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Novel Mg_2SiO_4 structures

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We describe the formation of novel, leaf-like Mg_2SiO_4 structures, *via* iodine vapour transport of magnesium onto quartz substrates.

Mg_2SiO_4 (Forsterite) is a major component of the earth's upper mantle,[1–3] an insulator under high-frequency irradiation[4] and chromium-doped Forsterite has found potential use in laser optics.[5] Focus to-date has been towards the high-pressure production of Mg_2SiO_4, with occasional reports highlighting the formation of particulate nano- and micro-meter-scale crystals.[6–8]

Mg powder (Alfa, 99.8% −325 mesh, 85 mg) was finely mixed with I_2 (Aldrich, 99.9+%, 15 mg) under an inert atmosphere. The powder was placed in a quartz boat, within a quartz tube, approximately 20 cm from a horizontal quartz substrate containing a fine deposit of amorphous SiO_2. The quartz tube was sealed under a He atmosphere (0.5 atm) and placed within a three-stage furnace. The mixed powders were heated to 800 °C and the substrate end of the tube to 600 °C, thus obtaining a temperature gradient of *ca.* 10 °C cm^{-1}. The reaction was left for 72 h after which the furnace was allowed to cool to room temperature. The quartz substrate was extracted for SEM analysis and a small amount of crystal deposit was carefully removed from the substrate and prepared for TEM investigations. A number of crystals were also observed on the walls of the reaction tube at the substrate end.

Fig. 1 shows SEM images (LEO Stereoscan) of the crystal deposits on top of the quartz substrate. The macro-structures (Fig. 1a) are typically *ca.* 60 μm in diameter and *ca.* 35 μm in height. Each of these structures is comprised of a myriad of tightly packed layers, rising from a central core on the quartz substrate. Their tips are discernible as triangular protrusions and their high aspect ratio is evident from the Mg_2SiO_4 leaves that lie parallel to the electron beam (Fig. 1b). Their depths are calculated to be less than 100 nm from SEM observations. Although the yield of these crystals is estimated to be less than 1%, identical structures were obtained in repeated experiments. Similar structures have also been observed for other chemical systems.[9,10]

The samples were also characterised by Energy Dispersive X-ray analysis (EDX, JEOL JSM-7400F), which showed signals from magnesium ($K\alpha = 1.25$ keV), silicon ($K\alpha = 1.74$ keV) and oxygen ($K\alpha = 0.53$ keV) arising from the structure, along with a minor contribution from iodine (Fig. 1c). The elemental analysis showed a ratio of 2.0 : 1.4 : 4.8 for Mg : Si : O, which, although points towards a magnesium silicate composition, is not consistent with that of Mg_2SiO_4. However, TEM observations showed that large parts of the underlying substrate were also removed from the quartz plate during sample preparation for TEM and EDX analysis. Subtracting a 2 : 1 : 4 ratio for Mg_2SiO_4, leaves a Si : O ratio of *ca.* 0.4 : 0.8 (*i.e.* SiO_2) and so the elemental analysis is consistent with these magnesium silicate crystals being contaminated with SiO_2, possibly attached to the base of the structure.

Fig. 2a shows a TEM (JEOL 200 CM and 4000EX) image of the fan-like crystal structure, that typifies a 2-D transmission view of the 3-D crystal. The triangular tips are clearly observed as the crystal protrudes away from the structure's core. The width varies considerably and is not always uniform down the length of the leaf-like crystal. The length of the leaf-like crystals also varies widely from *ca.* 100 nm to 35 μm. It can be seen that not all the crystal planes run to the full width of the leaf-like crystals, such that the layers are staggered in their packing and the thickness of the crystal thins towards its edges. (The premature endings of the planes can be seen by the broad fringes running parallel to the long axis, white arrows Fig. 2b.) Selected area electron diffraction (SAED) and electron diffraction modelling found that the crystal structure was

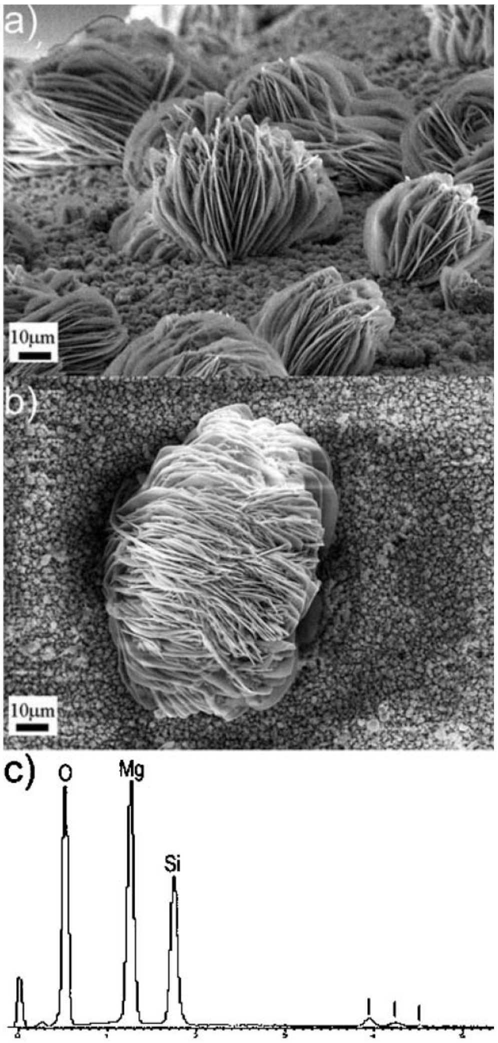

Fig. 1 a, b) SEM images of the fan-like structures protruding from the substrate, and c) EDX analysis of the individual crystals.

