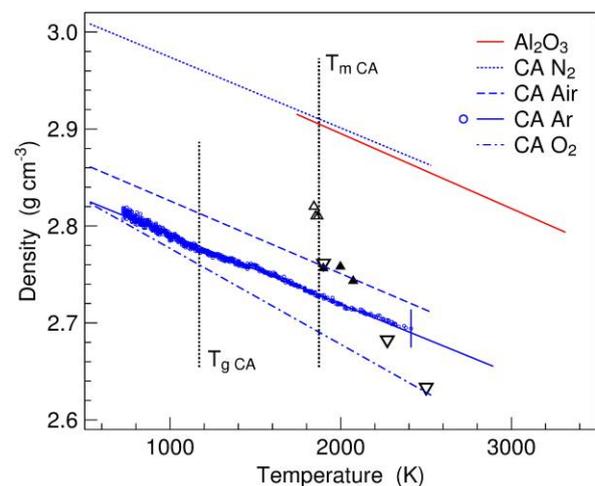


Fig. 3 Density of liquid Al_2O_3 (solid red line) and density of CA taken from Ref. 5) (N_2 , O_2 , and Air) compared with densities of CA determined as part of this study in Argon atmosphere (circles and solid line) and data determined using conventional methods (solid triangles Courtial and Dingwell³, open triangles pointing up Oliveira et al.¹⁴) as well as molecular dynamics simulations (open triangles pointing down Drewitt et al.¹⁵).

temperature dependence as the levitation experiments, the Oliveira et al.¹⁴⁾ and the Drewitt et al.¹⁵⁾ data deviate markedly. Both the melting and the glass transition temperatures of CA are indicated in the diagram. The Kumar et al. data are reported to show some kink close to the glass transition temperature. However, within error bars the data are described by a linear dependence over the entire measured temperature range as shown in the diagram. In our data the kink appears between T_g and T_m . This might indicate that the assumption of a constant emissivity over the entire temperature range of the measurement is not valid for CA. On the other hand a recent report on the cooling rate dependence of the glass transition temperature for CaO- Al_2O_3 glasses shows a rather strong cooling rate dependence of T_g for the CA sample investigated here¹⁶⁾. The wavelength of the pyrometer used for the measurements had a shorter wavelength compared with the measurement by Kumar et al. who made use of a 1.4 μm single wavelength pyrometer. Realigning the present data would shift the low temperature data closer to the measurements carried out in O_2 atmosphere, whereas the high temperature data would still fall in between the air and O_2 measurements of Kumar et al.. Moreover, it has to be noted that the density of CA processed in the same Argon atmosphere is significantly lower than the density of pure Al_2O_3 .

3.3 Viscosity of Al_2O_3 and CaAl_2O_4

Figure 4 shows the viscosity of Al_2O_3 and CaAl_2O_4 obtained by us in comparison to various literature data obtained both conventionally and through levitation. Our data were obtained by fitting of the decay of the amplitude of oscillation. In both cases the levitated droplets were excited close to their respective resonance frequencies of the ($l=2, m=0$) mode. For Al_2O_3 a undercooling of almost 200K was achieved before the sample started to crystallize. For CA apparently no undercooling was observed. The limitation in this case was the increasing viscosity and the range of maximal viscosity still accessible with the levitation setup which is about 200mPas at most. Compared with other levitation data by Glorieux et al.⁴⁾ the viscosity of Al_2O_3 is by about a factor 2 larger at higher temperatures. The reason is that Glorieux et al. used the width of the resonance curve of the damped harmonic oscillator to calculate viscosity which is known to result in values differing by about 50% of the real values. In addition data of Urbain¹⁷⁾ are shown that agree well with our ADL data. Moreover, results of electrostatic levitation experiments by Paradis and Ishikawa are shown as solid line underestimating viscosity slightly¹⁸⁾. Our ADL CaAl_2O_4 data show a pronounced increase of viscosity with decreasing temperature. Moreover, it differs from data of Urbain¹⁹⁾ reported in literature. However, compared with this data our data show similar temperature dependence. As already discussed for the density measurements, the temperature

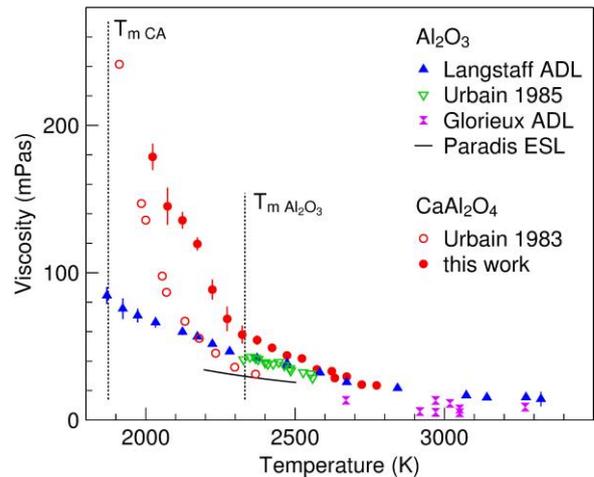


Fig. 4 Viscosity of liquid and undercooled Al_2O_3 and CaAl_2O_4 . Data of this work (red discs) are compared with literature data of Urbain¹⁶⁾. For Al_2O_3 data of Langstaff et al.⁷⁾ are compared with data of Urbain¹⁷⁾ and Glorieux⁴⁾ as well as Paradis¹⁸⁾.

calibration of the CaAl_2O_4 sample might have been affected by changing emissivity. Therefore, the difference in the data sets might be due to a difference between the real and the measured temperature. Shifting our data to lower temperatures will lead to an overlap with the Urbain et al. data within error bars. Considering the shift, our measurements still extend the available temperature range of Urbain towards higher temperatures. At the highest temperatures the data indicate merging viscosities of Al_2O_3 and CaAl_2O_4 . Most interesting, however, is that the data intersect in the supercooled liquid range of Al_2O_3 . It can be concluded that at lower temperatures the addition of CaO to Al_2O_3 leads to an increase in viscosity whereas at intermediate temperatures it leads to a decrease or almost no change at the highest temperatures.

4. Outlook and Conclusions

A laser-heated aerodynamic levitation setup has been presented, which enables accurate measurements of density and viscosity of liquid oxides to be made. Improvements compared with a previous levitation facility used to study liquid Al_2O_3 have been shown and discussed. Although the current setup works well in determining liquid oxide properties, which has been shown by first experimental results and their comparison with data from literature, there are some shortcomings inherent to the present technique. Due to the sample being partly hidden by the nozzle a full Legendre-polynomial fit to the sample surface cannot be carried out. Moreover, due to the gas pressure exerted on the sample from below, a deformation of the fraction of the sample hidden by the nozzle different from the elliptical shape observed otherwise cannot be completely ruled

out. In order to overcome these limitations lifting the sample off the nozzle providing a fully visible sample would be highly desired. This can in principle be achieved by using electrostatic levitation devices operated under pressure, as demonstrated by Kumar et al.⁵⁾ who reported densities for liquid CA. Concerning viscosities, CaO addition to Al₂O₃ leads apparently to an increase of viscosity at low temperatures and a decrease at intermediate temperatures. Further experiments for different CaO concentrations would be required to see whether such a behavior is manifested over the entire concentration range. An important question would be whether there are some structural changes on the atomic scale underlying this observation.

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