Fracture-induced amorphization of polycrystalline stishovite: Amorphization makes the ceramic tough

Silicon dioxide (SiO₂) has eight stable crystalline phases at conditions of the Earth's rocky parts. Many metastable phases including amorphous phases have been known, which indicates the presence of large kinetic barriers. As a consequence, some crystalline silica phases transform to amorphous phases by bypassing the liquid via two different pathways: heating under atmospheric pressure (temperature-induced amorphization) and compression at room temperature (pressure-induced amorphization). In the present study, we discovered a new pathway, a fracture-induced amorphization of stishovite that is a high-pressure polymorph [1]. The amorphization accompanies a huge volume expansion of ~100% and occurs in a thin layer whose thickness from the fracture surface is several tens of nanometers. Amorphous silica materials that look like strings or worms were observed on the fracture surfaces. The amount of amorphous silica near the fracture surfaces is positively correlated with fracture toughness (K_{lc}): in another words, the nanometer scale amorphization makes this material tough. A similar toughening mechanism has been known for a popular ceramic material, zirconia. In the case of zirconia, a huge tensile stress to cause fracture induces tetragonal to monoclinic transition. This transition accompanies a volume expansion of ~4%. This volume expansion generates compressional stress against the crack opening, which makes the material tougher (transformation toughening) [2]. In the case of stishovite, the huge volume expansion associated with fracture-induced amorphization is the origin of the toughening.

Stishovite is a high-pressure polymorph in silicon dioxide and is stable between 9 and 70 GPa. In 1996, it was reported that stishovite is the hardest oxide that can be utilized at ambient conditions [3]. The reported hardness values were ~30 GPa, which is 1.5 times as large as that of alumina, which is known as a hard ceramic and widely used in industry. However, stishovite has not been used for industrial applications because single-crystal stishovite is a very brittle material ($K_{\rm lc} = 1.6 \text{ MPa} \cdot \text{m}^{1/2}$). In general, hardness and toughness are mutually exclusive: hard materials are generally brittle (easy to break). The brittleness of single crystal stishovite hinders the usage in industry.

In 2012, we reported the synthesis of nanocrystalline bulk stishovite with very high fracture toughness ($K_{lc} > 10$ MPa·m^{1/2}) [4] (Fig. 1). Since single-crystal stishovite is very brittle, a toughening mechanism should be activated in the nanocrystalline bulk stishovite materials. However, the question "what does make this material tough?" had

remained unanswered. In the previous paper [4], we reported that fracture surfaces of this material look very different from those of other ceramics such as alumina. The fracture surfaces of this material show "worm-like texture." I thought that this unusual fracture surface can be an important key to answer this question.

In order to examine phenomena that happened on the fracture surfaces of nanocrystalline bulk stishovite, we performed Si-K XANES measurements for a series of stishovite polycrystals at soft X-ray photochemistry beamline BL27SU (Fig. 2). For each measurement, we collected two spectra simultaneously: a spectrum collected by the total electron yield (TEY) method and that by the partial fluorescence yield (PFY) method. The former is a surface-sensitive method: a XANES spectrum to a depth of ~10 nm from the surface can be obtained. The latter is a bulk-sensitive method: a spectrum to a depth of ~1 μ m can be obtained for silica materials. Since the peak position of XANES spectra of stishovite with silicon coordination number (CN) of 6 is quite different from those of silica materials with CN=4, these spectra can be used as fingerprints to distinguish silica materials with different CNs.

First, we performed a measurement for an unpolished (as sintered) surface of a nanocrystalline bulk stishovite material (v). The TEY and PFY spectra can be explained by the presence of a single phase of stishovite. On the other hand, two peaks indicating the presence of materials with CN=4 and 6 were clearly observed in a TEY spectrum obtained from a polished surface of a stishovite polycrystal (vi). Note that the CN=4 peak cannot be observed in the PFY spectrum. These results demonstrate that the CN=4 materials coexist with stishovite (CN=6) in a thin layer whose thickness is several tens of nanometers from the polished surface. A previous study reported that stishovite was inverted



Fig. 1. (a) A photograph of some representative samples of nanocrystalline bulk stishovite. (b) Relationship between hardness and fracture toughness of hard materials, tungsten carbides and ceramics. Single-crystal stishovite is brittle and nanocrystalline bulk stishovite has enhanced fracture toughness. A toughening mechanism is activated for nanocrystalline bulk stishovite.



