

Comprehensive Structural Study of Glassy BaTi₂O₅

The structures of glassy BaTi₂O₅ fabricated by the containerless method were comprehensively investigated by combined X-ray and neutron diffraction analyses, X-ray absorption near-edge structure (XANES) analyses and computer simulations. The three-dimensional atomic structure of glassy BaTi₂O₅ (*g*-BaTi₂O₅), simulated by reverse Monte Carlo (RMC) modelling using diffraction data, shows that extremely distorted TiO₅ polyhedra interconnected with both corner- and edge-shared oxygen formed a structure with a higher packing density than that of conventional silicate glass linked only by the corner-sharing of SiO₄ polyhedra. Our results show that the glass-forming ability enhanced by containerless processing, not by a 'strong glass former', resulted in the fabrication of new bulk oxide glasses with novel structures and properties.

BaTi₂O₅ glass spheres were fabricated using containerless processing in an aerodynamic levitation furnace (ALF) [1]. The X-ray diffraction experiments were performed at beamline BL04B2 of SPring-8 [2]. The neutron diffraction measurement for glassy sphere was carried out in the HIT-II spectrometer installed at the pulsed neutron source in the High Energy Accelerator Research Organization. The XANES spectra of the Ti *K*-edge were collected in the transmission mode at the undulator beamline NW14A of the PF-AR. The structure modelling of *g*-BaTi₂O₅ was performed by reverse Monte Carlo (RMC) simulation on an ensemble of 4000, starting with a random configuration.

Figure 1 shows the X-ray and neutron structure factors $S(Q)$ as a function of the wave vector of *g*-BaTi₂O₅ together with the results of RMC simulation. It is noted that the agreement between

the experimental data and the data obtained using the RMC model is excellent.

The derived total correlation functions $T(r)$ are shown in Fig. 2. The first peak in $T(r)$ was assigned to the Ti-O bond length, which is 1.92 Å in *g*-BaTi₂O₅, as determined from a positive peak of X-ray diffraction and a negative peak of neutron diffraction. The negative peak is due to the negative neutron scattering length of Ti. Intriguingly, the peak is skewed toward the high-*r* side, indicating the distribution of Ti-O distances from 1.60 Å to 2.50 Å due to highly distorted polyhedra. A fitting of the Ti-O peak using two Gaussian functions yielded two Ti-O correlation lengths at 1.91 Å and 2.13 Å, and the average coordination numbers $N_{\text{Ti-O}}$ obtained are 4.87 ± 0.15 for X-ray data and 5.05 ± 0.15 for neutron data. In the case of alkali titanium silicate glass, TiO₅ polyhedra generally exhibit a square pyramid having one shorter Ti-O bond and four longer Ti-O bonds [3]. In contrast to this, the partial pair distribution function $g_{ij}(r)$ of Ti-O derived using the RMC model shows a prominent peak at 1.90 Å that corresponds to the four shorter Ti-O bonds and a small peak at 2.10–2.5 Å corresponding to one longer Ti-O bond. A strong peak at 2.80 Å in the neutron data indicates the correlation length of O-O.

Figure 3(a) represents the distributions of Ti-O and Ba-O polyhedra obtained from the RMC configuration. Inhomogeneous distributions of Ti and Ba appear to exist within a space of 20 Å × 20 Å × 10 Å modeled by RMC simulation. The same tendency of forming Ti-rich and Ba-rich regions was observed by the RMC simulation of a titanium-silicate glass [4]. In the Ti-rich region, distorted trigonal bipyramidal TiO₅ was connected by both edge- and corner-sharing to form network rings (Fig. 3(b)). The Ti-O network was

