

Amorphous tantalum and its relationship with the molten state

O. L. G. Alderman,^{1,2,*} C. J. Benmore,² J. Neufeind,³ E. Coillet,⁴ A. Mermet,⁴ V. Martinez,⁴ A. Tamalonis,¹ and R. Weber^{1,2}¹Materials Development, Inc., Arlington Heights, Illinois 60004, USA²X-Ray Science Division, Advanced Photon Source, Argonne National Laboratory, Argonne, Illinois 60439, USA³Chemical and Engineering Materials Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37830, USA⁴Institut Lumière Matière, UMR 5306 Université Lyon 1, Centre National de la Recherche Scientifique, Université de Lyon, F-69622 Villeurbanne, France

(Received 4 March 2018; published 23 April 2018)

The structure factors of molten Ta₂O₅ and Nb₂O₅ have been measured by high-energy x-ray and pulsed neutron diffraction. These are compared to transmission-mode x-ray diffraction through a self-supported 15- μ m ion-beam sputtered amorphous tantalum film. Atomistic models derived from the diffraction data by means of empirical potential structure refinement reveal that tantalum and niobium liquids are very close to isomorphous, as confirmed by measurement of a molten mixture, Ta_{0.8}Nb_{1.2}O₅. Nonetheless, peak Nb-O bond lengths are about 1% shorter than those for Ta-O, at temperatures, $T^* = T/T_{\text{melt}}$, scaled to the melting points. Mean coordination numbers are $n_{MO} \simeq 5.6(1)$, $n_{OM} \simeq 2.23(4)$ in the liquid state, and $n_{TaO} \simeq 6.6(2)$, $n_{OTa} \simeq 2.63(8)$ in the solid. The liquids are built from five- and six-fold *M*-O polyhedra which connect principally by corner sharing, with a minority of edge sharing; α -Ta₂O₅ on the other hand has a local structure more akin to the crystalline polymorphs, built primarily from six- and seven-fold polyhedra, with a larger degree of edge sharing. The structural differences between liquid and amorphous Ta₂O₅, coupled with observations of *increasing* peak bond lengths upon cooling, are consistent with the interpretation that the amorphous film reaches a supercooled liquidlike metastable equilibrium during deposition. In other words, the amorphous film shares a common progenitor state with a hypothetical glass quenched from a fragile melt. In addition, we show that recent classical interatomic potentials do not fully reproduce the diffraction data, and infer that inclusion of attractive (non-Coulombic) Ta-Ta interactions is important, particularly for obtaining the correct degree of edge sharing, coordination numbers, and densities. Nanoscale inhomogeneity of the amorphous film is confirmed by the observation of small-angle x-ray scattering.

DOI: [10.1103/PhysRevMaterials.2.043602](https://doi.org/10.1103/PhysRevMaterials.2.043602)

I. INTRODUCTION

The structure of an amorphous solid can often be influenced by its synthesis method [1–3]. Such distinct amorphous forms of a given substance are often termed polyamorphs [2], in analogy to polymorphs in the crystalline state, with perhaps the most famous example being the different forms of amorphous water ice [3]. Conversely, amorphous oxides of *similar* structure, obtained via different, high-energy, synthesis routes have led to the idea that a common metastable equilibrium state is reached at some point in their thermal histories [4–6]. Furthermore, this metastable state may resemble the deeply supercooled liquid, as is the case for melt-quenched glasses. Here we use high-energy x-ray diffraction (XRD) and neutron diffraction (ND) to study *liquid* Ta₂O₅ and its putative isomorph—molten Nb₂O₅. Direct comparison is then made to the x-ray-diffraction pattern of ion-beam sputtered (IBS) α -Ta₂O₅ obtained in transmission geometry through a 15- μ m film. Such a comparison enables us to speculate on the structural relationship between the amorphous solid and hypothetical melt-quenched glass, two states often tacitly conflated in simulation studies [7–9]. Furthermore, the scattering data allow for direct testing of pair potentials used in classical molecular dynamics (MD) modeling, both in the equilibrium

high-temperature liquid as well as for the non-equilibrium amorphous solid.

Amorphous tantalum films have been used in the successful detection of gravitational waves, where they act as high index layers within the multilayer mirror coatings of large-scale interferometers [10–14]. For this application, among others, understanding the structural properties is key to reducing the internal friction and thermal noise and thereby increasing instrument sensitivity [14]. Amorphous transition-metal oxides, including those of tantalum and niobium, are also prime candidates for use in resistive random-access memory [15,16] as well as electrochromic [1] and energy storage applications. As such, the structure and properties of α -Ta₂O₅ have been studied quite extensively [6,17–25]. From a glass science perspective, α -Ta₂O₅ is an intriguing material, being an “intermediate” oxide composed of high-field-strength cations, which has not been melt quenched to form glass, but is typically formed by ion-beam sputtering. Nonetheless, glasses containing large molar amounts of Ta₂O₅ have been formed by melt quenching [26–31], with compositions including 60Ta₂O₅ · 10Ga₂O₃ · 30La₂O₃ [31], 50Ta₂O₅ · 50Li₂O [26], and 46Ta₂O₅ · 54Al₂O₃ [28], suggesting that Ta likely partakes in network formation. Understanding the structure of high-temperature melts ultimately facilitates fundamental understanding of glass formation (and crystallization)—how and why it occurs in certain compositions and not in others.

*Corresponding author: o.alderman@gmail.com

A second aspect of this paper concerns the structural similarity, or isomorphism, of molten tantalum and niobia. Nb^{5+} and Ta^{5+} have identical Shannon radii (0.64 Å for M -O octahedra [32]), and very similar bond-valence (BV) parameters [$R_{\text{NbO}} = 1.911(2)$ Å, $R_{\text{TaO}} = 1.920(5)$ Å [33]] and Pauling electronegativities ($\chi_{\text{Nb}} = 1.6$, $\chi_{\text{Ta}} = 1.5$). The melting points of the $M_2\text{O}_5$ oxides differ significantly, $T_{\text{melt}} = 1760$ K ($M = \text{Nb}$) and 2145 K ($M = \text{Ta}$), and both are strongly polymorphic [18,34–36], in part due to the possibility of nonstoichiometry, oxygen deficiency, and reduced M^{4+} states, which can lead to superlattice formation. The Ta_2O_5 - Nb_2O_5 phase diagram is rather complex [37]. While wide $(\text{Ta},\text{Nb})_2\text{O}_5$ solid-solution regions exist, these have different structures at either end of the phase diagram. Furthermore, a mixed $\text{Nb}_4\text{Ta}_2\text{O}_{15}$ phase, of unknown structure, exists over a limited temperature range above $T \approx 1680$ K, with a narrow solid-solution range. The known structures of ambient temperature $M_2\text{O}_5$ polymorphs typically contain M -O octahedra [38–42], but these are often distorted and may have additional, much longer, bonds. In coexistence with these octahedra, sevenfold sites are also found, e.g., in high-temperature Ta_2O_5 [43], and even fourfold tetrahedral sites are found, at low abundance, in high-temperature Nb_2O_5 [44].

Given the above information, one might expect similar, though not necessarily identical, structures for liquid and even amorphous tantalum and niobia. How similar they are is an open question addressed herein. Notably the surface tensions of the two liquids are identical, and they have similar atom number densities [45].

II. METHODS

A. Sample synthesis

A 15- μm -thick layer of amorphous Ta_2O_5 was deposited at Laboratoire des Matériaux Avancés, Villeurbanne, France, with a dual ion-beam sputtering coater. The coating was deposited on a silicon substrate, an area of 1.4×1.4 mm of which was later removed by etching in order to obtain a freestanding layer.

Ceramic beads of Ta_2O_5 and Nb_2O_5 , 2–4 mm in diameter, suitable for use in an aerodynamic levitation furnace, were obtained by laser melting of powders in a copper hearth open to air [46]. Starting reagents were 325 mesh Nb_2O_5 (Materion, 99.95%) and <20- μm Ta_2O_5 (Aldrich, 99.99%). In order to obtain mixed oxide beads, the two reagents were first baked at 873 K in Pt crucibles inside an electric furnace overnight. The dried powders were then weighed into a polyethylene bottle in proportions appropriate to the desired $2\text{Ta}_2\text{O}_5 \cdot 3\text{Nb}_2\text{O}_5$ molar composition. The 1.3-g batch was then tumble mixed with a single Al_2O_3 mixing bead. The powder mixture was then formed into beads within the laser hearth as for the single oxides.

B. Density

The density of molten niobia has been measured by Ikemiya *et al.* [45] over the $1810 \leq T \leq 1934$ -K temperature interval, with result

$$\rho_m = 4.280 - (4.09 \times 10^{-4})(T - T_{\text{melt}}) \quad (1)$$

in units of grams per cubic centimeter and Kelvin, and with $T_{\text{melt}} = 1760$ K. A contactless measurement on the more refractory liquid tantalum yielded a density of 6.55 g cm^{-3} at the melting point [47]. This translates into an atom number density 93% of that for liquid niobia at T_{melt} [45]. In lieu of more accurate experimental data we derive an equation for the density of molten Ta_2O_5 based on the assumption of identical atom number density to liquid Nb_2O_5 , at temperatures, $T^* = T/T_{\text{melt}}$, scaled to the melting points. This procedure yields

$$\rho_m = 7.116 - (5.58 \times 10^{-4})(T - T_{\text{melt}}) \quad (2)$$

where $T_{\text{melt}} = 2145$ K.

Densities of amorphous tantalum films have been measured between 7.30 and 7.68 g cm^{-3} [19,24,25,48]. For our analyses herein we have used the larger value of 7.68 g cm^{-3} [24,25]. Note that our proposed Eq. (2) for the density of molten Ta_2O_5 extrapolates to a room-temperature density of 8.15 g cm^{-3} , higher than measurements on amorphous films. This is exactly as should be expected because a hypothetical tantalum glass, derived by quenching the melt, would have a smaller thermal expansion coefficient than the liquid, and therefore a lower density than the extrapolation of the liquid curve. In addition, a- Ta_2O_5 films could be measured to have lower than their bulk densities if any porosity is present.

C. X-ray diffraction

High-energy x-ray-diffraction experiments were performed at beamline 6-ID-D of the Advanced Photon Source (APS), Argonne, IL, USA. Pair weighting factors for the different sample compositions are given in Table I. Cation-cation pair scattering typically dominates, followed by metal-oxygen and only a small contribution from O-O. Initial experiments used an x-ray energy of 100.315 keV ($\lambda = 0.123595$ Å), with beam cross section 200 μm high by 500 μm wide. X rays were detected by an a-Si Perkin-Elmer XRD1621 (2048 \times 2048 pixels of a 200 \times 200- μm TI-doped CsI scintillator) at a distance of 345.05 mm from the sample, calibrated with a cerium dioxide powder standard, giving access to a maximum $Q = (4\pi/\lambda) \sin \vartheta$ of $Q_{\text{max}} \simeq 24 \text{ \AA}^{-1}$ at scattering angle $2\vartheta_{\text{max}} = 27.3^\circ$. Only the above plane scattering was analyzed, owing to the increased absorption below the plane arising from the alignment of the x-ray beam at the top of the spheroidal sample. For Ta-bearing samples, a 1.5-mm-thick sheet of brass

TABLE I. Pair weighting factors for $M_2\text{O}_5$ materials based on the bound neutron coherent scattering lengths $\bar{b}_{\text{O}} = 5.803(4)$ fm, $\bar{b}_{\text{Ta}} = 6.91(7)$ fm, and $\bar{b}_{\text{Nb}} = 7.054(3)$ fm [100]. X-ray weightings are calculated at $Q = 0$, where $f_i(Q = 0) \approx Z_i$ and $Z_{\text{O}} = 8$, $Z_{\text{Ta}} = 73$, and $Z_{\text{Nb}} = 41$.

