

Formation of Forsterite Grains and Direct Observation of The Sublimation of Crystal Formation Grain

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Forsterite crystal fine grains have been produced by flushing SiO powders into the flame during MgO grain formation in mixture gas of Ar (80 %) and O₂ (20 %) at 13 kPa. Experimental studies on the sublimation of forsterite grains upon heating at 10⁻⁶ Pa have been carried out using a high-resolution transmission electron microscope. The spherical crystalline grains became polyhedral at 973 K, which corresponded to the temperature at which the stall state appeared. Coalescence and sublimation occurred at 1093 K. The sublimation rates of forsterite grains with a size of 40 to 100 nm with the structure of Mg₂SiO₄ were estimated. The sublimation of grains near the crystallization temperature indicates the reason that no crystal silicates appear in the interstellar medium.

1. Introduction

Submicron-sized silicate grains are present in the circumstellar outflows around oxygen-rich stars and within the interstellar medium. These grains may play an important role in the early evolution of the solar nebula, both as the starting material for the accumulation of planetary bodies and as the chief source of infrared opacity in the nebula. Since the estimated pressure of the solar nebula at 2-3 AU is low [1], experiments on grown metamorphism in vacuum are important for comparison with condensation, evaporation, melting and crystallization process observed in the primitive solar nebula [2 and 3].

IR spectra of red super giant (RSG), asymptotic giant branch (AGB) stars, post-AGB stars and planetary nebula (PNe) obtained by the infrared space observatory (ISO) project indicated a mixture of amorphous and crystalline silicates [4 and 5]. Spectroscopic and imaging observations of the structural and compositional properties of brown dwarf disks [6] showed that crystalline silicates are significantly more abundant in the outer part than in the deeper layers of the disk. In addition to the crystallization of amorphous grains, the reverse transformation from crystalline to amorphous species has become an important point of consideration.

We demonstrated that the crystallization of amorphous Mg-bearing silicate grains to crystalline Mg₂SiO₄ crystal takes place at 1075 K in vacuum [7]. The crystallization starts from the grain surface. We also found that prenucleation occurs in the 923-1003 K temperature range before the onset of crystallization at 1073 K. The phenomenon of a pre-nucleation state corresponds to the stall state, which was clarified by infrared spectroscopy [8]. Specific studies on the evaporation of forsterite at 1973 K have been performed recently. It was shown that forsterite evaporated congruently both in equilibrium in H₂ gas [1 and 3] and in vacuum [9]. The evaporation anisotropy of a synthetic single crystal of forsterite was investigated by high-vacuum experiments [10]. The intrinsic evaporation rates for the (100), (010) and (001) surfaces are different, and have a ratio of ~17, ~7 and 22 on μ m/hour. The evaporation rate along the c-axis is largest. The evaporation rate along the b axis is smallest due to the cross-packed direction of the MgO tetrahedron. In this paper, we report the direct observation of the sublimation of sub-micron scale, crystalline, Mg₂SiO₄ grains vacuum at a pressure of 10⁻⁶ Pa. The dynamic behavior of the submicron scale, crystalline, grains was recorded on videotape.

