Shock compression of synthetic opal

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Abstract. Structural change of synthetic opal by shock-wave compression up to 38.1 GPa has been investigated by using SEM, X-ray diffraction method (XRD), Infrared (IR) and Raman spectroscopies. Obtained information may indicate that the dehydration and polymerization of surface silanole due to high shock and residual temperature are very important factors in the structural evolution of synthetic opal by shock compression. Synthetic opal loses opalescence by 10.9 and 18.4 GPa of shock pressures. At 18.4 GPa, dehydration and polymerization of surface silanole and transformation of network structure may occur simultaneously. The 4-membered ring of T-O(T=Si/Al) tetrahedrons in as synthetic opal may be relaxed to larger ring such as 6-membered ring by high residual temperature. Therefore, the residual temperature may be significantly high at even 18.4 GPa of shock compression. At 23.9 GPa, opal sample recovered the opalescence. Origin of this opalescence may be its layer structure by shock compression. Finally, sample fuse by very high residual temperature at 38.1 GPa and the structure closes to that of fused SiO₂ glass. However, internal silanole groups still remain even at 38.1 GPa.

1. Introduction

Opal is made of low or non-crystalline SiO₂ with OH and H₂O. Jones and Segnit (1971) [1] classified opal into three well-defined structure groups, opal-C(well ordered low cristabalite), opal-CT(disordered low cristobalite/low tridymite) and opal-A(non-crystalline SiO₂ with OH and H₂O). Further, Langer and Flörke (1974)[2] classified opal-A into opal-AN(glass-like net work structure) and opal-AG(gel-like structure). Especially, non-crystalline opal-AG is made of regular stacking of small silica spheres with uniform size and show beautiful rainbow colours (opalescence). They also reported that opal-AG includes silanole groups(≡Si-OH) and H₂O at surface and interior. However, the structure of opal-AG did not investigate precisely until now.

On the other hand, meteorite impact on the earth gave strong influence for the materials on surface of the earth. The study of the structural change of SiO₂ glass by shock wave compression is important to know the formation process of craters on the earth and provides a model of structure evolution of non-crystalline SiO₂ by shock compression. Several scientists already investigated the structural evolution of shock compressed SiO₂ [3,4], and anorthite(CaAl₂Si₂O₈) glass [5]. They have reported densities of these glasses increase rapidly with shock compression above 15GPa and reach maxima at about 25GPa and these densification is attributed to the reductions of the average T-O-T (T=Si/Al) angle, which occurs first by collapse of large cavities in glass structure, and secondly by reduction of average size of TO₄ tetrahedrons. For higher shock pressure, increase of T-O-T angle was observed and
attributed to an annealing of densified structure due to high after shock residual temperature. However, structural change of silicate glass including silanole group by shock compression has not been investigated. Therefore, a study for shock compression of opal will give important information on deformation and transformation of hydrated non-crystalline materials.

In this study, structural change in synthetic non-crystalline opal by shock compression up to 38 GPa was investigated X-ray diffraction measurement, and IR and Raman spectroscopies.

2. Experimental

2.1. Sample preparation

Synthetic non-crystalline opal was prepared by using the procedure reported by Okudera and Hozumi[6] which includes the hydrolysis, dehydration and condensation of Si-tetraethoxide (Si[C2H5O]4, TEOS) in an aqueous solution of ethanol with ammonia as a catalyst at room temperature. This synthetic opal contains about 13.5 wt% of water and its density is 1.87 g/cm³.

X-ray powder diffraction profile of synthetic opal shows only very diffuse scattering maximum at about 23° in 2θ without any diffraction peaks of crystal. Therefore this opal may be classified as opal-A. SEM photograph of opal (Fig.1) shows a regular three-dimensional stacking of amorphous silica spheres whose diameter is about 400 nm. This regular stacking of silica spheres may lead to diffraction of visible light, exhibits play of colour (opalescence) as natural gem opal (Fig.2).