Material	Radiation	Pair weighting		
		M - M	M -O + O- M	O-O
Ta_2O_5	X-ray	0.616	0.338	0.046
$\text{Ta}_{0.8}\text{Nb}_{1.2}\text{O}_5$	X-ray	0.531	0.395	0.073
Nb_2O_5	X-ray	0.452	0.441	0.107
Ta_2O_5	Neutron	0.104	0.437	0.459
Nb_2O_5	Neutron	0.107	0.440	0.453

TABLE II. Summary of 100-keV x-ray and spallation neutron-diffraction measurements on the a-Ta₂O₅ IBS film and molten Ta₂O₅-Nb₂O₅ liquids. The densities shown are derived from measurements on molten niobia by Ikemiya *et al.* [45], and on the amorphous phase by Bassiri [25].

Material	Radiation	Gas	T (K)	T_{melt} (K)	T/T_{melt} (K)	Density (g cm ⁻³)	Density (atoms Å ⁻³)	r_1 (Å)
Ta ₂ O ₅	X-ray	O ₂	2287(10)	2145	1.066	7.0363	0.067124	1.910(8)
Ta ₂ O ₅	X-ray	O ₂	2339(18)	2145	1.09	7.0073	0.066847	1.913(11)
Ta ₂ O ₅	X-ray	O ₂	2400(32)	2145	1.119	6.9732	0.066522	1.910(8)
Ta ₂ O ₅	X-ray	O ₂	2458(17)	2145	1.146	6.9409	0.066214	1.907(8)
Ta ₂ O ₅	X-ray	O ₂	2504(26)	2145	1.167	6.9152	0.065969	1.908(8)
Ta ₂ O ₅	X-ray	O ₂	2538(32)	2145	1.183	6.8963	0.065788	1.907(8)
Ta ₂ O ₅	X-ray	O ₂	2595(26)	2145	1.21	6.8645	0.065484	1.905(7)
Ta _{0.8} Nb _{1.2} O ₅	X-ray	O ₂	2145(10)	1941	1.105	5.3186	0.066680	1.893(3)
Nb ₂ O ₅	X-ray	O ₂	1820(11)	1760	1.034	4.2556	0.06749	1.892(2)
Nb ₂ O ₅	X-ray	O ₂	1870(11)	1760	1.063	4.2352	0.067166	1.891(1)
Nb ₂ O ₅	X-ray	O ₂	1975(21)	1760	1.122	4.1922	0.066485	1.891(2)
Nb ₂ O ₅	X-ray	O ₂	2081(13)	1760	1.182	4.1489	0.065797	1.890(2)
Ta ₂ O ₅	X-ray	Ar	2234(16)	2145	1.041	7.0659	0.067406	
Ta ₂ O ₅	X-ray	Ar	2378(23)	2145	1.109	6.9855	0.066639	
Ta ₂ O ₅	X-ray	Ar	2478(19)	2145	1.155	6.9297	0.066107	1.924(18)
Nb ₂ O ₅	X-ray	Ar	2071(30)	1760	1.177	4.153	0.065862	1.888(1)
a-Ta ₂ O ₅	X-ray	Air	298(2)	2145	0.139	7.680	0.073264	1.957(6)
Ta ₂ O ₅	Neutron	Ar	2423(25)	2145	1.130	6.9604	0.066400	1.919(4)
Nb ₂ O ₅	Neutron	Ar	1923(25)	1760	1.093	4.2135	0.066822	1.912(5)

was used in front of the detector to selectively filter out fluorescence x rays from the Ta K edge. Samples were held within the converging-diverging conical nozzle of an enclosed aerodynamic levitation furnace [49]. Either pure O₂ or Ar gases were used to levitate the samples, at flow rates of ≈ 0.5 L/min. The different gases allow for comparison of measurements at different oxygen partial pressures to check for any influence of reduction of $M^{5+} \rightarrow M^{4+}$ at high temperature. Heating and melting were achieved using a 500-W, 10.6- μ m, CO₂ laser impinging onto the top of the sample bead, where the x-ray beam also passes, and where sample temperature was measured by optical pyrometry in the 0.9- μ m near-infrared region. Apparent temperature was corrected using Wien's displacement law approximation [50] with a spectral emissivity value of 0.87 estimated from the Fresnel losses for a material with a refractive index of 2.1 [51,52]. Correction was also made for reflection losses from a silica window and lens that were in the optical path. Measurements were made at fixed laser power, and were close to isothermal (see Table II). After initial melting, the temperature was typically lowered in 100-K steps, with measurements of 1-min duration (three captures using 0.2-s exposures averaging over 100 frames) at each step. Background measurements of the empty furnace were made, with either argon or oxygen gas flowing into the chamber.

The mixed oxide, Ta_{0.8}Nb_{1.2}O₅, sample was measured later with a slightly different setup. X-ray energy was 100.250 keV ($\lambda = 0.123675$ Å), with beam cross section 200 μ m high by 400 μ m wide. The sample-to-detector distance was 378.49 mm. The molten sample was measured in O₂ for 10 min in total during a single run (30 captures using 0.2-s exposures averaging over 100 frames).

Repeat measurements were made at the higher x-ray energy of 131.737 keV ($\lambda = 0.0941149$ Å), with beam cross section

200 μ m high by 500 μ m wide and sample-to-detector distance of 654.04 mm. The use of higher-energy x rays reduces the absorption and fluorescence problems associated with tantalum, but comes at the expense of greatly reduced x-ray beam intensity. Oxygen was used as the levitation gas, and measurements lasted 5 min (15 captures using 0.2-s exposures averaging over 100 frames).

Sample masses changed very little during each run, typically remaining within the measurement uncertainty of ± 0.1 mg, or about $\pm 0.1\%$. The largest change was observed for a Ta₂O₅ sample run several times in O₂, at $\Delta m = -0.21$ mg, or -0.25% .

The amorphous tantala film, with self-supported area of 1.4×1.4 mm, was suspended vertically and measured at nine points on its surface using an incident beam cross section of 250×250 μ m. The x-ray energy was 100.315 keV ($\lambda = 0.123595$ Å), and sample-to-detector distance was 329.76 mm. Of the diffraction patterns obtained at different locations, all showed some Bragg spots arising from residual Si substrate. The measurement with the smallest Si contribution was chosen for analysis, and the Bragg spots masked out of the data. A comparison of masked and unmasked data is given in Fig. S1 in Supplemental Material [53]. The silicon contribution is very small, and any remaining diffuse scattering can be neglected in the data analysis. Later measurements for comparison were also made at 131.737 keV ($\lambda = 0.0941149$ Å), and sample-to-detector distance of 682.81 mm, as well as at 60.0673 keV ($\lambda = 0.206409$ Å), which is below the Ta K edge (67.416 keV). Here the sample-to-detector distance was 469.46 mm. This final setup extended the measurement to lower Q , with concomitant reduction in Q_{max} .

Two-dimensional diffraction data were reduced, integrated, and corrected using FIT2D [54], additional angle and energy

TABLE III. Details of EPSR and MD models. Maximum amplitude of the empirical potential, U_E ; minimum cation-cation separation, r_{MM}^{\min} ; metal-oxygen and oxygen-metal coordination numbers with standard deviations of *their distributions* in parentheses; and goodness-of-fit parameters, $R\chi$. Values are given for the MD model for a-Ta₂O₅ of Ref. [9], while the 2400-K liquid was modeled using the refined potentials derived herein.

Model	EPSR					MD	
	a-Ta ₂ O ₅ A	a-Ta ₂ O ₅ B	a-Ta ₂ O ₅ C	Ta ₂ O ₅ 2458 K	Nb ₂ O ₅ 1975 K	a-Ta ₂ O ₅ [9]	Ta ₂ O ₅ 2400 K
U_E (kJ/mol)	547	912	547	534	534		
r_{MM}^{\min} (Å)	2.9	2.9	2.5	0.9	0.9		
n_{MO} ($r_{\text{cut}} = 2.75$ Å)	6.58(88)	6.74(97)	6.29(79)	5.52(63)	5.57(63)	5.72	5.84
n_{OM} ($r_{\text{cut}} = 2.75$ Å)	2.63(59)	2.70(62)	2.51(56)	2.21(49)	2.23(47)	2.29	2.34
$R\chi$ ($1.2 \leq r_{\text{cut}} \leq 8.0$ Å) XRD (%)	3.86	3.36	2.57	3.26	1.57	22.53	10.97
$R\chi$ ($1.2 \leq r_{\text{cut}} \leq 8.0$ Å) ND (%)				2.50	2.63		7.47

dependent corrections according to Ref. [55], and finally GUDRUNX [56] to obtain the x-ray structure factors. Residual background intensity varying slowly with Q was removed using the top-hat convolution method ($6.0\text{-}\text{Å}^{-1}$ top-hat width) and real-space intensity below 1.0 Å^{-1} was suppressed [56]. This amounts to an aesthetic correction which is nonetheless helpful for direct comparison to modeled functions.

D. Neutron diffraction

The coherent neutron-scattering cross sections for Ta and Nb are similar to that for oxygen, in contrast to the case for x rays where the heavy metal atoms dominate (see Table I). As such, combined neutron and x-ray scattering from tantalum and niobium pentoxide are highly complementary, and allow access to information from all three pair terms, M - M , M - O , and O - O . Moreover, the close similarity of the bound neutron coherent scattering lengths of Ta and Nb means that measurements on both of the M_2O_5 liquids make for a direct test of their putative isomorphism.

Neutron-diffraction measurements were made at the NOMAD beamline [57] of the Spallation Neutron Source (SNS), Oak Ridge, TN, USA. A reentrant well containing an aerodynamic levitation furnace similar to that described in Ref. [58] was used. Argon was used to fill the well and as levitation gas, on account of its reduced neutron scattering compared to air or oxygen, and thereby background scattering was reduced. The neutron beam was collimated and aligned to pass above the top of an Al nozzle within which the sample was floated. Measurements of vanadium beads of varying diameter, placed in the levitator nozzle, were used for normalization to absolute units. Each liquid was measured for a total of 60 min. After background subtraction, absorption corrections, and normalization, a further small renormalization, following the procedure in Refs. [59,60], was applied. This procedure forces the low r slope of $D(r)$ to be consistent with that expected based on the melt density. Finally, a Fourier filter was applied to reduce high-frequency noise and a small remaining low-frequency background. Comparisons of the data before and after this procedure are given in Fig. S2 in Supplemental Material [53].

E. Empirical potential structure refinement

Structural models were derived from the diffraction data using empirical potential structure refinement (EPSR) [61,62].