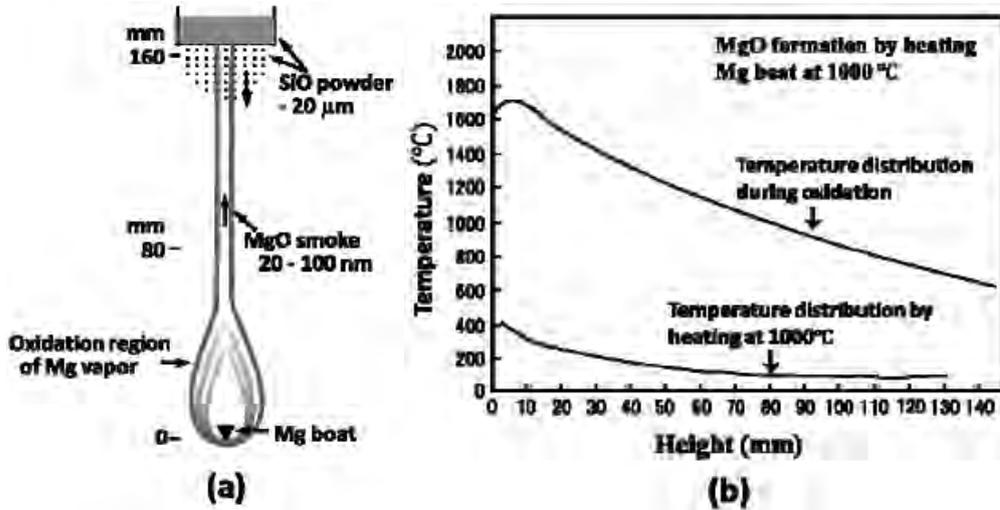


Fig.1. Schematic representation of method crystalline forsterite grain formation in magnetism oxidation smokes region by a tantalum boat (a). Temperature distribution during the appearance of MgO smoke in mixture gas of O₂ and Ar (b).

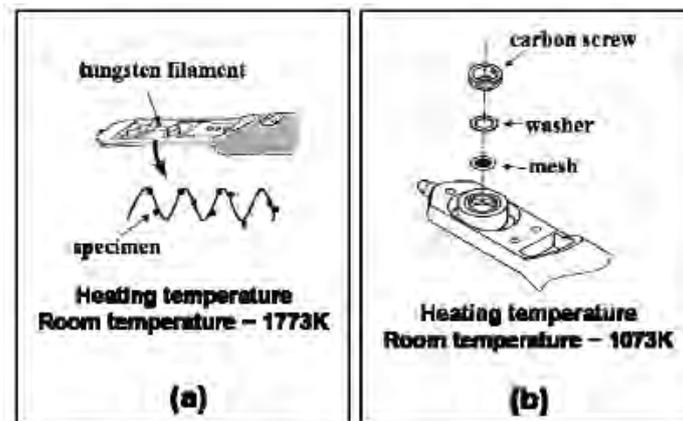


Fig.2. Schematic diagram of heating stages used in the present experiment in transmission electron microscope in vacuum

2. Experimental Procedure

The crystalline Mg₂SiO₄ samples were produced by an advanced gas evaporation smoke method, i.e., SiO powder was flashed into a magnesium oxide flame as shown in Fig. 1(a) [11]. The sample preparation chamber was a glass cylinder of inner diameter 17 cm and height 33 cm. MgO smoke was produced by the oxidation of evaporated magnesium from the evaporation source of tantalum boat in mixture gas of O₂ (20 Torr) and Ar (80 Torr) in gas pressure of 13 kPa. SiO powders were sprinkled on the smoke stream rising straight up from the evaporation source. MgO fine grains were produced by evaporating Mg powder at 1000°C in the mixture gas. During the evaporation of Mg, the temperature in atmosphere becomes higher than the source temperature due to the exothermic reaction of Mg vapor as shown in Fig. 1(b). SiO powder sprinkled from the top of the smoke was evaporated in MgO oxidation region in Fig. 1(b). If the evaporation of Mg powder finished, the temperature becomes the general shape of gas flow temperature at 1000°C as indicated in Fig. 1(b). The evaporation of SiO powder occurred during the oxidation of Mg. Two heating stages were used, as shown in Fig. 2. Specimen Mg₂SiO₄ crystal grains were placed on the tungsten heater (Fig. 2 (a)). This holder can be used to heat the specimen to 1773 K, whereas the holder shown in Fig. 2(b) can be used for heating to approximately 1073 K. The specimen was dispersed on the carbon holey film. The specimen holder in Fig. 2(b) can also be used for the method of covering the specimen with a thin carbon film [12]. The sublimation process was observed by high-resolution transmission microscopy (Hitachi H-9000 NAR) using the specimen holder in Fig.2.

