3. D. G. RICKERBY and N. H. MACMILLAN, Mechanisms of Solid Particle Erosion in Crystalline Materials, in "Proceedings of the Fifth International Conference on Erosion by Solid and Liquid Impact", Cambridge, England, September (1979).
4. K. L. JOHNSON, J. J. O'CONNOR and A. C. WOODWARD, *Proc. Roy. Soc.* A334 (1973) 95.
5. B. LAWN and R. WILSHAW, *J. Mater. Sci.* 10 (1975) 1049.

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The central region of the calcium oxide–gallium oxide system

During attempts to grow single crystal calcium gallate ($CaGa_2O_4$) from the melt using the Czochralski technique, it became necessary to check the phase diagram in the region of the compound, $CaGa_2O_4$ since different authors have variously assigned to this mole ratio, no compound [1], two compounds [2], and three compounds [3], nominally all with the formula $CaGa_2O_4$. This communication describes investigations on this system and attempts to rationalize the results obtained and those already published.

Mixtures of calcium carbonate and gallium oxide of the highest commercially available quality, with a total metallic impurity content about 10 ppm, were made in the range 35 to 65 mol% Ga_2O_3, sixteen mixtures in all. Each sample was subsequently placed in a differential thermal analysis (DTA) unit heated until molten and then cooled. The temperature was then recycled and a DTA trace obtained, the heating and cooling rate being 10° C min^{-1}. The samples

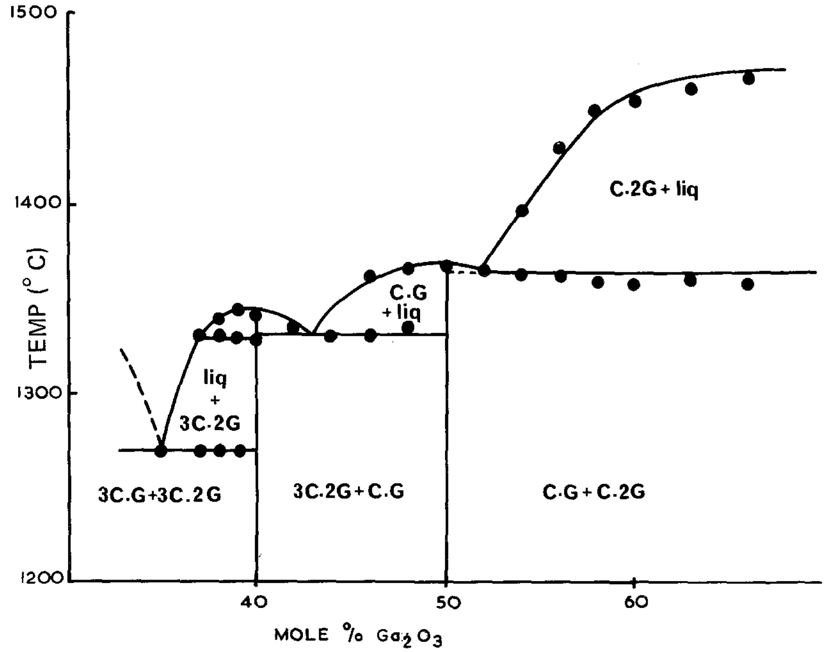

Figure 1 The $CaO–Ga_2O_3$ system. C = CaO, G = Ga_2O_3. Eutectic between 3C.G and 3C.2G at 35 mol% Ga_2O_3 1270 ± 3° C. Maximum melting point 35 to 45 mol% 1345 ± 3° C. Eutectic between 3C.2G and C.G at 43 mol% Ga_2O_3 1332 ± 3° C. Melting point 50 mol% mixture 1368 ± 3° C.

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were then subjected to X-ray powder diffraction photography (Debye–Scherrer). The results of the DTA runs are shown in Fig. 1. The shape of the liquidus in Fig. 1, although showing a maxima at 50 mol% at about 1370° C, which agrees well with [3], differs considerably on either side of this maxima, decreasing to eutectic about 43 mol% Ga_2O_3. The liquidus temperature was then found to rise and reach a maxima about 40 mol% Ga_2O_3, decreasing to a further eutectic at 37.5 mol% which is the same composition as reported in [3]; On the gallium oxide-rich side of 50 mol%, the current work suggests the presence of a eutectic about 52 mol% Ga_2O_3, but an incongruent melting compound $CaGa_2O_4$ is also possible.

The observations on a number of the Debye–Scherrer photographs taken are summarized below in Table I.

Attempts to grow crystals from the melt, using the vertical lift (Czochralski) technique were apparently quite successful, until cooling of the crystal was in progress. In every case, at some time during the cooling period, the crystal cracked severely, giving it a crazed appearance. This cracking, which did not apparently occur at a fixed temperature, could not be alleviated even with extensive after-heating and using cooling rates of a few degrees per hour. In only one case did the crystal cool through as much as 400° C before cracking commenced. Attempts were made to grow crystals from melts slightly rich in one or other component, but again cracking was encountered. A sample of pulled crystal was subjected to repeated cycling in the DTA apparatus, showing only one endothermic peak on the heating cycle. An X-ray powder photograph was also taken see Table I. A fragment of single crystal was further investigated by means of a STOE X-ray precession goniometer, which confirmed the cell dimensions previously obtained [2, 4] and also agreed with the proposed alternative space groups.

TABLE I 3:1 – $3CaO \cdot Ga_2O_3$; 1:2 – $CaO \cdot 2Ga_2O_3$. I, II, meta, phase designation after [3], see text.