For the liquids, neutron and x-ray data were both used as input simultaneously, while for the amorphous solid only x-ray data were available. Initial random configurations of 4900 atoms were equilibrated using Monte Carlo under Coulombic plus Lennard-Jones 12-6 reference potentials to give reasonable starting points for the refinements. The reference force-field parametrizations were based on the Lorentz-Berthelot mixing rules and the following atomic parameters: $\epsilon_O = 0.92\text{ kJ mol}^{-1}$, $\sigma_O = 3.16\text{ Å}$, $q_O = -e$, $\epsilon_M = 2.23\text{ kJ mol}^{-1}$, $\sigma_M = 1.48\text{ Å}$, and $q_M = +2.5e$, where e is the proton charge. Temperatures and densities were fixed at 2458 K, 6.941 g cm^{-3} for Ta₂O₅; 1975 K, 4.192 g cm^{-3} for Nb₂O₅; or 298 K, 7.680 g cm^{-3} for a-Ta₂O₅. Following equilibration, empirical potential refinement was used to progressively modify the atomic configuration such that the experimental scattering data were reproduced. Once the goodness of fit parameter was minimized, statistical structural data were collected over ensembles of $>2 \times 10^3$ configurations. It was necessary to enforce a minimum Ta-Ta separation in the models of a-Ta₂O₅, and ultimately three models were produced with different r_{TaTa}^{\min} , or maximum energy amplitudes of the empirical potential (see Table III).

F. Molecular dynamics

Pair potentials for Ta₂O₅ have been developed by Trinastic *et al.* [8] and used by those authors [7] and others [9] to predict the structure and properties of a-Ta₂O₅. Trinastic *et al.* [8] based their potentials on the O-O pair potential for BKS (named for van Beest, Kramer, and van Santen) silica [63], which takes the Buckingham form. An additional Morse interaction term was included for Ta-O, while Ta-Ta pairs interacted solely via Coulombic forces. The Ta-O pair potential was fitted to lattice and elastic constants of β -Ta₂O₅ derived from density functional theoretic calculations [34].

Herein we compare existing models of a-Ta₂O₅ [8,9] to our x-ray-diffraction data, and use the Trinastic *et al.* [8] potentials, and derivatives thereof, to model molten tantalum. The simulations were conducted using the DL_POLY classic code [64] in the isothermal-isobaric (N - P - T) ensemble at 2400 K and 1 atm pressure. An initial configuration of 1400 atoms was derived using a Monte Carlo procedure under the EPSR reference potentials described above. An equilibration period (forces capped) of 25 ps was followed by a 50-ps production run from which results were derived. A time step of 1 fs was used throughout.

A modified set of potentials was derived, starting from those of Trinastic *et al.* [8]. These were based on the as-published Ta-O pair potential, an increased O-O Buckingham interaction amplitude $A_{OO} = 2110.935$ eV, and inclusion of an attractive Ta-Ta pair interaction of the form

$$\varphi_{\text{TaTa}}(r) = A_{\text{TaTa}} \exp\left(\frac{-r}{\rho_{\text{TaTa}}}\right) - \frac{C_{\text{TaTa}}}{r^6} - \frac{D_{\text{TaTa}}}{r^8} \quad (3)$$

with $A_{\text{TaTa}} = 2.4 \times 10^4$ eV, $\rho_{\text{TaTa}} = 0.25$ Å, $C_{\text{TaTa}} = 1.6 \times 10^3$ eV Å⁶, and $D_{\text{TaTa}} = -1.6 \times 10^3$ eV Å⁸. The modified potentials were derived in order to obtain the correct system density, as given by Eq. (2), and to improve the agreement with diffraction data, primarily in terms of the nearest-neighbor Ta-Ta distance distribution.

III. RESULTS

A. Reciprocal-space functions

Comparison of the Q -weighted structure factors, or interference functions, plotted in Fig. 1, reveals a number of insights. First, the great similarity between the two neutron-diffraction measurements lends strong support to the idea that the tantala and niobia liquids are isomorphous. The bound neutron coherent scattering lengths (see Table I) of Ta and Nb differ by only $\sim 2\%$, and as such the structure factors are expected to differ beyond this level only if the atomic

arrangements themselves do so. The similarity carries over into the x-ray scattering functions, but in this case the larger number of electrons of the Ta atoms ($Z_{\text{Ta}} = 73$) leads to a larger weighting of the M - M pair scattering compared to Nb ($Z_{\text{Nb}} = 41$) (see Table I). Therefore there are clear differences in the modulation of the relative peak heights between the Ta_2O_5 , Nb_2O_5 , and $\text{Ta}_{0.8}\text{Nb}_{1.2}\text{O}_5$ liquids in the x-ray scattering curves.

A second insight garnered from Fig. 1 is that the effect of temperature, at least over the ~ 300 -K range explored, is small for both molten tantala and niobia. Although the structure factors at this scale are barely distinguishable between different temperature points, some subtle systematics do exist and will be explored in the discussion.

Third, the a- Ta_2O_5 x-ray-diffraction data reveal a much greater degree of ordering compared to the liquids, as is expected from the greatly reduced thermal disordering at room temperature. The first peak also becomes clearly split into two peaks at 1.87 and 2.42 Å⁻¹, something not observed in related materials such as a- HfO_2 [65].

It is also evident in Fig. 1 that the x-ray data for liquid tantala are somewhat noisier than for liquid niobia. This is a consequence of the greater absorption cross section of Ta_2O_5 compared with Nb_2O_5 . The measurements were made using x rays with energies greater than those of the K edges of Nb (18.986 keV) and Ta (67.416 keV). At 100 keV, the absorption

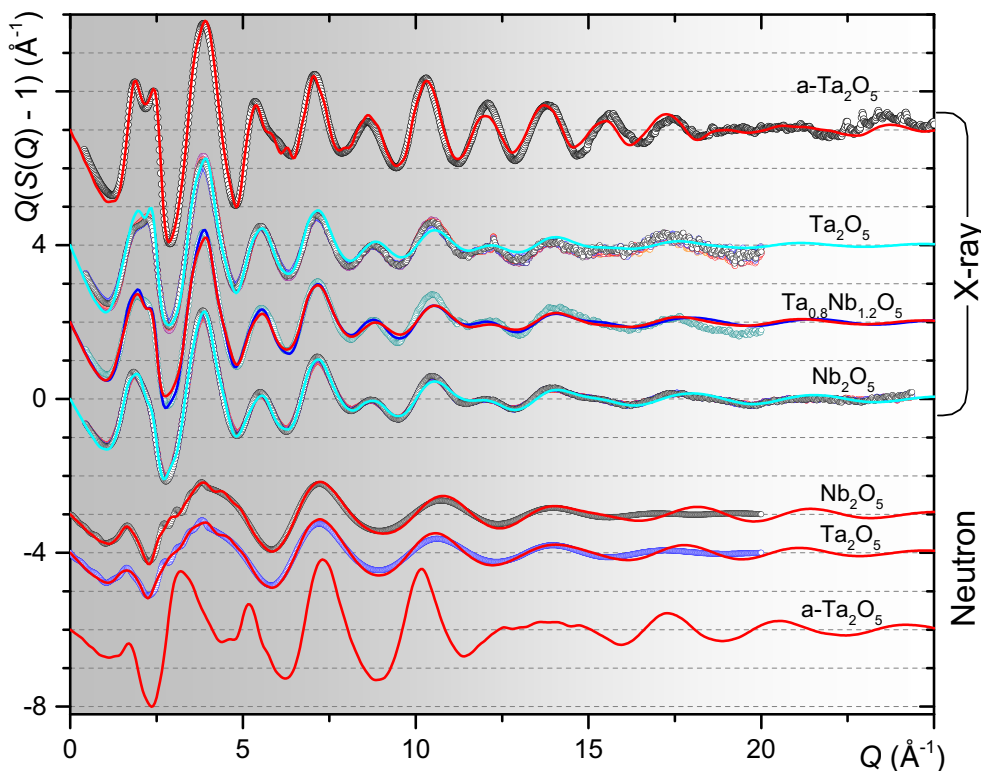


FIG. 1. Interference functions, $Q[S(Q) - 1]$, for the a- Ta_2O_5 IBS film and molten Ta_2O_5 - Nb_2O_5 liquids. Measurements (open points) in O_2 gas using 100-keV x rays and in Ar gas using spallation neutrons are shown. The solid curves (red or cyan) overlaid are derived by EPSR. In the case of a- Ta_2O_5 , only the predicted neutron function is shown. Seven liquid Ta_2O_5 and four liquid Nb_2O_5 datasets obtained at different temperatures are shown overlaid in different colors. For the $\text{Ta}_{0.8}\text{Nb}_{1.2}\text{O}_5$ molten solution, two solid curves are overlaid, obtained by reweighting and summing the partial structure factors derived by EPSR for the Ta_2O_5 (red) and Nb_2O_5 (blue) end members, assuming isomorphism. Vertical offsets have been applied for clarity.

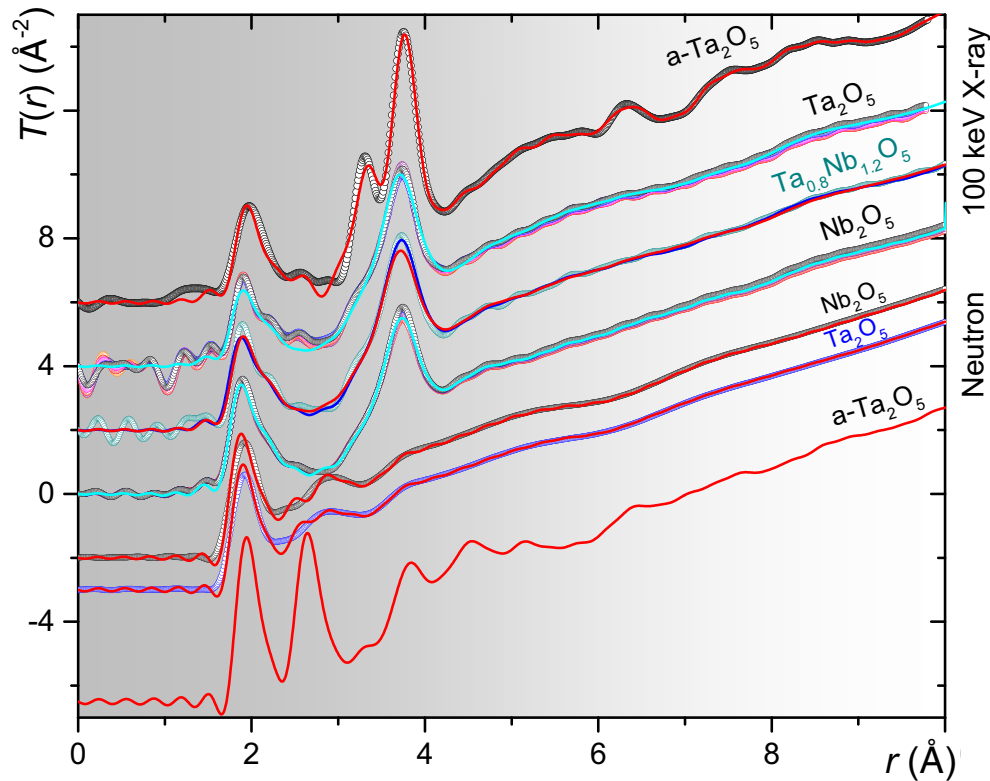


FIG. 2. The total correlation functions obtained by sine Fourier transform of the data in Fig. 1. In all cases a $Q_{\max} = 20.0 \text{ \AA}^{-1}$ was used, without any additional window or modification function. Vertical offsets have been applied for clarity.

length of molten Ta_2O_5 (0.40 mm) is almost an order of magnitude smaller than for molten Nb_2O_5 (3.03 mm) and the fluorescence energy ($\sim 57 \text{ keV}$) and yield are correspondingly greater. This results in an attenuated signal as well as a fluorescence background for the Ta_2O_5 measurements, which increase the uncertainty in the result.