2.2. Shock-wave experiments

Shock-wave experiments for synthetic opal were performed using a single-stage propellant gun at Shock Wave and Condensed Matter Research Centre of Kumamoto University, Japan. Synthetic opal is formed to a disk, 12 mm in diameter and 2 mm in thickness, which was encased in a stainless container. The specimen containers were hit by tungsten or copper flyers, which were accelerated to velocities up to 1.67 km/s. Five shock-wave experiments were performed with shock pressures of 10.9, 18.4, 23.9, 27.3, and 38.1 GPa. These pressures were estimated from measured projectile velocities, using the impedance matching method. Sample recovered from shock-wave experiment 10.9 GPa is opaque white block with partial translucent part. Samples form 18.4, 23.9, 27.3 GPa, 38.1 GPa are shown in Fig.3.
27.3, and 38.1 GPa are white blocks (Fig.3). The densities of shock compressed opals were also measured as 1.870(2), 1.984(1), 2.05(7), 1.99(7), 2.08(2) and 1.57(6) g/cm$^3$ of 10.9, 18.4, 23.9, 27.3, 38.1 GPa sample, respectively.

2.3. X-ray diffraction measurement
The X-ray powder diffraction measurements were performed using an X-ray powder diffractometer Rigaku Rint 2200 with CuKα radiation. Scan step was set a 0.05° in 2θ range of 2°-45° ($S$=0.14-2.79Å$^{-1}$, $S$=4πsinθ/λ).

2.4. Infrared and Raman spectroscopy
The infrared absorption measurements were performed by the KBr micro pellet method, using JASCO FT-IR (610V) Fourier transformed IR spectrometer. Spectra were recorded in the range of $\nu$ =400-7000 cm$^{-1}$ with a band pass of 4 cm$^{-1}$.

Raman spectra were recorded by micro-Raman spectrometer, Ramanor T-6400(Jovin Yvon) of Japan Advanced Institute of Science and Technology for shocked samples, original one and silica glass. The 514.5 nm line (green) of the Ar$^+$ laser was used to excite Raman scattering, and the Raman light was collected in the backscattering geometry. Spectra were accumulated for 180 s in the range of 100-700 cm$^{-1}$ with a band pass of 0.5 cm$^{-1}$. All observed Raman spectra were corrected for background.

2.5. Scanning electron microscopy (SEM)
A scanning electron microscope (JEOL JSM-5310) was used to observe the micro surface structures of shocked synthetic opals and original one. Samples were mounted on brass specimen supports and coated with gold.

3. Results

3.1. SEM observation
Fig.4 shows the SEM images of shocked opals. The SEM image of 10.9 GPa sample shows initial microstructure of silica sphere stacking. However, some heavy distorted spheres are also recognized. The smooth textures are dominant in 18.4 and 23.9 GPa samples. A few silica spheres may be recognized in 18.4 GPa sample. On the other hand, stacking structure of thin sheet was observed at 23.9 GPa. In contrast, 27.3 GPa sample has a rough surface structure, 38.1 GPa sample shows many submicron size pores which may indicate melting during shock compression.

3.2. X-ray diffraction pattern
XRD patterns for shock compressed opals are shown in Figure 5. The position of first sharp diffraction peak (FSDP) for synthetic opal ($S$=1.638Å$^{-1}$) is very similar to that of silica gel ($S$=1.60-1.67Å$^{-1}$)[7]. With increasing in shock pressure, FSDP position shifts toward smaller $S$.

3.3. Infrared absorbance spectra
IR spectra of shocked opal are shown in Figure 6.
Three major bands observed at around $\nu=470, 800$ and $1100\text{cm}^{-1}$. These bands can be assigned to O-Si-O and Si-O-Si bending vibrations and Si-O antisymmetric stretching vibration, respectively. The intensity of weak band at $\nu=950\text{cm}^{-1}$ attributed for Si-OH stretching decreased rapidly up to 18.4 GPa and weak shoulder remains even at higher pressure. IR spectra in the range of $\nu=2500-4500\text{ cm}^{-1}$ are shown in Fig 7. Almost all water remained at 10.9 GPa. This is consistent with the pressure variation of $\nu=950\text{ cm}^{-1}$ band. At 18.4 GPa, the broad band at $\nu=3400\text{cm}^{-1}$ is almost disappeared, but the weak band at $\nu=3650\text{cm}^{-1}$ remains.