3.Results and Discussion

3-1 Formation of forsterite grain

One of experimental methods used to produce ultrafine growth is the gas evaporation technique. If the Mg and SiO is evaporated on the mixture gas of O₂ (20 Torr) and Ar (80 Torr) from the evaporation source of tantalum boat at 1000 °C (Mg) and 1600 °C (SiO), the typical electron microscopic image of MgO and SiO₂ were produced as shown in Fig. 3. MgO particles were cubic shape compound of 8 {100} planes. By the evaporation of SiO powder in the mixture gas, amorphous oxidation of SiO is preferentially produced beta-SiO₂ amorphous spherical structure as indicated diffractions pattern. The detail formation of silicon oxide will be published elsewhere.

If the SiO powder were introduced into the Mg oxidation region in smoke, the reaction between magnesium oxide and SiO water took place as indicated previous paper [11]. The heating of Mg at 1000 °C, the reaction of Mg with oxygen gas becomes at 1600 °C as indicated in Fig. 1. The produced particles were MgO and Mg₂SiO₄. The amorphous Mg₂SiO₄ particles were hardly produced in the present method against another method [7].

Figure 4 shows a mixture of forsterite particles indicated A (Mg₂SiO₄, a = 0.47553, b = 1.01978, c = 059817 nm), the same lattice constants as those in the studies on the evaporation anisotropy of single crystal forsterite (Nagahara and Ozawa, 1999) and of periclase particles (MgO indicated B) produced by dropping SiO powder into the MgO smoke flame [11]. Since the MgO flame due to the oxidation of Mg vapor reaches 1873 K [13], the SiO powder becomes SiO vapor in the flame.

Figure 5 (a), (b) and (c) show the high-resolution transmission electron microscopic images of Mg₂SiO₄ crystal. Most of the spherical grain had a plate shape, and the crystallographic orientation is shown in the images. The electron diffraction pattern (ED) showed the single-crystal grain growth of forsterite.

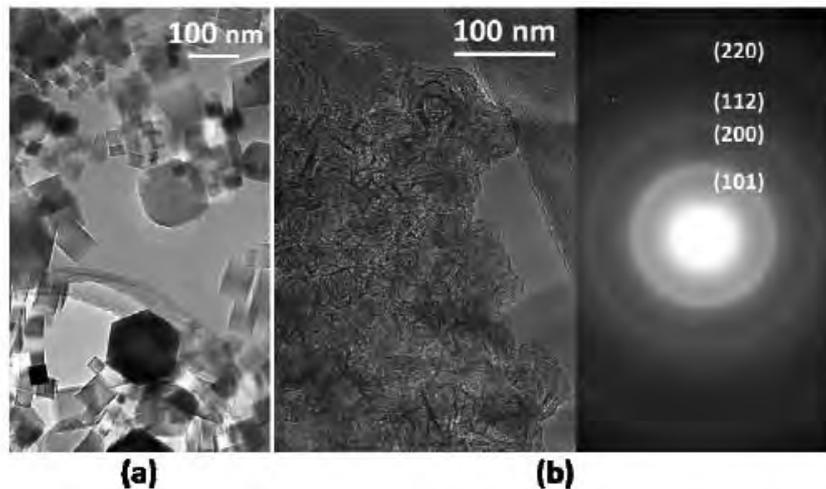


Fig. 3. Typical produced grains of MgO and amorphous, β — SiO₂ by heating in the present system.

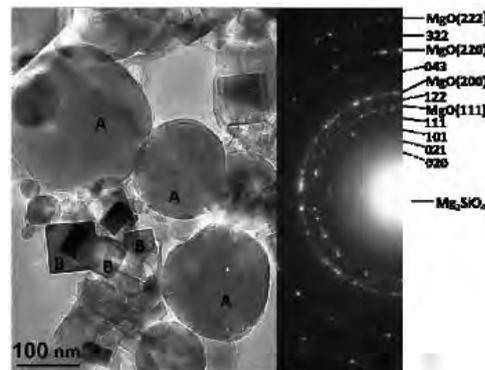


Fig. 4. Typical electron microscopic images of MgO and Mg₂SiO₄ crystal grains produced by the present system in Fig. 1. A and B shows Mg₂SiO₄ and MgO particles.