Fig. 2. Representative Si-K XANES spectra of a series of stishovite polycrystals and those obtained by first-principles calculations. TEY and PFY spectra collected simultaneously from one measurement are shown side by side. (i), a-quartz by firstprinciples calculation; (ii), ordinary silica glass; (iii) densified silica glass; (iv), stishovite by first-principles calculation; (v), unpolished surface of a polycrystalline stishovite sample with synthesis temperature (T_S) of 1300°C; (vi), polished surface T_S = 1300°C; (vii), fracture surface $T_{\rm S}$ = 1300°C; (viii), fracture surface $T_{\rm S} = 1600$ °C; (ix), fracture surface $T_{\rm S} = 1800$ °C; (x) fracture surface $T_{\rm S} = 2000^{\circ}$ C. *, a pre-edge peak of stishovite.

to silica glass (CN=4) by mechanical grinding, which supports our observations. Similar features were observed in the spectra obtained from fracture surfaces of nanopolycrystalline bulk stishovite materials synthesized at different temperatures (vii, viii), demonstrating the coexistence of the CN=4 material with stishovite (CN=6) in thin layers (several tens of nanometer thick) adjacent to the fracture surfaces. We observed a decrease of relative intensity of the CN=4 peak with respect to the CN=6 peak intensity in TEY spectra with increasing synthesis temperature ($T_{\rm S}$) above 1700°C (ix). At the highest $T_{\rm S}$ of 2000°C, we observed the complete absence of the CN=4 peak (x). The fracture surface of this sample did not show "worm-like texture." The fracture surface looks similar to that of alumina showing intergranular fracture. The results of XANES measurements clearly show that thin layers (several tens of nanometer thick) which contain CN=4 silica material exist on fracture surfaces of nanocrystalline bulk stishovite.

In order to identify the CN=4 phase, we performed TEM and SEM observations (Fig. 3) of crashed pieces of nanocrystalline bulk stishovite. A low magnification image shows the presence of worm-like textures (Fig. 3(a)). Selected-area electron diffraction patterns of the worm-like textures have a halo and an example of

X-ray fluorescence spectra show the presence of only silicon and oxygen (Fig. 3(b)). These results indicate that fracture of nanocrystalline bulk stishovite induces transformation from stishovite (CN=6) to amorphous silica (CN=4), which results in the coexistence of the CN=4 and CN=6 peaks in the TEY-XANES spectrum. Figure 3(c) shows a high-magnification SEM image of the amorphous silica that exists on the fracture surface of the nanocrystalline bulk stishovite.

Nanocrystalline bulk stishovite with simultaneous high-hardness and high-toughness with composition of SiO₂ meets the requirement for managing the scarcity of chemical elements [5].



Fig. 3. Amorphous silica on fracture surfaces of nanocrystalline bulk stishovite. (a) A low-magnification TEM micrograph of worm-like texture on a fracture surface of a broken piece of nanocrystalline bulk stishovite. (b) A magnified TEM image of worm-like textures. Electron diffraction patterns (ED1 and 2) and an X-ray fluorescence spectrum by energy dispersive X-ray spectroscopy (EDS) show presence of an amorphous silica phase on the fracture surface. An electron diffraction pattern (ED3) that is collected at the interface between the amorphous and stishovite shows coexistence of halo and diffracted spots from a stishovite crystal. (c) A magnified SEI micrograph on a fractured stishovite grain. String-shaped amorphous silica materials are observed. They could be one of the sources of the worm-like texture.

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53