Sinoite (Si$_2$N$_2$O) shocked at pressures of 28 to 64 GPa

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ABSTRACT

Shock recovery experiments of sinoite (Si$_2$N$_2$O) were carried out in a pressure range of 28–64 GPa. Post-shock samples were investigated by optical microscopy, X-ray diffraction, micro Raman spectroscopy, and transmission electron microscopy coupled with energy dispersive X-ray analysis. Sinoite was stable up to ~28 GPa, being partially amorphous at 34 GPa, and almost completely amorphized above 41 GPa. These results are consistent with the observation that sinoite is found in enstatite chondrites classified into shock stage S2, and imply that sinoite may not be a crystallization product from impact melts and that it may be a metamorphic product of high temperatures and relatively low pressure.

Keywords: Sinoite, shock metamorphism, oxynitride, amorphization, high-pressure transition

INTRODUCTION

Silicon oxynitrite (Si$_2$N$_2$O) is a mineral known as sinoite, identified by Andersen et al. (1964) and Keil and Andersen (1965a, 1965b), in some enstatite chondrites. It has been observed as 200 μm-size irregular grains or euhedral lath-like grains associated with metallic Fe-Ni and enstatite (Keil and Andersen 1965b; Alexander et al. 1994). The structure was originally determined by Idrestedt and Brosset (1964) and Brosset and Idrestedt (1964). The structure and compressibility of sinoite have been studied in detail and sinoite adopts an orthorhombic structure with space group $Cmc2_1$ (36) and is built of SiN$_3$O tetrahedral linked with puckered hexagonal Si$_2$N$_2$ layers through O atoms (Srinivasa et al. 1977; Sjberg et al. 1991). The origin of sinoite is not fully understood, although there are several proposals such as the product of condensation at high temperature and pressure from a gas of solar nebular (Herndon and Suess 1976; Sears 1980), the product of metamorphism at temperatures not so high as the artificial synthesis of Si$_2$N$_2$O (~1400 °C) (Khodakovsky and Petaev 1981; Petaev and Khodakovsky 1986; Fogel et al. 1989) or at lower temperature (~950 °C) over geologic time scales by the help of a catalyst (Muenow et al. 1992), and the product of crystallization from an impact melt (Rubin 1997).

Sinoite has been observed in EL6 chondrites and EL4 chondrite and these enstatite chondrites indicate higher bulk nitrogen contents than the others. All known EL6 chondrites are classified into shock stage S2 although the proto-EL6 materials may have experienced intensive shock levels of S3-S5 (Rubin et al. 1997). A petrographic classification of progressive stages S1 (unshocked)-S6 (highly shocked) of shock metamorphism for the ordinary chondrites has been proposed by Stffer et al. (1991). The scale defined by six stages of shock is based on shock effects in the typical minerals and a critical evaluation of data from shock recovery experiments. There are no experimental data available on sinoite shocked in laboratory. It is important to investigate shock metamorphism of sinoite experimentally and to understand the effect of shock on sinoite. Recently theoretical simulations on the stability and the high-pressure transformations of sinoite have been performed and indicate a series of phase transformations including decompositions (Kroll and Milko 2003). Compositionally, sinoite can be considered to be a mixture of SiO$_2$ and Si$_3$N$_4$. With increasing pressure SiO$_2$ displays various phases such as quartz, coesite, stishovite, and others (Prakapenka et al. 2004), while Si$_3$N$_4$ yields α-type, β-type, spinel-type, and others (Tatsumi et al. 2002). Therefore high-pressure studies are required to know the high-pressure stability of sinoite and to check whether sinoite is a possible host mineral of nitrogen under various conditions similar to those at time of formation of enstatite chondrites.

Here we report the experimental results on shocked sinoite up to a peak shock pressure of ~65 GPa, which covers the shock stage levels up to S5.

