film, an effect confirmed in the case of iron both for the oxidation of silicon, and in the nitridation of high purity silicon [9, 10]. Further work is now needed to clarify the origins of the later, faster, "β-stage" process responsible for large scale β-silicon nitride formation in powder B [3]. This was assumed earlier to be due to an enhanced release of silicon vapour from a clean silicon surface. The possibility now needs to be examined that this feature is due to a liquid phase reaction consequent upon the rapid, widespread, wetting of silicon surfaces free from silica.

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References

1. D. CAMPOS-LORIZ, Ph.D. Thesis, Department of Ceramics, University of Leeds (1976).
2. R. B. GUTHRIE and F. L. RILEY, *J. Mater. Sci.* 9 (1974) 1363.
3. D. CAMPOS-LORIZ and F. L. RILEY *ibid* **11** (1976) 195.
4. R. B. GUTHRIE and F. L. RILEY, *Proc. Brit. Ceram. Soc.* **22** (1973) 275.
5. JANAF, Thermochemical Tables, 2nd edition, NBS (1971).
6. D. J. GODFREY, Society of Automotive Engineers Paper No. 740238, New York (1974).
7. K. H. JACK, *J. Mater. Sci.* **11** (1976) 1135.
8. M. HANSON, "The Constitution of Binary Alloys" (McGraw–Hill, 1958).
9. S. M. BOYER and A. J. MOULSON, *J. Mater. Sci.* (to be published).
10. S. M. BOYER, D. SANG and A. J. MOULSON. "Nitrogen Ceramics" edited by F. L. Riley (Noordhoff, 1977) p. 297.

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A new compound in the Ge–Te system

The Ge–Te phase diagram as described by Klemm and Frischmuth [1] has just one compound, GeTe, which has a range of stoichiometry [2]. Its structure has been described [3–5] using a rhombohedral cell with $a = 5.96$ Å, $\alpha = 88°16'$ and $Z = 4$, derived by small distortions of a basic NaCl fcc structure. Stoemenos *et al.* [6] have shown that further structural distortions exist resulting in a doubled cell edge and giving a rhombohedral cell containing ideally 32 Ge and 32 Te atoms. These authors also suggest that the vacant Ge sites, which are implied by the small Ge deficiency always found for low temperature GeTe, may be accommodated along the antiphase domain boundaries present in thin films of the material. While studying the eutectic between GeTe and Te, a new compound has been found and is described here.

15 g batches, prepared from the pure elements with nominal concentrations 15, 16.5, 17.5, 19, 20, 21.5, 22.5 at.% Ge, were melted in evacuated sealed silica tubes at 950° C in a horizontal rocking furnace. Oxidation and volatilization were assumed to be minimal. After quenching and crushing, the specimens were subdivided into five and remelted under the same conditions to ensure homogeneity. The quenched glassy specimens were heat treated at five temperatures in the range 170 to 400° C for 24 h, again in evacuated sealed silica tubes, and then examined by reflected light microscopy and X-ray powder diffractometry.

For samples of composition 20% Ge–80% Te crystallized at 300° C and higher, the diffractometer traces showed GeTe and Te peaks as expected, but treatment at 180° C gave a completely new powder pattern shown in Table I. The appearance of the sample in reflected light is shown in Fig. 1 and can be easily distinguished from the normal GeTe/Te crystals shown in Fig. 2. A sample heat treated at 240° C showed no X-ray evidence of the new phase but using a reflected light microscope it was discovered in small amounts developing as surface crystallization, a characteristic of the 20% Ge–80% Te composition. The new phase was also found in the specimen 19% Ge–81% Te, often nucleated internally, and was present in quantities below the limit of X-ray detection at compositions 17.5% Ge–82.5% Te and 21.5% Ge–78.5% Te. Crystallization of this new species was predominant at the composition 20% Ge–80% Te suggesting a possible stoichiometry of $GeTe_4$. Since on either side of the composition 20% Ge–80% Te, GeTe and Te precipitate from the glass, even for some low temperature heat treatments, kinetic factors are clearly involved in the crystallization processes and equilibrium is not attained. The results of heat treatment at different temperatures also suggest that the new phase is not stable above 240° C.

