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BRIDGMAN GROWTH OF AgGaS\textsubscript{2} WITH IMPROVED OPTICAL PROPERTIES (*)

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Résumé. — Le sulfite ternaire AgGaS\textsubscript{2} est d'un intérêt spécial pour les utilisations optiques non linéaires. Cependant, les monocristaux d'une qualité optique élevée et de grandes dimensions n'étaient pas disponibles jusqu'à présent. C'est pourquoi la fabrication de ce genre de mono-cristaux a fait l'objet du présent examen. La méthode Bridgman a permis d'obtenir des échantillons suffisamment grands (5 \times 5 \times 5 \text{mm}^3) exempts de fêlures, d'inclusions et de macles après avoir optimisé la composition du bain, le profil de température du four et la géométrie des ampoules. Grâce à une malleabilité ultérieure, l'absorption a pu être réduite à des valeurs $\alpha < 0.1 \text{ cm}^{-1}$ dans la partie essentielle de la zone de transmission.

Abstract. — The ternary sulfide AgGaS\textsubscript{2} is of special interest for nonlinear optical applications. Single crystals of high optical quality and large size, however, were not available. Therefore we investigated the growth process to obtain such crystals. Using the Bridgman technique by optimizing composition of the melt, temperature profile and geometry of the quartz ampoule it was possible to get sufficiently large (5 \times 5 \times 5 \text{mm}^3) samples free of cracks, voids and lamellar twins. By a subsequent annealing process, absorption could be reduced to $\alpha < 0.1 \text{ cm}^{-1}$ for the most important part of the transmission range.

1. Introduction. — Tunable infrared laser sources in the spectral range between about 2 and 10 \text{ }\mu\text{m} are of great interest for detecting pollutant gases by optical methods. A very promising laser source might be an optical parametric oscillator, pumped by a convenient Nd: YAG laser. The main part of the oscillator is a nonlinear optical crystal, which allows transformation of the constant pump frequency to tunable emission at lower frequencies. For this application crystals from the group of ternary I-III-VI\textsubscript{2} semiconductors are of special interest [1].

AgGaS\textsubscript{2} is very promising for use in such an optical parametric oscillator by reasons of high nonlinear coefficients, sufficiently high optical birefringence for phasematching and its transparency ranging from 0.5 to about 12 \text{ }\mu\text{m} [2, 3]. The phasematching range of AgGaS\textsubscript{2} allows pumping of the oscillator by a Nd: YAG laser ($\lambda = 1.06 \text{ }\mu\text{m}$), in order to obtain tunable emission in the range of about 2 to 10 \text{ }\mu\text{m}. However, single crystals of AgGaS\textsubscript{2} of the desired high optical quality and sufficiently extended size of twin free cubes were not available until now. Problems in growing AgGaS\textsubscript{2} crystals by the Bridgman-Stockbarger technique were:

1. pronounced tendency of lamellar twin formation during crystallization [4].

2. too high an optical absorption with absorption coefficient $\alpha > 1 \text{ cm}^{-1}$ in the whole transparency range (0.5-12 \text{ }\mu\text{m}) [3, 5]. The upper limit for the special application of a parametric oscillator is estimated to be about $\alpha = 0.1 \text{ cm}^{-1}$ in the wavelength range of infrared emission [3].

We tried first the liquid encapsulation Czochralski technique as a different growth method [6] to overcome these difficulties. The resulting crystals, however, showed no significant improvement. Therefore we again used the Bridgman technique to obtain the desired crystal properties. Growing performance and results are reported in the following.

2. Crystal growth conditions. — The polycrystalline AgGaS\textsubscript{2} for Bridgman growth was synthesized by a pre-melting procedure. Due to the requirement of high crystal transparency the starting material should be of highest purity. Because of the high vapor pressure of sulphur when starting with elemental components it was necessary to synthesize AgGaS\textsubscript{2} from the binary sulphides Ag\textsubscript{2}S\textsubscript{3} and Ga\textsubscript{2}S\textsubscript{3}. The binary components, however, were available only in 4-N to 5-N grade compared to 6-N quality of the elements. The starting composition was chosen stoichiometric and in several deviating ratios. For synthesis double-walled quartz ampoules were used in order to prevent oxidation of the compound which can occur by fracture of the internal ampoule during cooling. The ampoules were degreased with acetone, etched in a mixture of HF and HNO\textsubscript{3} in a ratio 1 : 1, and then baked at 1 000 °C for 24 hours in vacuum. They were filled with the sulphide mixtures in charges of 60 g, evacuated to $10^{-5}$ torr and sealed. The binary