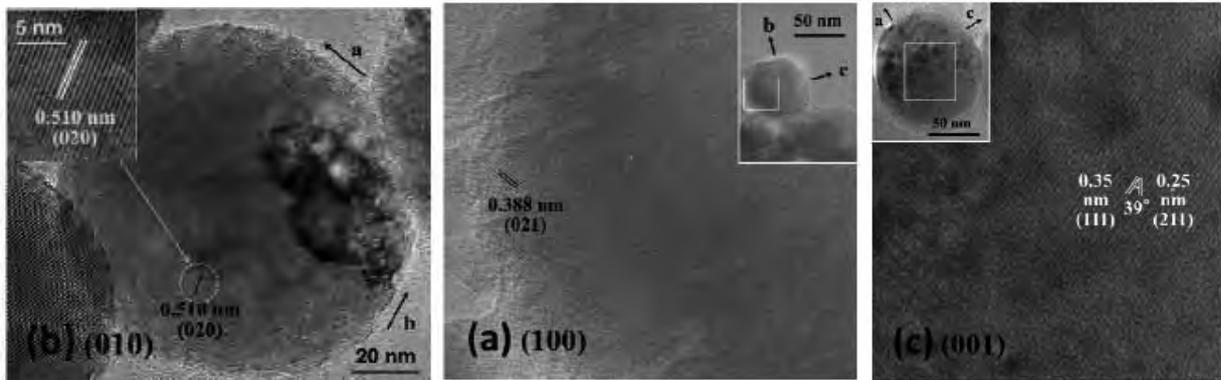


Fig. 5. High resolution electron microscopic image of (100), (010) and (001) direction images of Mg_2SiO_4 nano particles.

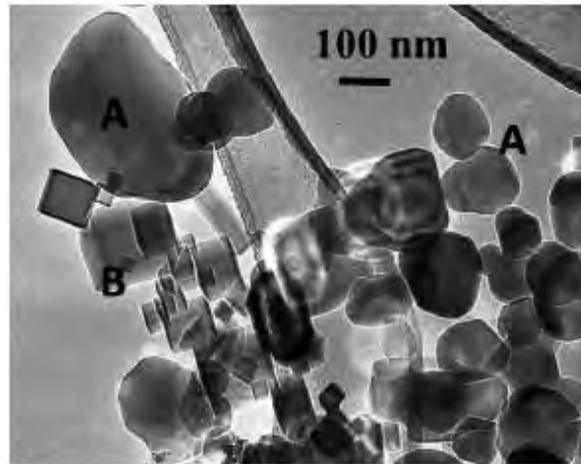


Fig. 6. Typical image after heating using the hole in Fig. 2 (b). Spherical grains became polyhedral upon cooling in vacuum. A and B shows Mg_2SiO_4 and MgO particles.

3-2 The sublimation of crystal forsterite grains

The morphological alteration started at 973 K. The spherical crystal indicated in Fig. 4 became polyhedral shapes as indicated in Fig. 6. This shows that the higher order crystal plane started to sublimation or be remolded. Fig. 7 shows the direct observation on the alteration process of forsterite crystal. The shape of the particle indicated by arrows A and B were altered at 973 K. The alteration of the spherical shape crystal B than the spherical shape crystal A was clearly seen. The black dots and the coagulated cubic particles indicated by arrows suggest the formation of MgO crystallites, i.e., the decomposition of Mg_2SiO_4 spherical particle into MgO and SiO_2 took place as well as prenucleation of amorphous forsterite grains, i. e., surface decomposition is prominent above 973 K. The b and c or a axes of the forsterite crystals are appeared. This shows that the higher order crystal plane started to sublimation or be remolded. From the difference in evaporation along the a. b and c axes of the forsterite crystal [10], the (001) and (100) planes, with higher rates of evaporation, both evaporated.

