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Dedicated to Prof. Antonius Kettrup on the occasion of his 60th birthday

THE INFLUENCE OF THE THERMAL BEHAVIOUR OF $AgGaS_2$ ON THE CRYSTAL GROWTH PROCESS

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Abstract

Differential thermal analysis has been carried out on $AgGaS_2$ samples in order to investigate the relationship between the superheating of the melt and the supercooling behaviour of the material leading to an improvement of crystal growth conditions. The knowledge gained will be correlated to the crystal growth experiments which had been carried out by using the gradient freezing method.

Keywords: $AgGaS_2$, crystal growth, differential thermal analysis

Introduction

The ternary compound $AgGaS_2$ is a representative of the A^I-B^{III}-C^{VI}_2 semiconductor family (*A*=Cu, Ag, Li, Na, K; *B*=Al, Ga, In; *C*=S, Se, Te). The high non-linear susceptibility, a wide area of transparency in the far infrared region, and the possibility of phase matching are of special interest for non-linear applications.

Hitherto it was impossible to grow orientated large scale $AgGaS_2$ single crystals in the dimension of centimetres reproducible. The crystallisation of the material is influenced by supercooling effects in the melt (T_{melt}=1268 K). As generally known the structure of the molten state will also affect the supercooling behaviour.

The scientific object of this paper therefore will be the investigation of the thermal behaviour of $AgGaS_2$ and the correlation of the results to the crystal growth conditions and the crystal quality.

Experimental

$AgGaS_2$ was synthesised from the elements silver (5N), gallium (5N), and sulphur (5N) by reaction of the molten silver gallium alloy with the sulphur va-

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pour. In order to avoid a reaction between the $AgGaS_2$ and the quartz wall, the ampoules were always carbon coated. The synthesis followed the instructions described in [1]. Seeded and non-seeded growth from the melt using the gradient freezing method was carried out. The ampoules used had a diameter of 10 mm and a length of 100 mm. Square ampoules had an edge length of 10 mm and a length of 100 mm.

The supercooling-superheating behaviour as well as the dependence of the supercooling on the cooling rate of $AgGaS_2$ were investigated in order to understand the crystallisation behaviour. The thermal behaviour was analysed by measurements using a DTA 404 (Netzsch Gerätebau GmbH). The $AgGaS_2$ probes were sealed in carbon coated and evacuated quartz ampoules. These ampoules were placed in Pt crucibles. The thermal curves were taken in the temperature range from 300 to 1350 K.

Results and discussion

In carrying out the investigations of the dependence of the supercooling on the cooling rate the samples were always superheated 40 K above the melting point. $AgGaS_2$ shows in contrast to other materials (e.g. CdTe, $LiInSe_2$,...) a different behaviour (Fig. 1). Even small values of the cooling rate do not avoid supercooling (Fig. 5). At higher values of the cooling rate (>10 K) the supercooling of the melt will approximate to 55 K.

As known from the II–VI semiconductors the structure of the molten state will affect the supercooling behaviour and therefore the crystal growth conditions [2]. Polycrystalline growth and formation of twins are assumed to be caused by associated particles, which exist in the melt at low superheating above the melting point. It is assumed that these particles reduce the nucleation energy

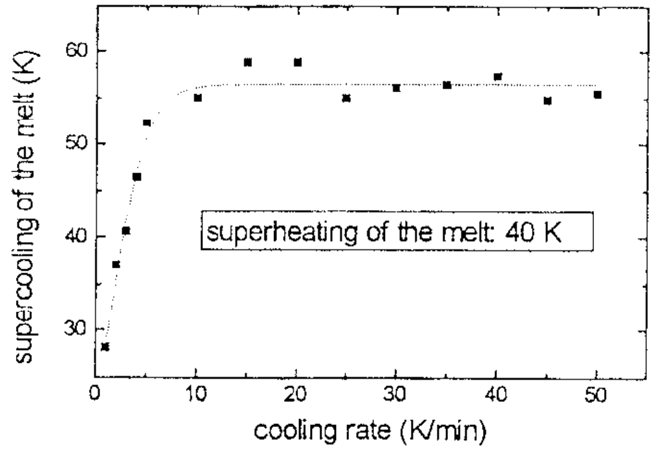

Fig. 1 Dependence of the supercooling of the melt on the cooling rate

and therefore the supercooling will be suppressed [2]. At a high superheating the associated particles will be destroyed resulting in a higher supercooling of the melt. No supercooling has been observed at small values of superheating (<10 K) (Fig. 2). At higher values of superheating (<10 K) supercooling occurs up to 55 K.

