

Short-Range Disorder in TeO₂ Melt and Glass

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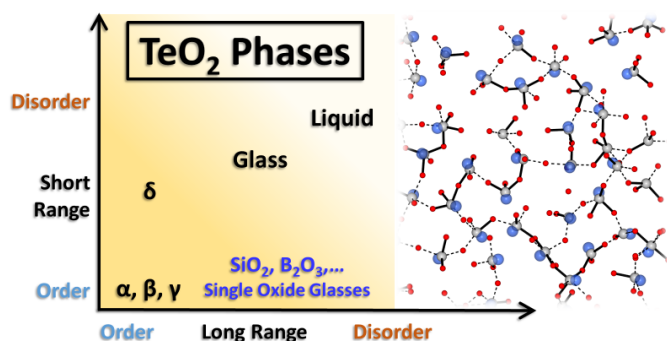
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Abstract

*High-resolution x-ray pair distribution functions for molten and glassy TeO₂ reveal coordination numbers $n_{\text{TeO}} \approx 4$. However, distinct from the known α -, β - and γ -TeO₂ polymorphs, there is considerable short-range disorder such that no clear cutoff distance between bonded and non-bonded interactions exists. We suggest that this is likely similar to disorder in δ -TeO₂ and arises from a broad distribution of asymmetric Te–O–Te bridges, something that we observe becomes increasingly asymmetric with increasing liquid temperature. Such behavior is qualitatively consistent with existing interpretations of Raman scattering spectra, and equivalent to temperature-induced coordination number reduction, for sufficiently large cutoff radii. Therefore, TeO₂ contains a distribution of local environments that are, furthermore, temperature dependent, making it distinct from the canonical single-oxide glass formers. Our results are in good agreement with high-level *ab initio* cluster calculations.*

TOC Graphic



Tellurium dioxide is an enigmatic compound with several known crystalline polymorphs and which can, reluctantly, be melt-quenched to form a single-oxide glass in bulk.¹ This latter property is shared by only a handful of oxides (B_2O_3 , SiO_2 , GeO_2 , P_2O_5 , V_2O_5 , As_2O_3 , Sb_2O_3 , TeO_2) and of these only the latter three are based on lone-pair cations with non-bonding s -electron pairs. Stereochemical activity of the cationic lone-pairs leads to highly asymmetrical coordination polyhedra with just a few short, strong bonds to oxygen forming on the opposite side of the cation. As such, at least the first two of Zachariasen's topological rules² for glass formation are satisfied in the 'lone-pair oxide' glasses. While diffraction measurements on the lone-pair oxide glasses indicate well-defined trigonal pyramidal coordination polyhedra for As^{3+} ,³ and Sb^{3+} ,⁴ the coordination of Te^{4+} to oxygen is less clear-cut, with a range of values between $3.6 < n_{TeO} \lesssim 4.0$ reported.⁵⁻¹⁰ The differences are important because $n_{TeO} < 4$ implies the existence of non-bridging, or terminal, $Te=O$ groups, the fraction of oxygen in such groups being $f_{TO} = 2 - n_{TeO}/2 = 2 - n_{OTe}$.⁵ Clarifying the local coordination environment in TeO_2 glass is therefore important for understanding structure-property relationships in tellurite glasses and enabling property prediction and optimization. Indeed, considering their wide infrared transmission windows, high refractive indices and non-linear optical susceptibilities,¹¹ glasses based on TeO_2 are promising materials for various optical devices, including photonic switches. The optical non-linearity in particular is strongly influenced by the local structural arrangements.¹²⁻¹³

It can often be conducive to consider the melt structure alongside that of the ambient glass,^{8,14} especially considering that glasses are always derived by (sufficiently rapid) cooling from the liquid state. The structure and transport properties of the (supercooled) liquid phase also control crystal growth and are required for its optimization.¹⁵ Moreover, molten oxides are important materials in their own right as high-temperature hermetic seals and oxide ion conducting electrolytes for fuel cells and gas separation membranes, including those based on molten TeO_2 .¹⁶⁻¹⁷ Although the structure of molten TeO_2 is less well studied than that of the glass, a recent Raman spectroscopic investigation⁸ has been interpreted in terms of a declining $Te-O$ coordination number with increasing temperature, along with a concomitant increase in the number of $Te=O$ doubly bonded terminal oxygen groups. *Ab-initio* molecular dynamics (MD) simulations¹⁸ support this interpretation to some extent, although the liquid states studied were highly pressurized due to the use of a fixed density, something which likely suppresses the coordination decrease. The existence of $Te=O$ groups in TeO_2 glass, based on values of $n_{TeO} < 4$,⁵ has been somewhat contentious⁶ and it has been recognized that the method of determination of n_{TeO} ,⁹ as well as the definition of what constitutes a bonded interaction⁶ must be considered.