Comparison of x-ray-diffraction measurements made in oxygen and argon atmospheres (see Fig. S3 in Supplemental Material [53]) reveals negligible changes due to the change in oxygen partial pressure, from 1 atm down to $\sim 10^{-6}$ atm in ultrahigh-purity Ar. This implies that thermal reduction of pentavalent M^{5+} to lower valence states can be neglected in our structural analyses. Nonetheless, while materials processed in O_2 appeared white on recovery, those melted in argon were blackened, implying a small abundance of M^{4+} defects, sufficient to strongly influence the optical properties. The slightly larger changes observed for molten Ta_2O_5 compared to Nb_2O_5 are attributed to the lower signal-to-noise ratio of the former measurements, rather than any difference in redox behavior.

X-ray-diffraction measurements were conducted at 100 and 132 keV and direct comparisons are plotted in Fig. S4 in Supplemental Material [53]. The higher-energy measurements were undertaken in order to reduce the absorption and fluorescence associated with tantalum. However, despite this advantage, the incident x-ray flux is also lowered by almost two orders of magnitude, which could not practically be fully compensated for by increasing the measurement times. As such, the 132-keV measurements have a lower signal-to-noise ratio, and serve mainly to verify the 100-keV measurements, without improving upon them.

The structure factor of a- Ta_2O_5 is plotted in Fig. S1 in Supplemental Material [53], where it can be seen that at $Q \lesssim 0.8 \text{ \AA}^{-1}$ the intensity increases from a minimum value. This can be seen more clearly in the 60-keV data (see Fig. S5 in Supplemental Material [53]), which extend to lower Q by virtue of the lower energy and longer sample-detector distance. This small-angle x-ray scattering (SAXS) implies inhomogeneity within the amorphous film, possibly nanoscale porosity built in during the deposition process. A much larger SAXS signal has recently been observed in a- HfO_2 grown by gas phase condensation [65].

B. Real-space functions

Total correlation functions are plotted in Fig. 2. Again, a comparative inspection reveals a remarkable amount of information, even beyond that gleaned from the reciprocal-space data plotted in Fig. 1. Perhaps the most striking feature is the split Ta-Ta nearest-neighbor peak in a- Ta_2O_5 , with clearly resolved peaks at 3.312(2) and 3.750(1) Å. The area ratio of short to long Ta-Ta distances is approximately 1:2 and they are loosely ascribed to edge- and corner-sharing TaO_n polyhedra, respectively. The shorter metal-metal distance remains present as an unresolved shoulder in the x-ray data for the Ta_2O_5 - Nb_2O_5 liquids.

The M -O nearest-neighbor peaks are clearly asymmetric, with modal distances of $\sim 1.9 \text{ \AA}$ and a tail, or shoulder, to higher r . This asymmetry of the M -O bond-length distribution is common to many molten and amorphous oxides [65–68], with the exceptions being the highest-field-strength network-

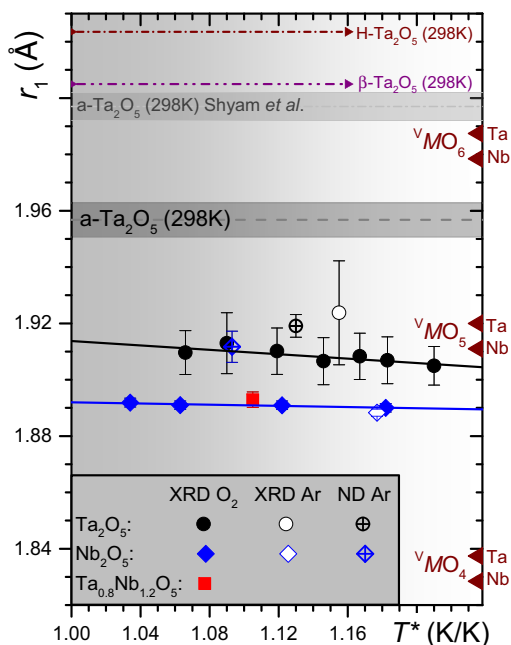


FIG. 3. Peak (modal) bond lengths for a-Ta₂O₅ IBS film and molten Ta₂O₅ and Nb₂O₅ liquids, as a function of $T^* = T/T_{\text{melt}}$. Solid lines are linear regressions of the XRD data collected in O₂ gas. Crystallographic mean bond lengths for H-Ta₂O₅ [43] and β -Ta₂O₅ [40] are shown for comparison. Also shown to the right-hand side are bond-valence derived bond lengths for four-, five-, and six-fold pentavalent cations, relevant to ambient temperature and calculated assuming equivalency of all bonds within the polyhedron. Note that this equivalency of bonds does not exist in the liquids or the amorphous film, where the mean and modal bond lengths differ significantly. Nonetheless, the bond-valence derived values serve as a useful reference point.

forming cations such as Si⁴⁺ and B³⁺. Notably the peak position is slightly larger in a-Ta₂O₅ compared to the liquids, possibly indicative of a higher average M -O coordination. Analysis of the full bond-length distributions is made by EPSR (see below). The modal peak positions have been extracted using PFIT [69], by fitting the leading edge up to 1.95 Å, and these are recorded in Table II and Fig. 3. The shorter distances in the liquids compared to the solid film are clear, and indeed a larger cutoff radius of 2.0 Å was required in fitting the data for the solid. Also revealed is a difference between the niobia and tantala liquids, whereby the Nb-O peak bond length is slightly shorter compared to Ta-O, by about 0.02 Å. The reasons for this are discussed below in Sec. IV A.

C. EPSR models

The EPSR method derives ensembles of atomic configurations at fixed density that are consistent with diffraction data. The solid curves overlaid on the data in Figs. 1 and 2 demonstrate that EPSR has been successful in deriving chemically feasible atomic arrangements in all cases. Note that for the liquids the models are more highly constrained, by both neutron and x-ray data, whereas for the a-Ta₂O₅ only x-ray data were available, and the predicted neutron data are given at the bottom of each plot.

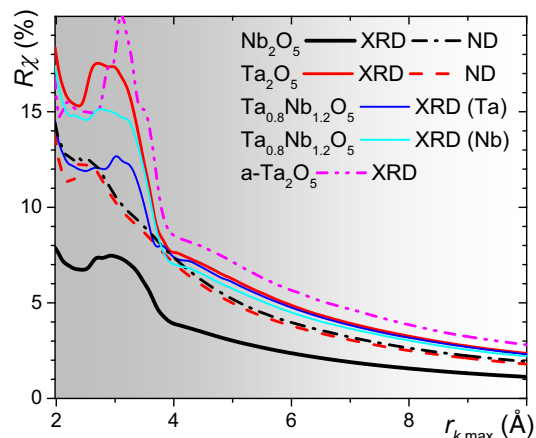


FIG. 4. Goodness-of-fit parameters as a function of summation cutoff radius for various EPSR models.

The real-space goodness of fit can be calculated using [70]

$$R_{\chi}(r_{k, \max}) = \left(\frac{\sum_{k, \min}^{k, \max} [T_{\text{exp}}(r_k) - T_{\text{mod}}(r_k)]^2}{\sum_{k, \min}^{k, \max} T_{\text{exp}}^2(r_k)} \right)^{1/2}, \quad (4)$$

where subscripts “exp” and “mod” denote experimental and modeled functions, respectively. This parameter is plotted as a function of $r_{k, \max}$ in Fig. 4 ($r_{k, \min} = 1.2$ Å) and given numerically for $r_{k, \max} = 8.0$ Å in Table III. The molten Nb₂O₅ XRD data are most well reproduced, followed by the ND data, molten Ta₂O₅ XRD, and finally a-Ta₂O₅ XRD. The ordering of the XRD datasets can be rationalized based on the higher quality of the Nb₂O₅ data compared to Ta₂O₅ where absorption and fluorescence have a greater effect. The a-Ta₂O₅ is least well reproduced, despite the lack of constraint by neutron-diffraction data, likely because it is more ordered—it is always easier to reproduce a highly disordered (high temperature, high entropy) structure than an ordered one.

EPSR derived partial pair distribution functions $g_{ij}(r)$ are plotted in Fig. 5, coordination number distributions are plotted in Fig. 6, and bond angle distributions are plotted in Fig. 7. It is quite clear that the independently derived structures of molten tantala and molten niobia are very similar; they are essentially the same—*isomorphous*—within measurement uncertainties. Amorphous tantala, however, has a structure quite distinct from the high-temperature melts. Indeed, the melts have mean M -O coordination numbers (see Table III) of 5.6, compared to $n_{\text{TaO}} \simeq 6.6(2)$ in the amorphous phase. Figure 6(a) shows that the melts are largely composed of five- and six-fold Ta or Nb, with most oxygen being twofold, bridging oxygen, at shared corners of M -O polyhedra. By contrast a-Ta₂O₅ is composed largely of six-, seven- and some eight-fold Ta, and there are more threefold oxygen than twofold, indicating a higher degree of edge sharing of polyhedra than in the melts.

IV. DISCUSSION

A. Isomorphism of molten Ta₂O₅ and Nb₂O₅

Molten tantala and niobia appear to have very similar structures at the level of the atomic arrangements, and can therefore be considered as *isomorphs*. An additional test of

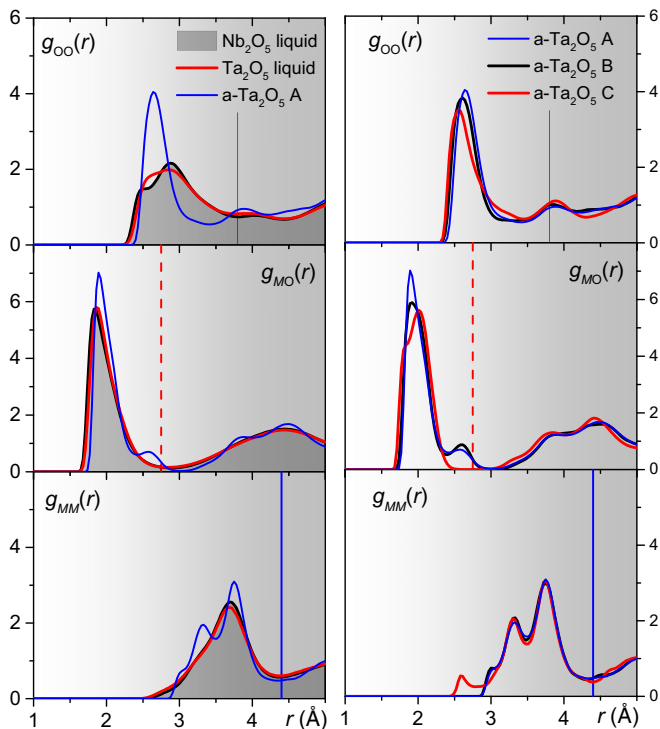


FIG. 5. Partial pair distribution functions derived by EPSR for the a-Ta₂O₅ IBS film and molten Ta₂O₅ and Nb₂O₅ liquids. Vertical lines correspond to cutoff radii for which coordination number and bond-angle distributions were calculated.

this comprises the simulation of the x-ray data for the mixed molten oxide, Ta_{0.8}Nb_{1.2}O₅, using the appropriately weighted partial structure factors derived from EPSR of the end-member oxides. Figures 1 and 2 demonstrate that the diffraction data are predicted reasonably well in this manner. In fact, the real-space goodness-of-fit parameters are better than those of the pure Ta₂O₅ melt (see Fig. 4).