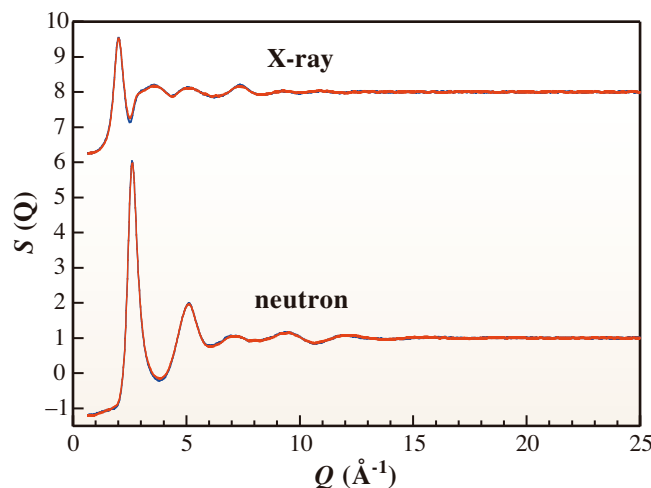


Fig. 1. Total structure factors $S(Q)$ of *g*-BaTi₂O₅ (blue, experimental data; red, RMC simulation data). The different features of the X-ray and neutron structure factors are due to the different scattering amplitudes of Ba, Ti, and O atoms, and the different weighting factors between the two techniques.

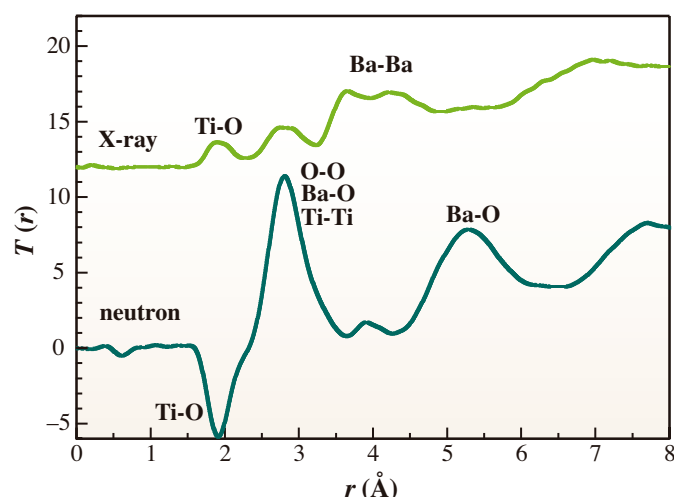


Fig. 2. Total correlation functions $T(r)$ of g -BaTi₂O₅.

dominated by small rings with the following distribution: threefold rings (35%), fourfold rings (25%) and fivefold rings (20%). This distribution is similar to that of chalcogenide glass exhibiting both corner- and edge-sharing [5], and is different from that of typical silicate glass linked only by the corner-sharing of SiO₄ tetrahedra [6].

Figure 3(c) depicts the Ba polyhedra connected by edge-, face- and vertex-sharing to form a random

dense packing. Similarly to Ti polyhedral linkage, Ba polyhedral linkages included threefold rings (35%), fourfold rings (22%) and fivefold rings (15%). In addition, the average coordination number $N_{\text{Ba-O}}$ in g -BaTi₂O₅ calculated using the RMC model was about 7.5, which is significantly higher than the values of 6 to 6.5 in barium silicate glass and is near 8 in crystalline β -BaTi₂O₅. This feature implies that the high-density packing of polyhedra is realized in g -BaTi₂O₅.

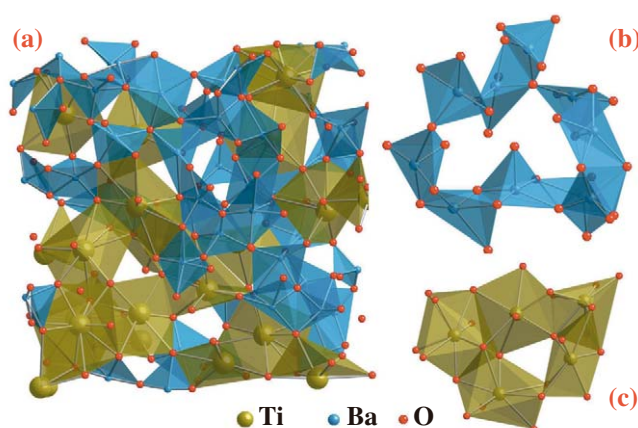


Fig. 3. (a) Representation of glass structure in slice (20 Å × 20 Å × 10 Å) modeled by RMC simulation. (b) Network configuration of TiO₅ polyhedra linked by both edge- and corner-sharing. (c) Network configuration of BaO_{*x*} (*x* > 7) polyhedra connected by edge-, face- and vertex-sharing to form random dense packing.

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