In this *Letter* we use high-energy x-ray diffraction to obtain high-resolution pair distribution functions for both molten and glassy TeO_2 . X-ray diffraction is relatively less sensitive to scattering contributions from $O-O$ pairs than is neutron diffraction,^{5, 10} and in this way, it is more sensitive to the $Te-O$ distance distribution, especially the longer $Te-O$ interatomic distances, as well as those of $Te-Te$ pairs. We are able to demonstrate unequivocally that the short $Te-O$ bonds present in TeO_2 glass become shorter, and stronger, in the high-temperature liquid, something which is typically associated with a reduction in coordination number,¹⁹⁻²⁰ and which is qualitatively consistent with interpretations of Raman scattering spectra.⁸ This has implications for the MD modelling of TeO_2 glass, because the hyperquenching necessitated by the short accessible timescales may freeze-in an unrealistically low $Te-O$ coordination

number. Furthermore, we show that a highly asymmetric Te–O distance distribution persists in the liquid state, such that no clear cutoff distance between bonded and non-bonded interactions exists. We support our findings with high-level *ab initio* relaxations of amorphous TeO₂ clusters, and discuss the consequences of this on the debate concerning TeO₂ glass structure. We favor a qualitative description within which $n_{\text{TeO}} \approx 4$ but with a wide distribution of asymmetric Te–O–Te bridges that becomes increasingly asymmetric with increasing temperature in the liquid, effectively lowering n_{TeO} below that of the glass, for sufficiently large cutoff radii.

High-energy x-ray diffraction measurements were made at beamline 6-ID-D of the Advanced Photon Source. TeO₂ glass was prepared as described elsewhere,^{1, 7} followed by grinding to a powder with an agate pestle and mortar. The fine powder was loaded into a thin-walled borosilicate glass capillary of 1.5 mm internal diameter and the diffraction pattern recorded using an incident beam energy of 100.36 keV and a flat-panel Varex 4343CT detector (2880 × 2880 pixels of 150 μm × 150 μm) for a total of 15 minutes. An empty capillary was also measured for the purpose of background subtraction. The sample-to-detector distance of 346.9 mm was calibrated by measurement of a sample of NIST standard CeO₂. For the study of molten TeO₂, polycrystalline samples were first formed from TeO₂ powder into beads of ~3 mm diameter using a laser hearth melter.²¹ A 53.93mg sample was floated on a stream of pure O₂ gas in a converging-diverging conical nozzle aerodynamic levitator.¹⁹⁻²⁰ A 10.6 μm CO₂ gas laser was weakly focused onto the top of the sample as the heating source, and the x-ray beam (200 μm high × 500 μm wide) passed through this upper portion of the levitated molten droplet. X-rays of 89.63 keV were used, along with a Perkin Elmer XRD1621 detector (2048 × 2048 pixels of 200 μm × 200 μm) for a measurement duration of 42 s. The empty levitator with gas flowing was also measured for the purpose of background subtraction, and the sample-to-detector distance of 345.3 mm was calibrated by measurement of a sample of NIST standard CeO₂. Temperature measurement was made using a 1.55 μm optical pyrometer, however, sample melting was clearly observed at apparent temperatures of ~800 K, far lower than the known melting point of $T_m = 1005$ K. Although the spectral emissivity of TeO₂ has been reported to be as low as 0.31,¹⁵ this does not account for such a low apparent temperature, and partial infrared transparency of the sample at 1.55 μm is implied. We estimate our measurement temperature to be ~1100 K since a moderate amount of overheating (above T_m) is required to overcome temperature gradients within the partially molten sample and obtain complete melting. Separate experiments using a 5 μm pyrometer were found to be consistent with an emissivity of 0.343, based on the temperature of recalescence observed during crystallization upon cooling. The temperature of the fully molten droplet calculated with this value for the emissivity was 1134 ± 46 K, however it is not clear if partial transparency, even at 5 μm, does not also contribute to the low apparent temperature. Retention of TeO₂ stoichiometry is supported by the white (not discolored) appearance of the recovered solidified bead within the levitator, and by x-ray diffraction of the same, with Bragg peak positions matching those expected for the thermodynamically stable α -TeO₂ polymorph (Fig. S1). It is also worth noting that separate experiments performed with high-purity argon as the levitation gas showed enhanced sample mass losses (10.1% over 20 s) compared to in oxygen (3.8% over 42 s), and diffraction data (100.32 keV) could not be effectively normalized assuming a stoichiometric TeO₂ composition. These observations, along with the known redox behavior of tellurium,²² suggest partial reduction of Te⁴⁺ to metallic Te⁰ in the melt in argon atmosphere.

