

Structural evolutions of a volcanic glass and synthetic metasilicate glasses under high pressure

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学 位 論 文 要 旨

Abstract

The present study has reported the pressure-induced structural changes of a volcanic glass and synthetic CaSiO_3 and $\text{CaMgSi}_2\text{O}_6$ glasses by using X-ray diffraction, Raman and infrared spectroscopy. Also, the structural evolutions of CaSiO_3 - MgSiO_3 glasses under pressure have been examined by molecular dynamics simulation.

The shock-wave compression for a rhyolitic volcanic glass resulted in the density increase with pressure up to 25GPa. The observed densification of 4–5 % was smaller than that reported for shocked SiO_2 glass. Modifier ions in the interstitial sites can prevent the large densification as in SiO_2 glass. The densification was attributed to the T-O-T angle reduction with a small contribution from the increase of small rings of TO_4 tetrahedra.

CaSiO_3 and $\text{CaMgSi}_2\text{O}_6$ glasses showed little shock-densifications. Static compressions for these glasses represented small densifications of 3% and 7%, respectively, which can be assigned to the small reductions of Si-O-Si bond angle. Molecular dynamics simulations revealed that the Si-O-Si angle decreased, and Ca and Mg coordination numbers increased under high pressure.

Small compactions of CaSiO_3 and $\text{CaMgSi}_2\text{O}_6$ glasses obtained by shock and static compressions were in strong contrast to the results on a volcanic glass and the previous studies. The difference could be explained in terms of the network polymerization. Modifier cations also prevent the large reduction of Si-O-Si angle.

Structural information on silicate glasses under high pressure is of geological importance for understanding the physical properties and predicting the dynamic behaviors of deep-seated magma within the Earth. To a first approximation of magmatic liquids, the pressure-induced structural changes in SiO_2 glass have been investigated by several workers (Hemley et al. 1986; Susman et al. 1990; Meade et al. 1992). On the other hand, there are only a few studies on the pressure evolutions

for silicate glasses with more complex compositions (Kubicki et al. 1992; Okuno et al. 1998). Therefore, the present study has reported the pressure-induced structural changes of a volcanic glass and synthetic CaSiO_3 and $\text{CaMgSi}_2\text{O}_6$ glasses by means of X-ray diffraction, Raman and infrared spectroscopy. Also, the structural evolutions of CaSiO_3 - MgSiO_3 glasses under pressure have been examined by molecular dynamics simulation.

The shock-induced densification of a rhyolitic volcanic glass was observed with pressure up to ~ 25 GPa. The observed densification of 4 – 5 % (Fig.1) was smaller than that reported for shocked SiO_2 glass (11 %: Okuno et al. 1999), and rather close to the shocked $\text{NaAlSi}_3\text{O}_8$ glass (4.2 %: Takabatake 2000). This reflects the structural similarity between rhyolitic volcanic glass and $\text{NaAlSi}_3\text{O}_8$ glass. Modifier ions as Na^+ , K^+ and Ca^{2+} in the interstitial sites can prevent the large densification as in SiO_2 glass (Reynard et al. 1999).

Raman spectra and X-ray first sharp diffraction peak (FSDP) analysis suggested that the densification observed at 20 – 25 GPa was attributable to T-O-T bond angle reduction (T = Al, Si), with a small contribution from the increase of small rings such as 3- and 4-membered rings. Above 25 GPa, partial relaxation of the densified structure, due to relatively high post-shock residual temperature, resulted in the density decrease of the shocked obsidian and fused glass.

A comparison between the present results and the previous studies (Okuno et al. 1999; Takabatake 2000) indicates that the highly polymerized silicate glasses have essentially similar shock-densification mechanisms. The degree of densification can be influenced by the existence of modifier cations and by ring distributions in the original structure. The present results also suggested the possibility that tektites had experienced shock-melting resulting from shock compression above 35 GPa by impact events, on the basis of the compositional and structural similarity between rhyolitic glass and tektite. The detailed paper of the shock densification of a volcanic glass is to be published (Shimoda et al. 2004).

I also studied shock-induced changes of CaSiO_3 and $\text{CaMgSi}_2\text{O}_6$ glasses as an analogue of basaltic glasses. The shock-recovered CaSiO_3 and $\text{CaMgSi}_2\text{O}_6$ glasses showed little densifications (within 0.5 %, Fig.1). Raman spectroscopy and X-ray FSDP analysis did not show any significant variations by shock compression.

On the other hand, static compressions for CaSiO_3 and $\text{CaMgSi}_2\text{O}_6$ glasses represented small densifications of about 3 % and 7 %, respectively (Fig.2). The small reductions of Si-O-Si angle were observed. The most interesting is the strong correlation between density and FSDP position. This means the changes in the medium-range ordering is of importance on densification of CaSiO_3 and $\text{CaMgSi}_2\text{O}_6$ glasses. This can be also originated from the compaction of SiO_4 tetrahedral linkage.

Molecular dynamics simulations of CaSiO_3 - MgSiO_3 glasses were performed by using empirical

potential parameters given by Miyake (1998). The potential function includes Coulombic, short-range repulsion, van der Waals attraction and Morse potential terms. The present MD simulation showed reasonable agreements with the experimental results. However, there is controversy about Mg-O coordination in Mg-containing silicate glasses. Some workers reported tetrahedral Mg species (Hanada et al. 1988; Taniguchi 1994). On the other hand, this study provided the Mg coordination number of 5.4, which is consistent with some experimental results (Kroeker and Stebbins 2000; Shimoda, personal datum).

