Structure of Liquid Aluminum Oxide

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The total structure factor, $S(Q)$, and the corresponding radial distribution function, $G(r)$, for supercooled and stable liquid aluminum oxide have been measured with x-ray synchrotron radiation. The specimens were levitated in a conical nozzle and melted with a laser, achieving temperatures in the range of 2200–2700 K. The first two peaks in $S(Q)$ reveal intermediate-range order and dense random packing of atoms, similar to that observed in many network liquids. The first two peaks in $G(r)$ are consistent with AlO_4^{5-} structural units and show that Al_2O_3 undergoes a major structural rearrangement on melting with an Al coordination change from octahedral to tetrahedral. The structure does not change appreciably with temperature in the stable and supercooled liquid. Implications of these results are discussed in connection with the solidification of aluminum oxide. [S0031-9007(96)02245-4]

Determination of high-temperature liquid structure is a challenging endeavor due to the reactivity of containers with the specimen materials of interest. Thus there are few detailed structural measurements on liquids at high temperature. Data exist for liquid metal [1], alloys [2], and molten salts [3] that melt at relatively low temperatures ($<1000\,°C$). Notable exceptions include the work of Enderby *et al.* [4] and Hensel [5]. The major difficulties in obtaining structural measurements at temperatures above $1000\,°C$ are the reactions of the specimens with their containers and the influence of the containers on the structural measurements. These difficulties become particularly severe at temperatures above $2000\,°C$. The problem of containment can be eliminated by using a conical nozzle levitation (CNL) technique [6] to position small liquid droplets with sufficient stability and duration to conduct x-ray diffraction measurements. Further, due to the absence of container-induced nucleation, structural measurements can be obtained on the metastable liquid. This paper reports x-ray diffraction measurements on liquid and supercooled Al_2O_3 (melting point 2327 K) in the temperature range 2200–2700 K.

The stable solid phase, α-aluminum oxide, exhibits the corundum structure with Al atoms in octahedral sites surrounded by six oxygen neighbors at a mean distance of 1.91 Å. The metastable phase γ-Al_2O_3, is described by a defect spinel structure in which the Al coordination varies from 3–5 [7], with tetrahedrally coordinated Al^{3+} predominating. For liquid Al_2O_3, the optical properties [8,9], solidification behavior [10], volume expansion on melting [11], and Al coordination number estimated from NMR measurements [12–15] have been reported. The solidification behavior of the deeply undercooled liquid was studied by Weber *et al.* [10] and was found to be strongly influenced by the oxygen potential. Tyrolerova and Lu [11] found a 20% volume expansion upon melting which would be expected to give rise to extensive structural re-

arrangements. The bonding in the liquid was recently investigated by Coutures *et al.* [12] and Massiot *et al.* [13] using ^{27}Al magic-angle spinning (MAS) NMR spectroscopy on liquid Al_2O_3. These studies inferred that the liquid consists of predominantly four-coordinated Al^{3+}, with an average Al coordination of 4.5 ± 1. Similar NMR results have been obtained for Al_2O_3-SiO_2 glasses quenched from the melt [14] and Al_2O_3-SiO_2 liquids [15].

The experimental setup was based on the earlier work of Winborne *et al.* [16], Coutures *et al.* [12], and recent developments made by Weber and Nordine [6], in which specimens are stably levitated by a gas jet in a divergent nozzle and laser heated to temperatures in excess of 2500 K. In this experiment, 3–4 mm diameter spheres were levitated in a nozzle in a flow of gas (air, oxygen, or nitrogen). A 270-W CO_2 laser beam was used for heating the specimen. Special care was given to the nozzle design so that the specimens occupied a stable positions above the plane of the top edge of the nozzle, allowing a clear path for the incident and diffracted x-ray beams. The specimen was maintained in a precise fixed position within ± 20 μm, by means of a feedback procedure derived from a signal on a phosphor screen placed downstream of the sample.

Specimen temperatures were measured by an optical pyrometer with an operating wavelength of 0.65 μm, and the temperatures were stable to about ± 10 K over the duration of the diffraction scans. The temperature gradient was less than 50 K between the top and bottom of the sample; the nominal temperature was measured on the specimen surface at the point illuminated by the x-ray beam. Emissivity corrections to the measured radiance temperature for liquid Al_2O_3 were based on reported values [9].