All collected diffraction patterns were corrected and reduced as described elsewhere²⁰ to obtain the x-ray structure factors $S(Q)$ plotted in Fig. 1 and total correlation functions $T(r)$ presented in Fig. 2.

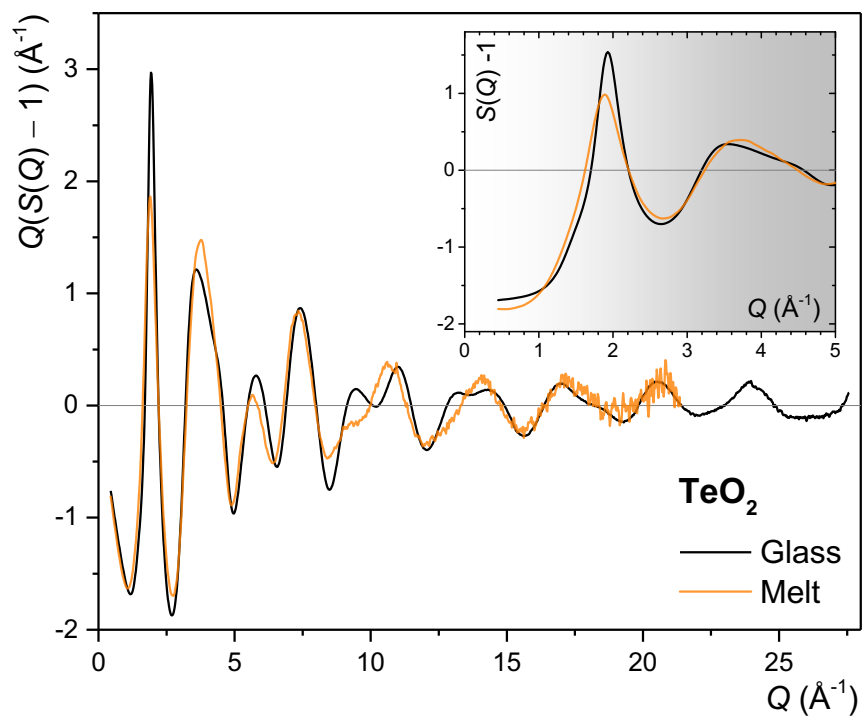


Figure 1: X-ray interference functions, $Q(S(Q) - 1)$, for molten and glassy TeO_2 . The structure factors, $S(Q) - 1$, are shown inset for $Q \leq 5 \text{\AA}^{-1}$, where the shift of the first diffraction peak to lower Q in the melt is more clearly visible.