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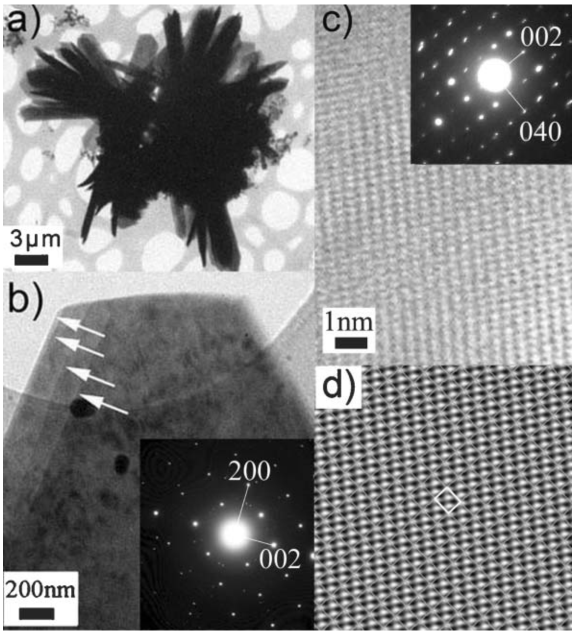

Fig. 2 a) TEM image of fan-like structure; b) a staggered-leaf under at high magnification with inset revealing the SAED from the [010] zone; c) HRTEM image from a staggered-leaf along the [100] zone, insert revealing the SAED; and d) the average image of part c (the unit cell is highlighted in white).

consistent with that of Forsterite (Mg_2SiO_4) with an orthorhombic unit cell possessing a *Pbnm* space group (no. 62) and lattice parameters of $a = 4.7$ Å, $b = 9.9$ Å and $c = 5.8$ Å. While the [010] zone gave the predicted *a*/*c* ratio (Fig. 2b inset), the [100] zone revealed a *ca.* 5% compression of the *b* lattice parameter compared to the published data (Fig. 2c inset). It should be noted, though, that there is a wide variation in the literature for the value of *b*, *e.g.* refs. 11 and 12. HRTEM images were taken parallel to the [100] zone axis, confirming the high degree of crystallinity within the leaves (Fig. 2c and 2d).

It is surmised that each leaf comprises of a number of smaller leaves that share a common stem but terminate at different intervals to each other, thus the leaf crystal, appearing in a staggered packing arrangement, has a single set of diffraction spots. This would also suggest that the stacking of four tips from the main leaf gives the impression of a much larger depth under SEM investigations and that each component of the leaf crystal has a depth of less than 20 nm. The overall geometry of a stacked growth within each leaf stabilises that leaf and similarly the closely packed layers lend stability to the whole structure arising from the substrate.

We have successfully repeated the experiment utilising MgB_2 as the starting material, in the attempt to produce nanoscale materials with the potential of superconductivity, which led to similar structures in the transported material and yielded identical ED patterns to those obtained using pure Mg. However, no B was detected in the crystals and so these structures highlight the dissociation of Mg from MgB_2 under the conditions reported above.[13] EDX mapping analyses reveal the presence of iodine within the sample although no iodine was obtained upon washing the final sample with toluene. The SAED pattern indicates that the crystal structure of orthorhombic Mg_2SiO_4 (*Pbnm*) is unaffected by the presence of iodine. In subsequent experiments the exclusion of iodine leads to the absence of fan-like structures.

XRD powder analysis on the mother material remaining in the boat after the experiment showed complete conversion of Mg powder to MgO. Given the relatively low temperature (600–800 °C) employed in the reaction in comparison to those favourably used for preparing Forsterite from the direct combination of MgO and SiO_2 powders (1100–1400 °C),[14] it is apparent that iodine plays a significant role in the growth of Mg_2SiO_4 crystals. Although undetected in the final sample, the formation of MgI_2 as an intermediate species towards the proliferation of fan-like Mg_2SiO_4 cannot be ruled out. The SiO_2 particles on the substrate are *ca.* 3 μm in diameter and are sometimes observed with small leaf-like crystals growing from their surface (Fig. 1a, lower right). We surmise that these structures represent the initial growth formation of Mg_2SiO_4 crystals from SiO_2 particles. Further investigations are being made to elucidate the growth mechanisms.

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