PREPARATION OF Cd$_3$As$_2$ AND CdAs$_2$ CRYSTALS BY TRANSPORT REACTION IN VAPOUR PHASE

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A method of preparation of Cd$_3$As$_2$ and CdAs$_2$ single crystals employing transport reaction in vapour phase without transport gas is described. Optimum conditions for growth of the crystals are determined. In the case of Cd$_3$As$_2$ the average temperature and the temperature gradient are 535 °C and 3-3 °C/cm respectively, in the case of CdAs$_2$ the corresponding values are 550 °C and 4 °C/cm. Bulk crystals as large as a few cm$^3$ can be obtained within several days using evacuated quartz tubes 150 mm in length and 20 mm in diameter. Furthermore, thermodynamical arguments indicating possible reaction mechanisms are presented. Sublimation appears to be the most probable mechanism of transport in the case of Cd$_3$As$_2$, whereas the process is more complicated in the case of involving the decay of CdAs$_2$ molecules.

I. INTRODUCTION

The classical way of growing Cd$_3$As$_2$ and CdAs$_2$ single crystals by means of crystallization from the melt faces some difficulties of experimental character. The technique by Bridgman yields always polycrystals with grains of various dimensions; modifications of the temperature gradient in the furnace and of the rate of lowering the ampoules did not lead to any satisfactory results. Another serious obstacle arises in the case of Cd$_3$As$_2$ where a phase transition in solid state takes place at 578 °C [1], resulting in appearance of small cracks and subsequent disintegration of eventually formed crystal. The technique by Czochralski that employs B$_2$O$_3$ melt has been reported for growth of Cd$_3$As$_2$ [2], but even here a number of technological problems arise. In the case of the growth of CdAs$_2$ from the melt one has to cope with relatively high partial pressure of arsenic vapours when the melting point of CdAs$_2$ is exceeded. This leads to the condensation of arsenic on the colder parts of apparatus and, consequently, to the violation of stoichiometry and the growth of polycrystalline inclusions. Moreover, CdAs$_2$ melt shows a trend to metastable solidification giving rise to Cd$_3$As$_2$ and As, which in turn leads to heterogenous nucleation. This phenomenon is responsible for the failure of Bridgman method to yield CdAs$_2$ single crystals from the melt.

We have, therefore, attempted to grow these crystals by transport in vapour phase. It is quite common technique for the growth of crystals of simple and more complex substances, nevertheless its application to cadmium arsenides has not yet been reported. We have tried to find optimum conditions of the growth of CdAs$_2$ and Cd$_3$As$_2$ single crystals and described, in a qualitative way, their growth mechanism from the thermodynamical viewpoint.

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2. EXPERIMENTAL

Transport reaction was performed in horizontal quartz tubes (15–20 mm dia., approx. 150 mm long) that were put in a furnace with temperature gradient. The tubes containing starting material were evacuated until pressure of approximately $10^{-6}$ Torr was reached. Heating up to about 300 °C and sealing off followed. Both cadmium and arsenic were of 6N purity and the corresponding starting cadmium arsenides were prepared by melting the stoichiometric mixtures of elements in evacuated and sealed quartz tubes. After the temperature was gradually raised up to about 800 °C and the melt was thoroughly mixed, the tube was left to cool freely in air.

In order to be able to observe the crystal growth and the process of transport, the furnaces were made from transparent quartz tubes provided with progressive resistance wire windings and with vacuum isolation shield that was made from transparent quartz tubes too. Temperatures were measured with ±5 °C precision by means of Pt–Pt.Rh thermocouple.

The transport of material takes place from the warmer towards the colder end of the tube. A series of experiments was performed under various reaction conditions; we were changing the temperatures $T_1$ (warmer end of the tube), $T_2$ (colder end of the tube), $T_{av}$ (average temperature) and the temperature gradient $\Delta T$. It has been corroborated both that the rate of transport, at given $\Delta T$, increases with increasing temperature ($T_{av}$) [2] and that the probability of single crystal growth is greater at lower temperature gradients.

As optimum growth condition of CdAs$_2$ from the vapour phase, the following temperature values have been found, viz.: $T_1 = 580$ °C, $T_2 = 520$ °C, $T_{av} = 550$ °C, the optimum gradient being 4.0 °C/cm. Obtained crystal exhibits natural growth faces as large as several tens of mm$^2$, its volume reaching even a few cm$^3$. To prove the identity of the grown crystals X-ray analysis was used. The transport rate amounts approximately to 1 g/day in the case of Cd$_3$As$_2$ while a half of this value is typical of CdAs$_2$.

Together with transport of CdAs$_2$ and its crystallization in the colder end of the tube, recrystallization of starting charge takes place in the warmer end giving rise to tiny single crystals of a few mm$^3$ in volume. Migration of grain boundaries appears to be responsible for this effect.

The same equipment as for CdAs$_2$ was used in the case of Cd$_3$As$_2$ too. The optimum temperature gradient for the growth of Cd$_3$As$_2$ single crystals was found to be 3.3 °C/mm, the colder end temperature $T_2 = 510$ °C, the warmer end temperature $T_1 = 560$ °C. Unfortunately, this value of the temperature gradient is not accompanied by the degree of supersaturation of the vapour phase that is necessary for the primary germ crystal to nucleate. Optimum temperatures for germ nucleation are as follows: $T_1 = 575$ °C and $T_2 = 520$ °C. Within a few hours small germ crystal forms; the tube is then moved into the lower temperature gradient ($\Delta T = 3.3$ °C/cm). Supersaturation, consequently, decreases below its critical value and the growth rate