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Growth of GaSe and GaS single crystals

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The paper describes principal manipulations to prepare single crystals of GaSe and GaS. A new simple method of synthesis with single-zone heating furnace is proposed. Growth of crystals was performed by modified Bridgman method with the use of rotating heat field. Raman and optical depth spectra show high structural and optical quality of obtained crystals.

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1 Introduction

GaSe crystals of ϵ -modification are the good candidates for laser frequency conversion from mid-IR to far IR and further to terahertz regions [1]. However, due to the perfect cleavage along {001} and very low hardness [2], the GaSe can not be cut and polished at arbitrary direction that limits its application. Doping is a well known technique to modify various physical properties of the crystals: transparency range; nonlinear and linear optical and mechanical properties; thermal conductivity, etc. GaSe doping with S [3,4], In [5-7] and Er [8-10] are mostly studied. Among these dopants the sulfur is likely to show best results for the compositions $\text{GaSe}_{1-x}\text{S}_x$, $x \leq 0.4$ [3].

The aim of this work is the preparation and study of monocrystalline samples of GaSe and GaS to compare then with mixed $\text{GaSe}_{1-x}\text{S}_x$ crystals. Generally, the whole procedure is divided into two stages: synthesis and growth. It should be mentioned that described operations are well fit for other chalcogenide compounds.

2 Experimental

All quartz ampoules for synthesis and growth were kept in the mixture of concentrated acids $\text{HNO}_3:\text{HF} = 1:1$ during 30 min. After repeated washing in bidistilled water and drying in air box, the ampoules were annealed at 1250 K during several hours. The starting materials for the synthesis: Ga 99.9997, S 99.99 and Se 99.99 were additionally purified by remelting in continuously evacuated ampoule. Weighing was performed with accuracy ± 0.1 mg. Both growth and synthesis ampoules were evacuated to residual pressure $\sim 10^{-4}$ torr.

High vapor pressure of volatile components is the main problem for synthesis of chalcogenide compounds. Though small quantities of chalcogenides may be prepared by direct fusion of starting components (e.g. AgGaS_2 [11], ZnGeP_2 [12]), for large amounts of material it is more convenient to use two-temperature (or two-zone) method [13-15]. In this method, an elongated ampoule with more and less volatile components in the opposite sides is heated in horizontal two-zone furnace. Temperature of the hot zone with less volatile components is quickly raised to the melting point of synthesizing compound, while increment of that of the cold zone is carried out more slowly according to the progress of synthesis reaction.

In this work we propose modification of synthesis method which is likely to make the process simpler. The method uses single-zone horizontal furnace. Temperature distribution is formed by heating wire wound around muffle with various frequency. The ampoule is partially inserted inside the furnace and the temperature is

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raised to the melting point of synthesizing compound (Fig. 1a). Maximum of the temperature distribution at the opened end of the furnace is necessary to compensate heat extraction through the ampoule. During heating the volatile compound (here S or Se) accumulates in the cold part of the ampoule. A distance between the ampoule and the muffle end is filled with the caoline wool which isolates volatiles from overheating. Also this wool makes the ampoule tilted which in turn keeps molten gallium in the hot part. But the ampoule incline is quite small ($\sim 3\text{--}5^\circ$) so molten sulfur (selenium) flows down slowly due to high viscosity. On the other hand, on reaching place with temperature of boiling, it evaporates and condensates back in the cold end of the ampoule. After finding the ampoule position when the rates of flowing down and evaporation of molten sulfur (selenium) are equal (Fig. 1b), the ampoule is gradually pushed inside the furnace. The rate of ampoule movement is controlled by vapor pressure of the volatiles which in turn may be estimated by the color of internal volume of the ampoule.

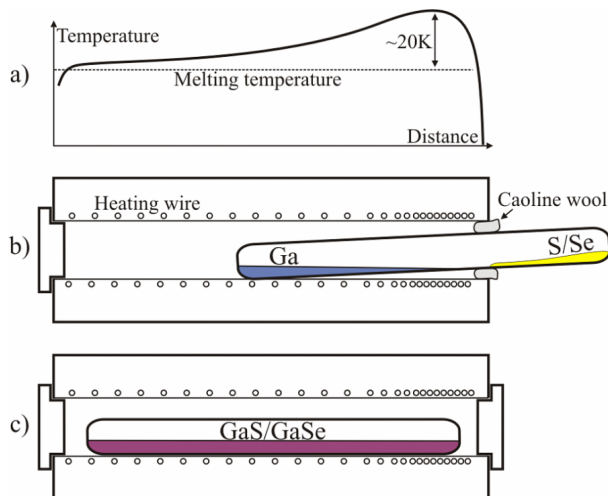


Fig. 1 Temperature distribution inside the furnace (a) for initial (b) and final (c) step of GaS/GaSe synthesis.

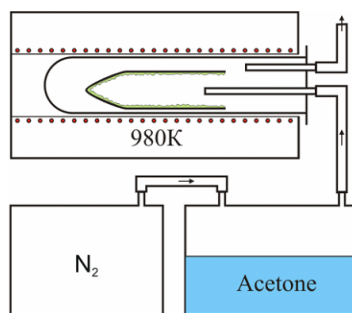


Fig. 2 Scheme of the carbon coating. (Online color for both figures at www.crt-journal.org)

When no liquid S/Se is observed in the cold part, the ampoule is entirely moved inside the furnace (Fig. 1c). After several hours of melt homogenization, the temperature is slowly decreased on 40 K below of melting point of compound at the rate ~ 10 K/h. Then the furnace is switched off. The melting temperatures of GaSe and GaS are assumed as 1213 K and 1233 K, correspondingly.