The $g_{ij}(r)$ for the two liquids (see Fig. 5) are very similar. The largest difference apparent here is in the first peak of $g_{OO}(r)$. Considering that this difference is not observed in the experimental neutron data, it is not considered a feature of the real liquids. Similarly, the small differences in coordination number distributions (see Fig. 6) and the 1% difference in mean coordination numbers (see Table III) are considered below the detection limit inherent in the experiments.

A true, subtle, difference in the structures does appear in the peak bond lengths (see Fig. 3 and Table II). Specifically, the peak Nb-O bond length is shorter than the Ta-O by about 0.02 Å, across the whole range of temperatures accessed. Although the Shannon radii for Nb⁵⁺ and Ta⁵⁺ are identical to the two significant figures they are given [32], a difference is apparent in the BV parameters of Nb⁵⁺ [1.911(2) Å] and Ta⁵⁺ [1.920(5) Å] [33] at the level of the third significant figure. What this means is that, for identical coordination geometries, one would expect niobium-oxygen bonds to be slightly shorter (by ~0.5%) than tantalum-oxygen bonds. Indeed, since the difference in BV parameters of $\Delta r_{BV} = 0.009(5)$ Å is very similar to the difference observed experimentally, $\Delta r_{xrd} = 0.018(8)$ Å, it can be ascribed to the intrinsic bonding difference alone, without invoking any difference in the mean

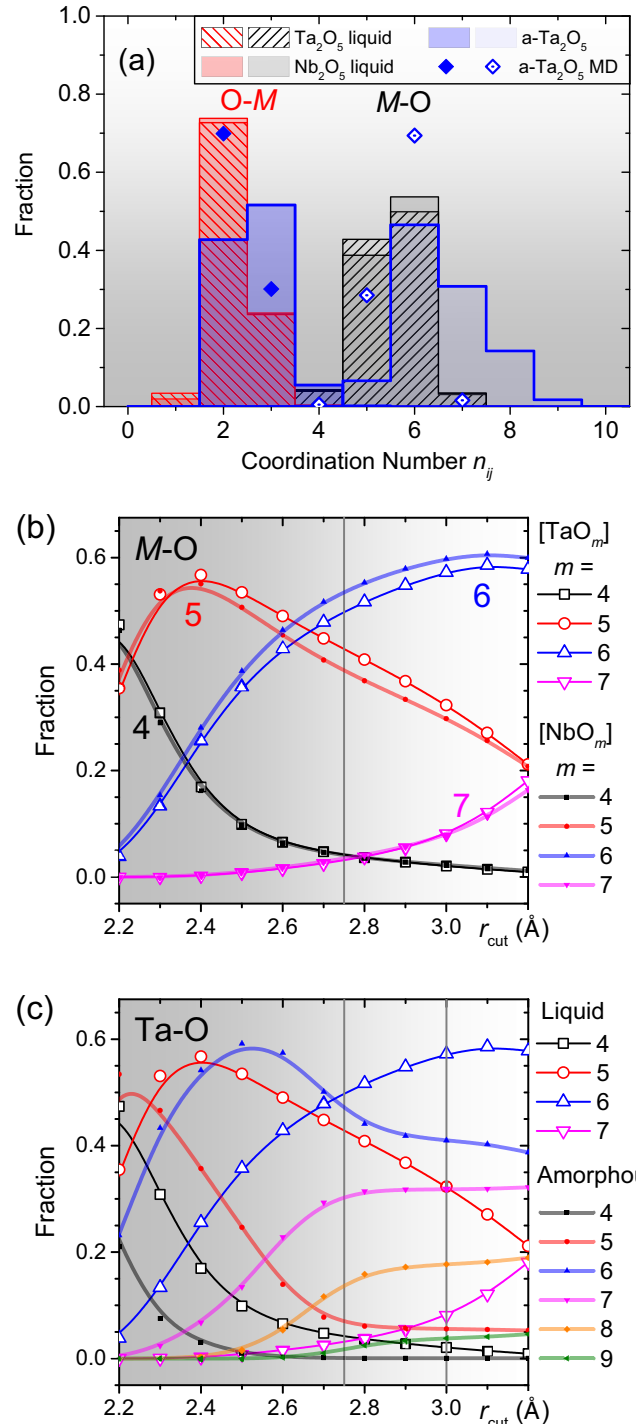


FIG. 6. Coordination number distributions for a-Ta₂O₅ IBS film and molten Ta₂O₅ and Nb₂O₅ liquids. (a) O-M and M-O distributions for a fixed cutoff radius of 2.75 Å. Results from the MD study of Damart *et al.* [9] are also shown. (b) As a function of cutoff radius for the two liquids. (c) As a function of cutoff radius for liquid and solid-amorphous tantalum.

coordination numbers or geometries. Again, differences in mean coordination environments at or below the 1% level cannot be ruled out.

Aleshina *et al.* [71] measured x-ray-diffraction patterns from *amorphous* Ta₂O₅ and Nb₂O₅ obtained by anodic

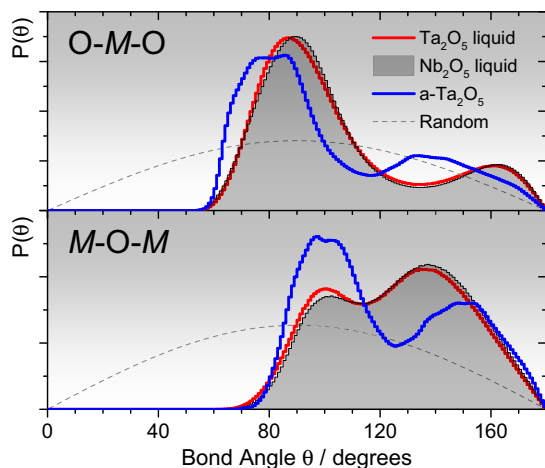


FIG. 7. Bond angle distributions for a-Ta₂O₅ IBS film and molten Ta₂O₅ and Nb₂O₅ liquids.

oxidation. Those authors found very similar bond lengths of $r_{\text{NbO}} = 1.98(2) \text{ \AA}$ and $r_{\text{TaO}} = 1.97(2) \text{ \AA}$, and a small difference in mean coordination number of $\Delta n_{MO} = 0.4(3)$, where $n_{\text{NbO}} = 7.1(2)$ and $n_{\text{TaO}} = 7.5(2)$. These results are slightly inconsistent, in that r and n typically scale together (logarithmically), and the slightly smaller BV parameter for Nb⁵⁺ [33] implies $r_{\text{NbO}} < r_{\text{TaO}}$, for $n_{\text{NbO}} \leq n_{\text{TaO}}$. The discrepancy may simply be a result of the low real-space resolution obtained by the conventional x-ray-diffraction technique, using relatively low-energy x rays from Fe, Cu, and Mo K_α transitions. Nonetheless, the results suggest similar structures for the amorphous solids, as well as for the liquids measured herein.

B. Structure of amorphous tantalum

X-ray-diffraction data presented herein reveal an amorphous tantalum structure distinct from that of the high-temperature melt. Beyond the decreased thermal disorder at ambient temperature, the denser solid phase also possesses more highly coordinated ions, the polyhedra of which link together by edge sharing as well as corner sharing, the latter being predominant in the melt phase.

The structure of a-Ta₂O₅ derived herein is not as well determined as those of the liquids. This is because only x-ray data were available, the unsupported area of the film ($\sim 2 \text{ mm}^2$) being too small compared to beams typically used for neutron diffraction. Partly as a consequence of this, it was necessary to enforce a minimum Ta-Ta separation during EPSR modeling. a-Ta₂O₅ models A and B (see Table III) were derived with $r_{\text{TaTa}}^{\text{min}} = 2.9 \text{ \AA}$ and differ only slightly on account of the larger maximum amplitude allowed for the empirical potential in a-Ta₂O₅ B. In model C, however, with $r_{\text{TaTa}}^{\text{min}} = 2.5 \text{ \AA}$, a large change is observed in the $g_{ij}(r)$ (see Fig. 5), whereby the peak of $\sim 2.6 \text{ \AA}$, which manifests in $g_{\text{TaO}}(r)$ in models A and B, is replaced by short Ta-Ta distances in $g_{\text{TaTa}}(r)$ in model C. Such short Ta-Ta distances are considered unlikely in the real material given that they are not found in the crystalline polymorphs of Ta₂O₅, while Ta-O bonds in this region are common.

The well-resolved split Ta-Ta peak observed in real-space x-ray-diffraction data for a-Ta₂O₅ (see Fig. 2) is a striking

feature. It is not something that is observed in ambient-pressure glass-forming oxides such as V₂O₅ [72], P₂O₅ [73], SiO₂ [74], GeO₂ [75], B₂O₃ [76], or even As₂O₃ [77]. Common to all of these glass formers is that their metal-oxygen coordination numbers are all low enough that an open network of corner-sharing polyhedra can be built up, within which oxygen bonds to an average of only two cations (or fewer in the case of phosphorus pentoxide). Stated concisely, for glass formers,

$$n_{OM} = \frac{c_M}{c_O} n_{MO} \leq 2, \quad (5)$$

where c_M/c_O is the metal-to-oxygen ratio. Equation (5) rearranges as

$$n_{MO} \leq 2 \frac{c_O}{c_M}. \quad (6)$$

In amorphous but non-glass-forming oxides the above inequality does not hold and the introduction of oxygen coordinated to more than two cations leads to mixed edge as well as corner sharing. This leads to two distinct populations of metal-metal distances, which are often resolved as a split peak in $g_{MM}(r)$. Such splitting is observed not only for a-Ta₂O₅ but also for a-HfO₂ [65] and a-TiO₂ [66,78], as well as glassy oxides (e.g., GeO₂) compressed to sufficiently high pressures that the M -O coordination increases above the $2(c_O/c_M)$ threshold [79,80]. Exceptionally, Al-Al distances in a-Al₂O₃ associated with edge and corner sharing are too similar to be resolved, but do lead to a clearly asymmetrical peak in $g_{\text{AlAl}}(r)$ [81–83].

Note that in related materials such as amorphous hafnia [65] the ratio of short to long metal-metal distances is rather different, being approximately 2:1 in a-HfO₂, as opposed to 1:2 in a-Ta₂O₅. This is primarily a consequence of the higher oxygen-to-metal ratio, c_O/c_M , in tantalum. A slightly lower M -O coordination number in a-Ta₂O₅, $n_{\text{TaO}} \approx 6.6(2)$ (see Table III), compared with $n_{\text{HfO}} \approx 6.8(6)$ in a-HfO₂, would also contribute to this observation.

a-Ta₂O₅ is therefore more similar to the glass-former oxides than is a-HfO₂, inasmuch as it has a higher proportion of corner-sharing M -O polyhedra. It might therefore be expected that tantalum could partake in oxide network formation in glasses, to a greater degree than hafnium, under the right circumstances, and in suitable compositions. This is borne out in observations of glass formation, with as much as 60 mol % Ta₂O₅ being incorporated into glassy La₃GaTa₆O₂₁ [31], 50 mol % in LiTaO₃ [26], and many other examples of tantalum-rich oxide glasses [27–31,84]. Meanwhile HfO₂ shows far less solubility in oxide glasses [85–87]. Niobium oxide can be incorporated into glasses even up to 75 mol % Nb₂O₅ in LaNb₃O₉ glass [31,88], which, like the equilibrium Ta₂O₅-Nb₂O₅ phase diagram, is suggestive of subtle differences between Ta and Nb. Similarly, ZrO₂ tends to be incorporated to slightly higher levels in glass [30,89,90], as compared to HfO₂.

