Table 3. *Polymorphism of* $SrB_2O_4$ *and* $CaB_2O_4$

| Phase | Approximate range of stability* | | Density (g.cm$^{-3}$) | | Symmetry | Lattice parameters (Å) | |
|---|---|---|---|---|---|---|---|
| | $SrB_2O_4$ | $CaB_2O_4$ | $SrB_2O_4$ | $CaB_2O_4$ | | $SrB_2O_4$ | $CaB_2O_4$ |
| I | 0–8 kbar | 0–12 kbar | 3·33 | 2·70 | Orthorhombic | $a=6·589$ $b=12·018$ $c=4·337$ | $a=6·214$ $b=11·604$ $c=4·285$ |
| II | – | 12–15 kbar | — | 2·89 | Orthorhombic | — — — | $a=8·369$ $b=13·816$ $c=5·007$ |
| III | 8–15 kbar | 15–25 kbar | 3·77 | 3·05 | Orthorhombic | $a=12·426$ $b=6·418$ $c=11·412$ | $a=11·380$ $b=6·382$ $c=11·304$ |
| IV | 15–40 kbar | 25–40 kbar | 4·38 | 3·43 | Cubic | $a=9·222$ | $a=9·008$ |

* Temperature $=600\,°C$ for $SrB_2O_4$ and $900\,°C$ for $CaB_2O_4$.

## Discussion

For ease of comparison between the $SrB_2O_4$ and $CaB_2O_4$ polymorphic series, crystal data and pressure ranges of stability are given in Table 3, and a plot of densities *versus* fraction of tetrahedral boron can be found in Fig.1. It can be seen from Table 3 as well as from Fig.1 that the behavior of $SrB_2O_4$ under pressure is very similar to that of $CaB_2O_4$.

One notable difference in the two polymorphic series is that an expected phase of $SrB_2O_4$ is missing, namely, $SrB_2O_4(II)$. It could be predicted from the data in Table 3 that this phase should exist at 6–8 kbar and 600°C. By further extrapolation of densities (see Fig.1) and analogy to $CaB_2O_4(II)$ (Zachariasen, 1967) one would expect this modification to be orthorhombic with a density of 3·6 g.cm$^{-3}$, a unit-cell volume of 650 Å$^3$, and very roughly, lattice parameters $a=8·9$, $b=14·3$, and $c=5·1$ Å. However, after considerable experimentation not a trace of $SrB_2O_4(II)$ could be detected in any of the X-ray powder films of the high pressure samples. It should be noted that $CaB_2O_4(II)$ was never obtained in the pure state from high pressure experiments at these laboratories. Instead, $CaB_2O_4(II)$ was always found as a mixture with $CaB_2O_4(I)$ or $CaB_2O_4(III)$. It seems reasonable to expect the pressure range of stability for $SrB_2O_4(II)$ to be narrower than $CaB_2O_4(II)$. From Table

3 and from the known coordination changes for $CaB_2O_4$ the implication is that the energy associated with the transition I → II should be about the same for both compounds since only the boron coordination is changing. However, for the transition II → III both cation coordinations are increasing and the energy required for this transition should be less for $SrB_2O_4$ than for $CaB_2O_4$.

In general it can be seen from Table 3 that considerably less energy is required, for each of the respective transitions, for $SrB_2O_4$ than for $CaB_2O_4$. Less energy is necessary to increase the strontium coordination than the calcium coordination since Sr is larger than Ca in ionic radius and is more easily accomodated in a larger lattice site. One would expect even lower energies for similar transitions for $BaB_2O_4$. However, preliminary experiments with $BaB_2O_4$ show that high pressure phases of this compound are not isostructural with any of the $SrB_2O_4$ phases.

Finally, a comparison of lattice parameters between isostructural compounds in Table 3 shows that for phase III a unique distortion of the unit cell occurs when strontium is substituted for calcium. Whereas the lattice parameters $a_0$ for $SrB_2O_4(III)$ is 9·2% larger than the corresponding parameter of $CaB_2O_4(III)$, the lattice parameters $b_0$ and $c_0$ are only 0·6% and 1·0% larger respectively. It is difficult to explain this unidirectional expansion without a knowledge of the structural details of $SrB_2O_4(III)$. Nevertheless, it can be speculated that second-nearest neighbor interactions in $CaB_2O_4(III)$ could become first-nearest neighbor interactions in $SrB_2O_4(III)$.

Fig. 1.

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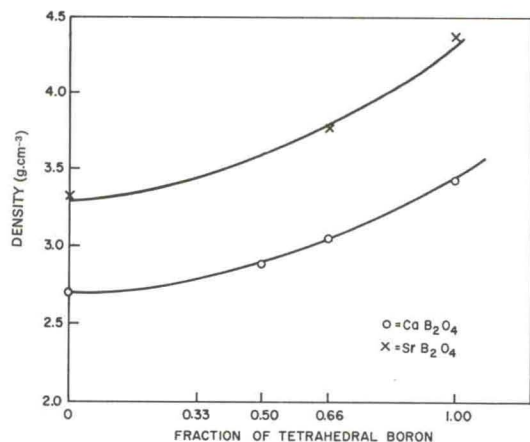ZACHARIASEN, W. H. (1967). *Acta Cryst.* **23**, 44.