Structural Change of a Volcanic Glass (obsidian) under High Pressure

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High pressure structural change of an obsidian from Iceland has been investigated using X-ray radial distribution function (RDF) analysis and Raman spectroscopy. Obsidians have been compressed under 4 GPa at 20 °C and 500 °C by a cubic anvil apparatus. The obsidian treated under 4 GPa-20 °C condition shows almost the same density and RDF curve as the original obsidian. However, the permanent densification of about 9% was observed by the compression under 4 GPa-500 °C. Based on RDF and Raman analyses, the structure of obsidian may change in the dominant TO₄ (T=Si and Al) from 5 and 6 to 4 and 3 membered rings by the compression at 500 °C.
[glass structure, obsidian, X-ray diffraction, Raman spectroscopy, high pressure]

1. Introduction

The study on structures of magmatic liquids under high pressure is very important for understanding the properties of magma in the earth crust. The structures of silicate glasses have been studied extensively [1-5]. Structural studies under high pressure have been carried out for synthesized SiO₂ glass and some silicate glasses [6-12]. Meade et al.[8] have reported that below about 10 GPa, Si-O-Si angle of SiO₂ glass structure decreases and the density increase, from about 10 GPa the coordination of Si atom increases and close to six at 42 GPa. However, there is almost no study on structure change of natural glass as obsidian under high pressure. In this study the structures of compressed natural volcanic glass (obsidian) have been analyzed by X-ray diffraction and Raman spectroscopy.

2. Experimental

Specimen

An obsidian from Krafra of Iceland was used for this work. This obsidian consists of glassy matrix only. However, the glassy matrix shows a small contrast such as glass-in-glass separation. The chemical composition averaged on 17 points of the obsidian sample was determined by SEM (Topcon Alpha-30A, 20 kV) with an EDAX analyzer. Even in the case of the existence of glass separation texture, only very small compositional variation was measured. Measured average chemical composition is shown on Table1. The CIPW norm of the obsidian sample was calculated from the chemical data of SiO₂, Al₂O₃, Na₂O, K₂O and CaO. This norm shows quartz (39.9 wt%), orthoclase (16.7 wt%), albite (33.0 wt%), anorthite (6.4 wt%) and corundum (0.5 wt%).

Table1. Chemical composition of obsidian.

composition	wt%	composition	wt%
SiO ₂	76.17	CaO	1.69
TiO ₂	0.30	Na ₂ O	3.99
Al ₂ O ₃	12.27	K ₂ O	2.82
Cr ₂ O ₃	0.06	P ₂ O ₅	0.29
FeO	3.29	NiO	0.01
MnO	0.11	Total	101.00.

High pressure experiments

The compacted samples were obtained under 30 minutes compression of 4 GPa at 20 °C and 500 °C by using a DIA-6 type cubic anvil apparatus of Tohoku University, Japan[13]. Densities were measured by the flotation method in acetone/CH₂I₂ solution. The measured densities are 2.41 g/cm³ (original obsidian, 20 °C), 2.41 g/cm³ (4 GPa, 20 °C) and 2.63 g/cm³ (4 GPa, 500 °C). These density data may indicate that the structure of this obsidian has not so largely changed by compression at 20 °C but permanently changed by compression at 500 °C.

X-ray diffraction measurements

Sphere-shaped ground samples with diameter of about 0.7 mm were used for the X-ray diffraction measurements. Measurements were carried out on a four-circle X-ray diffractometer (RIGAKU, AFC-5, Japan) with MoK α radiation monochromated by pyrolytic graphite, in the step scan mode at every 0.5° in 2 θ in the range of 5°≤2 θ ≤120° (Fig.1). The measured intensities were corrected for polarization and absorption factors, and for Compton scattering and normalized to S-i(S) data [14] (Fig.2). Radial distribution function (RDF(r)) and correlation function (G(r)) curves were calculated from S-i(S) data.

Raman spectroscopy

Raman spectra of normal and 4 GPa-500 °C obsidians were recorded on a Raman spectrometer equipped with a single premonochromator (1800 gr/mm gratings) and CCD nitrogen-cooled detector at NIRIM, Japan by using small fragments. The 514.5 nm line of Ar⁺ laser was used to excite Raman scattering. Operating laser power was 100 mW and a band pass is about 1 cm⁻¹. Raman spectra in the range of 150-1300 cm⁻¹ were recorded for each specimen. The observed Raman spectra were corrected for temperature and frequency dependence of the first order (Stokes) Raman scattering [15,16].