Ga_2O_3	Diffraction lines visible in the powder photograph
38%	mainly 3:1 – strongest line of II just visible
40%	mainly II – strongest lines of I just detectable, no 3:1 apparent
46%	mainly I + II, with meta weakly visible
50%	mainly I with meta also evident
Crystal	all lines index on cell dimensions of I
52%	mainly I + 1:2 now detectable – trace of meta still present
58%	mainly 1:2 – three strongest lines of I just detectable

It was originally reported [1] that gallium oxide would form gallates, by sintering with a number of other oxides, at various temperatures, but apparently $CaGa_2O_4$ did not form by sintering, although the temperature at which this was attempted was not recorded. Subsequent workers [3], in studying the CaO/Ga_2O_3 system, claimed to identify three distinct modifications of $CaGa_2O_4$, depending on the conditions of preparation, in addition to the phases $3CaO \cdot Ga_2O_3$ and $CaO \cdot 2Ga_2O_3$; Their modifications of $CaGa_2O_4$ they described as calcium gallate I, calcium gallate II and metal-calcium gallate. Two of the variations described, calcium gallate I and meta-calcium, were physically similar under optical examination and shown subsequently [4] to have a similar cell size and *Z* number. The third variation, calcium gallate II, was physically different in appearance and structurally different, none of the cell dimensions suggesting any ready analogy with other $RO \cdot R'_2O_3$ compounds. Other workers [2] were only able to prepare the forms $CaGa_2O_4$I and *m*-$CaGa_2O_4$ from a stoichiometric mix, suggesting that $CaGa_2O_4$II has a different stoichiometry. Jeevaratnam and Glasser [3], however, point out that $CaGa_2O_4$II was only obtained where there was a slight excess of either of the starting materials over the stoichiometric composition.

The current investigation in the region 35 to 55 mol% Ga_2O_3 identified all five previously recorded phases, the DTA results suggesting that a congruent compound exists about 40 mol% Ga_2O_3, with the 50 mol% compound possibly incongruent. The X-ray results add support to the supposition that $CaGa_2O_4$II is the compound of stoichiometry about 40 mol%, existing only on the CaO-rich side of 50 mol% and that *m*-$CaGa_2O_4$ is indeed a metastable form of $CaGa_2O_4$I as the meta form is never present without $CaGa_2O_4$I. Jeevaratnam and Glasser [3] reported that if a 50 mol% mixture was quenched, a glass was formed, but if a melt was cooled through the liquidus temperature 2 to 4° C min^{-1}, the meta modification would be formed. This was shown to transform to $CaGa_2O_4$I on standing, the higher the temperature the quicker the transformation took place. The DTA equipment used for the current work has a cooling rate of 10° C min^{-1} from which one might expect to produce some metastable phase, or initially all metastable phase some of which has transformed to phase I by the time the sample reached room temperature (Table I). The reason that the pulled crystal X-ray powder photograph can be indexed solely on phase I presumably follows from a similar argument, namely that the crystal, which is cooling at a rate the order of $\frac{1}{2}$° C min^{-1}. crystallizes in the metastable phase, but changes to phase I entirely during the cooling period which was at least 50 h. This could explain the cracking phenomena, which did not apparently onset at any fixed temperature. If $CaGa_2O_4$I is the stable phase, occurring during solidification, this would explain why no phase change was observed during the DTA heating cycle of phase I, the crystal being unable to revert to the meta phase once it had transformed to phase I. On cooling molten samples of crystal in the DTA unit, extensive supercooling was encountered and only one large exothermic peak was encountered about 200° C below the melting point. It is possible that under these conditions, crystallization and phase change occur simultaneously.

These results confirm the existence of the $3CaO·Ga_2O_3$ and $CaO·2Ga_2O_3$ compounds, and show there are two other compounds in the region of the system studied, the first, $CaGa_2O_4$ existing in two polymorphs, one metastable at all temperatures, the other being designated $CaGa_2O_4$I which is the phase obtained by Czochralski melt growth. The second, a phase previously described as calcium gallate II has the formula $3CaO·2Ga_2O_3$ and bears no similarity to the garnet-like compound nominally $12CaO·7Al_2O_3$. This work also indicates that the growth of single $CaGa_2O_4$ from the melt will not be possible as a result of the nature of the phase diagram in the region around 50 mol% and the probability of a phase change on cooling causing internal strain and subsequent severe cracking.

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References

1. T. MOELLER and G. L. KING, *J. Amer. Chem. Soc.* 75 (1953) 6060.
2. H. J. DEISEROTH and Hk. MULLER-BUSCHBAUM *Z. Anorg. Allgen. Chem.* 396 (1973) 157.
3. J. JEEVARATNAM and F. P. GLASSER, *J. Amer. Ceram. Soc.* 44 (1961) 563.
4. J. JEEVARATNAM, F. P. GLASSER and L. S. DENT GLASSER, *Z. Krist. Bd.* 118 S (1963) 257.

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Characterization of fused silica powders

Silica exists in several crystalline forms in nature. The most abundant forms are quartz sand and quartz crystals. Fused silica is an amorphous (non-crystalline) form of silica and can be prepared by arc fusion of quartz sand. The resulting fused silica retains some porosity, is translucent to opaque, and ranges in colour from off white to black.

Since 1956, a technique involving the process of slip casting and producing a rebounded form of fused silica [1] has been used. Some of the physical properties of the rebonded fused silica are considerably different from the conventional fused silica while some, such as thermal expansion and specific heat are unchanged. The majority of the work with slip cast fused silica has been directed to aerospace applications, although rebonded fused silica has found applications in the refractory industry. This letter concerns some studies on the characterization of fused silica powders (C.E.C. France) produced by industrial arc fusion melting, which enter the composition of commercial slip cast silica refractories. Arc fusion of quartz sand is performed using graphite electrodes. After being melted and cooled down to room

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