EXPERIMENTAL METHODS

Sinoite was prepared from an equimolar mixture of Si$_3$N$_4$ (TS-7 grade, α-type, Tosoh Co., Tokyo) and SiO$_2$ (precipitated from silicic anhydrite, Koso Chem. Co., Osaka) at 1850 °C for 30 min under a nitrogen pressure of 0.98 MPa (Mitomo et al. 1989). The weight loss was 0.6 wt% and the X-ray diffraction (XRD) spectrum of the product indicated ~90% sinoite and ~10% β-Si$_3$N$_4$ (Fig. 1a). The powdered sample was mixed with a large amount (90 wt%) of copper powder (Sekine et al. 1987) and pressed as a disk (18Φ × ~1 mm thick) in copper containers (30Φ × 30 mm long). The roles of the copper mixtures are temperature control, pressure enhancement, quick quenching because copper has a high compressibility, high shock impedance and high thermal conductivity.

A propellant gun was used to accelerate a projectile with a flyer metal (3 mm thick copper or 2 mm thick tungsten), and the velocity just before impact was measured. The peak shock pressure was calculated by the impedance match method assuming the sample pressure reached equilibrium with the container pressure. The detailed procedure has been described elsewhere (Sekine 1997). The experimental

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conditions are listed in Table 1. After successful recovery of sample container, the container was cut open to remove the sample. The sample was then immersed in nitric acid solution to dissolve the copper, washed with a large amount of water, and dried in an oven at 120 °C. The samples thus obtained were investigated by an optical microscopy, XRD, Raman spectroscopy, transmission electron microscopy (TEM), and EDX analysis. Raman spectroscopy used an Ar ion laser (~30 μm beam diameter, 514.5 nm wavelength).

RESULTS AND DISCUSSION

Figure 1 depicts a series of XRD patterns. The starting material consists of a mixture of sinoite and β-Si_3N_4. The spectrum of the post-shock sample at 28.4 GPa (Fig. 1b) indicated no appreciable change in peak shift and intensity except for the peak broadenings. Under a polarizing microscope there were no amorphous grains found in this sample. Post-shock sample at 34.3 GPa contained a few amorphous grains (5–100 μm size), found under a microscope. The XRD pattern showed severe peak broadening and intensity variation. The peak intensity for Si_3N_4 increased and the one for Si_2N_2O decreased relatively (Fig. 1c). This can be interpreted as partial amorphization of sinoite. Post-shock samples above 41 GPa displayed intensive

amorphization as shown in Figure 1d, although the strongest peaks for sinoite around 20 and 27 degrees remained and some strong peaks for cubic spinel appeared weakly. The cubic spinel has a lattice constant of 0.775 ± 0.002 nm based on the observed (3 1 1), (4 0 0), and (4 4 0) peaks, corresponding to 2θs of ~39, ~48 and ~69, respectively. There is no appreciable shift of the lattice constant from pure spinel-type Si_3N_4 (a = 0.7744 nm) that is synthesized from α-Si_3N_4 or β-Si_3N_4 under similar shock conditions (Sekine et al. 2000). The amounts of cubic spinel in the post-shock samples remain small and did not indicate the possible decomposition of sinoite into SiO_2 and cubic Si_3N_4.

Three post-shock samples above 41 GPa display similar Raman spectra as shown in Figure 2. The Raman spectra also indicate that sinoite peaks became weak with increasing shock pressure and the main peak at 520 cm⁻¹ remained weak in the three samples. No new peaks appeared in the Raman shift range between 150 and 850 cm⁻¹. The Raman spectrum for cubic Si_3N_4 synthesized by the shock compression method shows a high background and the peaks are not easily observed even in pure cubic Si_3N_4 that was confirmed by XRD. The micro Raman data for shock-amorphized quartz (Champagnon et al. 1996) indicated a gradual decrease in its intensity in the range of 50~600 cm⁻¹ with increasing shock pressure. Although we did not assign the lines for sinoite (Mirgorodsky et al. 1989), a comparison of the Raman data between quartz and sinoite indicate that most of sinoite amorphized by shock compression, because the Raman patterns for quartz and sinoite are similar and the detailed data for shock-amorphized quartz are available (Gucsik et al. 2003).

