

## Ring-chain Intergrowths in the System (Ca,Sr)(Si,Ge)O<sub>3</sub>

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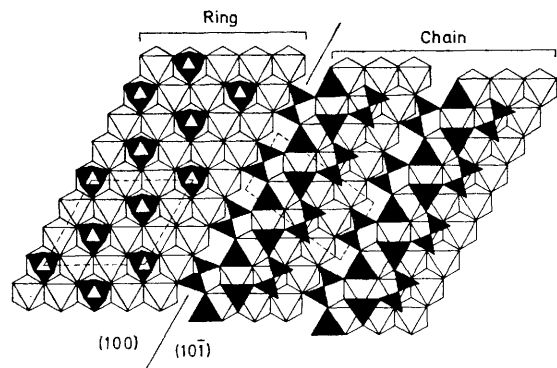
High-resolution electron microscopic and electron diffraction studies in the system (Ca,Sr)(Si,Ge)O<sub>3</sub> reveal that, at certain compositions, hitherto unknown intergrowths of ring- and chain-structures occur, the orientation and type of these intergrowths being described.

Studies of chain metasilicates (general formula MSiO<sub>3</sub>) have confirmed that their structural configurations are determined by the size of the M<sup>2+</sup> cations.<sup>1-3</sup> It has been postulated that both chain and ring metasilicates are part of a continuous series,<sup>4</sup> the ring structure arising when the ratio of the dimensions of MO<sub>6</sub> octahedra and SiO<sub>4</sub> tetrahedra becomes so great that a chain structure is no longer possible. If this is the case, at a certain value of this ratio both types of structure should co-exist, and even form oriented intergrowths. Recent work has confirmed that ring structures of the SrSiO<sub>3</sub> type<sup>5</sup> can be produced by only a slight degree of substitution of the larger Sr<sup>2+</sup> into CaSiO<sub>3</sub>;<sup>6</sup> however attempts to find oriented intergrowths of chains and rings in CaSiO<sub>3</sub> at high temperatures, where the stability fields of both phases overlap, have failed.<sup>7</sup> Such intergrowths do occur though, if Ge replaces Si, as described below.

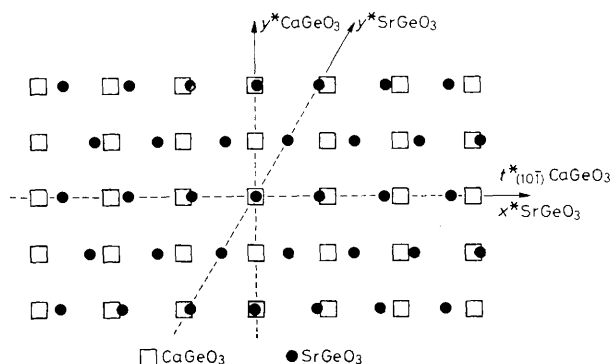
Glasses of known composition in the system (Ca,Sr)-(Si,Ge)O<sub>3</sub> were prepared by quenching from oxide melts, and

were annealed at a range of temperatures from 800 to 1250 °C for up to 48 h. Resulting specimens were examined by X-ray powder diffractometry, followed by analytical and high-resolution electron microscopic studies. Analytical electron microscopy was used to confirm the starting composition and check the compositional homogeneity, on areas as little as 2000 Å in diameter, of all the phases prepared. On this scale, all crystals were found to be of the same stoichiometry within any given sample. Possible compositional variations in intergrowth structures observed by high-resolution microscopy (described below) could not be investigated in this way as the scale of the intergrowths was excessively fine. The findings broadly confirm the above hypotheses. With no Ge present, even 5% replacement of Ca<sup>2+</sup> by Sr<sup>2+</sup> produced ring structures at all annealing temperatures. With no replacement of Ca<sup>2+</sup>, substitution of Ge for Si up to a figure of 20% produced little change in the known structural behaviour, a ring form being stable at high temperatures and the characteristic stacking disorder<sup>8</sup> of the low-temperature chain structure persisting, but for greater replacement these features were no longer observed and ordered chain structures prevailed at all temperatures. When

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**Figure 1.** Schematic illustration of a ring-chain intergrowth in  $(\text{Ca,Sr})\text{GeO}_3$ . For clarity,  $\text{MO}_6$  octahedra are shown as polyhedra of constant size. Tetrahedra (solid triangles) therefore differ greatly in size in the two phases.



**Figure 2.** Schematic reciprocal lattice section of an intergrowth crystal, viewed down  $[001]$  (ring structure) or  $[101]$  (chain structure).

substitutions of both  $\text{Sr}^{2+}$  for  $\text{Ca}^{2+}$  and Ge for Si were allowed, the  $\text{Sr}^{2+}/\text{Ca}^{2+}$  ratio at which rings became the stable configuration increased, with ultimately, in  $(\text{Ca,Sr})\text{GeO}_3$ , 50% replacement of  $\text{Ca}^{2+}$  being necessary to stabilise this structure. With less than 50% replacement of Si by Ge, specimens exhibiting both ring- and chain-structures contained separate crystallites of each, along with a glassy phase, but with still higher Ge contents, oriented intergrowths of the type shown in Figure 1 were observed. Structural co-

existence of the two forms in an oriented fashion has not hitherto been reported.

Within the limited annealing times possible (*ca.* 200 h) these intergrowths could not be removed by heat treatment at  $1250^\circ\text{C}$ . Their orientation, determined from lattice images and electron diffraction patterns, was  $(100)$  ring/ $(10\bar{1})$  chain, with the layers of  $\text{MO}_6$  octahedra being common to both phases. Lamellae of one phase within another were frequently as narrow as  $15\text{ \AA}$ , but no regular repeating patterns of chain and ring forms were observed. A schematic reciprocal lattice for an intergrowth of relatively coarse lamellae is shown in Figure 2. This was derived from observed electron diffraction patterns where considerable streaking parallel to  $[100]$  (ring structure) was noted, but the maxima indicated were nevertheless clearly discernible.

The results described above are merely preliminary, and a full account will be published elsewhere. They do indicate, however, that separate classification into ring silicates or chain silicates may not be as clear-cut as was once believed, and suggest that an intermediate family of silicates, such as the biopyriboles,<sup>9</sup> may exist in the metasilicate composition range. Substitution of non-divalent cations into  $\text{CaSiO}_3$ , such as  $\text{Al}^{3+}$ , also appears to stabilise these intergrowths and further work is continuing.

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