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Growth and the Phase Transition of Indium Sulfide Ultrafine Particle

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Indium sulfide particles produced in smoke have been analyzed by transmission electron microscopy. Three phases, α, β and β' with the different external shapes were produced. A mixture phase of β and β' was found and the lattice relation was elucidated. The phase transition temperatures were assigned to be 400°C (α to β) and 500°C (β' to β).

KEYWORDS: α-In_2S_3, β-In_2S_3, phase transition, ultrafine particle, advanced gas evaporation method, indium sulfide, electron microscopy
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1. Introduction

In a previous paper, we proposed a new method of producing metallic sulfide ultrafine particles and noted that some sulfide particles grew as the mixture particles of polymorphic phases independent of the reversible and irreversible transformation seen in bulk materials.[1,2] The morphological studies on ultrafine particles on metal,[3] metallic oxides[4] and metallic sulfides[2] indicated that the structural differences appear as morphological differences. In addition to the interest on the sulfide particles in the fields of astrophysics and mineralogy indium sulfide compounds are also interesting as the solar cell materials[5,6] and the optical catalyst replacing the TiO_2. The temperature of the polymorphic transformation is generally lower in sulfide compounds than metal and metallic oxides. In case of In_2S_3 crystal, the α to β transformation is known to occur at 360°C and is irreversible. In the present paper, in addition to α and β phases of In_2S_3 particles, the existence of a β' phase is shown. The phase transition temperature relationships of α, β and β' phases have been elucidated by the successive heating in vacuum.

2. Experimental

The sample production chamber is a glass cylinder of 17 cm i.d. and 33 cm height. Two tantalum boats, U and D, were set in the chamber as shown schematically in Fig. 1. When boat U was heated to 1400°C in Ar gas pressure of 13 kPa, the temperature distribution around the heater became as shown in Fig. 1. The temperature distribution curve was measured using a specially designed chromel-alumel thermocouple of 20 μm diameter.[7] Heater U was used as the evaporation source of indium. Sulfur powder was charged into boat D.

By heating boat U at 1400°C, the vapor pressure of indium in boat U and sulfur in boat D, which is defined by the atmospheric temperature, became on the order of 1 Torr. Then the reaction between sulfur vapor and indium vapor took place near boat U and smoke could be seen by the naked eye. Convective flow was produced due to the presence of boat U. The samples collected 100 mm above boat U were examined using Hitachi H-7100R and Hitachi H-9000NAR electron microscopes.

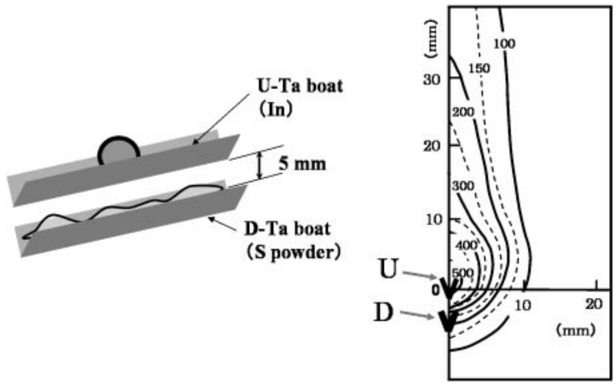

Fig. 1. Schematic of the set up for producing the sulfide particle by making use of the temperature distribution and convection flow in smoke. This method is called the advanced gas evaporation method (AGEM).

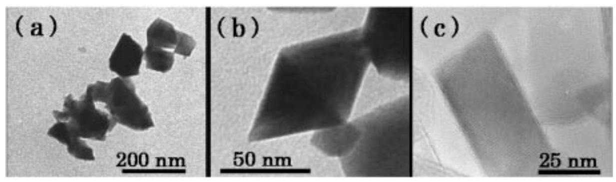

Fig. 2. (a) α, (b) β and (c) β' of In_2S_3 phases electron microscopic images of typical In_2S_3 particles. The difference in the morphology reflects the structural difference.

3. Results and Discussion

In addition to typical complicated polyhedral and octahedral shape particles reported in a previous report[2] and indicated in Figs. 2(a) and 2(b), plate-shaped particles were observed, as shown in Fig. 2(c). The lattice image can be identified as that of the β' phase with a tetragonal structure having lattice parameters $a = 1.073$ and $b = 3.232$ nm.[8] The α and β phases indicated in Figs. 2(a) and (b) are the low- and high-temperature phase. The bulk data showed that the α to β phase transition occurs at 360°C and is irreversible. Three phases are mixed in the collected particles. Since the phase transition temperature is lower than those of the elements or oxides, the difference in the

