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STRUCTURAL AND INFRARED SPECTRAL CHANGES OF SILICON OXIDE GRAINS BY HEAT TREATMENTS

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Abstract: In order to elucidate the relationship between crystallographic structures of amorphous silicon oxide grains and infrared (IR) spectra, ultrafine grains produced by the gas evaporation method have been studied on the basis of IR spectral measurements and electron microscopic (EM) observations. The shifts and disappearance in the IR absorption peaks of specimen heat-treated in air have been found. The spectral changes have been discussed in the relation with the polymorphism of silica.

1. Introduction

On the basis of absorption spectra from infrared objects (WOOLF and NEY, 1969), oxygen-rich stars (FORREST *et al.*, 1979) and the galactic center (MCCARTHY *et al.*, 1980), it is recognized that the 10 and 20 μm bands are due to silicate minerals. Siliceous dust is also thought to exist in the interstellar space. Infrared Astronomical Satellite, IRAS, provided a few thousand spectra from infrared sources, most of which exhibited a single broad absorption band at 10 μm and an 18 μm absorption band. Both 10 and 18 μm bands are attributed to the silicon-oxygen bond. The broadness of the 10 μm absorption band is attributed to siliceous dust with an amorphous structure. IR spectra of some amorphous silicates have been measured by one of the present authors (KOIKE and HASEGAWA, 1987; KOIKE *et al.*, 1987; KOIKE and TSUCHIYAMA, 1992). Some materials were synthesized by evaporation of olivine, pyroxene and quartz. All the materials produced by evaporation in the laboratory were amorphous (DAY and DONN, 1978; NUTH and DONN, 1982).

The most fundamental information needed to understand various properties of materials is the structural arrangement of the constituent atoms. In crystalline solids, the position of each atom in the unit cell can be accurately determined by X-ray diffraction in conjuction with the knowledge of a finite number of space groups associated with the long-range periodicity of the lattice. In a disordered solid, there is no long-range order and the structure is usually characterized by short-range order such as nearest-neighbor coordination number, average bond length and bond angle of coordinated atoms and ring structures. If electron and X-ray diffraction patterns were halo, it is called amorphous matter because of a lack of long-range order. When

ZACHARIAZEN (1932) considered the problem of the formation of glass, he predicted that compounds with corner-sharing structural units would form glasses. The best examples is SiO_2, whose structure is thought to be a continuous random network (CRN) composed of corner-sharing silica tetrahedra. The CRN model of inorganic glass has overwhelming support at present, but many experimental results explained by the CRN models have been criticized by PHILLIPS (1982). Our systematic studies by high-resolution electron microscopy (HREM) on amorphous oxides have shown that the microcrystallite structural model is useful in describing the structure of some so-called amorphous materials (SAITO, 1984; KAITO *et al.*, 1984, 1985a, b, 1986; SAITO *et al.*, 1985, 1987; KAITO and SAITO, 1986).

Most of the discussion on the structure of amorphous films have been made by means of the interpretation of a structure sensitive intensity or a radial distribution function (RDF). Observations of the local structure of the amorphous films are necessary to elucidate the structure of the films. In the case of an amorphous WO_3 film, a HREM observation and an analysis of the halo electron diffraction (ED) patterns have been carried out (KAITO *et al.*, 1984). It has been concluded the film was composed of the microcrystallites distributed at random in the film. HREM studies on typical SiO_2, fused quartz and $Li_2O \cdot 3SiO_2$ glasses also showed that the films consist of microcrystallites (KAITO *et al.*, 1986). It has been believed that the most important compounds in interstellar dusts were carbonaceous and siliceous materials. SAKATA and WADA (1993) reported the IR spectra of SiO film-like condensates and discussed the feature of H_2O trapped on them. Our recent studies on the optical properties of amorphous carbon grains showed the dependence of absolute values of absorption and spectral index on the microcrystallite size (KOIKE *et al.*, 1994, 1995a, b).

By experiments on SiC and alumina grains, it became apparent that the absorption peak shifts are due to the difference in crystal structures and defects in crystal (KAITO *et al.*, 1995; KOIKE *et al.*, 1995a, b; KIMURA *et al.*, 1996). In the case of alumina, the IR absorption peak position made no change between amorphous and crystal.

