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ELECTRON MICROSCOPIC AND INFRARED SPECTRAL STUDIES ON THE STRUCTURE OF ALUMINA PHASES

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Abstract: Alumina produced by oxidation of aluminum in air was studied by infrared spectroscopy and electron microscopy. Infrared spectra of both alumina particles and alumina film oxidized in air showed an absorption peak at 10.8 μm, though that of γ-Al_2O_3 particles showed a broad 13 μm peak. On the basis of the infrared spectra and electron diffraction pattern, it was concluded that alumina produced by the oxidation of aluminum in air is η-Al_2O_3. The phase transition from η-phase to γ-phase and to α-phase took place at 900°C and 1100°C, respectively. The relationships between infrared spectra and crystal structure of some alumina phases are discussed.

1. Introduction

Corundum (Al_2O_3) is the refractory phase predicted to condense first from a cooling gas of solar composition before the appearance of minerals such as perovskite, melilite and spinel (GROSSMAN, 1972). According to the condensation theory, it is suggested that corundum disappears at 1240°C due to the formation of spinel. Actually, corundum had not been reported their existence in meteorites until quite recently. However, numerous twenty-six corundum grains were found in the Murchison C2 chondrites, ranging in size from 3 to 15 μm (ANDERS *et al.*, 1991). The analysis of grains by ion microprobe mass spectrometry indicated the existence of ^{26}Al and ^{16}O in the early solar system. Moreover, the presence of corundum grains in space is also suggested from astronomical observation and theoretical calculations (VARDYA *et al.*, 1986; ONAKA *et al.*, 1989; KOZASA *et al.*, 1989). For example, the broad 12 μm feature observed in a spectra of Mira variables is identified as a characteristic band of aluminum oxide grains. It is also suggested that corundum grains may have condensed in the ejecta of SN 1987A. However, it is not obvious at present whether alumina grains in the ejecta of SN 1987A are amorphous or crystalline, or whether they are α-Al_2O_3 or γ-Al_2O_3. In spite of increasing interest in optical constants of alumina grains, very few spectral studies of alumina grains have been performed thus far. In a previous study, spectra of two types of γ-Al_2O_3 particles were measured (KOIKE *et al.*, 1995). The spectra showed very broad peaks around 13 μm. It was shown that the features agreed very well with those of spectra calculated using bulk data of amorphous γ-Al_2O_3. In general, it is well known that γ-Al_2O_3 can be produced by many techniques including vacuum evaporation of Al_2O_3, sputtering, chemi-

cal vapor deposition, anodization to form barrier-type coatings and oxidation of aluminum. However, in the present experiment, it is shown that alumina produced by the oxidation of metallic aluminum in air is not γ-Al_2O_3 but η-Al_2O_3, and that the η-Al_2O_3 phase is transformed to γ-Al_2O_3 or α-Al_2O_3 by heating above 900°C. Various alumina particles and alumina films have been studied by infrared (IR) spectroscopy. The relationships between IR spectrum and the crystal structure of alumina particles and alumina film are also discussed.

2. Experiments

At first Al particles and Al film were prepared by the gas evaporation method and vacuum evaporation method, respectively. Al particles were produced by evaporating metallic aluminum in Ar gas of pressure about 13 kPa. Al particles were oxidized by heating in air at 400–1100°C for 20 hours. For electron microscopic analysis, particles were dispersed in ethyl alcohol and mounted on a standard electron microscopic grid covered with carbon film. Particles were also mixed into KBr powder in order to measure IR spectrum, then KBr pellets embedded the particles were formed using a tablet punching device. On the other hand, Al film was produced by evaporating metallic aluminum in vacuum of 10^{-3} Pa on KBr substrate. The vacuum-evaporated Al film on KBr substrate was oxidized by heating in air at 550°C for several hours. In addition to those samples, two types of commercial alumina particles were examined. One is γ-Al_2O_3 particles from Nippon Aerosil Co. Ltd. The other is α-Al_2O_3 sample from National Bureau of Standards, which is used as a standard sample for checking the intensity of X-ray diffraction pattern. The transmittance of KBr pellets was measured with a Fourier transform infrared spectrometer (Horiba Inc., FT-210). The observation of the specimens was carried out using Hitachi H-7100R and H-800 electron microscopes.