Our data are compared directly in Fig. S6 in Supplemental Material [53] to those of Shyam *et al.* [20], who employed a rather different approach for obtaining the x-ray structure factor of a-Ta₂O₅. Those authors used a grazing-incidence (GI) technique which does not require any substrate removal, probing only the top 50–100 nm of the film. Overall the results are very similar. The transmission measurement has a higher

signal-to-noise ratio, which might explain the more clearly resolved split in the first diffraction peaks at 1.87 and 2.42 \AA^{-1} . The reduced Q range of the grazing-incidence measurement means that it is not clear if small-angle scattering is present, as for the transmission measurement, although the lowest-few- Q data points do show a slight upturn. In real space the differences in the $T(r)$ are at the noise level. A slightly longer Ta-O peak bond length is observed in the GI data (see also Fig. 3). However, this may come down to systematic uncertainties, e.g., in calibration of the scattering geometry, rather than any real difference in structure arising from slight differences in thermal history. As such, the liquid-amorphous comparison in Fig. 3 is better made between our measurements which use very similar experimental setups. Since the GI measurement is sensitive to a depth of many tens of nanometers, it is a bulk probe, as is the transmission measurement through the 15000 nm film, and differences on the grounds of different bulk or surface sensitivities are not expected.

Shyam *et al.* [20] did not quote numerical coordination numbers, but they cite a similar short-range structure to the crystalline phase also measured, likely β -Ta₂O₅, with sixfold Ta coordination. However, based on the great similarity between the GI and transmission x-ray-diffraction measurements (see Fig. S6 in Supplemental Material [53]), we can conclude that our models with $n_{\text{TaO}} \approx 6.6(2)$ are consistent with both datasets. Using a combination of first-principles MD and electron diffraction, Bassiri *et al.* [24] obtained an average coordination number in IBS amorphous tantalum of $n_{\text{TaO}} = 6.53$, in excellent agreement with the present findings.

Aleshina *et al.* [71] found $n_{\text{TaO}} = 7.5(2)$, somewhat higher than the value obtained herein. The difference could arise from the synthesis method of the anodic films, which is rather different from that for IBS films, and could lead to incorporation of water and/or hydroxyls. Furthermore, the conventional x-ray-diffraction technique could be subject to larger uncertainties than those quoted. Indeed, $n_{\text{TaO}} = 7.5(2)$ is closer to the sevenfold Ta sites found in high-pressure Z-Ta₂O₅ [91,92] than to any ambient pressure polymorphs. Notably Maeng *et al.* [93], based on extended x-ray-absorption fine-structure (EXAFS) data, suggested a similar local structure for anodic a-Ta₂O₅ as for the β -Ta₂O₅ polymorph containing sixfold Ta. This does not completely refute the findings of Aleshina *et al.* [71], however, given that EXAFS has also yielded comparatively low $n_{\text{TaO}} \simeq 5$ in IBS a-Ta₂O₅ [18], which can be at least partially attributed to the difficulties and uncertainties associated with extraction of quantitative coordination numbers from EXAFS data. Studies using ¹⁷O NMR [94] suggest an O-Ta coordination number $n_{\text{OTa}} = 2.43(12)$, as derived from the relative areas of resonances assigned to two- and three-fold oxygen. The corresponding $n_{\text{TaO}} = 6.1(3)$ is only slightly smaller than found herein by high-energy x-ray diffraction and EPSR.

Finally, the presence of inhomogeneity in the IBS film is implied by the observed rise in SAXS (see Figs. S1 and S5 in Supplemental Material [53]), which specifically suggests scattering density fluctuations on the nanometer length scale. The same conclusion has recently been reached by Hart *et al.* [21] using fluctuation electron microscopy and virtual dark-field imaging. Those authors found inhomogeneity on the 5-nm length scale, and furthermore that it increased with

thermal annealing. Structure on this scale is difficult to capture in atomistic models, given that even a $5 \times 5 \times 5\text{-nm}$ cube contains more than 9000 atoms. To capture any fluctuations would likely require an increase in linear dimension of an order of magnitude, which is 10^3 in volume, or a total atom count on the order of 10^7 . Simultaneously modeling atomic to nanoscale (or larger) structure clearly poses a general problem in the computational modeling of materials.

C. Temperature dependence of the liquid structure and relationship with a-Ta₂O₅

The changes in liquid x-ray-diffraction patterns with temperature are very small, partly due to the relatively small temperature ranges of $\Delta T \approx 300 \text{ K}$ accessed. Nonetheless, Table II and Fig. 3 reveal subtle, systematic trends toward shorter peak M -O bond lengths at higher T . In other melts, this phenomenon has been associated with a reduction in coordination number with increasing temperature [49,95]. The gradients obtained by linear regression are $-1.8(5) \times 10^{-5}$ and $-0.6(2) \times 10^{-5} \text{ \AA K}^{-1}$ for Ta-O and Nb-O respectively. These correspond to negative bond-length thermal expansion coefficients of $-10(3) \times 10^{-6}$ and $-3.2(9) \times 10^{-6} \text{ K}^{-1}$. These are imperfect measures, owing to the asymmetry of the M -O bond length distributions (see also Ref. [96]), but nonetheless can be compared instructively to the magnitude of changes observed in other systems. For example, in molten BaTi₂O₅, $\alpha_{\text{TiO}} = -8(2) \times 10^{-6} \text{ K}^{-1}$ (from the mean r_{TiO} , not the mode) [49], and, in Na₂B₄O₇, $\alpha_{\text{BO}} = -23(3) \times 10^{-6} \text{ K}^{-1}$ (mean is approximately equal to mode) [95,97]. Therefore the values found for α_{TaO} and α_{NbO} are entirely reasonable, and imply a reduction in n_{TaO} and n_{NbO} with increasing temperature. Note that in liquid B₂O₃ a *positive* B-O bond expansion is observed, with $\alpha_{\text{BO}} = +3.7(2) \times 10^{-6} \text{ K}^{-1}$, owing to the constancy of the B-O coordination number ($n_{\text{BO}} = 3$) [76].

A coordination number which increases during cooling is exactly what would be expected from the structural differences between liquid and amorphous tantalum, *if* a-Ta₂O₅ is considered an analog for a hypothetical melt-quenched glass. If this is indeed the case, then the Ta-O bond length and coordination number would have to increase more rapidly during cooling in the supercooled regime, as opposed to the equilibrium liquid regime accessed experimentally herein. The reasoning behind this statement is that the extrapolation of the linear trend in Ta-O bond length in the melt does not reach that measured for the solid, even at 0 K , let alone at a putative glass transition in the vicinity of 900 K (based on crystallization during annealing above this temperature [6,10]). A qualitatively similar result was found in molten BaTi₂O₅ [49]. This type of behavior is associated with fragile melts—those that display super-Arrhenius temperature dependence of the liquid viscosity.

The idea that amorphous materials can attain a supercooled liquidlike metastable equilibrium structure is often tacitly assumed in their computational modeling. Identical MD modeling methodologies involving melt quenching are often applied for both amorphous materials as well as glasses (materials which experimentally melt quench without crystallization). This concept has been advanced by Kim *et al.* [4–6,94], who have shown that amorphous materials obtained by different synthesis routes often converge upon a common

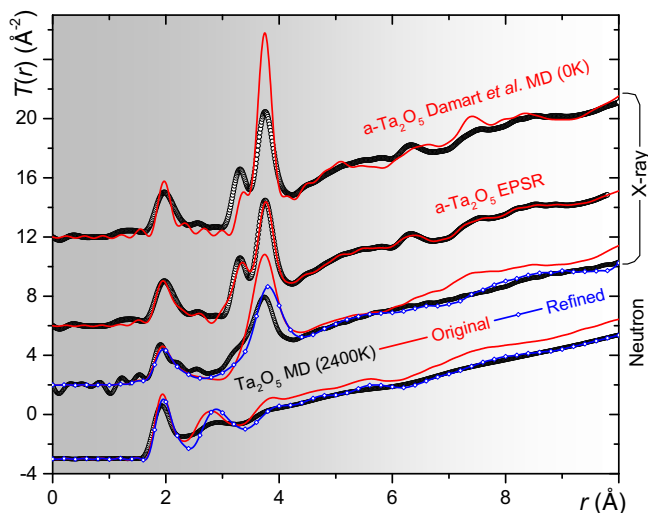


FIG. 8. Total correlation functions for liquid and solid-amorphous tantalum. The experimental data are repeated from Fig. 2, along with the a-Ta₂O₅ EPSR model, while the remaining solid curves represent MD models derived herein for the liquid and by Damart *et al.* [9] for the solid, in both cases using the potentials of Trinastic *et al.* [8], or refinements thereof.

structural arrangement. Notably these synthesis routes involve high-energy processes, in terms of the ion kinetic energy in the (dual-) IBS technique, or the thermal energy supplied during annealing of sol-gel materials. We therefore expect liquid and amorphous tantalum and niobia to display a phenomenology common with other single oxides. That is, coordination numbers which decrease during cooling of the liquid until frozen at a “glass transition,” engendering a denser amorphous phase constructed from more highly coordinated ions. This has recently been demonstrated experimentally for some binary-oxide glass formers [49,95] and explicitly in MD models of liquid and amorphous TiO₂ [66]. We have chosen not to perform an analogous MD study herein, based on the inability of existing, and modified, classical interatomic potentials to adequately reproduce the diffraction data, as discussed below.

D. Need for improved interatomic potentials

The a-Ta₂O₅ model derived by Damart *et al.* [9] is compared directly to real-space x-ray-diffraction data in Fig. 8. The position and asymmetry of the Ta-O peak are well reproduced. The fact that the model peak is somewhat narrower can be partially attributed to the temperature difference between the 0-K model and the room-temperature x-ray measurement. However, an additional factor is the smaller Ta-O (and O-Ta) coordination numbers in the MD model [see Fig. 6(a)]. The mean $n_{\text{TaO}} = 5.72$ and $n_{\text{OTa}} = 2.29$ of the MD a-Ta₂O₅ are more similar to our experimental findings for the liquid than for the amorphous solid (see Table III). Larger differences are evident in the Ta-Ta peaks (see Fig. 8). Although both model and experiment show a split Ta-Ta peak, the MD model has a much larger proportion of the Ta-Ta distances falling under the higher separation, “corner-sharing,” peak. This is consistent with the lower coordination numbers found for the

MD model, as compared to the experiment and EPSR models [see Fig. 6(a)].

A similar situation is observed in the liquid state. The position and asymmetry of the Ta-O peak are nicely reproduced, but the Ta-Ta peak appears biased to longer corner-sharing distances. The neutron-diffraction data show a less-sharp O-O peak as compared to the MD model. Notably the coordination numbers do not differ greatly between the liquid and amorphous solid states in the MD model, having mean values of $n_{\text{TaO}} = 5.84$ and $n_{\text{OTa}} = 2.34$ in the melt. This is in stark contrast to our findings, whereby a-Ta₂O₅ contains more highly coordinated ions than the melts (see Table III).

