STABILITY, LATTICE PARAMETERS AND THERMAL EXPANSION OF β-CRISTOBALITE: REPLY

F. Aumento

I regret any ill feelings engendered by my phraseology, but I firmly believed in the integrity of my statement at the time of writing. It appears that having made every effort to vindicate Lukesh's calculation on mathematical and arithmetical grounds, I overlooked the simple solution of the presence of printer's error.

The value obtained by Lukesh for the coefficient of thermal expansion of β-cristobalite, both before and after correction of typographical errors, is comparable to those of other workers, and is indeed quite acceptable. The same applies for that of Büssem *et al.* (1935); at no time did I state or imply that the latter was unacceptable. One has only to observe the approximate parallelism of the thermal expansion graphs in Figure 1 (Aumento, 1966) to note that the orders of magnitude of the thermal expansion, between similar temperature intervals, obtained by different workers, are very similar. Figure 1 unfortunately would require a vertical extension to permit the values of Lukesh to be included.

Lukesh omitted from his abstract (1942) the pertinent fact that his sample was of high purity. This led me to assume that the sample was of the same general character as those used by others, and therefore to discount the apparently low values obtained. On the basis of the additional information submitted by Lukesh, which suggests that he was dealing with a special case, one can now better evaluate his results.

My expansion graph is that of a β-cristobalite with the minimum necessary solid solution to guarantee survival of the phase below the inversion temperature. I stated at the time that the material used for the graph only approximated ideal purity. Büssem's graph, displaced vertically from mine in the direction of the values of Lukesh, was possibly derived from material with less solid solution than mine; the crystallinity of Büssem's β-cristobalite suffered on cooling, giving poor room-temperature diffraction patterns. One must therefore assume that, since all previous values fall between these two graphs, all the β-cristobalites used by previous workers, including the author's, but excluding Lukesh's, are subject to some degree of solid solution. Admittedly the values reported by Büssem *et al.* lie between those of the author and those of Lukesh; one must concede, however, that they are somewhat biased towards the former!

We are faced with two distribution fields for the lattice parameter

values of β-cristobalite: the lower field, characterized by the determinations of Lukesh alone, represents pure β-cristobalite, whilst the upper field is characterized by a large number of determinations by various workers on material with varying amounts of impurities. The two fields are only theoretically connected by my straight line graph, representing the lattice parameters at room temperature plotted against maximum temperature of annealing. Indeed, the purer the material synthesized, the smaller the lattice parameters obtained. Had it been possible to continue the graph beyond the minimum value for a — 7.106 Å (β-cristobalite that might have given a lower value did not survive below the inversion point), the complete range of cell parameters down to that of pure β-cristobalite could have been recorded. If one may be allowed to extrapolate a theoretical curve from Lukesh's values, one may expect a room temperature value at around 7.00 Å for the pure β-cristobalite. A similar straight line graph could presumably be plotted for the cell parameter at some other temperature, more conveniently above the inversion point. There exists, therefore, a gap of the order of 0.1 Å between the lowest values recorded by the author and those of Lukesh, whilst the maximum range of variations found by the author and other workers is only of the order of 0.04 Å. It is now easier to understand why the values of Lukesh are somewhat lower than those of the author and other workers. Lukesh himself (1942) suggests that "the discrepancy may be due to any or all of these causes; material used, previous thermal history of the sample, or technique used in measurement." I have demonstrated (Aumento, 1966) that the effects of the first two causes will explain part of the discrepancy. I am still not convinced, however, that these effects are of sufficient magnitude to close the gap between the two distribution fields for the lattice parameters of β-cristobalite.

References

Aumento, F. (1966) Stability, lattice parameters, and thermal expansion of β-cristobalite. *Amer. Mineral.* **51**, 1167.

Büssem, W., M. Bluth, and G. Grochtmann (1935) Röntgenographische Ausdehnungemessungen kristalliner Massen I. *Ber. Deut. Keram. Ges.* **16**, 381–392.

Fenner, C. N. (1913) The stability relations of the silica minerals. *Amer. J. Sci.* (4) **36**, 331–384.

Lukesh, J. S. (1942) The size of the unit cell and the coefficient of expansion of high cristobalite (abs.). *Amer. Mineral.* **27**, 226.

Sosman, R. B. (1927) *The properties of silica.* Chemical Catalogue Co., New York.