When the temperature was increased to 1103 K, which is slightly higher than the crystallization temperature of 1073 K [7], coalescence growth and sublimation were prominently observed. Figure 8 shows the process of alteration and sublimation. The convex region indicated by the arrow in Fig.8 was flattered by the sintering process (Kimura,1960). By increasing the temperature by only about 10 K, two polyhedral grains of size 500 nm in contact were observed to coalescence, and alter shape as shown in Fig.8. The particles indicated by the arrow A altered their shapes.

The black dots seen in Fig.7 hardly observed. The sublimation of the Mg_2SiO_4 crystal took place congruently, which means that the residue has the same composition as the starting material [1]. The grain indicated by arrow A sublimated

and disappeared with 430 s as shown in Fig.8. If we assumed that the particle size indicated by arrow A at 210 sec is a sphere with a radius of 42 nm, then the mean evaporation rate of the forsterite crystal is 2.04×10^4 molecule/sec. From the coalescence of grains at 1103 K, it was estimated that a spherical grain of 172 nm was absorbed in 810 sec by diffusion to the substrate grain. The alteration in shape suggests that this may be the result of the differences in evaporation rates along the different axes. The sublimation rate before the diffusion process merged the two grains was 3.6×10^4 molecule/sec.

Figure 9 shows a grain of 100 nm radius on the top of a MgO crystal sublimated in 380 sec. The mean evaporation rate for the particle in Fig.9 is 1.5×10^5 molecule / sec.

To observe the evaporation along the [010] direction, the surface of the particles was covered with a thin carbon layer using the heating shape (b) in Fig.2 (b). The specimen grains were dispersed on holey carbon film. A typical grains covered by a thin carbon layer (4 nm) is shown in Fig.10. The carbon layer was also evaporated above 973 K (Ishikawa et al., 2003). The evaporation state of the forsterite along to the (010) plane was observed using a high resolution transmission electron microscopic image of the (101) lattice image in the temperature range between 1033 to 1113 K as shown in Fig.11. The lattice image of (101) lattice image in the temperature range between 1033 to 1113 K as shown in Fig.11. The lattice image of (101) is distorted upon the evaporation of the (010) surface. The thickness alteration causes the lattice image to disappear. Therefore the focus of the grain in the TEM was altered. However all of the (101) lattice images disappeared within 1063 sec. The disappearance of the lattice images left to right suggests that sublimation took place by layer. At about 1113 K, the crystal structure of Mg_2SiO_4 was destroyed and most of the particles became MgO crystallites. After heat treatment of the sample, the particles dispersed on the carbon holey film had changed in

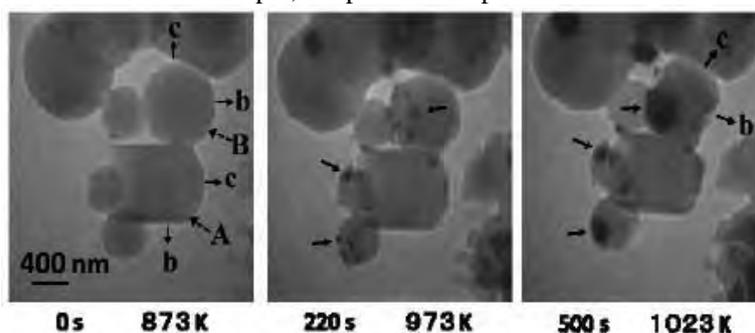


Fig. 7. Morphological alteration of forsterite grains by heating to the prenucleation temperature (stall state)