A computer program similar to that of Werner [7] was used to index the powder diffraction pattern. Hesse [8] and Lipson [9] pointed out that for an $(h\,k\,l)$ reflection

$$\sin^2\theta = h^2A + k^2B + l^2C$$

if the material being examined has orthogonal axes. A, B and C are constants related to cell dimensions and wavelength. Thus for pairs of reflections $(h_1\,k\,l)$ and $(h_2\,k\,l)$

$$\sin^2\theta\,(h_1\,k\,l) - \sin^2\theta\,(h_2\,k\,l) = (h_1^2 - h_2^2)A$$

and the set of differences between all pairs of $\sin^2\theta$ values should frequently equal A, $3A$, $4A$, $5A$, $8A$, $9A$ etc. for crystals with orthogonal axes. A similar result holds for multiples of B and C. Such a set of differences were therefore computed and the number occurring within a small range of each of x, $3x$, $4x$, $5x$, $8x$ and $9x$ were counted. The totals were multiplied together and the products scanned for particularly large values which should occur when x coincides with A, B or C. In the present case large values occurred at values of x which were in simple ratios implying a cubic pattern. This led to a successful indexing of the reflections on a cell with

$$a = 11.09 \pm 0.02\,\text{Å}.$$

The indexing scheme, the intensities measured at peak heights and the d-spacings for unindexed reflections are shown in Table I. The many absent lines and the few unindexed lines prevented an earlier recognition of the pattern as cubic.

Diffractometer traces of the new compound prepared from 20% Ge–80% Te samples show no major glassy humps. Furthermore, any Te or Ge rich glass produced if the new phase had a composition very different from the matrix, should have given rise to Te and/or GeTe in the X-ray diffraction pattern, since glasses with compositions on either side of 20% Ge–80% Te crystallize quite rapidly to give Te and GeTe even at low temperatures. The few unindexed reflections occurring indicate the presence of another unidentified phase but their low intensity suggest only small quantities are present. Thus the new phase can differ little from the composition $GeTe_4$, confirming the earlier conclusion. The fine scale of the dendritic crystallization pattern has made a reliable determination of composition by electron

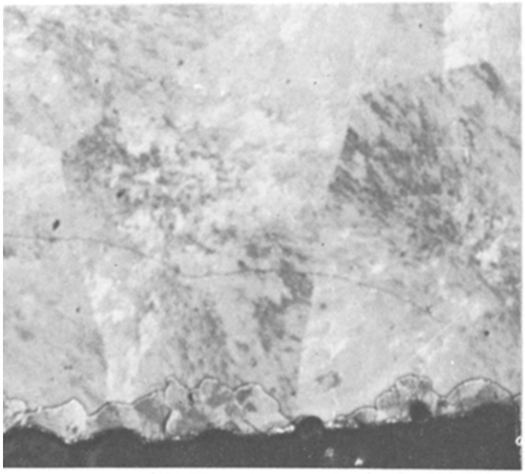

Figure 1 A reflected light micrograph using polarized light of a specimen of composition 20% Ge–80% Te heat treated for 24 h at 180° C (X 45).

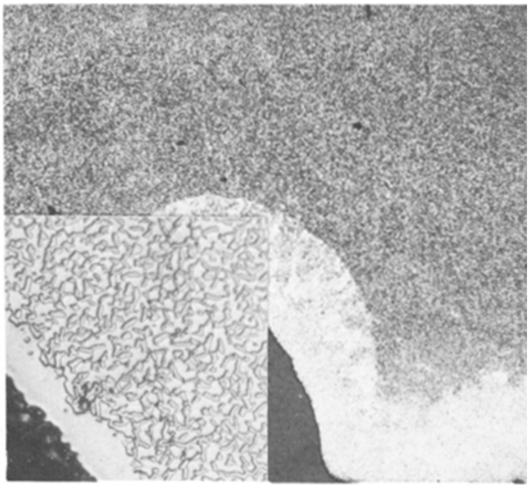

Figure 2 A reflected light micrograph of a specimen heat treated for 24 h at 300° C (X 50, Inset X 450).

microprobe or similar technique impossible.

The bulk density of the crystallized specimen was determined by Archimedes' method as 5.5 g cm^{-3}. Taking this as the density for the new phase gives $Z = 8$ and a unit cell content of 8 Ge and 32 Te atoms, which are easily accommodated within the constraints of cubic symmetry. The number of tellurium atoms suggests a relationship with the proposed GeTe supercell [6] although the cell volume is 21% lower, reflecting the removal of the smaller Ge atoms from their interstitial sites and the increased degree of bonding between Te atoms as the Te content increases. In Fig. 3 is plotted Te content versus volume per Te atom calculated using published cell dimensions [3, 10] and the very large volume changes probably reflect the changing bond character.