3. Results and Discussion

Figure 1 is electron microscopic (EM) images and electron diffraction (ED) patterns of Aerosil γ-Al_2O_3 particles and standard α-Al_2O_3 sample. Aerosil γ-Al_2O_3 particles of a mean diameter 20 nm are spherical in shape. ED pattern in Fig. 1a shows strong rings due to γ-Al_2O_3 crystal and weak rings due to α-Al_2O_3 crystal. This indicates that the particles are composed predominantly of γ-Al_2O_3 crystal and of a small amount of α-Al_2O_3 crystal. As shown in Fig. 1b, the standard sample contains a small amount of γ-Al_2O_3 particles. α-Al_2O_3 particles shown in Fig. 1b have size less than 1 μm and are spherical in shape. Small particles with a mean size of 30 nm pointed by arrows in Fig. 1b were identified as γ-Al_2O_3 structure by ED pattern of the region of the coagulated small particles. The IR spectrum of Aerosil γ-Al_2O_3 particles in Fig. 2 shows a very broad peak at about 13 μm. This feature agrees very well with that of the spectrum calculated using bulk data of amorphous γ-Al_2O_3 (KOIKE *et al.*, 1995). Characteristic absorption peaks appear at 13.7, 15.6, 17, 20.4 and 22.4 μm in the IR spectrum of the standard α-Al_2O_3 sample.

Figure 3 shows IR spectra of Al film heated in air at 550°C for 5 hours (curve a) and Al particles heated in air at 400°C for 20 hours (curve b). The IR spectra of both film and

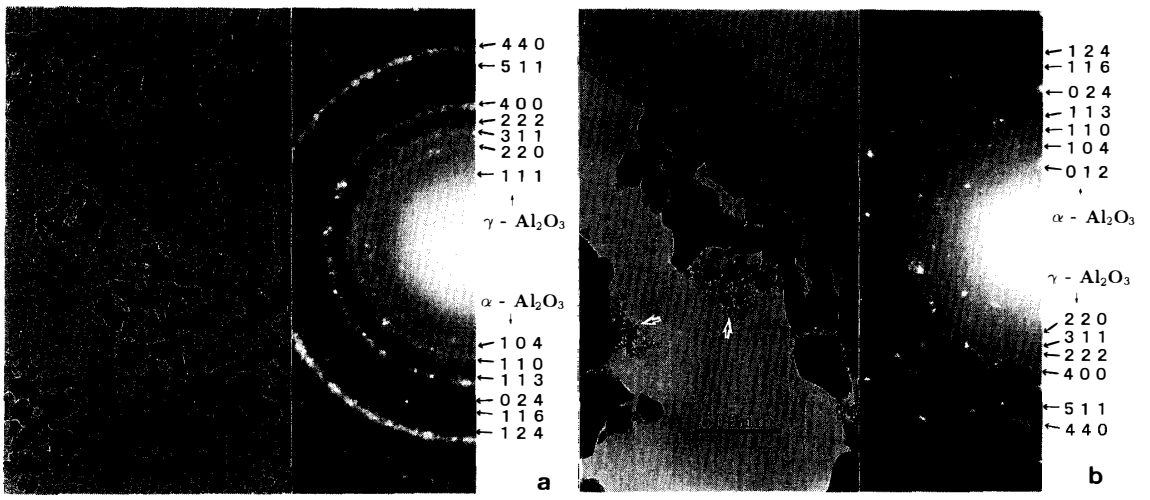

Fig. 1. EM images and ED patterns of (a) Aerosil γ-Al_2O_3 particles and (b) standard α-Al_2O_3 sample.