The x-ray measurements were carried out at the X-6B beam line at the National Synchrotron Light Source (NSLS), using a monochromator with beam focusing

optics and suitable slits to provide a focused 0.5×0.6 mm rectangular beam. The x-ray energy ranged from 6–9.25 keV with an uncertainty of 2 eV. Scattered x rays were detected with a wide band detector which viewed the specimen through Soller slits, and scattered photons were recorded with the aid of a position-sensitive detector.

We have found no examples in the literature of x-ray diffraction studies conducted on spherical surfaces. The general principles by which such a specimen geometry can be analyzed have been established by Warren [17]. The computation is complicated by the lack of symmetry implicit in flat plate and cyclindrical geometries. Two nonstandard checks were carried out to establish the validity of the correction procedures. First, measurements were made with the top of the sample only partially illuminated. The corrected results agreed within error with those obtained using full x-ray illumination of the specimen top. Second, an SiO_2 glass sphere was run, and the corrected results were in good agreement with literature data [18].

Direct volume integration methods were used to determine attenuation coefficients, and the multiple scattering contribution was calculated with a Monte Carlo method. Incoherent scattering was included in the multiple scattering and attenuation corrections using the methods and formalism of Wagner [19]. The form factors, incoherent scattering factors, and photoelectric and pair production terms were approximated using the tables of Baro et al. [20]. The data for the liquid and supercooled liquid were corrected with the same procedure, using identical air-scatter subtractions and form factors. The number density was taken as 0.0937 atom/Å^3 for both stable and supercooled liquids, based on the crystal density of 3.97 g cm^{-3} and taking into account the 20% density decrease on melting [11].

The x-ray weighted total structure factor $S(Q)$ for liquid Al_2O_3 at 2223 and 2662 K is shown in Fig. 1. The sharp rise in $S(Q)$ at low Q arises from inexact subtraction of the air scatter and should be ignored. The two prominent peaks in $S(Q)$ are at 2.05 and 4.50 Å^{-1}. The corresponding radial distribution function $G(r)$, given in Fig. 2, was determined from the $S(Q)$ results using the maximum entropy Fourier transform method [21]. $G(r)$ shows a strong peak at 1.76 Å, and progressively weaker peaks at 3.08 and 4.25 Å. In the supercooled liquid longer-range correlations are observed at distances up to 7 Å, which are less evident in the stable liquid.

The positions of the peaks in the $S(Q)$ data may be used to classify the ordering in the liquid along the lines proposed by Price et al. [22]. The first peak at $Q_1 = 2.05$ Å^{-1} is typical of the first sharp diffraction peak found in many network liquids and glasses. A number density of 0.0937 implies a mean interatomic spacing d_s of 2.73 Å, and the first peak at 1.76 Å may be taken as the value of r_1, the nearest neighbor distance. The reduced wave-vector values $Q_1 r_1 = 3.61$
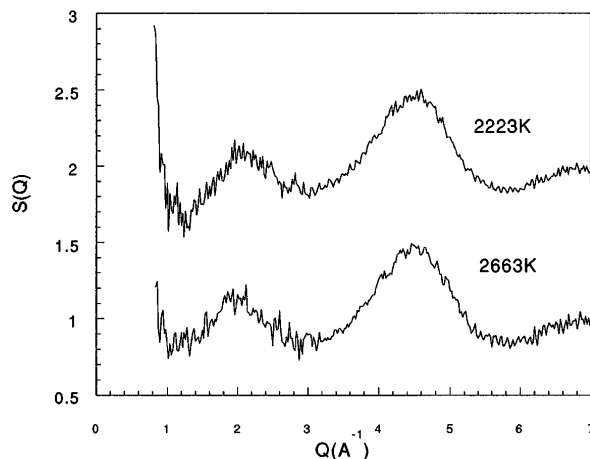

FIG. 1. Total x-ray structure factor for supercooled liquid Al_2O_3 at 2223 K (upper curve) and stable liquid Al_2O_3 at 2663 K (lower curve). The values for the lower curve have been shifted down by 1 for clarity.

and $Q_1 d_s = 5.60$ classify the first peak in $S(Q)$ as arising from intermediate-range order. The second peak at $Q_2 = 4.5$ Å^{-1} gives the reduced values $Q_2 r_1 = 7.9$ and $Q_2 d_s = 12.30$, which are indicative of topological short-range order arising from touching Al-O pairs.