Silicon monoxide (SiO) has been used as a protective layer and antireflection coating in optical applications and as a dielectric material in certain microelectronic devices. The SiO layer is generally prepared by the rapid evaporation of SiO under high-vacuum conditions. The silicon atoms in a silicate mineral and silicate glass are fully oxidized and surrounded by 4 oxygen atoms, rendering them chemically stable. On the other hand, silicon atoms that are not fully oxidized react exothermally with oxygen atoms contained in other oxides to form fully oxidized silicates, as suggested by CLAYTON (1980).

In a previous paper, we proposed the production method of SiO_2 grains and showed that β-cristobalite crystal grains can be obtained by evaporating SiO powder in a mixture gas of Ar and O_2 (KAITO *et al.*, 1987). The purpose of the present study is to prove the correlation between IR spectra and structures of SiO grains produced by the gas evaporation method.

2. Experimental

The chamber used for sample preparation was a glass cylinder 17 cm in diameter and 33 cm high. A tungsten V-boat was used as the evaporation source. A vacuum in the chamber was made ~10^{-6} Torr, and then Ar gas was introduced into the chamber. SiO powder was evaporated by heating to above 1300°C in Ar gas. SiO grains were produced by evaporating commercial SiO powder in Ar gas at 100 Torr, and were got from a collector fixed above the evaporation source. Some of the collected samples were oxidized by furnace heating at various temperatures in air. Samples were examined using Hitachi H-7100R and H-800 electron microscopes. Each of the samples was mixed with KBr to form a pellet, and the spectrum was measured using a Horiba Fourier transform infrared spectrometer FT-210 in the wavelength region from 2.5 to 25 μm.

3. Results and Discussion

The color of commercial SiO powder used for evaporation was silver gray. As shown in Fig. 1, the IR spectrum of commercial SiO shows four typical peaks at 9.2, 12.5, 15.3 and 21.3 μm. The strongest peak at 9.2 μm is due to Si-O stretching vibrations, the peak at 12.5 μm due to Si-Si stretching vibrations and that at 21.3 μm due to O-Si-O bending vibrations, which correspond to those of quartz (Gürtler *et al.*, 1981). X-ray diffraction pattern of commercial SiO powder obtained using the Debye diffraction technique showed that the SiO powder consists of a mixture of fused silicon and fused quartz containing about 1% silicon and quartz crystals. The crystal structure of silicon dioxide has many interstices which can be occupied by some other atoms. As the absorption intensity due to Si-O stretching vibrations is stronger than that due to Si-Si stretching vibrations, the peak at 15.3 μm may be due to Si-O stretching vibrations, where Si corresponds to interstitial silicon in quartz. Powder sizes were distributed in the range between 50 nm and 1 μm.

SiO grains produced by the gas evaporation method were brown. Figure 2 shows

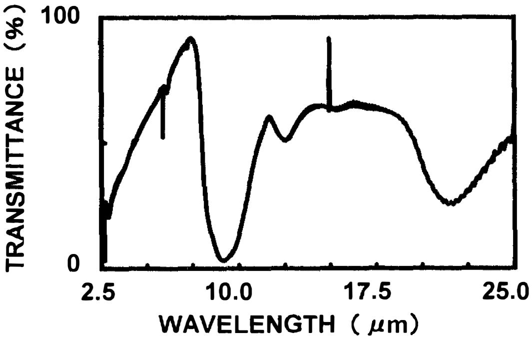

Fig. 1. IR spectrum of commercial SiO powder. Peaks at 2.7 and 6.3 μm are due to H_2O, and that at 4.3 μm due to CO_2, but that at 7.2 μm can be identified in all figures. These peaks may appear due to the treatment of the specimens in air.