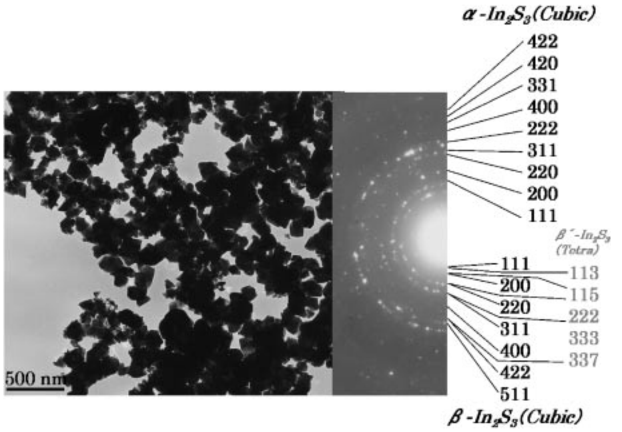

Fig. 3. TEM image of collected particles and corresponding electron diffraction pattern. The electron diffraction rings indicate the growth of three polytypes.

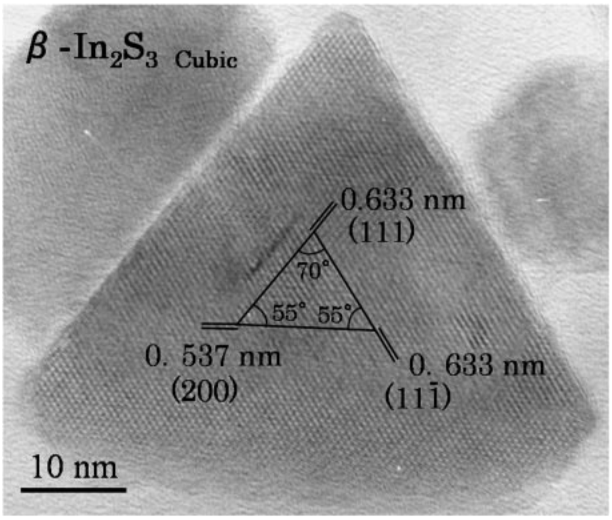

Fig. 4. HRTEM image of a particle. The lattice distance and crossed angles indicate the growth of the β phase.

cooling velocities in the smoke[9] may have produced the three phases. The amount of the β' phase is very little; therefore we could not identify it in the previous study. The electron microscopic image and electron diffraction pattern of the three phases is shown in Fig. 3. The diffraction pattern can also be indexed as a mixture of the three phases. The morphologies of the three phases were found to be different. In the present experiment, the truncated tetrahedral particles seen in small In_2O_3 particles are also observed, as shown in Fig. 4. The particle is identified as the β phase from the crossed lattice image and the crossed lattice angles.

Figure 5 shows the coalesced particle of two octahedral particles with parallel relationship. The electron diffraction pattern was indexed as that of the β' phase with the zone axis of [110], since the β' phase can be explained as the superstructure of the β phase with three times the lattice constant along the *b*-axis direction of β. Therefore the β and β' phases may coexist. By high resolution transmission electron microscope (HRTEM) analysis, the β and β' phase mixtures are examined as follows.

Figures 6 and 7 show HRTEM images that indicate the

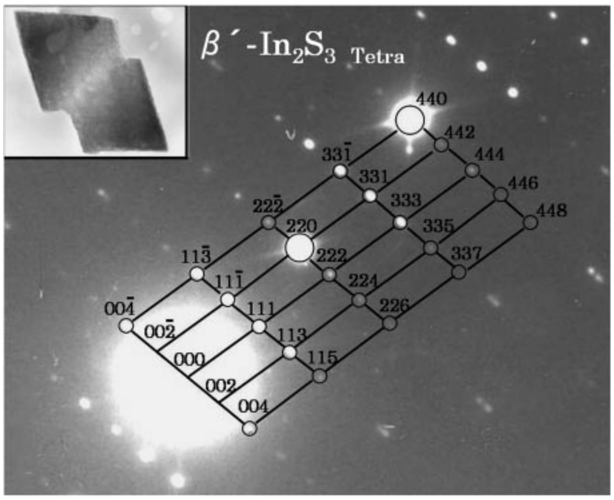

Fig. 5. TEM and ED images of the coalesced particle of two octahedral particles with parallel relationship. The super-diffraction spots can be indexed as those of the β' phase.

lattice relation between the two phases, β and β'. The image in Fig. 6 shows tetragonal particles surrounded by a layer of weak contrast. This surrounding region of weak contrast region was composed of β' phase and the central region was composed of β phase with the lattice relation $(111)_{\beta} \parallel (113)_{\beta'}$. Figure 7(a) shows the mixture region of mixed β and β' phases. Guinier–Prestin (G.P.) zone like contrast[10–13] indicated by arrows can be seen in the β' phase region. Figure 7(c) shows that the misfit dislocations can also be seen in the boundary between the two phases. These contrasts suggest that the β' phases were gradually altered to the β phases. Since the crystal structure of In_2S_3 is similar to that of In_2O_3, the phases produced may be n-type sulfides;[14] therefore the presence of excess metals may result in the G.P. contrasts.