The present MD study revealed that Si-O-Si bond angle decreased under high pressure as reported by Kubicki et al. (1992). The coordination change of Si atoms was small, whereas Ca and Mg coordination numbers increased with pressure accompanying with slight contractions of cation-anion pair distances. The pressure-induced evolutions in the medium-range structural components were also indicated. The present MD study suggested that the FSDP of CaSiO₃ and CaMgSi₂O₆ glasses included the information of Ca-related structural components as well as medium-range units of SiO₄ tetrahedra.

The above experimental and theoretical results support the suggestion that the reduction of Si-O-Si bond angle under high pressure is elastic and revert to relaxed angle during decompression in CaSiO₃-MgSiO₃ glasses (Kubicki et al. 1992). This can result in the small compaction of CaSiO₃ and CaMgSi₂O₆ glasses obtained by shock and static compression. It is in strong contrast to SiO₂ glass and obsidian, in which relatively large densifications were reported (Couty 1977; Okuno et al. 1998; Shimada et al. 2002; Shimoda et al. 2004). The difference could be explained in terms of network connectivity; the degree of polymerization can influence the degree of the densification. The polymerized network structure as in SiO₂ glass and rhyolitic volcanic glass (obsidian) can easily compacted by the collapse of open voids and by the formation of small rings. However, the depolymerized network of chain- and sheet-like structural units with interstitial cations as in CaSiO₃ and CaMgSi₂O₆ glasses (and also basaltic glass) can not allow the large rings with open voids (Taniguchi 1994). Therefore, the compaction due to the collapse of large rings can not be allowed. Also, modifier cations, especially with large ionic radius as Ca, can prevent the large reduction of Si-O-Si bond angle.

This study implies that the shock-recovered silicate glass with more depolymerized network such as Mg₂SiO₄ glass also shows no significant densification.

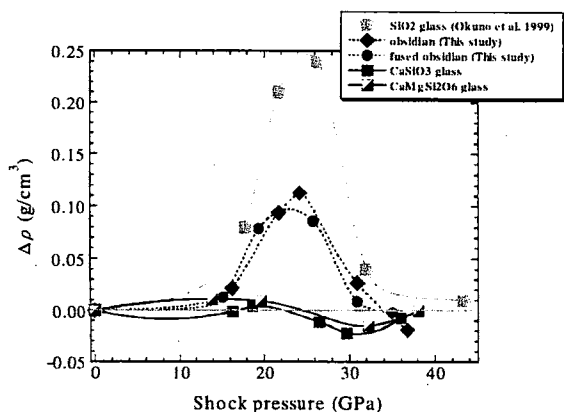


Fig.1 Density differences between shocked SiO₂ glass (Okuno et al. 1999), obsidian and its fused glass and CaSiO₃ and CaMgSi₂O₆ glasses (this study).

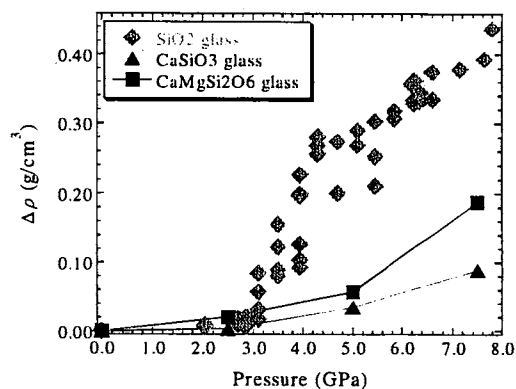


Fig.2 Density differences between SiO₂ glass (Couty 1977) and CaSiO₃ and CaMgSi₂O₆ glasses (this study) as a function of pressure.

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学位論文審査結果の要旨

本学位請求論文に対する各審査委員による予備審査の後、平成 16 年 7 月 30 日に口頭発表会を開催し、終了後直ちに論文審査委員会を開催し以下のように判定した。本論文は、火山ガラス及び合成メタ珪酸塩ガラスの静的及び動的圧縮による構造変化についての研究をまとめたものである。高圧力下での珪酸塩ガラス構造の情報は、マグマの物理的特性ならびにクレータ形成過程での物質変化の研究に必須である。しかし、複雑な組成を持つ珪酸塩ガラスならびに衝撃圧縮による構造変化の研究報告は少ない。本論文ではまず、複雑な化学組成を持つ火山ガラス等について衝撃圧縮実験を行い、その圧縮挙動が静水圧下での挙動と異なっており、密度増加率のガラスによる違いは化学組成と原子レベルの構造の差に起因することを示した。また、合成 $CaSiO_3$ 及び $CaMgSi_2O_6$ ガラスは衝撃圧縮での密度増加は極めて小さく、 SiO_4 四面体の重合度が小さく圧縮構造が緩和されやすいことがその原因であると結論づけている。さらに、分子動力学計算によって、 $CaSiO_3 - MgSiO_3$ 系ガラスの圧縮挙動を調べ、 $CaSiO_3 - MgSiO_3$ 系ガラスの高密度化には中距離構造の変化が大きく寄与し、 SiO_4 四面体結合角の変化の寄与は小さいことを明らかにした。本論文は、隕石衝突などの衝撃圧力下での珪酸塩物質の挙動と地球内部での珪酸塩融体の挙動の解明に大きく寄与するものである。よって本論文は博士論文に値するものと考え、合格と判定した。