The starting powder and the post-shock sample of 793 (64 GPa) were investigated by TEM coupled with EDX analysis. The average grain size of the starting powder is about 10 μm and the grains in the post-shock sample were relatively smaller. Selected area electron diffraction indicated most of grains are

TABLE 1. Shock conditions for a mixture of 90 wt% copper and 10 wt% sinoite*

Shot no.	Flyer	Impact velocity (km/s)	Sample		
			Density (g/cm³)	Thickness (mm)	Pressure (GPa)
1219	3 mm Cu	1.30	7.03	0.85	28.4
1221	3 mm Cu	1.52	7.07	0.90	34.3
786	3 mm Cu	1.78	6.71	0.93	41.7
779	3 mm Cu	2.04	5.17	1.99	49.6
793	2 mm W	1.93	7.08	0.99	64.3

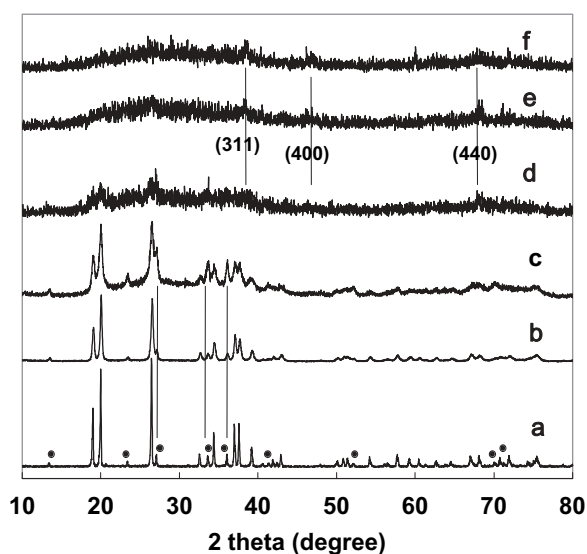* This sinoite sample contains about 10 wt% β-Si_3N_4.

FIGURE 1. XRD patterns of starting material and post shock samples. (**a**) Starting material, (**b**) 28.4, (**c**) 34.3, (**d**) 41.7, (**e**) 49.6, and (**f**) 64.3 GPa. The starting material is sinoite containing β-Si_3N_4 (peaks are marked by dots). Peaks with index (311), (400), and (440) are for cubic spinel-type Si_3N_4. CuKα radiation was used at 40 kV and 40 mA.
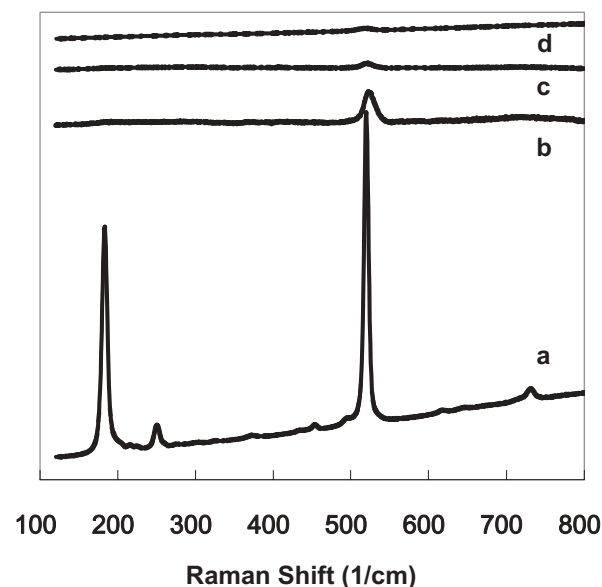

FIGURE 2. Raman spectra of starting material and post-shock samples. (**a**) Starting material, (**b**) 41.7, (**c**) 49.6, and (**d**) 64.3 GPa.

amorphous. High-magnification TEM images for some grains showed ordered atomic arrangements corresponding to a cubic spinel structure, but the atomic arrangements in most of areas were disordered and looked like the trail of a slug due to the amorphous state. EDX analyses of typical grains were carried out to check the compositions. We found that generally spinel grains are poor in oxygen and the glassy regions are relatively rich in oxygen, although it was difficult to separate mixed grains of spinel and glass completely. There were rare glass grains of SiO$_2$ without significant amount of nitrogen and the observed coexistence of the SiO$_2$ glass and spinel-type Si$_3$N$_4$ in the post-shock samples was not always explained as shock-induced decomposition products. The amounts were too small. XRD, Raman and EDX analyses indicate that sinoite becomes amorphous without significant decomposition into SiO$_2$ and Si$_3$N$_4$ by shock loadings.