Figure 8 shows the results of the heat treatment of collected samples. The electron diffraction pattern of the specimen heated at 200°C showed the existence of three phases. On heating at 400°C, the α phase disappeared. The β and β' phases remained. On heating at 500°C, all the phases had become the β phase. The phase transition of α to β' is concluded to occur at 400°C. The β' to β phase transition occurred at 500°C. All the phase transitions were irreversible. The formation of three phases may be due to the size effect and the difference in the cooling velocity in smoke. The shape of the particles was not negligibly altered to the phase transition from α to β' and β. This suggests that the three polytypes of In_2S_3 were very similar structures. During the growth process in smoke, the local temperature difference and cooling speed difference in different regions of smoke may have caused the different shapes and structures.

4. Summary

The indium sulfide particles were of mixture of α, β and β' of In_2S_3. The basic morphology was different in three phases, i.e. complicated polyhedron (α), octahedron or truncated tetrahedron (β) and plate-shape (β'). The lattice relationship between the β and β' phases was elucidated. The phase transition temperatures and the three phases were clarified to be 400°C (α to β) and 500°C (β' to β).

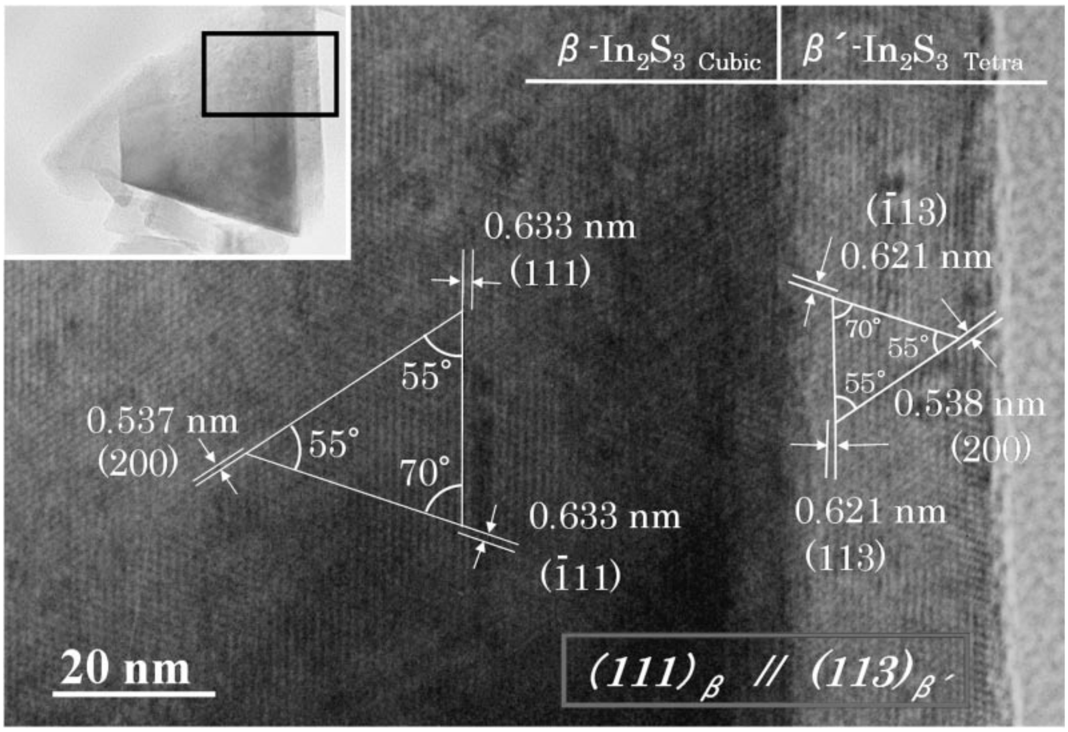

Fig. 6. Two-phase particle of β and β' phases. The β' phase grew on the β phase with the parallel relationship of $(111)_{\beta} \parallel (113)_{\beta'}$.

