

**NON-EQUILIBRIUM CRYSTALLIZATION OF AMORPHOUS POROUS DIOPSIDE DUST ANALOGS.**

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**Introduction:** Silicate dusts in the ISM are thought to be porous aggregates of amorphous magnesium rich silicates. As they are incorporated into the protostellar nebula, these structural properties likely influence their crystallization behavior during simple annealing. In this study we illustrate the way such amorphous material crystallizes by the sequence of alkaline-earth rich minerals that nucleate from porous and amorphous diopside precursors. This original behavior provides new insights into the formation of minerals studied in infrared observatories or found in natural objects.

**Experiments:** Amorphous and porous diopside was synthesized by a Sol-Gel route developed in our laboratory. Samples show a fluffy microstructure with a domain size of about 10 nm which confer to the material a high surface/volume ratio, comparable to silicate smokes. In-situ XRD experiments were carried out on powders in a Guinier-Lenné diffraction chamber furnace from ambient temperature to 1000°C at 7°C/h. In addition powders were also annealed at 740°C (~10°C above T<sub>g</sub> of diopside glass) for 10 days. Recovered samples were analyzed by TEM and X-ray EDS.

**Results:** In-situ XRD annealing of the sample reveals the successive crystallization of merwinite (Ca<sub>3</sub>Mg[SiO<sub>4</sub>]<sub>2</sub>) at ~705°C, akermanite (Ca<sub>2</sub>MgSi<sub>2</sub>O<sub>7</sub>) and diopside (CaMgSi<sub>2</sub>O<sub>6</sub>) at ~800°C, forsterite (Mg<sub>2</sub>SiO<sub>4</sub>) at ~825°C and probably cristobalite (SiO<sub>2</sub>) at ~950°C. Note that all these phases coexist in the final annealed samples. When the annealing temperature increases, the Ca-rich phases nucleate first, which leads to a significant CaO depletion of the residual amorphous material. At higher temperature, the Mg-rich mineral (forsterite) subsequently appears. This sequence is completed by the formation of crystalline silica from the SiO<sub>2</sub>-rich amorphous residue.

TEM associated with X-ray EDS analysis show that amorphous porous diopside annealed at 740°C for 10 days forms crystalline merwinite, akermanite, diopside and forsterite. Phase morphologies strongly depend on the mineral formed. Akermanite and merwinite are found as fine-grained polycrystalline aggregates (typical grain size = 100nm) while forsterite and diopside are micron-sized. A Mg- and Ca-poor amorphous phase also remains, usually intermingled with nanocrystals. These observations are fully consistent with the XRD results. Around T<sub>g</sub> bulk diffusion is very slow and dominated by alkaline and alkaline-earth cation diffusion. On the other hand surface diffusion is faster and probably still significant at such moderate temperatures. Therefore, the high surface/volume ratio of the material probably enhances diffusion processes and allows Ca and Mg cations to form alkaline earth-rich phases faster than more stable but silicic phases.