ON THE SYNTHESIS OF THE COMPOUND $Ge_3Bi_2S_6$

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The preparation of the recently reported compound $Ge_3Bi_2S_6$ was studied. From the results of differential thermal analysis and Debye–Scherrer and microstructural analyses it follows that no compound $Ge_3Bi_2S_6$ is formed in the system GeS–Bi_2S_3. Heterogeneous mixtures, predominantly of germanium disulfide and metallic bismuth, resulted from all syntheses.

During systematic study of semiconducting compounds constituted by Groups IV-V-VI elements, attention was paid also to the system Ge–Bi–S. According to Odin and coworkers[1], a single compound $Ge_3Bi_2S_6$ with congruent melting point 655 ± 5°C, is formed in this system. This compound undergoes a phase transformation at 215–221°C, and its X-ray diffraction patterns differ[1] from those of GeS and Bi_2S_3. No detailed structural data, however, have been reported.

In the present work, the procedure[1] was exactly reproduced: a stoichiometric mixture of GeS and Bi_2S_3 was heated in the molten state (850°C) for 48 h, cooled,

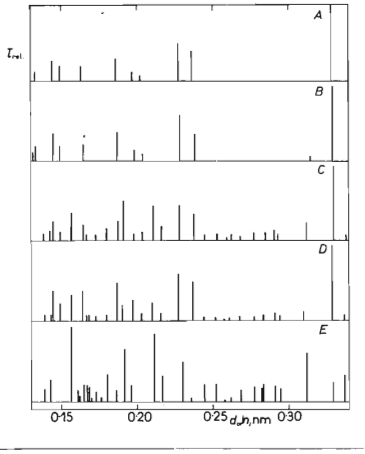

FIG. 1

Interplanar Crystal Spacing $d\alpha/n$

A pure Bi; *B* a part of the sample after the zone refining of $Ge_3Bi_2S_6$ virtually pure Bi; *C*, *D* parts of the samples $Ge_3Bi_2S_6$ prepared according to Odin[1]; *E* sample containing a relatively higher amount of Bi, *D* pure GeS_2.

and annealed at 400°C for 1 000 h. Samples of "$Ge_3Bi_2S_6$" were prepared in addition by direct synthesis from the elements (850°, 100 h) with successive slow cooling of the melt. In all cases the synthesis was performed in evacuated quartz ampoules from materials 5N purity (99·999%).

The samples obtained were grey colour, with a laminated structure, and were evidently inhomogeneous. The Debye–Scherrer analysis revealed that the samples were multiphase and contained predominantly germanium disulfide and metallic bismuth, formed according to the scheme $3\ GeS + Bi_2S_3 = 3\ GeS_2 + 2\ Bi$, or $3\ Ge + 2\ Bi + 6\ S = 3\ GeS_2 + 2\ Bi$.

The zone refining of the "compound" $Ge_3Bi_2S_6$ prepared according to[1] gave again a heterogeneous sample. A part of it – formed by Bi – was metallically lustrous (Fig. 1). The remaining part of the sample was represented predominantly by germanium disulfide. Small quantities of GeS and Bi_2S_3 could be identified in the zone refining products, too.

Heterogeneous samples resulted also from a slow directed solidification of the melt $Ge_3Bi_2S_6$ ($v = 2-4$ mm/h) in a conical ampoule according to Bridgman[2]. The bottom part was formed by GeS_2, the central part was clearly multiphase, the upper part contained metallic bismuth.

From the two latter experiments it follows unambiguously that the melt $Ge_3Bi_2S_6$ does not solidify congruently. Moreover, the compound $Ge_3Bi_2S_6$ is formed neither by applying the procedure described in[1], nor by direct synthesis from the elements, even if the samples are annealed below their melting point. In all cases multiphase samples originate, constituted predominantly by GeS_2 and Bi. In this sense the data of the paper[1] are to be reconsidered.

REFERENCES

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