At this point the densities of the various models should be discussed. The MD potentials yield densities of amorphous tantalum of 7.96 [9] to 8.10 g cm⁻³ [8] that are higher than the experimental values of 7.30 to 7.68 g cm⁻³ [19,25,48]. While a degree of porosity in the amorphous films might lower their measured densities below the intrinsic bulk value, such a situation cannot be expected in the liquid state. At 2400 K, the molten tantalum MD model obtained herein converged to a density of 7.86 g cm⁻³. This is only slightly lower than the solid phase MD model, and much higher than the liquid tantalum density of 6.97 g cm⁻³ predicted on the basis of measurements on molten Nb₂O₅ [45] [see Eq. (2)]. Indeed, the MD liquid is denser than a-Ta₂O₅, as measured.

Therefore it can be concluded that the MD potentials lead to models of liquid and amorphous tantalum which are more dense than expected experimentally, that underestimate the thermal expansion, and that underestimate the coordination numbers and possibly their changes upon melt quenching as well.

It should not be too surprising that the Ta-O peak is well reproduced while the Ta-Ta peaks are not. After all, the Ta-O potential was refined in order to reproduce the structure and elastic constants of β - and δ -Ta₂O₅, as predicted from density functional theory, while the Ta-Ta interaction was not [8].

In order to improve on the set of interatomic potentials for tantalum, it seems highly likely that attractive non-Coulombic interactions between Ta-Ta pairs are necessary, in order to promote a larger degree of edge sharing of polyhedra. Such interactions have been shown to be important in a number of other molten oxides [66,67]. Results of a preliminary refinement, including non-Coulombic Ta-Ta interactions, are plotted in Fig. 8. The final density of the system was 6.98 g cm⁻³, in excellent agreement with the predicted 6.97 g cm⁻³ [45], by construction. While there is also improved agreement with the x-ray- and neutron-diffraction data, further room for improvement remains. It is possible that alternative forms of the Ta-Ta potential are necessary, or else polarizable or many-body potentials may be required. Indeed, differences in the polarizability of niobium and tantalum [98,99] may be the key to explaining many of the observed differences between niobite and tantalate materials.

V. CONCLUSIONS

Neutron and x-ray scattering data have been used to test existing molecular dynamics models based on classical interatomic potentials, and to derive models by empirical potential structure refinement of liquid and amorphous tantalum, as well as molten niobia, leading to the following conclusions.

(i) Molten Ta₂O₅ and Nb₂O₅ are isomorphous, with any differences at or below the 1% level. Their short-range structure comprises a mixture of five- and six-fold metal-oxygen polyhedra which are linked primarily by corner sharing, with a minority of edge sharing.

(ii) The main difference observed between the two melts is a Nb-O bond length 1% shorter than for Ta-O, at temperatures $T^* = T/T_{\text{melt}}$ scaled to the melting points.

(iii) Amorphous tantalum is denser than the liquid, and has higher coordination numbers, being built primarily from six- and seven-fold Ta-O polyhedra which link by edge sharing as well as corner sharing.

(iv) Ta-O and Nb-O peak bond lengths contract slightly with increasing temperature, implying a coordination decrease.

(v) The structural differences between the solid amorphous and liquid states are consistent with the phenomenology observed for some other molten oxides, both glass-forming and non-glass-forming, whereby coordination numbers increase during melt quenching to form an amorphous glassy phase. This in turn is consistent with the idea that a common progenitor metastable state is obtained during certain high-energy synthesis routes for amorphous solids, and that this may be identified with the supercooled liquid state from which traditional glasses are formed.

(vi) Existing classical interatomic potentials for tantalum oxide fail to completely reproduce the scattering data and expected densities. It is suggested that attractive (non-Coulombic) Ta-Ta interactions are important, particularly for obtaining the correct degree of edge sharing.

(vii) Ion-beam sputtered amorphous Ta₂O₅ causes small-angle x-ray scattering, consistent with other measurements which imply inhomogeneity on the nanometer scale. This poses

another, separate, challenge for molecular dynamics modeling, since very large numbers of atoms, $\sim 10^7$, are required to capture such density fluctuations.

Future work should include development of improved interatomic potentials for tantalum and niobium pentoxides which reproduce experimental data, including the observed differences between analogous tantalate and niobate systems; modeling of the structural changes accompanying melt quenching; detailed measurements and understanding of the nanometer scale inhomogeneity in a-Ta₂O₅; and neutron scattering from a-Ta₂O₅ to further constrain models and to test the predicted structure factor derived herein.

ACKNOWLEDGMENTS

Thanks to Prof. Gianpiero Cagnoli, director of the Institut Lumière Matière, France, for provision of the original amorphous tantalum film. Leighanne Gallington and Sam Sendelbach are thanked for assistance with beamline measurements at the SNS and APS, respectively. Thanks also to Stuart Reid of the University of the West of Scotland for bringing a-Ta₂O₅ to the attention of O.L.G.A. at a 2015 meeting of the Society of Glass Technology, UK. Work was supported by U.S. Department of Energy (DOE) under Grant No. SBIR DE-SC0015241 (O.L.G.A., A.T., and R.W.). This research used resources of the Advanced Photon Source, a DOE Office of Science User Facility operated for the DOE Office of Science by Argonne National Laboratory under Contract No. DE-AC02-06CH11357, and of the Spallation Neutron Source, a DOE Office of Science User Facility operated by the Oak Ridge National Laboratory.

-
- [1] A. Llodes, Y. Wang, A. Fernandez-Martinez, P. Xiao, T. Lee, A. Poulain, O. Zandi, C. A. Saez Cabezas, G. Henkelman, and D. J. Milliron, *Nat. Mater.* **15**, 1267 (2016).
- [2] J. H. Cartwright, A. G. Checa, J. D. Gale, D. Gebauer, and C. I. Sainz-Díaz, *Angew. Chem. Int. Ed.* **51**, 11960 (2012).
- [3] T. Bartels-Rausch, V. Bergeron, J. H. E. Cartwright, R. Escribano, J. L. Finney, H. Grothe, P. J. Gutiérrez, J. Haapala, W. F. Kuhs, J. B. C. Pettersson, S. D. Price, C. I. Sainz-Díaz, D. J. Stokes, G. Strazzulla, E. S. Thomson, H. Trinks, and N. Uras-Aytemiz, *Rev. Mod. Phys.* **84**, 885 (2012).
- [4] N. Kim, R. Bassiri, M. M. Fejer, and J. F. Stebbins, *J. Non-Cryst. Solids* **429**, 5 (2015).
- [5] N. Kim, R. Bassiri, M. M. Fejer, and J. F. Stebbins, *J. Non-Cryst. Solids* **405**, 1 (2014).
- [6] N. Kim and J. F. Stebbins, *J. Non-Cryst. Solids* **378**, 158 (2013).
- [7] J. P. Trinastic, R. Hamdan, C. Billman, and H.-P. Cheng, *Phys. Rev. B* **93**, 014105 (2016).
- [8] J. Trinastic, R. Hamdan, Y. Wu, L. Zhang, and H.-P. Cheng, *J. Chem. Phys.* **139**, 154506 (2013).
- [9] T. Damart, E. Coillet, A. Tanguy, and D. Rodney, *J. Appl. Phys.* **119**, 175106 (2016).
- [10] I. W. Martin, R. Bassiri, R. Nawrodt, M. M. Fejer, A. Gretarsson, E. Gustafson, G. Harry, J. Hough, I. MacLaren, S. Penn, S. Reid, R. Route, S. Rowan, C. Schwarz, P. Seidel, J. Scott, and A. L. Woodcraft, *Classical Quant. Grav.* **27**, 225020 (2010).
- [11] D. Crooks, P. Sneddon, G. Cagnoli, J. Hough, S. Rowan, M. Fejer, E. Gustafson, R. Route, N. Nakagawa, and D. Coyne, *Classical Quant. Grav.* **19**, 883 (2002).
- [12] S. D. Penn, P. H. Sneddon, H. Armandula, J. C. Betzwieser, G. Cagnoli, J. Camp, D. Crooks, M. M. Fejer, A. M. Gretarsson, and G. M. Harry, *Classical Quant. Grav.* **20**, 2917 (2003).
- [13] M. H. Gregory, R. A. Matthew, E. B.-T. Andres, A. Helena, B. Eric, D. Kate, E. Matt, N. Chinyere, V. Akira, D. R. M. Crooks *et al.*, *Classical Quant. Grav.* **24**, 405 (2007).
- [14] M. Granata, E. Saracco, N. Morgado, A. Cajgfinger, G. Cagnoli, J. Degallaix, V. Dolique, D. Forest, J. Franc, C. Michel, L. Pinard, and R. Flaminio, *Phys. Rev. D* **93**, 012007 (2016).
- [15] L. Zhu, J. Zhou, Z. Guo, and Z. Sun, *J. Phys. Chem. C* **120**, 2456 (2016).
- [16] J. H. Ju, S. K. Jang, H. Son, J.-H. Park, and S. Lee, *Nanoscale* **9**, 8373 (2017).
- [17] R. Bassiri, M. R. Abernathy, F. Liou, A. Mehta, E. K. Gustafson, M. J. Hart, H. N. Isa, N. Kim, A. C. Lin, I. MacLaren, I. W. Martin, R. K. Route, S. Rowan, B. Shyam, J. F. Stebbins, and M. M. Fejer, *J. Non-Cryst. Solids* **438**, 59 (2016).
- [18] R. Bassiri, F. Liou, M. R. Abernathy, A. C. Lin, N. Kim, A. Mehta, B. Shyam, R. L. Byer, E. K. Gustafson, M. Hart, I. MacLaren, I. W. Martin, R. K. Route, S. Rowan, J. F. Stebbins, and M. M. Fejer, *APL Mater.* **3**, 036103 (2015).