The first peak in $G(r)$ at 1.76 Å can be compared with the distance of closest approach, 1.72 Å, based on the 0.36 and 1.36 Å ionic radii of Al^{3+} and O^{2-} ions, respectively [23]. Octahedrally coordinated α-Al_2O_3 has an Al-O nearest neighbor distance of 1.91 Å. This difference between the nearest-neighbor distances in the liquid and α solid is equal to the observed difference between nearest-neighbor distances in octahedrally and tetrahedrally coordinated SiO_2 [24] and strongly suggests that the Al^{3+} is tetrahedrally coordinated. In this case the shortest O-O distance should be $r_{Al-O} \times 1.732 = 3.05$ Å, which agrees well with the
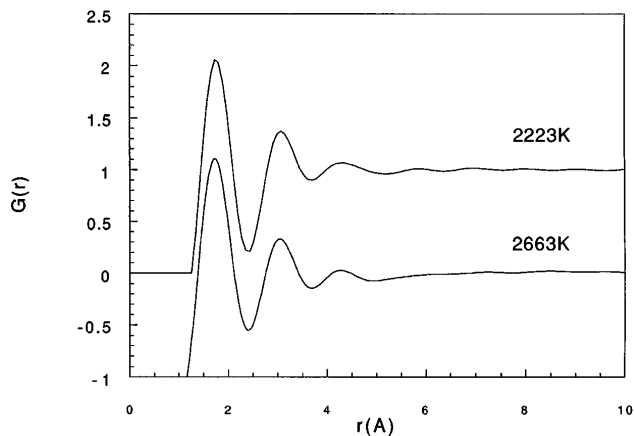

FIG. 2. The radial distribution function for supercooled liquid Al_2O_3 at 2223 K (upper curve) and stable liquid Al_2O_3 at 2663 K (lower curve). The values for the lower curve have been shifted down by 1 for clarity.

second peak in $G(r)$ at 3.08 Å. Furthermore, integration under the first peak in $G(r)$ gives an Al-O coordination number of 4.4 ± 1.0 atoms, compared with the value of four expected from tetrahedral coordination. A small number of these AlO_4^{5-} tetrahedra may then be linked to other tetrahedra by a combination of edge and corner sharing similar to that seen in γ-Al_2O_3. This would explain the small peak in $G(r)$ at 4.25 Å, which would then arise from O-O next-nearest-neighbor correlations when the AlO_4 groups share a corner O and the average base to vertex angle is around 45°. Such an extended network would produce nearly stoichiometric Al_2O_3 if it were extended in three dimensions.

The position of the second peak in $S(Q)$ and the first two peaks in $G(r)$ are independent of temperatures over the range 2200–2650 K. At the lower temperature, additional features can be observed in $G(r)$ at distances up to 7 Å, which may arise from small local networks or clusters that form when the liquid is supercooled.

These results show that melting of aluminum oxide in its stable α form is accompanied by drastic changes in structure and coordination. These structural changes explain the complex solidification behavior reported on cooling the melt. When the cooling rates approach 10^5 K/s, amorphous aluminum oxide can be formed [25]. At somewhat lower cooling rates, the metastable γ phase can be formed directly from the melt [25], while at cooling rates in the range of 1–100 K/s only α-Al_2O_3 forms [10]. The present measurements show that liquid Al_2O_3 exhibits a real structure similar to γ-Al_2O_3, enabling the formation of an intermediate γ phase on cooling from the melt, prior to the formation of the stable α phase.

In conclusion, we report the first measurements of the structure of liquid aluminum oxide. These results show that melting of Al_2O_3 is accompanied by major structural rearrangements and a change in the Al coordination from octahedral to tectrahedral. The measurements indicate Al-O and O-O nearest-neighbor distances of 1.76 and 3.08 Å, respectively, are consistent with a structure based on AlO_4^{5-} tetrahedral units. These main structural features were found to be temperature independent over a temperature range of 500 K.

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