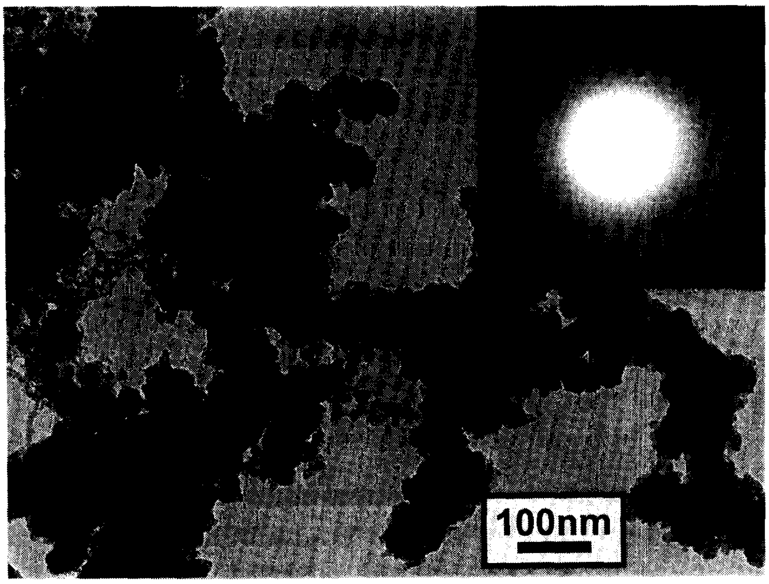

Fig. 2. EM image and ED pattern of the as-prepared SiO grains.

an EM image and an ED pattern of the SiO grains. Since the ED pattern shows halo rings, the grain is the so-called amorphous. Mean grain size is 50 nm.

Figure 3a shows the IR spectrum of the grains. The spectrum shows peaks at 9.2, 11.4, 12.7 and 21.8 μm, and differs from that of commercial SiO powder.

COLEMAN and THOMAS (1967), who studied the structure of amorphous SiO_x films ($x=0.7-1.7$) by the RDF analysis, reported that films prepared by vacuum deposition and the glow-discharge method consisted of microcrystallites with both silicon atoms and silica structures. Using HREM, one of the present authors (KAITO and SHIMIZU, 1984) confirmed that an amorphous SiO film was composed of microcrystallites of silicon and α-cristobalite with size of ~2 nm.

To compare IR spectra of SiO grains and films, a vacuum-deposited SiO film was produced onto a KBr pellet. Figure 4a shows the IR spectrum of the SiO film. The spectrum has a strong absorption peak at 10.2 μm and three weak peaks at 13.5, 15.0 and 19.5 μm. This indicates that the structure of the SiO film differs from both that of commercial SiO powder and that of the produced SiO grains. Since the film was prepared by the same method as the previous experiment, the film must have been composed of silicon and α-cristobalite microcrystallites. Thus, the spectrum corresponds to that of α-cristobalite. Cristobalite is one of the polymorphs of silicon dioxide. Needless to say, interatomic distances in cristobalite differ from those in quartz. The difference in crystal structures caused the difference in the peak positions. In the IR spectrum of α-cristobalite, the absorption peak at 10.2 μm is due to Si-O stretching vibrations, that at 13.5 μm due to Si-Si stretching vibrations and that at 19.5 μm due to O-Si-O bending vibrations. The peak at 15.0 μm may be due to silicon which occupies the interstices in α-cristobalite.

The phase transition from α-cristobalite to β-cristobalite is above 250°C. The as-deposited SiO film was heat-treated at 300°C for 30 hours in air. Since an ED pattern of the film also showed halo rings, the film remained also amorphous. Figure 4b shows

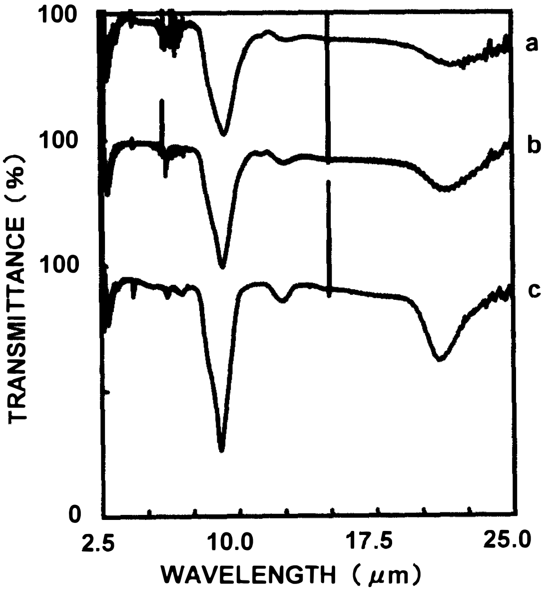

Fig. 3. IR spectra of, (a) as-prepared SiO grains, (b) grains heated at 300°C for 30 hours, and (c) those at 500°C for 30 hours.

