

Table 3. *Polymorphism of SrB₂O₄ and CaB₂O₄*

Phase	Approximate range of stability*		Density (g.cm ⁻³)		Symmetry	Lattice parameters (Å)	
	SrB ₂ O ₄	CaB ₂ O ₄	SrB ₂ O ₄	CaB ₂ O ₄		SrB ₂ O ₄	CaB ₂ O 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 SrB₂O₄ and 900°C for CaB₂O₄.

Discussion

For ease of comparison between the SrB₂O₄ and CaB₂O₄ 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 SrB₂O₄ under pressure is very similar to that of CaB₂O₄.

One notable difference in the two polymorphic series is that an expected phase of SrB₂O₄ is missing, namely, SrB₂O₄(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 CaB₂O₄(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 Å³, and very roughly, lattice parameters *a* = 8.9, *b* = 14.3, and *c* = 5.1 Å. However, after considerable experimentation not a trace of SrB₂O₄(II) could be detected in any of the X-ray powder films of the high pressure samples. It should be noted that CaB₂O₄(II) was never obtained in the pure state from high pressure experiments at these laboratories. Instead, CaB₂O₄(II) was always found as a mixture with CaB₂O₄(I) or CaB₂O₄(III). It seems reasonable to expect the pressure range of stability for SrB₂O₄(II) to be narrower than CaB₂O₄(II). From Table

3 and from the known coordination changes for CaB₂O₄ 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 SrB₂O₄ than for CaB₂O₄.

In general it can be seen from Table 3 that considerably less energy is required, for each of the respective transitions, for SrB₂O₄ than for CaB₂O₄. 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 accommodated in a larger lattice site. One would expect even lower energies for similar transitions for BaB₂O₄. However, preliminary experiments with BaB₂O₄ show that high pressure phases of this compound are not isostructural with any of the SrB₂O₄ 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 SrB₂O₄(III) is 9.2% larger than the corresponding parameter of CaB₂O₄(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 SrB₂O₄(III). Nevertheless, it can be speculated that second-nearest neighbor interactions in CaB₂O₄(III) could become first-nearest neighbor interactions in SrB₂O₄(III).

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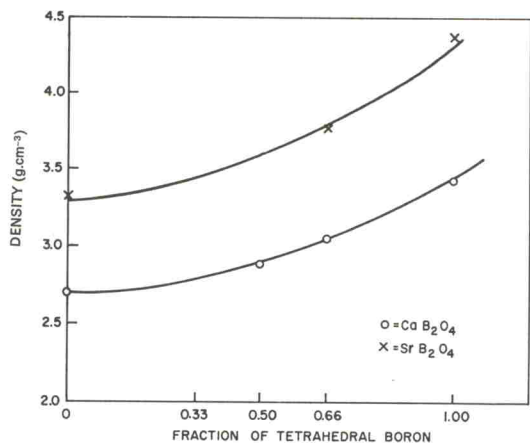


Fig. 1.