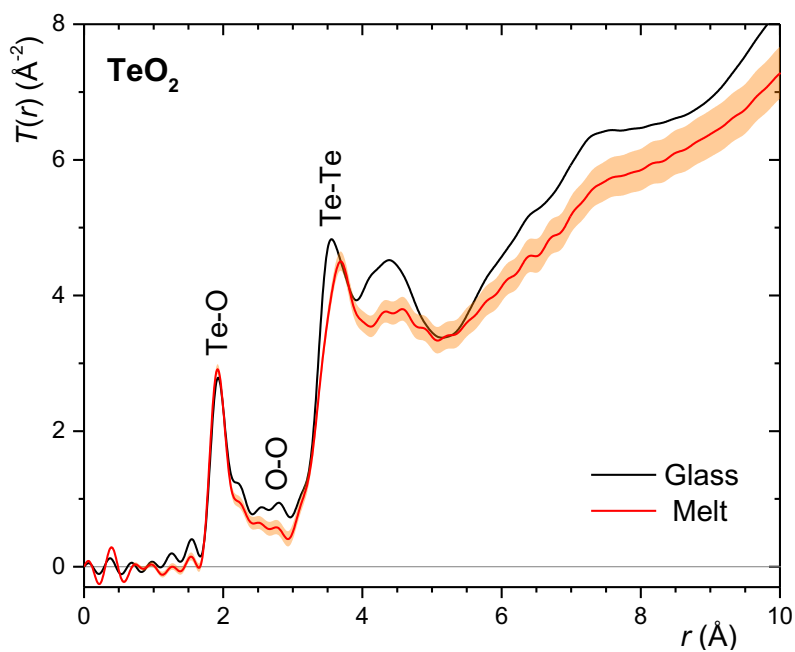


Figure 2: X-ray total correlation functions obtained by sine Fourier transform of the interference functions of Fig. 1, using a $Q_{\max} = 21.39 \text{ \AA}^{-1}$ and step modification function which yields the highest possible resolution. The shaded region represents the range of results based on a melt density of $5.09 \pm 0.27 \text{ gcm}^{-3}$.

In order to quantitatively interpret total scattering diffraction data the bulk density is required.²⁰ For TeO_2 glass we take the density to be 5.65 gcm^{-3} , in good agreement with direct measurements^{1, 7, 9} as well as linear extrapolation of binary tellurite glass densities.²³ For molten TeO_2 we are aware of only a single, unverified value of 5.5 gcm^{-3} at an unspecified temperature.¹⁵ Based on the thermal expansion of paratellurite ($\alpha\text{-TeO}_2$)²⁴ however, a lower melt density might be expected, see Fig. S2. As such, we analyze our data for molten TeO_2 for a range of densities of $5.09 \pm 0.27 \text{ gcm}^{-3}$.

We note that a melt density lower than that of the glass is supported by the shift of the first diffraction peak (FDP) to lower Q in the melt, Fig. 1 (inset). Lower Q corresponds to a larger real-space periodicity, in this case of the Te–Te pair distribution, which can be seen in the $D(r)$ of Fig. S4, as well as in the increased nearest-neighbor Te–Te distance in the melt clearly evident in Fig. 2. If the melt were denser than the glass, the TeO_2 (supercooled) liquid would have to display negative thermal expansion, which would put it into the category of anomalous liquids such as supercooled liquid silica or water.

In order to gain detailed insight into the distribution of Te–O distances in molten and glassy TeO_2 , we deconvolute the $T(r)$ and obtain the radial distribution function $\text{RDF}_{\text{TeO}}(r) = c_{\text{O}}T_{\text{TeO}}(r)$ as described in the supporting information (SI), and plotted in Fig. 3. By combining our x-ray diffraction data for TeO_2 glass with published neutron diffraction data⁵ we are able to show that the contribution from the O–O pair term is negligible for $r \lesssim 2.4 \text{ \AA}$, Fig. S7, and small beyond this. Thus, the running coordination numbers $n_{\text{TeO}}(r)$, also plotted in Fig. 3, truly correspond to the Te–O coordination number up to $r \approx 2.4 \text{ \AA}$. Clearly the $n_{\text{TeO}}(r)$ show no indication of a plateau and therefore no unambiguous delineation between bonded and non-bonded coordination shells. Based on the x-ray-neutron difference function, Fig. S7, this conclusion holds for the glass out to at least 3.0 \AA (where the Te–Te pair term starts to contribute), and is consistent with our *ab initio* calculations of the structure of amorphous TeO_2 clusters (Fig. 3, see SI). This is in contrast to the known structures of the α -, β - and γ - TeO_2 crystalline polymorphs, all of which show a plateau at $n_{\text{TeO}}(r \approx 2.4 \text{ \AA}) = 4$, even when accounting for thermal and instrumental broadening effects (see e.g. γ - TeO_2 in Fig. 3). This difference between the amorphous and crystalline structures is likely due to the presence of a distribution of local coordination environments in liquid and glassy TeO_2 , perhaps similar to that expected in the disordered δ - TeO_2 phase.²⁵⁻²⁶