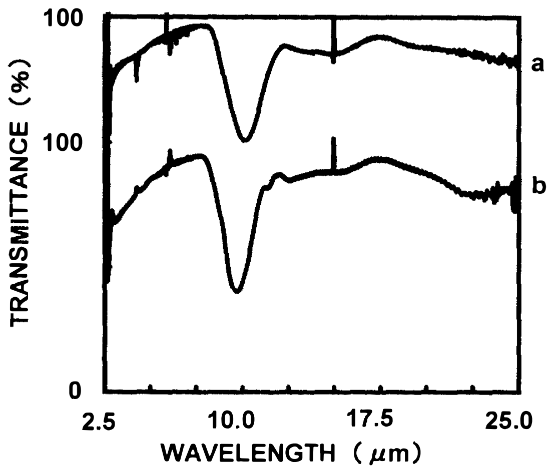

Fig. 4. IR spectra of, (a) as-deposited SiO film, and (b) the film heated at 300°C for 30 hours.

the IR spectrum of the heat-treated film. The spectrum gives peaks at 9.6, 11.4, 12.5, 15.3 and 22.5 μm, and differs from that of the as-deposited SiO film. This indicates that the heat treatment caused a structural change of film, that is, the phase transition from α- to β-cristobalite took place. The spectrum could be interpreted as that of β-cristobalite. Two crystal structures have been reported in β-cristobalite (WYCKOFF, 1965); one is a highly symmetrical cubic structure (O_h^7 (*Fd3m*)), and the other is a structure slightly distorted from the highly symmetrical positions (T^4 ($P2_13$)). Since the amorphous materials such as as-deposited and heat-treated specimens have strain fields even if the film is composed of microcrystallites (SAITO, 1984), the present heat-treated film may have β-cristobalite structure with low symmetry. In the low-symmetry structure, the Si-Si distances are 2.89 and 3.09 Å, and the Si-O distances are between 1.52 and 1.58 Å. By the phase transformation, the peak corresponding to Si-O stretching vibrations shifted from 10.2 to 9.6 μm, and that corresponding to O-Si-O bendings shifted from 19.5 to 22.5 μm. The single peak at 13.5 μm due to Si-Si stretching vibrations in the α-phase split into two peaks at 11.4 and 12.5 μm, because the difference between the shortest and the longest Si-Si distance is about 3.3 times as large as than that of Si-O distance in the β-cristobalite structure. The weak peak at 15.3 μm may be due to interstitial silicon in β-cristobalite. In fact, since the film hardly showed the color change, initial silicon remains in the film.

The two spectra in Figs. 3a and 4b are similar to each other. Thus, it was concluded that the SiO grains are composed of silicon and β-cristobalite.

The as-produced phases by the vacuum evaporated film and the grains are different. Difference in structures between SiO grains and SiO film produced by the evaporation of same material resulted from difference in the formation conditions. Figure 5 shows the temperature distribution around the heater at 1400°C in Ar gas at 100

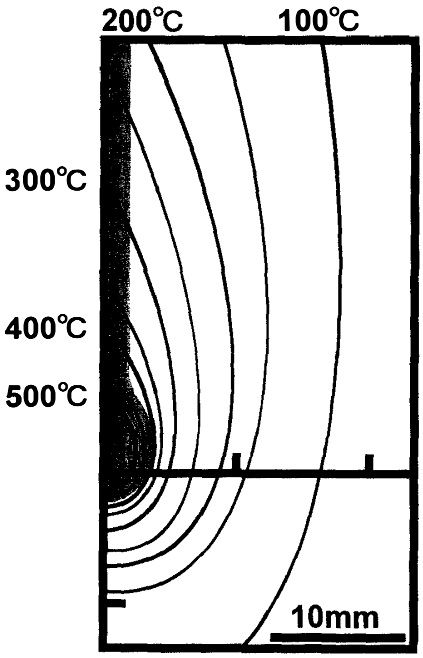

Fig. 5. The temperature distribution around the heater at 1400°C in Ar gas at 100 Torr and the produced grains flowing along a convection stream of Ar gas.

