

### Comment on "First-Principles Studies on Structural Properties of $\beta$ -Cristobalite"

In a recent Letter [1] Liu *et al.* reported first-principles electronic structure calculations related to the crystal structure of the  $\beta$  phase of cristobalite,  $\text{SiO}_2$ . They provide evidence that a structure composed of domains of  $I\bar{4}2d$  [2] is to be preferred over the "ideal"  $Fd\bar{3}m$  structure. Using an argument based on the energies of domain walls they exclude an alternative model [3] based on domains of the low-temperature ( $\alpha$ )  $P4_12_12$  structure. No comment was made on the size of these domains, but to be recognizable as such they presumably contain at least a few unit cells, and they need to exist for times that are longer than typical phonon periods. The problem of the structure of the  $\beta$  phase of cristobalite is important since cristobalite is a model system for the study of the technologically important silicate glasses.

In this Comment we will present an alternative model to the domain models cited above. First, however, we note two pieces of evidence against a domain model.

(a) Raman and infrared spectroscopic studies of the  $\alpha$ - $\beta$  phase transition in cristobalite [4,5] show no evidence for the existence of domains of symmetry lower than  $Fd\bar{3}m$ . It has been shown that spectroscopic studies of high frequency modes with weak dependence on wave vector probe correlations on length scales of the order of one or two unit cell lengths [5,6]. In our spectroscopic studies we found that almost all the modes we measured that are systematically absent in the  $Fd\bar{3}m$  structure disappear completely in the  $\beta$  phase, apart from one which has a lifetime of less than 0.6 ps. If static domains of symmetry lower than  $Fd\bar{3}m$  are present in the  $\beta$  phase we would expect to see additional peaks in the  $\beta$  phase spectra that are much sharper than the one additional mode observed.

(b) Molecular dynamics simulations of the  $\beta$  phase of cristobalite [4,7] show that the Si-O bonds are orientated at about  $17^\circ$  from the orientation in the ideal  $Fd\bar{3}m$  structure, [111], but the orientational probability distribution function is isotropic with respect to rotations about [111]. No domain structure was found.

A more realistic model for the  $\beta$  phase of cristobalite is given by the so-called "rigid unit mode" model [7-9]. A rigid unit mode (RUM) is a vibrational mode that propagates with no distortion of the  $\text{SiO}_4$  tetrahedra, and is therefore of low energy. RUMs are analogous to the "floppy modes" found in glasses, although RUMs are collective rather than local. Calculations of the RUM spectrum for cristobalite in the  $Fd\bar{3}m$  structure show that

there is a RUM at every wave vector in the  $\langle 110 \rangle$  zones [7-9]. The proposed  $I\bar{4}2d$  structure [1,2] and the  $P4_12_12$  structure of the  $\alpha$  phase can be generated from the ideal  $Fd\bar{3}m$  structure by condensation of the  $\Gamma_5^-$  and  $X_4$  RUMs respectively, which are part of the same phonon branch. However, in principle, a RUM with any wave vector in the  $\langle 110 \rangle$  zone can condense. Accordingly we suggest that the structure of  $\beta$ -cristobalite is dynamically disordered with average structure  $Fd\bar{3}m$ , the disorder arising from the existence of a large number of large-amplitude RUMs. Given that the ideal  $Fd\bar{3}m$  structure is a maximum in the lattice energy, and that the RUMs are low frequency modes, the system will be highly anharmonic. There will be no domains of any lower symmetry except those that form as transient fluctuations. It is worth noting that an appropriate linear combination of condensed RUMs will give low-energy domain walls between domains of different orientations as required by Liu *et al.* [1].

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