Fig.1. X-ray scattering intensities of obsidians.

Fig. 2. S-i(S) curves of obsidians.

Fig. 3. RDF(r) curves of obsidians.

Fig. 4. G(r) curves of obsidians.

3. Results and discussion

Density

The density of 4 GPa-20 °C obsidian is equal to that of the original obsidian. However, the density of 4 GPa-500 °C obsidian is larger than that of the original obsidian by about 9%. These indicate that the compression at 20 °C is elastic compression and permanent densification is realized by compression at high temperature. Therefore, the compression at 500 °C may give some structure change on the obsidian.

RDF analyses

The S-i(S) and RDF curves of 4 GPa-20 °C obsidian are very similar to these of the original obsidian (Fig.2, 3). On the other hand, those of 4 GPa-500 °C obsidian show some difference from those of original obsidian. These results are consistent with that of densities. Peaks and shoulders are observed at 0.168, 0.25, 0.32 nm in the RDF curve of original obsidian, 0.170, 2.5, 3.2 nm in 4 GPa-20 °C obsidian, and 0.166, 0.24, 0.316 in 4 GPa-500 °C obsidian. On the basis of the data of ionic radii [17] and chemical composition, these peaks could be assigned as follows. The first peaks correspond to the nearest T-O (T=Si/Al) pairs. The average coordination numbers of T atoms are about 4. Therefore, these three obsidians have TO_4 tetrahedra as basic structure units. The weak peaks at 0.24 - 0.25 nm perhaps correspond to the average (Na,K,Ca)-O pairs. The peaks at 0.316 - 0.320 nm may be assigned to the nearest T-T pairs.

The density data and RDF curves suggest that the structure has not changed by room temperature compression and changed by compression at 500 °C. For detail discussion of structure, we compare G(r) curves of these three obsidians carefully (Fig.4). The G(r) curve of 4 GPa-500 °C obsidian in the range of $r < 0.35$ nm is similar to that of original obsidian. However, the G(r) curve of 4 GPa-500 °C obsidian is not similar at $r > 0.35$ nm to that of original obsidian. RDF curve of 4 GPa-500 °C is more intense in the range of $0.40 < r < 0.45$ nm. The 2nd neighboring T-T distance of ideal 4-membered rings of TO_4 tetrahedra could be calculated about 0.44 nm. Yamana (1980) [18] reported a similar change on RDF curves of compressed SiO_2 glasses and concluded that this change could be explained

by the change from 5 or 6 membered rings of TO₄ tetrahedra to 4 membered rings dominant structure. Therefore, similar change of RDF curve on obsidian may suggest an increase of 4 membered rings of TO₄ tetrahedra in obsidian structure by compression under 4 GPa and 500 °C.

Raman spectroscopy

The corrected and normalized spectra ($200 < \nu < 700 \text{ cm}^{-1}$) are shown in Fig.5. In Fig.5, the Raman intensity at $\nu=450\text{--}600 \text{ cm}^{-1}$ of obsidian increases by 4 GPa-500 °C compression. On SiO₂ glass, the bands near 600 cm^{-1} and 490 cm^{-1} have been assigned to the symmetric Si-O-Si bending mode of 3 and 4 membered rings of SiO₄ tetrahedra, respectively [19]. Therefore, these intensity increases may indicate increases of 3 and 4 membered rings of TO₄ tetrahedra and decrease of average T-O-T angles by compression at 500 °C. This is consistent with the result by X-ray analyses. On the other hand, the peak of 660 cm^{-1} band becomes weak and broad by compression at 500 °C. Although this band could not be assigned clearly, the previously reported Raman spectra of MgCaSi₂O₆ and CaSiO₃ composition glasses show strong band at $\nu=600\text{--}700 \text{ cm}^{-1}$ [20]. We suppose that this band is related to the chain structure of TO₄ tetrahedra and this chain structure unit is included in very small nuclei of crystallization. Therefore, we could conclude that the chain structure of original obsidian decrease and 3 and 4 membered rings in polymerized network structure increase by the compression at 500 °C to increase its density.

Fig. 5. Raman spectra of obsidians.

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