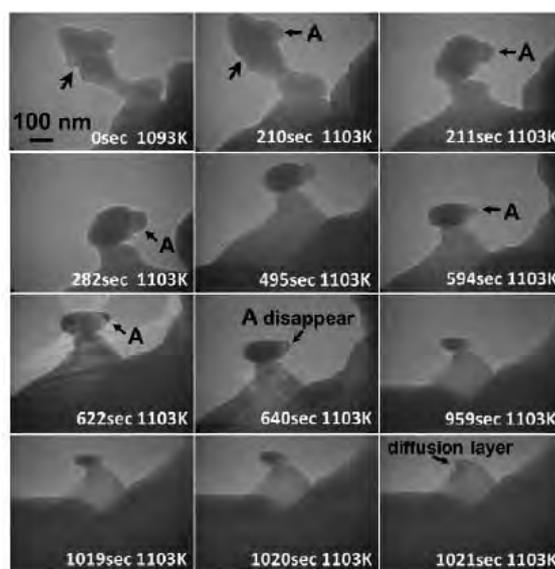


Fig. 8. Coalescence and sublimation at the temperature range of crystallization

shape and MgO crystals were predominately observed as shown in Fig. 6. Figure 12 shows the high resolution electron microscopic image corresponding to the grain in Fig.11, fine stable and dissolved MgO crystallites was predominately seen. The layer – by layer- alteration along the b-axis was mainly due to the decomposition of Mg_2SiO_4 and MgO and SiO_2 . The metamorphism of SiO_2 phase [14] was clearly took place at 1173 K. More detail based on an experiment using

the same apparatus in Fig.2(a) will be published in near future for the SiO₂ plane.

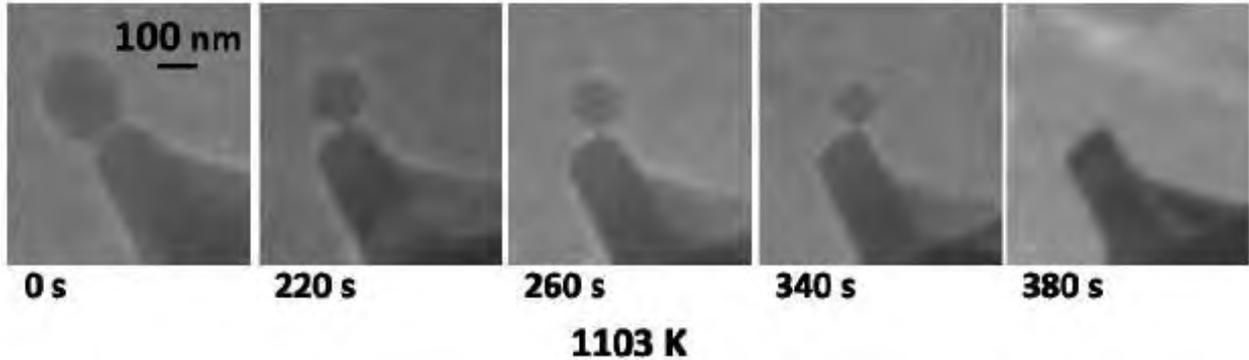


Fig. 9. During the sublimation process, the shape of crystal was altered.

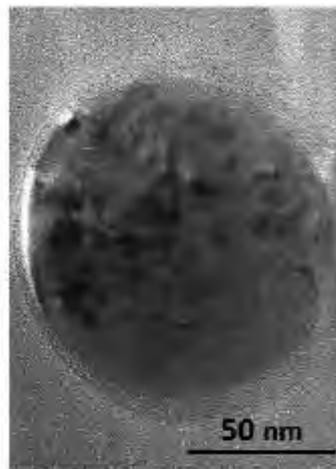


Fig. 10. Typical grains covered with amorphous carbon layer of 5 nm thickness. A grains covered with a carbon layer can be easily produced using the heating stage in Fig.2 (b) by heating at 373-673K.

4. General Discussion

The evaporation coefficient for forsterite in vacuum is between 0.09 – 0.16 at temperature of 1900 ~2163 K [9, 15]. Extrapolation of these to the sublimation temperature at 1093 K is impossible. Evaporation experiments on single crystals have mainly been performed at temperature of 1973 K [10]. The present result is about 0.51 times lower and suggests that the sublimation temperature of the dust is different these that of the bulk material. The main reason for this is that the surface energy of the grains causes a decrease in sublimation temperature. The surfaces to volume ratio of grains with size of 10,100 and 1000 nm are 2.75, 0.275 and 0.0275 % respectively. The coalescence and growth of particles in the smoke cloud is also a low temperature phenomenon in nanoparticle physics [16, 17]). Spontaneous alloying at room temperature [18] and the spontaneous mixing of alkali halide crystals [19] involve atomic diffusion at low temperatures. The alteration of the surface structure and low temperature sublimation become prominent in grains of size less than 500 nm. The present results are in good agreement with the schematical diagram of dust metamorphism in a protostellar disk and the processes involved therein [20]. The authors thank T .Yamamoto and Joseph A. Nuth III of NASA/GSFC for the reviewers for valuable comments.

