Glass formation in chalcopyrite structured semiconducting compounds

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The II-IV-V₂ and I-III-VI₂ elements in the Periodic Table, which commonly adopt the chalcopyrite structure, have been studied with regard to their glass-forming tendency. CdGeP₂ [1-3], CdGeAs₂ [4, 5] and CdSiAs₂ [6] have been frequently investigated. Other investigators have studied glass-forming tendency in the CdGe₁₋ₓSiₓAs₂ and CdGe₁₋ₓSbxAs₂ systems [7]. Hruby et al. [8] found that CdGeAs₂ can be formed into glass more easily, in many cases, with a decrease in the germanium content.

Chalcopyrite compounds generally have at least one toxic constituent, which makes it necessary to synthesize in a closed system. This also prevents oxidation and volatilization of batch components. A systematic effort has been undertaken, and described in this letter, to vitrify a wide range of II-IV-V₂ as well as I-III-VI₂ group chalcopyrites.

Fused silica tubes of 10 mm i.d., 1 mm wall thickness and ~ 200 mm length were sealed at one end. A neck of ~ 8 mm diameter was formed in each tube at a distance of ~ 80 mm from the closed end, by heating the tube with an oxy-propane torch. The tubes were cleaned using trichloroethane-acetone methanol, respectively (TAM), and then with distilled water. The inner surfaces of the tubes below the sealing neck were then carbon-coated by pyrolysis of acetone.

Stoichiometric quantities of high-purity elemental constituents were weighed and placed in these fused silica tubes, and a ~ 25 mm long, 9 mm diameter fused silica rod was inserted in the tube to minimize excess void space and to facilitate proper sealing. The tubes were evacuated with a mechanical/diffusion pump system to ~ 10⁻⁶ torr and then sealed to form ampoules. These ampoules were suspended in a vertical globar furnace and slowly heated to a temperature approximately 200°C above their melting temperatures and held there for approximately 24 h for homogenization.

This synthesis technique was found to be inefficient and had drawbacks: there was inadequate contact between the vapour phase and unreacted liquid phase, and the homogenization was due to sluggish diffusion processes only. Long exposure of ampoules to high temperatures occasionally caused solid state fluxing, hence failure of fused silica tubes.

Occasional explosion of the fused silica tubes initially occurred due to excessive build-up of pressure inside the tube. The vapour pressure of the most volatile constituents used was calculated based on the Clausius–Clapeyron equation.

\[
\ln \left( \frac{p}{p^*} \right) = \frac{\Delta H_{\text{sub}}}{R} \left( \frac{1}{T_{\text{sub/vap}}} - \frac{1}{T} \right)
\]  (1)

where, \( p^* \) is 1 atm, \( \Delta H_{\text{sub}} \) is the enthalpy change during sublimation, \( T_{\text{sub/vap}} \) the sublimation temperature at 1 atm and \( R \) is the gas constant. Plots from this expression shown in Fig. 1 demonstrate the increase in vapour pressure of arsenic, sulphur and precipitously phosphorus with temperature in a closed system.

To overcome these problems, a horizontal Kanthal-wound 100 mm diameter melting tube furnace, shown in Fig. 2, was designed, which reduced the homogenizing time by ~ 50%. A fused silica rod of 9 mm diameter was heated at one end with the oxy-propane flame and bent to form a shape of an “S”. The sealed ampoule was attached to this end of the rod by fusing the ends, such that the ampoule was at ~ 45° with the axis of the rod. The ampoule was placed within the furnace such that the rod extended outside the furnace through a hole in the lid concentric with the furnace tube. The guide tube placed in the lid hole kept the rod parallel to the furnace axis. The extended end of the rod was connected to a 1 r.p.m. electric motor through a flexible coupling. As the sample rod was rotated, the constituents inside the ampoule mixed from one end to the other during melting and homogenizing.

Generally, homogenization was complete in 8 h and the ampoule, along with the rod, was removed from the furnace after releasing the rod from the coupling. The compound removed from the fused silica container appeared homogeneous. This made it possible to synthesize a variety of compounds containing arsenic, sulphur, selenium, etc. Most remarkably, vitreous CdGeAs₂, which was previously reported to be formed in 3 mm diameter ingots after quenching the melt in refrigerated glycol-water mixture [9], was obtained in 10 mm diameter ingots simply by air quenching the melt homogenized in this furnace.

The implication of this finding is that glass formation tendency in chalcopyrite compounds in prior literature studies may have been more severely limited by variable stoichiometry than by the choice of rapid solidification techniques. This also points towards the feasibility of glass fibre formation with CdGeAs₂, perhaps followed by aligned devitrification for use as a laser up-converter.

The homogenized compound was crushed using a clean mullite mortar and pestle and then resealed in individual 2 mm i.d. and 0.5 mm thick fused silica tubes under similar vacuum conditions. The individual tubes were once again attached to a fused silica rod, but concentric to the rod, and placed in another similar furnace of 50 mm diameter. This time, the furnace was heated rapidly to ~ 200°C above the melting point of the compound, and held at that
temperature for about 2h. The ampoule was then quenched in a glycol–water solution-encapsulated mercury quench bath at −30°C [10] by tilting the furnace and releasing the rod from the holder. CdSiAs₂, ZnGeAs₂, and ZnSiAs₂ were obtained in the partially vitreous form when homogenized compounds in 2 mm i.d. ampoules were quenched in the glycol–water bath at −20°C.

To obtain an improved quenching rate, the roller splat-quenching method was used as shown in Fig. 3. Homogenized compounds were crushed and then put into carbon-coated fused silica tubes (10 mm i.d.). The tubes had a small hole (~1 mm diameter) on one side and an opening on the other side, to which a nitrogen intake gas hose was connected. The tube was heated above the melting temperature of the compounds using a Kanthal wire heating element from outside in the nitrogen atmosphere. Molten compounds were injected on to the surface of a rotating aluminium wheel by nitrogen gas pressure. Ribbons of amorphous CdGeAs₂, 2 mm wide and 30 μm thick, were obtained under the conditions of 100 kPa nitrogen gas pressure, 200 mm diameter aluminium wheel rotating at 1850 r.p.m., and ~850°C melting temperature. Glass formation of other chalcopyrite compounds is currently under investigation in our laboratory.

The compounds with phosphorus were not investigated in view of their explosoive nature. Some sulphides were homogenized in 200 mm long ampoules by controlling the sulphur vapour inside the tube. Initially about three-quarters of the ampoule was inserted in the furnace. The ampoule was rotated through the fused silica rod attached to it and the furnace was heated to the melting temperature of the compound. The vapour across the length of the tube was not under thermal equilibrium because the low-temperature end tended towards low pressure while the high-temperature end tended towards high pressure. Because the pressure had to be equal throughout, a compromising lower equilibrium pressure developed than if the entire tube was in the furnace. Thus as the reaction of the sulphur with other batch constituents proceeded, the ampoule was slowly inserted inside the furnace, generally at 2 to 4 mm h⁻¹ until the entire ampoule was in the hot zone of the furnace. Assuming a Raultian solution, the vapour pressure of sulphur was reduced by half as it went into solution. The compound was further homogenized for 2 h and then air quenched.

Some compounds were not attempted in view of their high melting temperatures. One compound containing aluminium (AgAlTe₂) was attempted, but it reacted badly with the fused silica tube. Other aluminium compounds were also abandoned as a precautionary measure.

X-ray diffraction was used to determine the amorphous nature of as-quenched bulk compounds. Samples were crushed using a clean mortar and pestle and −200 mesh material was used for powder diffraction. A Philips (Philips Electron Instruments, Mount