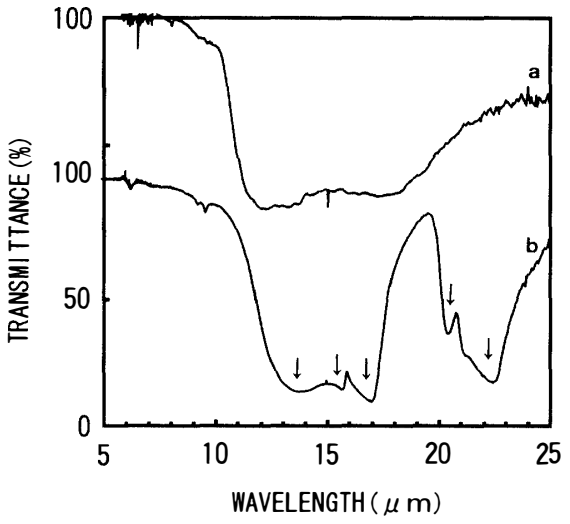

Fig. 2. IR spectra of (a) Aerosil γ-Al_2O_3 particles and (b) standard α-Al_2O_3 sample. Typical peak positions of α-phase are indicated in figure.

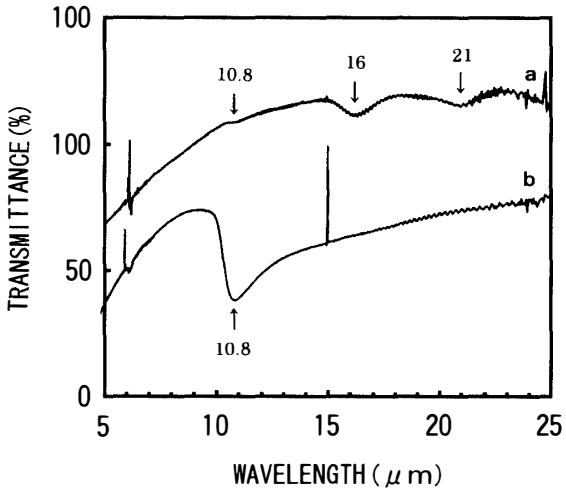

Fig. 3. IR spectra of (a) Al film heated in air at 550°C for 5 hours and (b) Al particles heated in air at 400°C for 20 hours. Peak positions are indicated by arrows.

particles have an absorption peak at 10.8 μm, different from the IR spectrum of Aerosil γ-Al_2O_3 particles. In general, alumina produced by the oxidation of aluminum has been considered to be γ-alumina. The difference of the peak positions at 13 μm (IR spectrum of Aerosil γ-Al_2O_3 particles) and 10.8 μm (IR spectrum of alumina produced by the oxidation of aluminum) suggests that the structure of oxides produced from both metallic particles and film is neither γ- nor α-structure.

Figure 4 is EM image and ED pattern of Al film heated in air at 550°C for 5 hours. ED pattern was indexed as the η-structure. Diffraction patterns of η-phase are very similar to that of γ-phase, because of the same cubic structure with nearly the same lattice constant. The difference of the structure may be due to the position of Al atoms, though

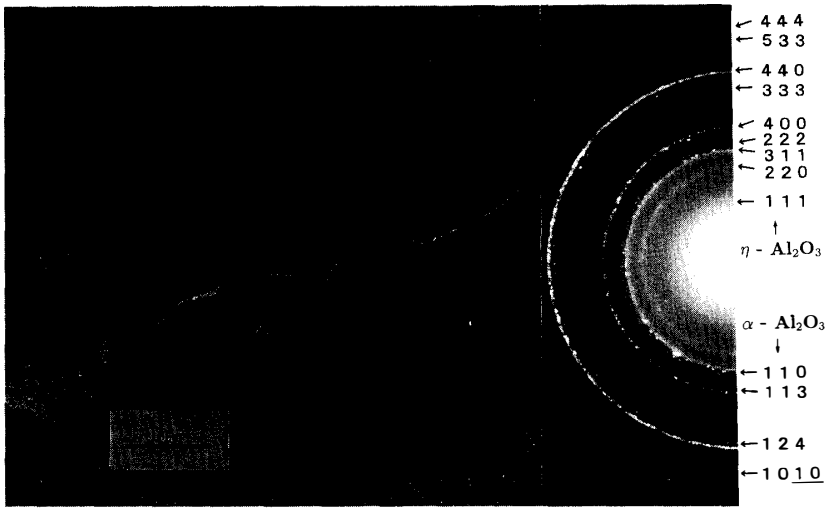

Fig. 4. EM image and ED pattern of Al film heated in air at 550°C for 5 hours. ED pattern can be indexed by η-phase.

