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Abstract

Full Text

PHYSICAL CHEMISTRY

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NEW GLASS-LIKE COMPOUNDS

(Presented by Academician B. P. Konstantinov, 16 VIII 1964)

Most of the glass-like compounds known at present, with the exception of a small group of fluoroberyllate glasses, belong to oxide or chalcogenide glasses. For substances with a diamond-like structure, glass formation is not characteristic. Thus, neither elements of group IV nor compounds of the types $A^{III}B^V$, $A^{II}B^{VI}$, or $A^I B^{VII}$ have been obtained in the glass-like state (thin amorphous films are not considered). It was therefore quite unexpected that we discovered glass formation in ternary semiconductor compounds of the type $A^{II}B^{IV}C_2^V$, which are structural analogues of A^{IV} and $A^{III}B^V$.

We observed the presence of allotropic transformations in some ternary compounds of this type. The glass-like state was detected in the study of high-temperature transformations in them. The glass-like state is manifested most clearly in the compound CdGeAs₂: conchoidal fracture (Fig. 1), optical homogeneity, and the presence on Debye diagrams of only diffuse maxima (Fig. 2).

Fig. 1. Conchoidal fracture of glass-like CdGeAs₂

In some quenched ingots one can observe the coexistence of crystalline and glass-like phases simultaneously. In the compound CdGeAs₂, a single-phase glass-like ingot can be obtained in an ampoule with an internal diameter of no more than 6 mm or in a flat-bottomed quartz vessel at a melt height of no more than 3–4 mm. At a greater height of the molten layer of the substance, the regions of the melt directly adjacent to the ampoule walls vitrify more readily, and the boundary between the crystalline part and the glass becomes distinguishable. This is especially characteristic of CdGeP₂, which in the glass-like state forms as a thin layer. Consequently, for vitrification of these compounds a high cooling rate is necessary (more than 200° per sec).

Crystallization of CdGeAs₂ begins soon after the softening temperature ($T_g = 410^\circ\text{C}$). Crystallization does not occur in a temperature interval—

Table 1

Properties of CdGeAs₂ in the crystalline and glass-like states

	Density, g/cm ³	M.p. (softening), °C	Microhardness, kg/mm ²	Conductivity type	Specific resistance (ohm · cm) at 300°K
Crystal	5.60	700	470	<i>n</i> and <i>p</i>	~ 10 ⁻¹
Glass	5.35	410	320	<i>n</i>	~ 10 ⁶

temperatures, but almost instantaneously at a temperature of about 460°, and is thus strongly shifted toward T_g .

An extremely important question is whether the tetrahedral, “diamond-like” structure is preserved in $A^{II}B^{IV}C_2^V$ compounds in the glassy state. A change in the short-range structure is usually accompanied by a change in density. We present some characteristics of glassy CdGeAs₂ in comparison with its properties in the crystalline state (see Table 1).

Fig. 2. Distribution of the intensity of X-radiation scattered by glassy and polycrystalline CdGeAs₂. Debyeogram according to the data of [1].

As can be seen, the densities measured by us differ from one another; the density of the crystalline substance is close to the density calculated from X-ray data, 5.612 g/cm³. A comparatively small change in density is characteristic of transitions to the glassy state that are not accompanied by a change in the short-range structure.

The similarity of the short-range order in crystalline and glassy CdGeAs₂ can be judged by comparing the intensity distribution of X-radiation scattered by the glass with the X-ray diffraction pattern of a polycrystalline specimen (Fig. 2). The correspondence of the positions of the diffuse maxima indicates the presence of such similarity.

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Note: Figure translations are in progress. See original paper for figures.

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