

Crystal structure of protoenstatite quenched to ambient temperature

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Protoenstatite (MgSiO_3) is generally thought that it cannot be quenched to ambient temperature, however, there are several reports on quenched protoenstatite (e.g., Lee and Heuer, 1987). We also observed protoenstatite using ^{29}Si MAS NMR spectroscopy of MgSiO_3 sample taken out from a furnace and cooled down (Xue et al., 2002). However, there is no study on crystal structure of quenched protoenstatite nor quantitative analysis on proportion of enstatite polymorphs in the quenched samples. In this study, four samples with different cooling rates were studied by powder X-ray diffraction and micro-Raman spectroscopy.

Starting enstatite sample was prepared from reagent-grade MgO and SiO_2 , and they were mixed, and pelletized, and treated at 1500°C twice. In previous reports (Lee and Heuer, 1987; Reynard et al., 2008), glass or melt was quenched to obtain protoenstatite, but in the present study, ordinary solid state synthesis method was employed. The starting material was kept at 1500°C for 5h, and cooled down to ambient temperature with four different cooling rates (150 K/h, 15 K/h, taken out from the furnace and bottom of Pt crucible was dipped into water, sample directly dipped into water). It is known that protoenstatite would transform to low-clinoenstatite by grinding. So the samples were handled gently. Since recovered samples were powder, no special treatment was necessary to put into sample holder for powder X-ray diffraction measurement. Grain size of all samples are similar, and are about 5 micrometer with angular shapes. The Rietveld method was used to refine crystal structure of protoenstatite, and quantitative analysis of the samples (RIETAN-FP program used). For Raman spectroscopic measurement, recipe proposed by Reynard et al. (2008) is used to identify enstatite polymorphs.

From X-ray diffraction, it was found that all samples contain both protoenstatite and low-clinoenstatite. Their existence was also confirmed by micro-Raman spectroscopy including the starting material. Structural refinement was conducted using protoenstatite-rich sample. Obtained lattice parameters are consistent with extrapolated values of high-temperature data (Jiang et al., 2002), suggesting no major structural change with temperature. Refined crystal structure of protoenstatite is essentially same as that determined at high temperature, and is consistent with simulated structure using the DFT calculation (at 0 K). Quantitative analysis by the Rietveld method revealed that about 40% protoenstatite exists in Pt crucible bottom dipped into water sample, and about 30% for slowly cooled sample (15 K/h), and there is cooling rate dependence for the proportion. However, supposedly most rapidly quenched sample, directly dipped into water, showed lowest proportion (30%).

Present study revealed that even using common synthesis technique, significant amount of protoenstatite is remained in so-called low-clinoenstatite sample. This implies that previous phase equilibrium studies of the MgSiO_3 system might used such samples, and reassessment of those studies may be necessary. As a such example, a possibility of incorrect phase relation between low-clinoenstatite and orthoenstatite due to overlooked protoenstatite will be discussed.

Jiang, D. et al. (2002) *J. Min. Petrol. Sci.*, 97, 20

Lee, W.E. and Heuer, A.H. (1987) *J. Am. Ceram. Soc.*, 70, 349

Reynard, B. et al. (2008) *J. Euro. Ceram. Soc.*, 28, 2459

Xue, X. et al. (2002) *Geochim. Cosmochim. Acta*, 66, A853

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