The present shock recovery experiments on Si$_2$N$_2$O have indicated that sinoite is stable up to a pressure of ~28 GPa, and that it becomes amorphous with increasing shock pressure and the amorphization is almost complete above ~41 GPa. The present experimental results are consistent with the observation that sinoite-bearing chondrites EL6 are classified into shock stage S2 of which pressure is below ~10 GPa (Stffler et al. 1991; Rubin et al. 1997), although proto-EL6 parental body may have been shocked to S3-S5 levels and even higher levels. Shock amorphization of sinoite commences sharply around a pressure between 28 and 34 GPa. The onset pressure is significantly higher than that for quartz in the mixture with copper powders (Sekine et al. 1987). With increasing shock pressure the amount of amorphous form increases rapidly and it becomes almost complete above 42 GPa. Therefore the presence of sinoite in chondrite suggests the parental body has never experienced shock effect over ~30 GPa after crystallization.

Our starting material was a mixture of sinoite and β-silicon nitride. The shock experimental results on β-Si$_3$N$_4$ were reported previously (Sekine et al. 2000) and β-Si$_3$N$_4$ has been known to be transformed into a cubic spinel phase above pressures of ~20 GPa, although much high shock pressures are required to obtain as high yields as detected by XRD. In the present experiments we also detected a cubic spinel as one of shock products and a relative increase of β-Si$_3$N$_4$ in the XRD spectrum at 34 GPa where sinoite starts to amorphize. The increase is due to amorphization of sinoite only. This amorphization of sinoite by shock compression may imply a high-pressure phase transformation, although it would be possible for sinoite to melt by shock heating. We have no enough data to check due to lack of Hugoniot data and melting curve as a function of pressure. Many materials including silicates (Arora 2002) display high-pressure amorphization that has been considered due to destabilization of the low-pressure phase at high pressure and a kinetic mechanism of the phase change.

The stability of sinoite at high pressures has never investigated experimentally. In the paper by Li et al. (2001), they have successfully prepared sinoite from oxidized amorphous Si$_3$N$_4$ powders (5.8 wt% O) at 1 GPa and 1400 °C. They have no discussion on the high-pressure stability on sinoite. The calculations by Kroll and Milko (2003) indicate positive enthalpy of formation above a high pressure (~6 GPa), but their calculations

of free energy of formation at high temperatures and high pressure suggest it to be negative due to an entropy effect. As a result they summarized two possible high-pressure candidates (defect spinel and corundum types), although two phase assemblages [coesite (or stishovite) + β-Si$_3$N$_4$ and stishovite + spinel-type Si$_3$N$_4$] are proposed in the intermediate pressure ranges of 6–11 GPa and 40–80 GPa, respectively. It is known that quartz is quenched mostly as an amorphous form by shock loadings, but Si$_3$N$_4$ does not amorphize up to a shock pressure of 63 GPa. If sinoite decomposes into SiO$_2$ and Si$_3$N$_4$ by shock loadings, then we will observe a large amount of spinel-type Si$_3$N$_4$. Therefore the present results indicate that sinoite does not decompose under shock.

Finally we make a note on osbornite TiN that is considered to be a nitrogen source for the formation of sinoite. TiN is easily oxidized into rutile TiO$_2$ in the presence of some oxides even during the microsecond duration of the shock compression process (Li et al. 2004). Therefore osbornite may not be a nitrogen source for sinoite and nierite. The presence of osbornite may simply imply that the formation and subsequent conditions were kept reducing, more than the presence of sinoite.

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