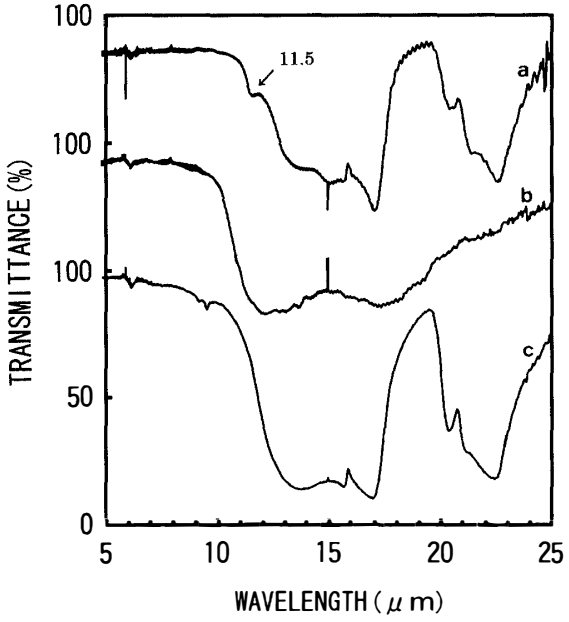

Fig. 5. IR spectra of (a) η-phase particles and (b) Aerosil γ-Al_2O_3 particles heated at 1100°C for 20 hours. IR spectrum of (c) standard α-Al_2O_3 sample is also shown.

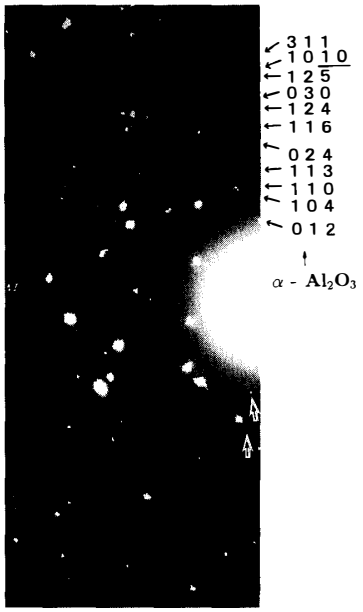

Fig. 6. ED pattern of η-phase particles heated in air at 1100°C for 20 hours. ED pattern shows the transformation to α-phase.

the fine structure of η-phase has not been clarified. On the basis of IR spectral data, it was concluded that alumina produced by the oxidation of aluminum in air is not γ-Al_2O_3 but η-Al_2O_3. In addition to the absorption peak at 10.8 μm, the absorption peaks at 16 and 21 μm in curve a in Fig. 3 were observed. According to the theoretical calculation of PEARCE and EVANS (1984) for vacuum, the absorption peaks at 16 and 21μm correspond to those of α-Al_2O_3. These peaks agreed well with two peaks measured using the standard α-Al_2O_3 sample (Fig. 2). The appearance of the two peaks may be due to the preferred orientation of the oxide film on Al film. Appearance of α-Al_2O_3 was also confirmed from ED pattern. Although the α-Al_2O_3 has been considered to be a stable phase

above 1500°C, it turns out that a part of η-Al_2O_3 film changes to α-Al_2O_3 upon heating at 550°C. Difference in the absorption peak between α-Al_2O_3 crystal from Al film and the standard α-Al_2O_3 sample is due to the measurement in vacuum (film) and in KBr medium.