For the growth process, the polycrystalline material was loaded into double wall ampoule. The internal conical container has a layer of pyrolytic carbon which protects the melt from reaction with quartz. Carbon coating was performed according to the scheme presented at figure 2. A mixture of gaseous nitrogen and acetone enters the furnace heated up to 980 K. Gaseous products of decomposition are removed outside while elementary carbon deposits inside the reactor. In this work the amount of acetone used for coating of one container was ~ 50 ml.

The unseeded crystal growth was performed both by classical and modified vertical Bridgman-Stockbarger methods. In the modified configuration the method of heat field symmetry change and rotation was used. Details of application of that approach to Bridgman-Stockbarger crystal growth are described in [16].

The sealed growth ampoule was loaded into the furnace with temperature gradient ~ 15 K/cm at the estimated level of crystallization front. A thermocouple of S-type was attached to the bottom of the ampoule in order to control the processes of melting and growth. After homogenization of the melt at the temperature 30 K above the melting point, the ampoule was mechanically lowered with the speed 10 mm/day. When the growth was completed, the furnace was switched off.

3 Results and discussion

Since there is a temperature gradient along the synthesis ampoule (Fig. 1a), the melt solidifies directionally provides polycrystalline ingots (Fig. 3a,b). After optimization of solidification regime, a growth of single crystal is likely to be possible directly on the stage of post-synthesis cooling.

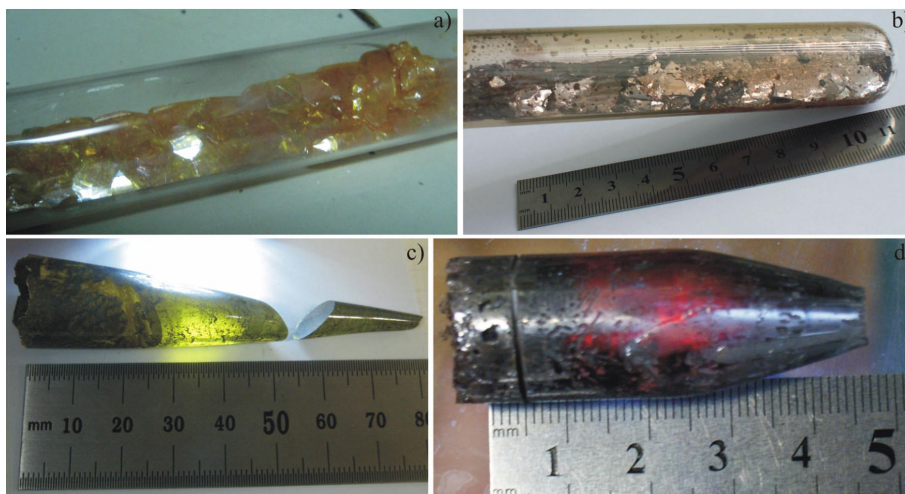


Fig. 3 Synthesized material and grown crystals of GaS (a,c) and GaSe (b,d). (Online color at www.crt-journal.org)

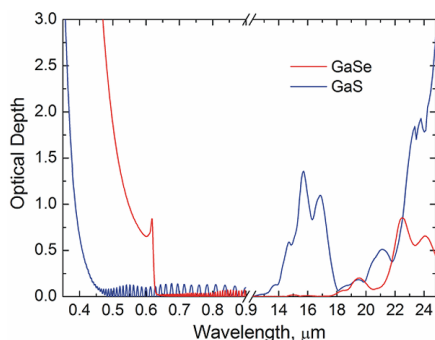


Fig. 4 Optical depth spectra of 17 μm GaSe and 4.9 μm GaS crystals. (Online color at www.crt-journal.org)

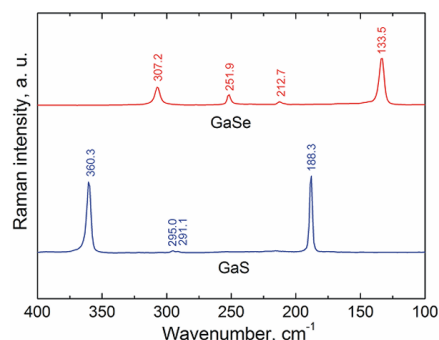


Fig. 5 Raman spectra of GaSe and GaS crystals. (Online color at www.crt-journal.org)

The single crystals were obtained with the use of rotating heat field (Fig. 3c,d). Large volumes up to several cm^3 without visible defects may be found inside the crystals. For optical analysis, the crystals were split along cleavage planes $\{001\}$.

Optical depth spectra of the grown crystals show no impurity and defect absorption bands (Fig. 4). Cm-length samples of both compounds were characterized as high optical quality crystals; determined absorption coefficients were as low as $\leq 0.1 \text{ cm}^{-1}$. Then the crystals were examined by Raman spectroscopy (Fig. 5). The results are in a good agreement with the spectra of defect free pure ϵ -GaSe and β -GaS polytypes (e.g. see [17,18]).

4 Conclusion

The main stages of preparation of GaS and GaSe were outlined in this work. With the use of modified Bridgman-Stockbarger technique, high quality single crystals were grown. The described procedures may be useful for preparation of other chalcogenide compounds.

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