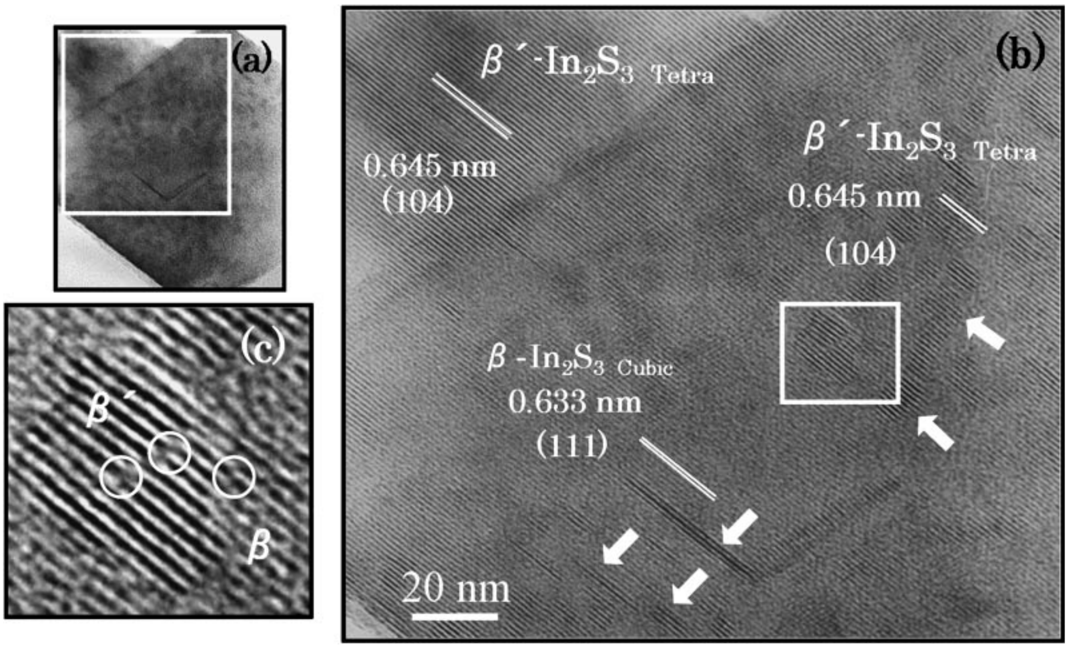

Fig. 7. HREM image of octahedral particle. The G.P. contrast and misfit dislocations are seen with the coexistence of two phases.

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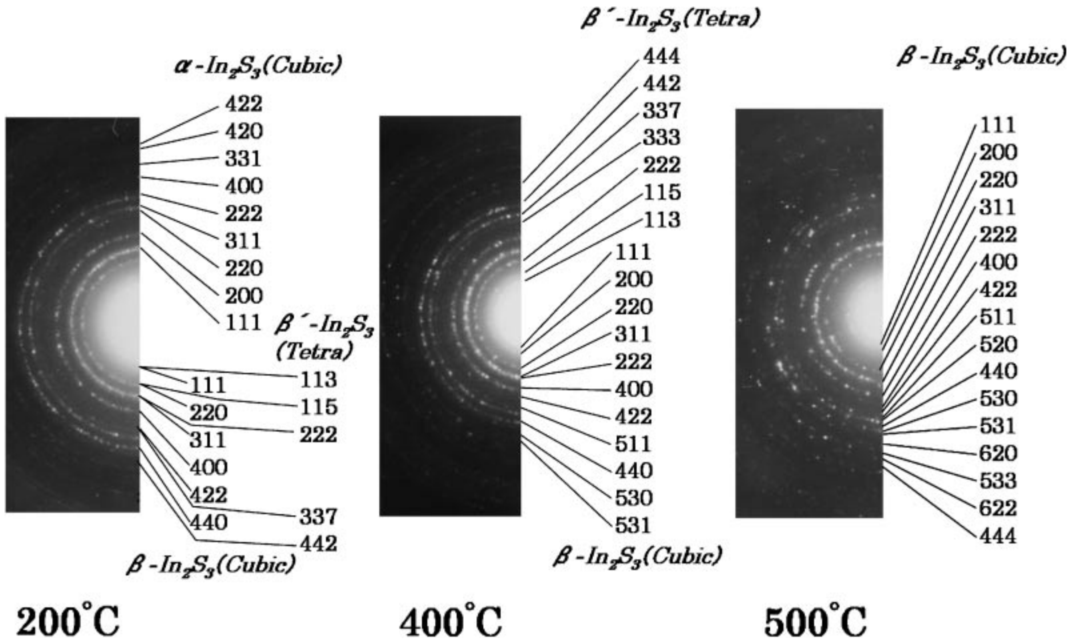

Fig. 8. ED patterns of the heat-treated collected samples. Phase transition temperatures of α, β and β' were determined. The α phase disappeared at 400°C. The β' transformed to the β phase at 500°C.