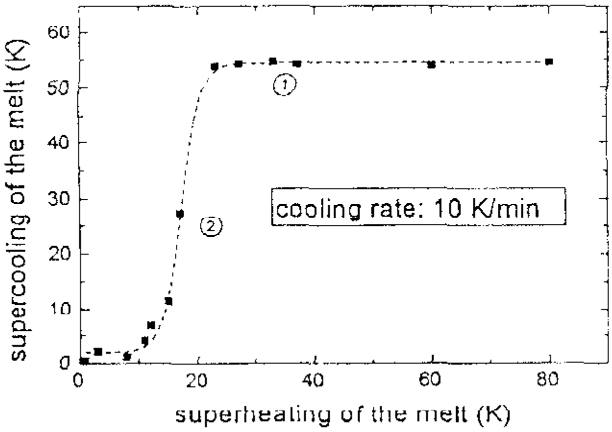

Fig. 2 Dependence of the supercooling of the melt on the superheating of the melt

Figure 3 shows $AgGaS_2$ material grown from a highly superheated melt (position 1 in Fig. 2) without a seed. The high superheating results in a high supercooling of the melt and therefore in totally polycrystalline growth because the crystal was supercooled over the whole length. Growing $AgGaS_2$ under the same conditions but superheating the melt less than 20 K (position 2 in Fig. 2) instead, polycrystalline growth at the beginning will occur resulting in single crystal growth (Fig. 4). Due to the associated particles in the melt the nucleation energy will be reduced leading to accelerated crystallisation and therefore the supercooling of the melt will be decreased. Grain growth proceeds single crystal growth.

Carrying out seeded growth using the gradient freezing or the Bridgman method will be an alternative method to avoid supercooling of the melt and to grow large scale $AgGaS_2$ single crystals. The grown single crystals always

Fig. 3 Polycrystalline crystallisation of $AgGaS_2$ resulting from high superheating of the melt (pos. 1 in Fig. 2)

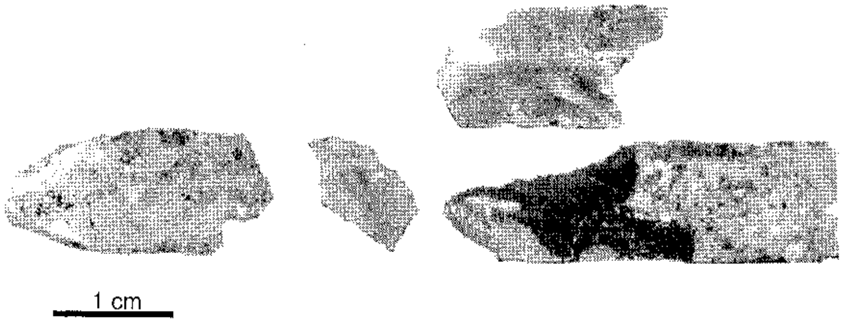

Fig. 4 $AgGaS_2$ crystals: Polycrystalline crystallisation at the beginning leading to single crystal growth resulting from less superheating of the melt (pos. 2 in Fig. 2)

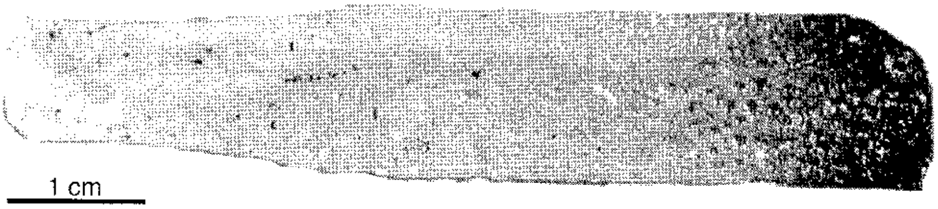

Fig. 5 Alternative method: seeded growth of $AgGaS_2$

showed a homogenous yellow colour and were up to 55 mm in length and 12 mm in diameter. They showed a high transparency in the visible (Fig. 5). Twin formations were not observed.

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