TABLE I Powder data for a specimen of composition 20% Ge–80% Te heat treated for 93 h at 215° C. The intensities given are peak heights corrected for background and 2θ values are for CuKα radiation.

2θ	I	d_{obs}	d_{calc}	$(h\,k\,l)$
13.87	3	6.385	6.405	(1 1 1)
19.66	31	4.515	4.529	(2 1 1)
21.48	4	4.137		
22.63	22	3.929	3.922	(2 2 0)
24.53	2	3.629		
25.35	28	3.513	3.508	(3 1 0)
26.67	6	3.342	3.345	(3 1 1)
27.85	100	3.203	3.203	(2 2 2)
28.47	5	3.135		
30.13	76	2.966	2.965	(3 2 1)
30.90	6	2.894		
32.28	15	2.773	2.774	(4 0 0)
53.28	2	2.692	2.691	(4 1 0) and (3 2 2)
34.44	19	2.604	2.615	(4 1 1)
35.28	10	2.544	2.545	(3 3 1)
36.14	2	2.485	2.481	(4 2 0)
37.11	6	2.423	2.421	(4 2 1)
38.34	6	2.348		
39.80	9	2.265	2.265	(4 2 2)
40.52	4	2.226	2.219	(5 0 0) and (4 3 0)
41.56	26	2.173	2.176	(4 3 1) and (5 1 0)
42.29	5	2.137	2.135	(5 1 1) and (3 3 3)
44.68	8	2.028	2.025	(5 2 1)
46.28	9	1.962	1.961	(4 4 0)
47.74	12	1.905	1.903	(5 3 0) and (4 3 3)
49.31	28	1.848	1.849	(6 0 0) and (4 4 2)
50.68	8	1.801	1.800	(6 1 1) and (5 3 2)
52.11	13	1.755	1.754	(6 2 0)
53.55	3	1.711	1.712	(5 4 1)
56.35	5	1.633	1.636	(6 3 1)
58.80	6	1.570	1.569	(7 1 0), (5 5 0) and (5 4 3)
61.29	6	1.512	1.510	(7 2 1), (6 3 3) and (5 5 2)
62.71	5	1.482	1.482	(6 4 2)

No AB$_4$ compounds have been reported for other combinations of Group IV and Group VI elements although there are many examples of AB and AB$_2$ compounds. GeS and GeSe both have structures related to that of black P which in turn is a derivative of the NaCl structure [11], while GeS$_2$ has a structure of linked GeS$_4$ tetrahedra [12, 13] and GeSe$_2$ is reported as being a deformed CdI$_2$ structure [14]. By analogy with GeTe, however, a possible model for the GeTe$_4$ structure has cubic close packing of tellurium atoms. Indeed, Te itself adopts a distorted cubic close packing scheme but only at very high pressures where the volume/Te atom is relatively small [15]. Assuming this model and neglecting the scattering from the Ge atoms, having fewer electrons, the only reflections within the angular range examined would be those indexed as (2 2 2), (4 0 0), (4 4 0), (6 2 2) and (4 4 4). In fact the (2 2 2) reflection is easily the most intense observed and (4 0 0) the second most intense after applying Lp corrections and allowing for multiplicity factors. (4 4 0) is relatively intense but (6 2 2) and (4 4 4) are missing. These observations suggest that the proposed model may well be correct but that considerable distortions from the

