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Synthesis of enstatite single crystals at high pressure

ROLAND STALDER*
Naturhistoriska riksmuseet, Sektionen för mineralogi, Box 50007, SE-10405 Stockholm, Sweden

Abstract: mm-sized crystals of enstatite were synthesized under H_2O-saturated conditions at 25 kbar in a piston-cylinder apparatus. The bulk starting composition corresponded to enstatite, silica and water in the respective proportions of 60, 20 and 20 wt.%. The most successful synthesis runs were heated above the liquidus (1400°C), followed by a slow temperature ramp (6°/h) down to 1100°C. Enstatite was the only crystallising phase, having exclusively been in contact with a silica-rich fluid or melt during the whole run. Synthesis products were analysed by X-ray diffraction and electron microprobe. IR-spectroscopy revealed that the enstatite contains approximately 280 ppm H_2O.

Key-words: enstatite, high-pressure synthesis.

Introduction

The aim of this study was the development of a strategy to synthesize large single crystals of enstatite. Large crystals are needed as standards and for example for H-diffusion studies on oriented samples (*i.e.*, profile measurements using FTIR-spectroscopy should be possible), as previously carried out on other minerals (olivine: Mackwell & Kohlstedt, 1990; clinopyroxene: Ingrin *et al.*, 1995). Dimensions of at least several hundreds of μm in each direction are desirable.

Synthesis of enstatite at high temperatures from a melt, which would lead to the generation of large crystals, is problematic due to several reasons. On the one hand, enstatite melts incongruently to a silica-rich melt and forsterite up to 5 kbar (Boyd *et al.*, 1964) under anhydrous conditions, excluding the possibility to crystallize enstatite from a dry melt with enstatite composition. Even if a dry synthesis at higher pressures is principally possible, the required temperatures (*i.e.*, > 1700°C at 15 kbar; Boyd *et al.*, 1964) make this strategy rather uncomfortable. Under hydrous conditions melting of enstatite is shifted down to 1275°C at 30 kbar, but the incongruent melting persists to more than 30 kbar (Kushiro *et al.*, 1968). To avoid incongruent melting, syntheses are often conducted at subsolidus conditions using H_2O as flux. However, starting compositions then have to contain some excess silica, as the aqueous fluid dissolves much more silica than MgO up to 30 kbar (Nakamura & Kushiro, 1974; Ryabchikov *et al.*, 1982). In previous studies pure enstatite was synthesized at 15 kbar at constant temperatures under subsolidus conditions (Kohn, 1996, Keppler & Rauch, 2000), using an aqueous fluid as flux. Crystal dimensions were up to 100 μm. Synthesis from gels at 25 kbar and 800°C lead to crystals of about 5 μm (Fockenberg & Schreyer, 1997).

Experimental strategy

In order to optimise the synthesis conditions several parameters have to be taken into account. In general, at the beginning of each run temperatures have to be above the liquidus for a while to dissolve all starting oxides and destroy existing nuclei of potentially formed silicates during heating. Thereafter, crystallisation is initiated during a ramp with a slow temperature decrease, until approximately 50-70 wt.% of the system has crystallised. Finally, the run is terminated by quenching. In order to avoid separation problems after recovering of the synthesis products, the starting composition has to be chosen in such a way that the system contains a free aqueous fluid phase before quenching. Quenching of an assemblage enstatite + hydrous melt could lead to a solid overgrowth on the crystals which may be hard to remove. For the choice of pressure several aspects were considered. Firstly, the pressure should be outside the stability field of any hydrous silicate, including potentially occurring quench phases. Talc is the most common reported quench product in the MSH-system; its stability decreases strongly with increasing pressure (Ulmer & Trommsdorff, 1999). On the other hand, to yield a larger amount of synthesis products and bigger crystals, syntheses should be run in a large assembly.

*Present address: Geowissenschaftliches Zentrum der Universität Göttingen, Abteilung Angewandte und Experimentelle Mineralogie, Goldschmidtstr. 1, D-37077 Göttingen. E-mail: rstalder@gwdg.de

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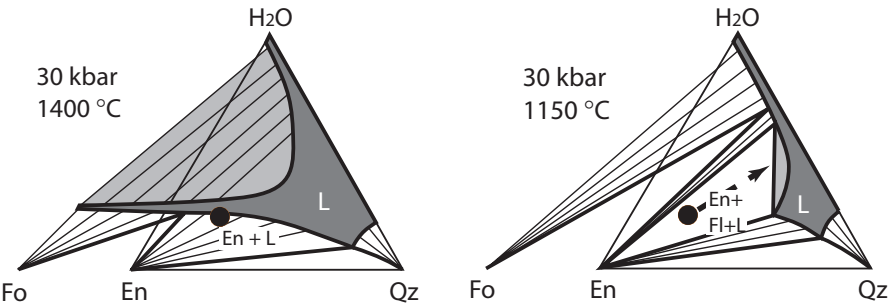

Fig. 1. Schematic phase diagrams of the system MgO-SiO_2-H_2O at 30 kbar, compiled from Kushiro *et al.* (1968), Nakamura & Kushiro (1974), Ryabchikov *et al.* (1982) and Inoue (1994). "L" denotes a melt, "Fl" denotes a fluid phase. The solid dot represents the approximate starting composition for all synthesis runs.