Torr. The temperature distribution was measured by a specially designed chromel-alumel thermocouple of 20 μm diameter (Kaito *et al.*, 1976). As vapor near the heat source cools rapidly due to collision with inert gas, the nucleation and growth stop within a few mm around the heater. The grain produced near the heat source flow along a convection stream of Ar gas produced by the heater. Therefore, we can see the convection flow of the gas as a smoke through the produced grains (Kaito *et al.*, 1992). The grains produced in high-temperature regions are cooled by convection flow as shown in Fig. 5. A crystal of α-quartz is produced without any impurity (Saito, 1984). Since commercial SiO powder was composed of silicon and quartz, Si vapor, some of which would become interstitial atoms acting as impurities, was also contained during the grain production. Therefore, β-cristobalite, which is high-temperature phase, was produced in high-temperature regions. The cooling process for films differs widely from that for grains, that is, the vapor evaporated from the heat source is cooled on the pellet in vacuum. Since the pellet temperature is kept at room temperature, the evaporated vapor cooled rapidly on the pellet. Therefore, the low-temperature phase has been produced.

The SiO grains were oxidized by heating at 300°C or 500°C for 30 hours in air. The grains heated at 300°C remained nearly brown, which might represent that the interstitial silicon atoms in β-cristobalite and the silicon microcrystallites do not be oxidized to form SiO_4 tetrahedra. By the heating at 500°C the grains changed white. This indicated the formation of only SiO_2 grains (Kato, 1976). Morphological change (shape) of the grains was hardly seen. ED patterns also showed halo rings. Mean grain size of the specimens became larger, that is, the size of the grains heat-treated at 300°C was 70 nm and that at 500°C 75 nm. Grain size increment due to the heat treatments may be a result of grain growth induced by absorbing the strain connected small grains.

Figure 3b and 3c shows IR spectra of the grains heated at 300 and 500°C in air, respectively. Comparing Fig. 3a and 3b, it was found that the feature hardly changed by the heating, because both heated at 300°C and as-prepared SiO grains had been β-cristobalite. On the other hand, a comparison of Fig. 3a with 3c indicates that the three peaks at 9.2, 12.7 and 21.8 μm shifted to 9.0, 12.5 and 21.0 μm, which shows typical quartz peaks, respectively. The characteristic peak at 11.4 μm due to Si-Si stretching vibrations in β-cristobalite disappeared. This suggests that β-cristobalite might have fully transformed into α-quartz. This transformation would have resulted from the oxidation of the interstitial silicon atoms in β-cristobalite and the silicon microcrystallites, and been accelerated by the heat produced in the exothermic reaction by the heating at 500°C in air.

4. Conclusions

A summary of the present results is given in Table 1. It has been concluded that IR spectra changes were due to the difference in the crystal structures of amorphous grains. All of the discussion on IR spectral change in silicates have been considered that the difference of chemical components such as Mg, Fe, and Ca atoms in silicates is the origin of the IR spectral difference. Structure analyses on these amorphous materials have been hardly done. But the present results indicate that the phase transitions; *i.e.*, the crystal structural difference, result in IR spectral changes.

Table 1. Absorption peak positions from IR spectra.

Sample	Absorption peak positions (μm)			Composition of microcrystallite
Commercial SiO powder	9.2	12.5	21.3	Fused silicon and fused quartz
As-deposited SiO film	10.2	13.5	19.5	Silicon and α-cristobalite
300°C-heated film	9.6	11.4 12.5	22.5	Silicon and β-cristobalite
As-prepared SiO grains	9.2	11.4 12.7	21.8	Silicon and β-cristobalite
300°C-heated grains	9.2	11.4 12.4	21.5	Silicon and β-cristobalite
500°C-heated grains	9.0	12.5	21.0	α-quartz
Vibration corresponding to absorption peaks	Si-O stretching	Si-Si streching	O-Si-O bending	

As well, IR spectral changes due to the heat treatments give one of evidences that the structure of present amorphous specimens are not explained by the random network model, but by the microcrystallite model. At no distant date, to give enough evidences, we will report results of HREM observations and RDF analyses on as-prepared and heat-treated specimens. It is important that data on amorphous material with olivine, pyroxene and quartz compositions have to be rechecked from the point of structural consideration. We will do this systematically in the near future.

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