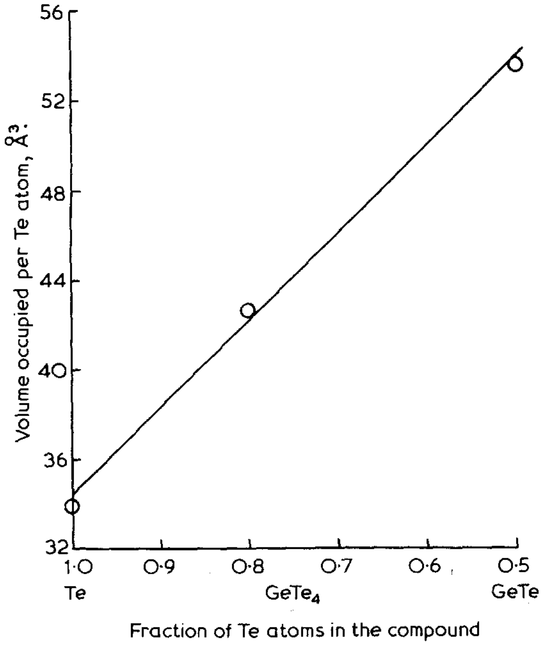

Figure 3 The volume available/Te atom is plotted as a function of Te content for the phases Te, GeTe$_4$, and GeTe showing a linear trend.

idealized arrangement must exist, just as is found for GeTe itself. The unidexed reflections reported could not be indexed on the basis of an hcp structure related to the cubic close packed model.

At this stage more detailed statements about these structural distortions or the Ge atoms positions cannot be made except to point out that the indexed powder pattern indicates an almost body centred cell and so a body centred arrangement of Ge atoms might be expected. Although the proposed model for $GeTe_4$ has three-quarters of the possible octahedral Ge sites unfilled it is pertinent to note that the non-stoichiometry of GeTe also implies vacant Ge sites. Indeed it is possible that the build-up of vacant germanium sites along antiphase domain boundaries as postulated by Stoemenos *et al.* for GeTe, in fact gives rise to a slab of structure related to that of $GeTe_4$.

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References

1. W. KLEMM and G. FRISCHMUTH, *Z. Anorg. Chem.* 218 (1934) 249.
2. I. R. McHUGH and W. A. TILLER, *Trans. Metallurg. Soc. AIME* 218 (1960) 187.
3. K. SCHUBERT and H. FRICKE, *Z. Metallkunde* 44 (1953) 457.
4. T. B. ZHUKOVA and A. I. ZASLAVSKII, *Soviet Phys. Crystallography* 12 (1967) 28.
5. J. GOLDAK, C. S. BARRET, D. INNES and W. YOUDELIS, *Chem. Phys.* 44 (1966) 3323.
6. J. STOEMENOS, S. KOKKOU and N. A. ECONOMOU, *Phys. Stat. Sol. (a)* 13 (1972) 265.
7. P. E. WERNER, *Zeit. Krist.* 120 (1964) 375.
8. R. HESSE, *Acta Cryst.* 1 (1948) 200.
9. H. LIPSON, *ibid* 2 (1949) 43.
10. A. J. BRADLEY, *Phil. Mag.* 48 (1924) 477.
11. S. N. DUTTA and C. A. JEFFREY, *Inorg. Chem.* 4 (1965) 1363.
12. W. H. ZACHARIASEN, *Phys. Rev.* 49 (1936) 884.
13. *Idem, J. Chem. Phys.* 4 (1936) 618.
14. LIU CH'UN-HUA, A. S. PASHINKIN and A. V. NOVOSELOVA, *Russ. J. Inorg. Chem. (Engl. Trans.)* 7 (1962) 1117.
15. J. C. JAMIESON and D. B. McWHAN, *J. Chem. Phys.* 43 (1965) 1149.

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Comments on "Glass-ceramics with random and oriented microstructures Part 2 The physical properties of a randomly oriented glass-ceramic"

Atkinson and McMillan have provided useful information on the mechanical, electrical and thermal properties of the glass ceramic material they studied [1]. However, consideration of their mechanical property results which are of particular interest to us, suggests that this aspect of their study is incomplete in a number of respects.

Before turning to a detailed consideration of their experimental data and its analysis it is appropriate to consider the theoretical background. A common basis for such analysis, as recognized by Atkinson and McMillan, is the Griffith equation:

$$\sigma = A_1\sqrt{(E\gamma/c)} \qquad (1)$$

where σ = the failure stress, A_1 = a flaw shape parameter, E = Young's modulus, γ = the fracture surface energy, and c is the flaw size. The first task is to determine whether or not the Griffith equation is valid for the particular conditions, or whether it can be made valid if appropriately modified. Validity can be established by measuring all parameters and showing that there is true equality.

Two conditions pertinent to the present material can make the above simple form of the Griffith equation invalid. The first is the contribution to failure that may be made to the failure stress by internal stresses resulting from the incompatible strains either between grains of the typically non-cubic phases that are produced, or