The samples of η-phase particles and Aerosil γ-Al_2O_3 particles were heated at 1100°C for 20 hours. IR spectra of those samples are shown in Fig. 5 together with that of the standard α-Al_2O_3 sample. The IR spectrum of the heated η-phase particles agrees very well with that of the standard α-Al_2O_3 sample, except for an absorption peak at 11.5 μm. On the other hand, IR spectrum of Aerosil γ-Al_2O_3 particles changed little. Figure 5 suggests that the structure of both particles heated in air is quite different from each other despite the same heat treatment. This result also supports the conclusion that alumina produced by the oxidation of aluminum is not γ-phase. From this experiment, it has been found that the phase transition from η-phase to α-phase take place upon heating at 1100°C. ED pattern after heat treatment of η-phase is given in Fig. 6. In addition to the α-phase, there exist two unidentified rings indicated by arrows except for α-phase rings. Since alumina phases have many polytypes, a small amount of another phase may

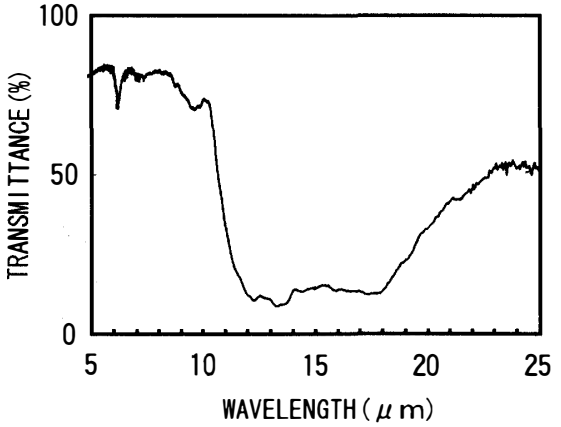

Fig. 7. IR spectrum of η-phase particles heated in air at 900°C for 20 hours. The spectrum indicates the phase transition to γ-phase.

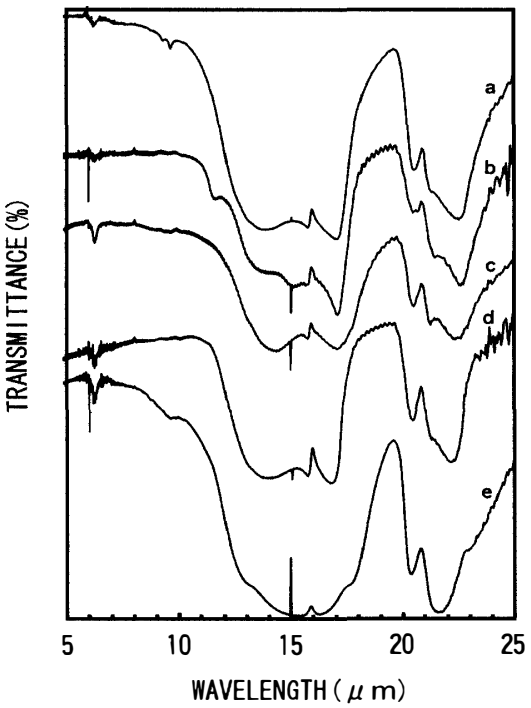

Fig. 8. IR spectra of α-Al_2O_3 particles produced under various experimental conditions. (a) the standard α-Al_2O_3 sample, (b) η-Al_2O_3 particles heated in air at 1100°C for 20 hours, (c) η-Al_2O_3 particles heated in Ar atmosphere at 1500°C for 10 hours, (d) Aerosil γ-Al_2O_3 particles heated in Ar atmosphere at 1500°C for 1 min and (e) Aerosil γ-Al_2O_3 particles heated in Ar atmosphere at 1500°C for 2 hours.