Therefore a pressure between 25 and 30 kbar, which can be conducted in large assemblies (0.75-inch in diameter), appears to be suitable. Occurring temperature gradients due to the application of large assemblies are not believed to have negative influence on the results, as the temperature of the system is changing with time anyway.

The starting mixture should fulfil the following requirements: 1) at the beginning of the run the system has to be above the liquidus; 2) an aqueous fluid should be present at the final temperature before quenching; 3) enstatite should be the only crystallizing phase during the whole run.

From the information given in the previous section tentative phase diagrams at different temperatures at 30 kbar can be drawn (Figure 1). At 1400°C both joins $MgSiO_3$-H_2O and Mg_2SiO_4-H_2O are supersolidus (Kushiro *et al.*, 1968, Inoue, 1994), and the hydrous silicate melt contains between 20 and 30 wt.% H_2O (Hodges, 1974). Therefore a bulk composition with these amounts of water is above the liquidus. A starting composition containing 60 wt.% enstatite, 20 wt.% silica, and 20 wt.% H_2O would meet all the requirements listed in the previous paragraph.

Enstatite synthesis

Starting materials were mixed from specpure-grade oxides. A mixture of 30 wt.% MgO and 70 wt.% SiO_2, corresponding to 75 wt.% enstatite and 25 wt.% quartz, was homogenized under acetone in an agate mortar. The mixture was used for syntheses "En7" and "En8". 200 mg of oxide mixture and 50 µl H_2O were loaded in a 12 mm-long Pt-capsule with an OD(ID) of 6.0 (5.6) mm, and welded shut. All high-pressure runs were carried out in an end-loaded 0.75-inch piston cylinder apparatus at the University of Bristol. Talc-pyrex assemblies were used as pressure medium, and W-Re thermocouples were used for temperature control; no pressure correction was applied to the EMF. To account for the friction of the talc-pyrex assemblies 10 % were added to the nominal load.

At the beginning of each run the pressure was increased to about 5 kbar; then, the temperature was increased automatically by 60°/min to 1400°C; simultaneously, the pressure was increased manually, until the final pressure (25 kbar) was reached. The pressure was then stable within less than ± 1kbar. Subsequently, the programmed Eurotherm-controller kept the temperature constant for a few minutes, followed by a ramp down to 1150°C (synthesis "En7") or 1100°C (synthesis "En8") with a rate of 6°/hour. When the final temperature was reached, the experiment was quenched manually by turning off the power supply. The recovered capsule were weighed, pierced, dried and weighed again; in average, about 70 % of the initial water could be released by this method, which means that the quench contains considerable amounts of water (≈10-15 wt%); alternatively partial leakage may have occurred at some stage of the experiment.

In an early stage of this study, a starting mixture with the same composition as described above was loaded in a 4.0 mm Pt-capsule and run at 30 kbar in a 14 mm, end-loaded piston cylinder apparatus at the ETH Zürich. In difference to the runs in Bristol the temperature was regulated manually with a cooling rate of 200°C/h down to 1200°C. This run is referred to as "En3".

Results

Run products consisted of approximately 50 wt.% enstatite crystals and 50 wt.% quenched solute from the fluid, which appeared as white, soft material that could easily be removed from the crystal surfaces. In runs "En3" and "En7" it occurred very rarely that crystals were assembled together, and even in those cases aggregates could be easily separated mechanically. In run "En8" this phenomenon was more widespread, even though most of the crystals could be recovered in the same way as from the other charges. Inspection of the recovered enstatites revealed that they were virtually free of fluid inclusions. In some specimens veins occurred, which were open towards both ends and contained some quench material. Crystals grown under a slow cooling rate (6°/h) are more than one order of magnitude (by volume) bigger than those crystallized during faster cooling (200°/h), as illustrated in Figure 2. The largest crystals reached dimensions of more than1 mm in each direction, being up to 3 mm long. All crystals were idiomorphic and elongated along the c-axis, developing predominantly the crystals faces (100), (010) and (hk0), which facilitated orientation for IR-analysis.