There are some subtle but clear differences between the bonding in glassy and molten TeO_2 . By peak fitting²⁷ to the $T(r)$ of Fig. 2, a slightly shorter peak bond distance of $1.919(2) \text{ \AA}$ can be found for the melt, compared to $1.926(1) \text{ \AA}$ in the glass. This is the opposite to what would be expected for *isotropic* thermal expansion of a fixed coordination environment. However, the long Te–O bonds will experience greater anisotropy in their thermal variations which can lead to an overall contraction of the short bonds to compensate. At a certain point, if the long bonds become long and weak enough, they will no longer ‘qualify’ as bonded interactions and the overall effect is a drop in coordination number. This is exactly what has been suggested based on detailed analysis of the Raman spectra of molten and glassy TeO_2 .⁸

The question as to how asymmetric a Te–O–Te bridge can become before it is considered broken to form a Te=O group may not have an unambiguous answer, and this has likely contributed to the debate over the structure of TeO₂ glass.

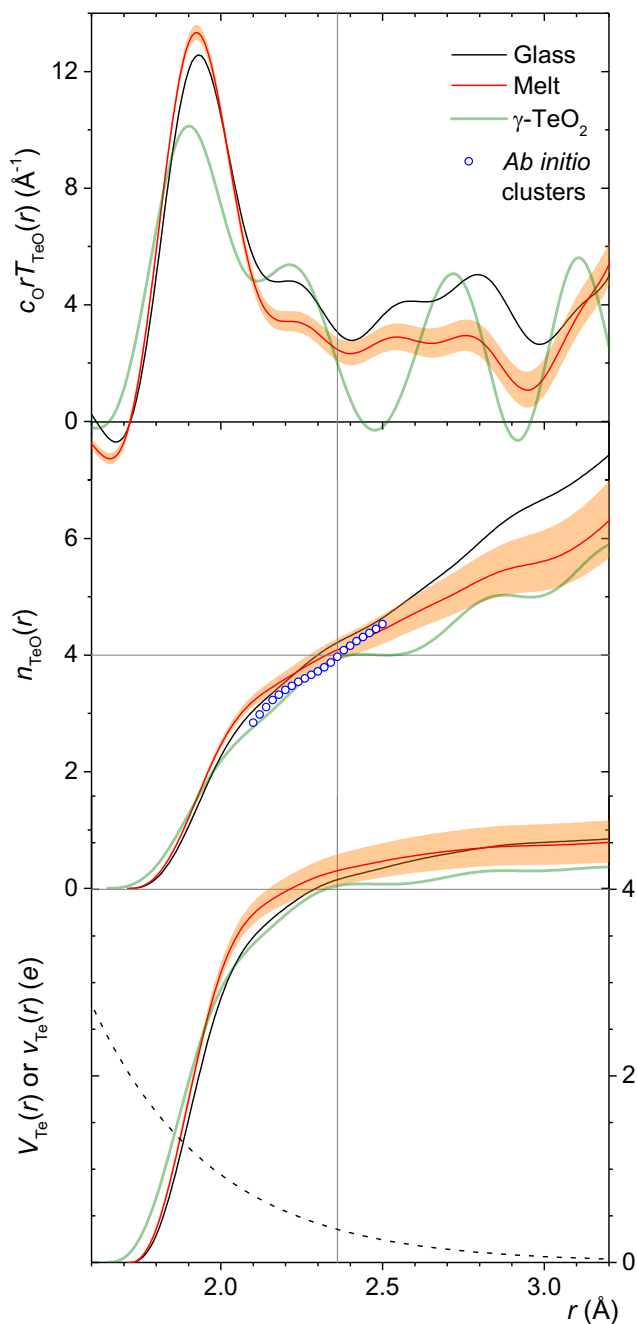


Figure 3: Upper panel: X-ray radial distribution functions (RDFs) with the Q -dependent Te–O pair weighting divided out, prior to sine Fourier transform of the interference functions of Fig. 1, using $Q_{\max} = 21.39 \text{ \AA}^{-1}$. Also shown is the Te–O RDF in $\gamma\text{-TeO}_2$,²⁸ calculated using the XTAL program,²⁹ and convolved with the same instrumental broadening as the x-ray data, and a thermal broadening of 0.07 \AA . Middle panel: Running Te–O coordination numbers ($n_{\text{TeO}}(r)$), obtained by integration of the RDFs with the lower

limit of the integral set to the zero-crossing at $\sim 1.72(1)$ Å. Results of our *ab initio* amorphous cluster calculations are also shown (blue circles, see supporting information). Lower panel: Running bond valence sums for Te obtained similarly to the $n_{\text{TeO}}(r)$, but after weighting by $v_{\text{Te}}(r) = \exp(R_{\text{TeO}} - r)/b$ (dashed line) prior to integration.³⁰