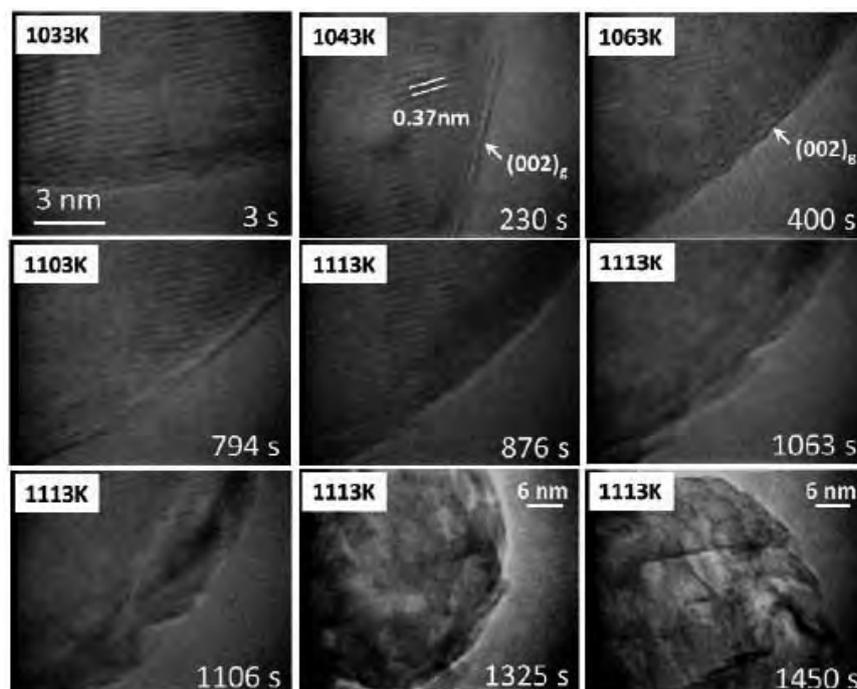


Fig. 11. High resolution transmission electron microscopic image slowing the evaporation of (010) forsterite.

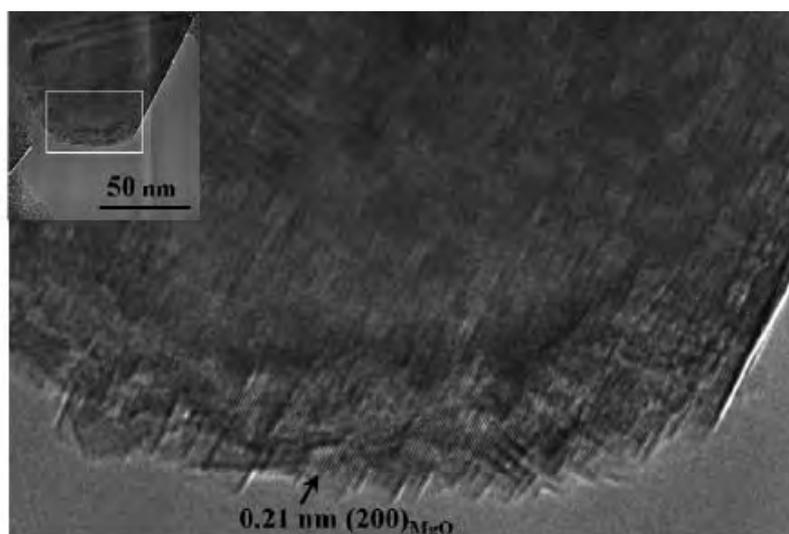


Fig. 12. High resolution transmission electron microscopic image after heating

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