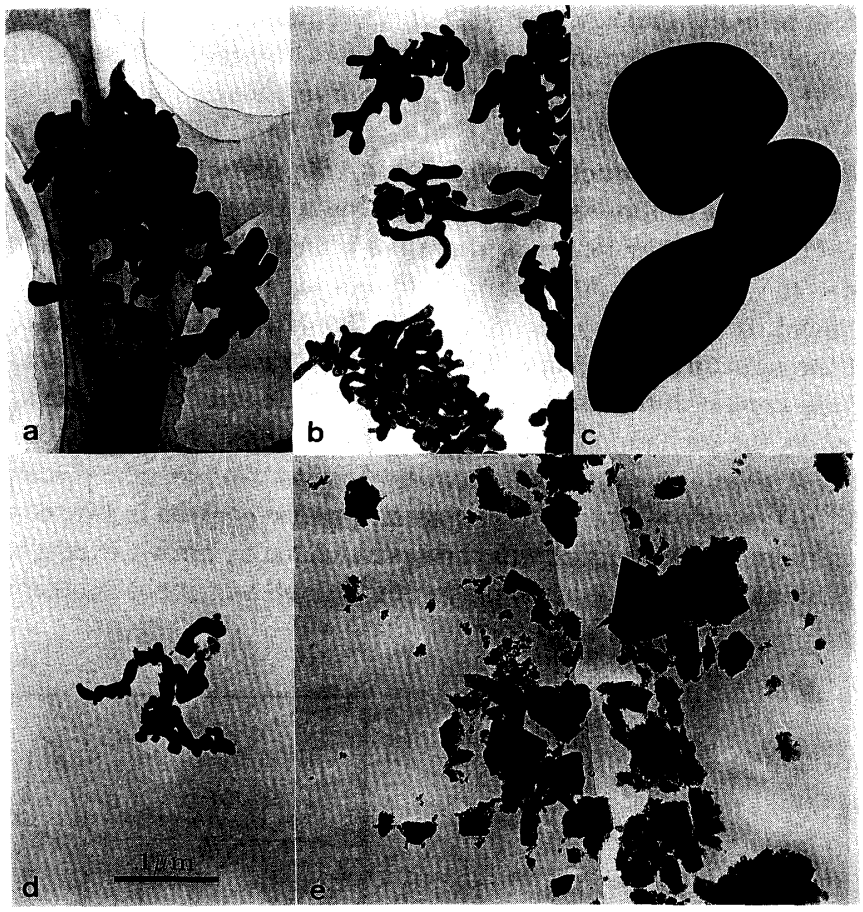

Fig. 9. EM images of α-Al_2O_3 particles produced under various experimental conditions. (a), (b), (c), (d) and (e) correspond to those indicated in Fig. 8. EM images are shown in the same scale.

appear upon heat treatment. Detailed analysis concerning this point is under way. The IR spectrum of η-phase particles heated at 900°C for 20 hours in air is shown in Fig. 7. It is in good agreement with that of Aerosil γ-Al_2O_3 particles. Therefore, it can be concluded that the phase transition from η-phase to γ-phase takes place upon heating at 900°C.

In this experiment, IR spectra of many kinds of α-Al_2O_3 particles produced under a different growth condition were measured. Figures 8 and 9 show, respectively, IR spectra and EM images of the α-Al_2O_3 particles. Although ED patterns of these samples showed α-Al_2O_3 phase, the features of IR spectra differ as seen in Fig. 8. IR spectra for the same crystal habits and sizes agreed well as seen in Fig. 8a, b, d. When the size of the particles becomes larger, the 17 μm peak in the IR spectrum becomes broad as seen in Fig. 8. This result indicates that the difference of the particle size and the crystal shape can influence the spectral features. However, IR spectral studies on the size and shape effects of particles for a single material have been little studied. The details of these effects will be published elsewhere, including the variation of the absolute absorption values due to the shape effect.

The presence of alumina grains in various astronomical objects have been listed in

Table II in previous paper (KOIKE *et al.*, 1995). As suggested in that paper, besides Mira variables, new emission features have been observed at 7.15, 10, 11.5, 13.1, 18 and 19.7 μm bands in other oxygen-rich circumstellar shells (GOEBEL *et al.*, 1994). The absorption peak of η, γ and α phases have been observed in the present experiments. Taking account of the shape effects in α-Al_2O_3 particle, except 7.15 μm peak, all other peaks may be assigned as the alumina phases. The absolute values of these phases may become important to correlate between the observation data and laboratory data. Details will be published elsewhere, including the shape effect on the spectrum.

Acknowledgments

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