Taking the somewhat arbitrary cutoff radius of 2.36 Å (similar to that used elsewhere)^{5, 9-10, 18} we obtain $n_{\text{TeO}}(2.36 \text{ Å}) = 4.22$ in the glass, and $n_{\text{TeO}}(2.36 \text{ Å}) = 4.09 \pm 0.20$ in the melt. Thus the coordination number is close to four with only a hint that it may be lower in the melt, especially considering that the statistical uncertainties are ~ 0.1 . However, using a single arbitrary cutoff can be misleading. Looking at the running $n_{\text{TeO}}(r)$ in Fig. 3 it is clear that the value initially rises more steeply for the melt than for the glass, crossing over somewhere between 2.15 Å and 2.55 Å such that the coordination number is larger in the glass only for sufficiently large cutoff radius. This means that the longer Te–O bonds are more important for satisfying the bonding requirements of Te^{4+} in the glass than in the melt, where the shorter bonds are stronger and more dominant.

Another way to consider the relative importance of bonds is through the running bond-valence sum:³⁰

$$V_{\text{Te}}(r) = c_{\text{O}} \int_0^r r' n_{\text{TeO}}(r') e^{\left(\frac{R_{\text{TeO}} - r'}{b}\right)} dr'. \quad (1)$$

Equation 1 is identical to the definition of the running coordination number, except for the inclusion of the bond-valence weighting factor, $v_{\text{Te}}(r) = \exp(R_{\text{TeO}} - r)/b$ (Fig. 3), where $R_{\text{TeO}} = 1.977$ Å is the bond-valence parameter and $b = 0.37$ Å a universal empirical constant.³¹ The results from applying equation 1 to our data are shown in Fig. 3. It is clearly evident that the bond-valence sum reaches the formal tellurium valence ($V_{\text{Te}} = 4$) at shorter radial cutoff in the melt than in the glass, and longer bonds are more important in the glass for bringing $V_{\text{Te}}(r)$ up to the same asymptotic value as in the liquid. We note that bond-valence parameters are expected to increase with temperature^{14, 20} due to thermal expansion, and that this would enhance the difference in $V_{\text{Te}}(r)$ between liquid and glass, as would any increase in the melt density.

In summary the TeO_2 liquid-glass system is distinct from other single-oxide glass formers, particularly the canonical network formers B_2O_3 , SiO_2 , GeO_2 and P_2O_5 , in that its structure incorporates short-range disorder. This is likely similar to that expected in disordered crystalline $\delta\text{-TeO}_2$,²⁵⁻²⁶ and leads to a poorly defined coordination number ($n_{\text{TeO}} \approx 4$) which has contributed to some confusion in the literature. We propose that the disorder manifests as a distribution of asymmetric Te–O–Te bridges, and that higher temperatures enhance this asymmetry. The latter is qualitatively consistent with coordination number reduction, as inferred from Raman spectroscopy,⁸ although this is only quantitatively observed by diffraction measurements when evaluating n_{TeO} out to sufficiently large cutoff radii. The extent to which doubly bonded Te=O groups are present is therefore somewhat subjective in that these may simply be oxygen ions within highly asymmetrical Te–O–Te bridges.

Supporting Information

Diffraction patterns of polycrystalline samples prior to and post melting experiments. Summary of density data for TeO₂ phases and estimates for the liquid. Comparison of independently measured x-ray diffraction datasets for TeO₂ glass. $D(r)$ functions showing medium range correlations out to 20 Å. Description of the derivation of the radial distribution functions, running Te–O coordination numbers and bond-valence sums. Description of the derivation of x-ray-neutron difference functions used for eliminating the contribution of O–O correlations from the diffraction data for TeO₂ glass. Computational details for amorphous TeO₂ cluster production and analysis.

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