Run products were furthermore analysed by X-ray powder diffraction and electron microprobe. XRD spectra were recorded from 5 to 50° 2θ. No phases other than enstatite were detected among the crystallized portion of the charges. The quench material contained besides enstatite significant amounts of amorphous material and traces of poorly crystallized talc. Most of the enstatite detected in the quench material crystallized probably before quenching, but could not be separated totally. The talc formed probably by the reaction enstatite+silica+H_2O = talc (Ulmer & Trommsdorff, 1999), with enstatite and silica as dissolved components in the aqueous fluid. Talc formation by the reaction enstatite+H_2O = forsterite+talc is improbable, as no forsterite has been observed.

Microprobe analyses of the synthesized enstatite crystals exhibit a weak systematic deviation from stoichiometry towards higher Mg/Si-ratios (1.016 ± 0.007), which is probably caused by a systematic analytical error rather than revealing a true significant deviation from stoichiometry, since the system was saturated with respect to silica. For infrared-analyses three enstatite crystals were embedded in a thermoplastic resin ("Quickstick"), oriented under a microscope according to the crystallographic axes, and polished on both sides. Polarised IR-spectra were recorded with a Bruker IFS 48 spectrometer at the University of Linköping. For each analysis 64-100 scans within the range 1000 – 5000 cm^{-1} were acquired in absorbance mode. The water content of 280 ppm was calculated by adding the three components α + β + γ using the calibration of Libowitzky & Rossman (1997). Peak positions, peak shapes and absorbance intensities are in very good agreement with Keppler & Rauch (2000); the determined water content is slightly higher than reported for enstatites synthesized at 15 kbar and 1100°C (240 ppm, Kohn, 1996; 200 ppm, Keppler & Rauch, 2000). A profile measured along [010] on a polished (100) plane of a clear, 80 µm thick crystal did not reveal any virtual zoning with respect to the H_2O-content.

The presented method allows crystal growth up to several mm^3, comparable to flux-grown crystals at 1 atmosphere (Ito, 1975). Like in other flux-growth methods the flux-component is incorporated to a certain extend into the synthesized crystals. Even if the absolute content is rather low (*e.g.*, one order of magnitude lower than in Li-V-flux synthesis – Ito, 1975), it has to be taken into account when the synthesis products are applied to further studies, as the presence of impurities can create additional defects in the lattice.

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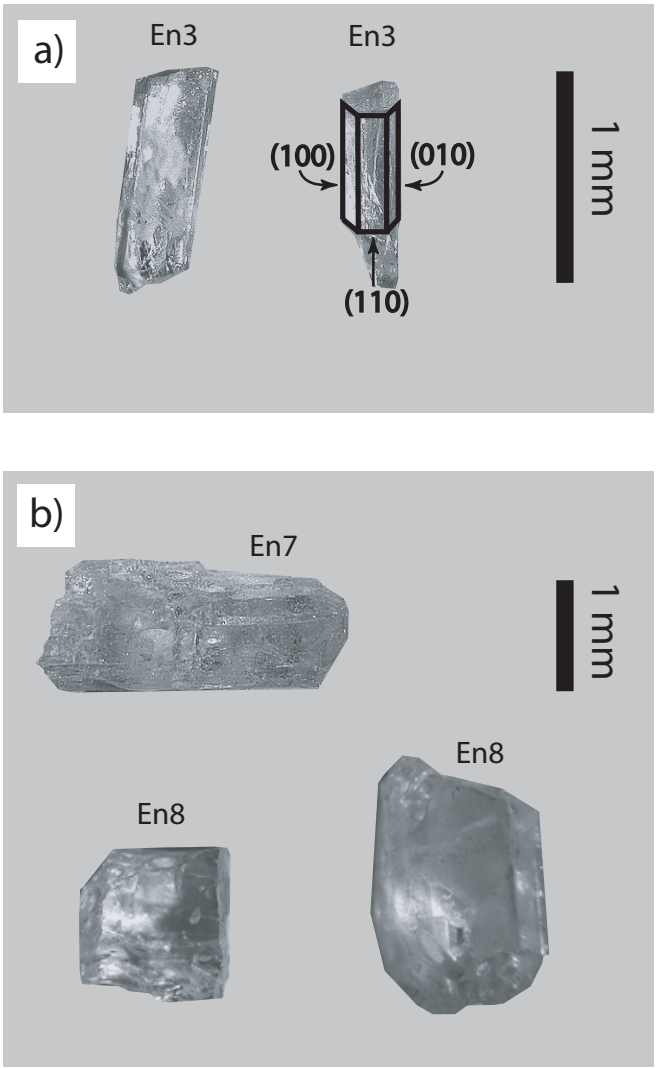

Fig. 2. Synthetic enstatites produced at 30 kbar and ΔT/Δt = 200°/h (a), and 25 kbar and 6°/h (b). Most crystals are elongated along the c-axis.

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