- [19] N. Banno, T. Sakamoto, N. Iguchi, M. Matsumoto, H. Imai, T. Ichihashi, S. Fujieda, K. Tanaka, S. Watanabe, S. Yamaguchi, T. Hasegawa, and M. Aono, *Appl. Phys. Lett.* **97**, 113507 (2010).
- [20] B. Shyam, K. H. Stone, R. Bassiri, M. M. Fejer, M. F. Toney, and A. Mehta, *Sci. Rep.* **6**, 32170 (2016).
- [21] M. J. Hart, R. Bassiri, K. B. Borisenko, M. Véron, E. F. Rauch, I. W. Martin, S. Rowan, M. M. Fejer, and I. MacLaren, *J. Non-Cryst. Solids* **438**, 10 (2016).
- [22] R. Bassiri, M. Hart, R. L. Byer, K. B. Borisenko, K. Evans, M. M. Fejer, A. C. Lin, I. MacLaren, A. S. Markosyan, and I. W. Martin, *J. Phys. Conf. Ser.* **522**, 012043 (2014).
- [23] R. Bassiri, K. Evans, K. Borisenko, M. Fejer, J. Hough, I. MacLaren, I. Martin, R. Route, and S. Rowan, *Acta Mater.* **61**, 1070 (2013).
- [24] R. Bassiri, K. Borisenko, D. Cockayne, J. Hough, I. MacLaren, and S. Rowan, *Appl. Phys. Lett.* **98**, 031904 (2011).
- [25] R. Bassiri, Ph.D. dissertation, University of Glasgow, 2011.
- [26] A. Glass, M. Lines, K. Nassau, and J. Shiever, *Appl. Phys. Lett.* **31**, 249 (1977).
- [27] K. M. Wetherall, P. Doughty, G. Mountjoy, M. Bettinelli, A. Speghini, M. F. Casula, F. Cesare-Marincola, E. Locci, and R. J. Newport, *J. Phys.: Condens. Matter.* **21**, 375106 (2009).
- [28] G. A. Rosales-Sosa, A. Masuno, Y. Higo, H. Inoue, Y. Yanaba, T. Mizoguchi, T. Umada, K. Okamura, K. Kato, and Y. Watanabe, *Sci. Rep.* **5**, 15233 (2015).
- [29] X. Ma, Z. Peng, and J. Li, *J. Am. Ceram. Soc.* **98**, 770 (2015).
- [30] T. Suzuki and A.-M. Anthony, *Mater. Res. Bull.* **9**, 745 (1974).
- [31] K. Yoshimoto, A. Masuno, M. Ueda, H. Inoue, H. Yamamoto, and T. Kawashima, *J. Am. Ceram. Soc.* (2018), doi:10.1111/jace.15484.
- [32] R. D. Shannon, *Acta Crystallogr. A* **32**, 751 (1976).
- [33] I. D. Brown and D. Altermatt, *Acta Crystallogr. B* **41**, 244 (1985).
- [34] Y.-N. Wu, L. Li, and H.-P. Cheng, *Phys. Rev. B* **83**, 144105 (2011).
- [35] L. A. Reznichenko, V. V. Akhnazarova, L. A. Shilkina, O. N. Razumovskaya, and S. I. Dudkina, *Crystallography Reports* **54**, 483 (2009).
- [36] Y. Yang and Y. Kawazoe, *Phys. Rev. Mater.* **2**, 034602 (2018).
- [37] G. Mohanty, L. Fiegel, and J. Healy, *J. Phys. Chem.* **68**, 208 (1964).
- [38] W. Mertin, S. Andersson, and R. Gruehn, *J. Solid State Chem.* **1**, 419 (1970).
- [39] F. Laves, W. Petter, and H. Wulf, *Naturwissenschaften* **51**, 633 (1964).
- [40] L. Aleshina and S. Loginova, *Crystallography Reports* **47**, 415 (2002).
- [41] S. Andersson, *Z. Anorg. Allg. Chem.* **351**, 106 (1967).
- [42] T. Ercit, *Mineral. Petrol.* **43**, 217 (1991).
- [43] N. Stephenson and R. Roth, *J. Solid State Chem.* **3**, 145 (1971).
- [44] K. Kato, *Acta Crystallogr. Sect. B* **32**, 764 (1976).
- [45] N. Ikemiya, J. Umemoto, S. Hara, and K. Ogino, *ISIJ Int.* **33**, 156 (1993).
- [46] J. K. R. Weber, J. J. Felten, and P. C. Nordine, *Rev. Sci. Instrum.* **67**, 522 (1996).
- [47] M. Maurakh, B. Mitin, and M. Roitberg, *Industrial Laboratory* **33**, 984 (1967).
- [48] T. Li, F. A. Aguilar Sandoval, M. Geitner, L. Bellon, G. Cagnoli, J. Degalliax, V. Dolique, R. Flaminio, D. Forest, M. Granata, C. Michel, N. Morgado, and L. Pinard, *Phys. Rev. D* **89**, 092004 (2014).
- [49] O. L. G. Alderman, C. J. Benmore, A. Tamalonis, S. Sendelbach, S. M. Heald, and R. Weber, *J. Phys. Chem. C* **120**, 26974 (2016).
- [50] J. K. R. Weber, S. Krishnan, C. D. Anderson, and P. C. Nordine, *J. Am. Ceram. Soc.* **78**, 583 (1995).
- [51] L. Gao, F. Lemarchand, and M. Lequime, *Opt. Express* **20**, 15734 (2012).
- [52] T. J. Bright, J. I. Watjen, Z. M. Zhang, C. Muratore, A. A. Voevodin, D. I. Koukis, D. B. Tanner, and D. J. Arenas, *J. Appl. Phys.* **114**, 083515 (2013).
- [53] See Supplemental Material at <http://link.aps.org/supplemental/10.1103/PhysRevMaterials.2.043602> for comparisons of diffraction data showing effects of substrate masking, Fourier filtering, atmospheric gas composition, incident x-ray energy, small-angle x-ray scattering, and comparison to published grazing incidence x-ray diffraction.
- [54] A. P. Hammersley, S. O. Svensson, M. Hanfland, A. N. Fitch, and D. Hausermann, *High Pressure Res.* **14**, 235 (1996).
- [55] L. B. Skinner, C. J. Benmore, and J. B. Parise, *Nucl. Instrum. Meth. A* **662**, 61 (2012).
- [56] A. K. Soper and E. R. Barney, *J. Appl. Cryst.* **44**, 714 (2011).
- [57] J. Neufeind, M. Feyngenson, J. Carruth, R. Hoffmann, and K. K. Chipley, *Nucl. Instrum. Meth. B* **287**, 68 (2012).
- [58] L. B. Skinner, C. J. Benmore, J. K. R. Weber, S. Tumber, L. Lazareva, J. Neufeind, L. Santodonato, J. Du, and J. B. Parise, *J. Phys. Chem. B* **116**, 13439 (2012).
- [59] O. L. G. Alderman, A. C. Hannon, D. Holland, and N. Umesaki, *J. Non-Cryst. Solids* **386**, 56 (2014).
- [60] A. C. Hannon, in *Modern Glass Characterisation*, edited by M. Affatigato (Wiley, New York, 2015), p. 1.
- [61] A. K. Soper, *Chem. Phys.* **202**, 295 (1996).
- [62] A. K. Soper, *Phys. Rev. B* **72**, 104204 (2005).
- [63] B. W. H. van Beest, G. J. Kramer, and R. A. van Santen, *Phys. Rev. Lett.* **64**, 1955 (1990).
- [64] W. Smith and T. R. Forester, *J. Mol. Graphics* **14**, 136 (1996).
- [65] L. Gallington, Y. Ghadar, L. Skinner, J. Weber, S. Ushakov, A. Navrotsky, A. Vazquez-Mayagoitia, J. Neufeind, M. Stan, J. Low, and C. Benmore, *Materials* **10**, 1290 (2017).
- [66] O. L. G. Alderman, L. B. Skinner, C. J. Benmore, A. Tamalonis, and J. K. R. Weber, *Phys. Rev. B* **90**, 094204 (2014).
- [67] L. B. Skinner, C. J. Benmore, J. K. R. Weber, J. Du, J. Neufeind, S. K. Tumber, and J. B. Parise, *Phys. Rev. Lett.* **112**, 157801 (2014).
- [68] L. B. Skinner, C. J. Benmore, J. K. R. Weber, M. A. Williamson, A. Tamalonis, A. Hebden, T. Wiencek, O. L. G. Alderman, M. Guthrie, L. Leibowitz, and J. B. Parise, *Science* **346**, 984 (2014).
- [69] PFIT, <http://www.alexhannon.co.uk/> (accessed 18 Jan. 2011).
- [70] A. C. Wright, in *Experimental Techniques of Glass Science*, edited by C. J. Simmons and O. H. El-Bayoumi (American Ceramic Society, Westerville, OH, 1993), p. 205.
- [71] L. A. Aleshina, V. P. Malinenko, A. D. Phouphanov, and N. M. Jakovleva, *J. Non-Cryst. Solids* **87**, 350 (1986).
- [72] U. Hoppe, R. Kranold, and E. Gattf, *Solid State Commun.* **108**, 71 (1998).

- [73] U. Hoppe, R. Kranold, A. Barz, D. Stachel, and J. Neuefeind, *Solid State Commun.* **115**, 559 (2000).
- [74] Q. Mei, C. J. Benmore, S. Sen, R. Sharma, and J. L. Yarger, *Phys. Rev. B* **78**, 144204 (2008).
- [75] M. Micoulaut, L. Cormier, and G. S. Henderson, *J. Phys.: Condens. Matter* **18**, R753 (2006).
- [76] O. L. G. Alderman, G. Ferlat, A. Baroni, M. Salanne, M. Micoulaut, C. J. Benmore, A. Lin, A. Tamalonis, and J. K. R. Weber, *J. Phys.: Condens. Matter* **27**, 455104 (2015).
- [77] Q. Mei, C. J. Benmore, E. Soignard, S. Amin, and J. L. Yarger, *J. Phys.: Condens. Matter* **19**, 415103 (2007).
- [78] V. Petkov, G. Holzhüter, U. Tröge, T. Gerber, and B. Himmel, *J. Non-Cryst. Solids* **231**, 17 (1998).
- [79] T. T. Duong, T. Iitaka, P. K. Hung, and N. Van Hong, *J. Non-Cryst. Solids* **459**, 103 (2017).
- [80] Y. Kono, C. Kenney-Benson, D. Ikuta, Y. Shibazaki, Y. Wang, and G. Shen, *Proc. Natl. Acad. Sci. USA* **113**, 3436 (2016).
- [81] P. Lamparter and R. Kniep, *Physica B* **234**, 405 (1997).
- [82] G. Gutierrez and B. Johansson, *Phys. Rev. B* **65**, 104202 (2002).
- [83] S. Davis and G. Gutiérrez, *J. Phys.: Condens. Matter* **23**, 495401 (2011).
- [84] T. Kokubo, M. Nishimura, and M. Tashiro, *J. Non-Cryst. Solids* **15**, 329 (1974).
- [85] M. Imaoka, T. Yamazaki, and I. Yasui, Rep. Inst. Ind. Sci. Univ. Tokyo, Japan **31**, 59 (1984).
- [86] T. Yamazaki, M. Imaoka, and I. Yasui, Rep. Inst. Ind. Sci. Univ. Tokyo, Japan **31**, 103 (1984).
- [87] M. Imaoka and T. Yamazaki, Rep. Inst. Ind. Sci. Univ. Tokyo, Japan **24**, 27 (1975).
- [88] A. Masuno, S. Kohara, A. C. Hannon, E. Bychkov, and H. Inoue, *Chem. Mater.* **25**, 3056 (2013).
- [89] M. Imaoka and T. Yamazaki, Rep. Inst. Ind. Sci. Univ. Tokyo, Japan **6**, 127 (1957).
- [90] M. Imaoka and T. Yamazaki, *J. Ceram. Assoc. Japan* **71**, 215 (1963).
- [91] V. Filonenko and I. Zibrov, *Inorg. Mater.* **37**, 953 (2001).
- [92] I. Zibrov, V. Filonenko, M. Sundberg, and P.-E. Werner, *Acta Crystallogr. Sect. B* **56**, 659 (2000).
- [93] S. Maeng, L. Axe, T. Tyson, and A. Jiang, *J. Electrochem. Soc.* **152**, B60 (2005).
- [94] N. Kim and J. F. Stebbins, *Chem. Mater.* **23**, 3460 (2011).
- [95] O. L. G. Alderman, M. Liska, J. Machacek, C. J. Benmore, A. Lin, A. Tamalonis, and J. K. R. Weber, *J. Phys. Chem. C* **120**, 553 (2016).
- [96] S. V. Sukhomlinov and M. H. Müser, *J. Chem. Phys.* **146**, 024506 (2017).
- [97] O. L. G. Alderman, C. J. Benmore, A. Lin, A. Tamalonis, and J. K. R. Weber, *J. Am. Ceram. Soc.* (2018), doi:10.1111/jace.15529.
- [98] L. Ma, J. Indergaard, B. Zhang, I. Larkin, R. Moro, and W. A. de Heer, *Phys. Rev. A* **91**, 010501 (2015).
- [99] T. Gould and T. Bučko, *J. Chem. Theory Comput.* **12**, 3603 (2016).
- [100] V. F. Sears, *Neutron News* **3**, 26 (1992).