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sulphides were brought to reaction by heating to 1020°-1050°C held for 3-5 days. For Bridgman growth the resulting reaction product was crushed, dried and again placed in a double walled ampoule with a conical bottom (cone angle 30°). After evacuating to $10^{-5}$ torr and filling with argon gas to 0.5 atm the ampoule was sealed and positioned into the top zone of the Bridgman furnace. It consists of a vertical 4-zone furnace with separately controlled heat zones, providing a long term stability better than ± 0.5 °C. The complete Bridgman apparatus is shown in figure 1. Separation of the upper and lower zone pairs by a variable air gap allows a steeper temperature gradient. The maximum value of this set-up was 55 °C/cm in the furnace, which resulted in 40 °C/cm within the ampoule. The temperature plateaus above and below this gradient were 1050 °C and 840 °C. The ampoules were lowered through the gradient at a speed of 4-6 mm per day. Crystals were cooled down to room-temperature at a rate less than 100 °C/h.

3. Results and discussion. — 3.1 Lamellar Twins. — Independent of the starting compositions the occurrence of twin lamellae in the resulting single crystals was observed. Figure 2a shows an example of such twin lamellae, which give regular interference structures in transmitted polarized light. Twin density, however, was not uniformly distributed throughout the whole cross section of the boule. Lamellae preferably started from the outer crystal surface. Termination towards the centre was observed. Figure 2b shows stopping of one lamella by running into an other one. In addition lamellae termination occurred merely by reducing thickness. From this latter observation it was concluded, that by increasing the ampoule diameter, twin free regions should be available from the centre of the boule. This expectation was verified experimentally. Ampoule diameters of about 2.5 cm gave twin free regions in the inner part of the boule with sizes of about 5 x 5 x 5 mm³.

3.2 Optical Transmission. — 3.2.1 As-grown material. — Single crystals grown by the technique described above gave different macroscopic appearances depending on the composition of the starting material. An exactly stoichiometric composition resulted in uniformly milky yellow boules. Absorption in the infrared region was rather high and comparable to earlier published data [3, 5].

Nonstoichiometric starting compositions with an excess of Ag₂S between 1 and 2 mol % gave crystals with improved appearance. Beside a milky yellow first region, we found an extended transparent one limited by a dark green terminating part.

Optical transmission measurements of samples cut from the transparent region, gave very low absorption coefficients in the whole transparency range, as shown in figure 3 in comparison to samples from the milky scattering region. At short wavelengths between 0.5 µm and 1.6 µm the absorption coefficient $\alpha$ is below the maximum desired value of 0.1 cm⁻¹ for
revealed the existence of included phases different from the surrounding material, as shown in figure 4a and 4b. Investigation by electron microprobe gave high metal content (Ag and Ga) for the bright inclusions in figure 4a (milky/transparent transition) compared to the surrounding transparent matrix. For the dark inclusions in figure 4b (transition transparent/dark-terminating-part), an eutectic with high excess of Ag compared to Ga was found. Electron microprobe data for metal content revealed, that the transparent region of the boule is characterizable by a higher sulphur content compared to the yellow milky scattering region.

3.2.2 Annealed material. — In order to reduce broadband absorption between 2 and 6 μm, we tried to increase sulphur content by additional annealing. For such experiments milky scattering samples were taken from boules grown with an excess of 2 mol % Ag₂S in the starting composition. Samples with additional elementary sulphur in evacuated ampoules were annealed at 750 °C for 120 hours. The visible effect of improved transparency is illustrated in figure 5 by two
samples. The smaller cube on the left shows the milky scattering material before annealing, whereas the one on the right shows the clear appearance after annealing. The greatly improved transparency, caused by annealing, is shown quantitatively in figure 6. Absorption is reduced below 0.1 cm$^{-1}$ in the range 0.9-8.5 μm, the most important range for parametric oscillator application of AgGaS$_2$. The origin of this effect has not yet been investigated in detail. To ensure, that improved transparency is not produced by heat effects alone, corresponding annealing in vacuum was carried out without additional sulphur. No significant changes in transparency could be observed. A partial improvement for short wavelengths was also found by annealing with additional Ag$_2$S (96 hours at 750° and 900 °C) as shown in figure 6 (dotted line for 750 °C, dash-dotted line for 900 °C). A residual absorption in the range 2-6 μm, however, still remained.

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