3.4. Raman spectra

Raman spectrum for shocked opal is shown in Figure 8. The Raman spectrum of synthetic opal is similar to that of silica gel [8]. The spectrum at 38.1 GPa shows broad band at around $\nu=400\text{ cm}^{-1}$, weak band at 480 cm$^{-1}$ and faint band at 590 cm$^{-1}$.

4. Discussion

SEM observation and opalescence

SEM image of original synthetic opal (Figure 1) shows that synthetic opal is composed of the regular three-dimensional stacking of amorphous silica spheres with diameter of about 400nm. This regular stacking of silica spheres may be responsible for opalescence.

Opal of 10.9 GPa keeps initial stacking of silica spheres and shows opalescence. Opal of 18.4 GPa lost almost of initial stacking and also lost opalescence.

However, opal of 23.9 GPa recovers splendor such as opalescence. This sample has the stacking of submicron size thin sheets. Probably, this sheet structure is responsible for the splendor.

Opal of 38.1 GPa has a number of pores. These pores may caused by evaporation of water at relative high residual temperature of shock compression.

Evolution of nano-structures of opals by shock compression

FSDP position of unshocked synthetic opal is similar to that of silica gel. Kamiya et al.[7] reported medium range structure of silica gel is more compact than silica glass and it may be composed of four-membered siloxane rings, mainly. Therefore, four-membered siloxane rings may be predominant in the structure of synthetic opal. Large shift of
FSDP position toward to small S-value is observed on the samples up to 23.9 GPa. At above 23.9 GPa, FSDP position is almost constant. It may indicate that the average structure of synthetic opal approach to that of silica glass with six-membered rings by shock compression. On the other hand, intensities of IR bands at $\nu=950\text{cm}^{-1}$ and $3400\text{cm}^{-1}$ which attributed to Si-OH and H-O stretching decreased rapidly up 18.4 GPa. Moreover, the intensity of Si-O-Si bending mode at $\nu=800\text{cm}^{-1}$ increase up to about 18.4 GPa. These results may indicate that surface silanole group are dehydrated and polymerized by shock compression and related high residual temperature. The high residual temperature may be explained low density of synthetic opal (1.87g/cm$^3$). Because high porosity is responsible for high residual temperature. These dehydration and polymerization processes are consistent with density increase by compression up to 27.3 GPa. Irregularly small density of shocked opal at 38.1 GPa can be explained by porous structure due to the melting by shock compression. However, intensity of $\nu=3650\text{cm}^{-1}$ band remains even at 38.1 GPa. This may indicate that internal silanole group remains even at 38.1 GPa and under high residual temperature condition. Probably, small duration of residual temperature is permits the remaining for silanole of 38.1 GPa sample. Raman spectrum of 38.1 GPa sample is similar to that of silica glass and show weak D1 and D2 bands at about $\nu=480\text{cm}^{-1}$ and $590\text{cm}^{-1}$. This is consistent with the results of IR analyses which show six-membered ring structure dominant in this sample.

5. Conclusions
The structural evolution of synthetic non-crystalline opal by shock compression can be summarized as follows.

Synthetic opal is composed of the regular three dimensional stacking of amorphous silica spheres and contains a great numbers of silanoles and molecular water, and the average structure can be characterized by four-membered rings of SiO$_4$ tetrahedrons and is similar to silica gel. Opal compressed at 10.9 GPa conserves initial stacking of silica sphere and shows opalescence. Their X-ray diffraction profile and IR spectrum are similar to those of original synthetic opal. By shock compression of 18.4 GPa, opal loses its opalescence and network structure of SiO$_4$ tetrahedrons increases with dehydration and polymerization of surface silanole groups. The average structure changes to six-membered rings of SiO$_4$ predominant structure. There is no large change in the nano-structure at 18.4–27.3 GPa. However, the sample at 23.9 GPa recovers opalescence. Probably, thin sheet structure of this sample is responsible for the opalescence. Above 27.3 GPa, samples lose opalescence, again. Opal shock compressed at 38.1 GPa seems to fuse by high residual temperature and its structure approach to that of silica glass. However, internal silanole groups may remain in the structure even at 38.1GPa.

6. References
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