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Synthesis and growth of AgGaGeS₄, a promising material for laser frequency conversions in the mid-IR range

Jérémy Rame*, Johan Petit

ONERA, 29 avenue de la division Leclerc, 92322 Châtillon Cedex

*jeremy.rame@onera.fr

Abstract: AgGaGeS₄ (AGGS) is a promising nonlinear crystal for mid-IR laser applications. This paper presents the processing steps of this material, the synthesis of polycrystals and the crystal growth using the Bridgman-Stockbarger technique. It also presents the solutions to obtain high quality single crystals taking into account the decomposition at high temperature of the AGGS phase due to the high volatility of GeS₂. AGGS crystals with 28 mm diameter and 70 mm length were grown. These crystals have a good homogeneity and high transparency in the 0.5-11.5 μm spectral range making its suitable for optical experiments.

1. Introduction

During the last decades, mid-infrared (3-12 μm) laser sources have attracted a particularly attention due to their potential application in different fields such as optical counter-measures (e.g: missile jamming) and remote chemical sensing (e.g: LIDAR). As transparency of common non linear oxide crystals is limited to about 4 μm, many researches have been focused on chalcopyrite compounds because of their wide transparency in mid-IR range and their high nonlinearity. There is a strong need of non linear materials able to convert efficiently 1.064 μm or 2.05 μm wavelengths from commercially available laser into wavelengths higher than 4 μm [1]. In the present work, we will describe the preparation of AgGaGeS₄ which is a promising nonlinear material for mid-IR applications, combining advantages of the well-known ZnGeP₂ and AgGaS₂ crystals. Indeed, AGGS has a high birefringence ($\Delta n=0.06$), is transparent in a wide spectral range (0.4-13.5 μm) and have shown high laser damage threshold [2,3]. In this paper, we will discuss about the main difficulties related to this material processing. Particularly, we will focus on GeS₂ volatility which can lead to a deviation from the starting composition and can be a limitation of the synthesis and growth of good optical quality single crystals.

2. Experimental details

a. Chemical Synthesis

AgGaGeS₄ synthesis was performed from high purity elements (silver, 99.9999 wt%; gallium, 99.999 wt%; germanium, 99.9999 wt%; sulfur, 99.9999 wt%). Starting elements were introduced into a quartz ampoule which was evacuated to 10⁻⁸ bar and sealed. Synthesis was carried out in a two-zone furnace in order to avoid reactor explosion which could be due to the high pressure of elements such as sulfur during the process. In the first step, the temperature is raised in the lower zone where the chemical reaction takes place: sulfur and compounds such as GeS₂ condenses in the upper zone (where the temperature is lower). This reduces the pressure rising into the quartz reactor. After 16 h at about 1220 K in the lower zone, the temperature is raised up to 1270 K in the upper zone in order to consume condensed sulfides on ampoule's walls. Then, after 12h, the ampoule is cooled down to room temperature and an AGGS polycrystalline ingot is obtained (Figure 1).



Figure 1 - AgGaGeS₄ polycrystalline ingot after the chemical synthesis

X-Ray diffraction pattern of polycrystalline sample was recorded (Figure 2). A pure orthorhombic AGGS phase was identified and the high intensity and narrow peaks indicated the good crystalline quality of the obtained sample.

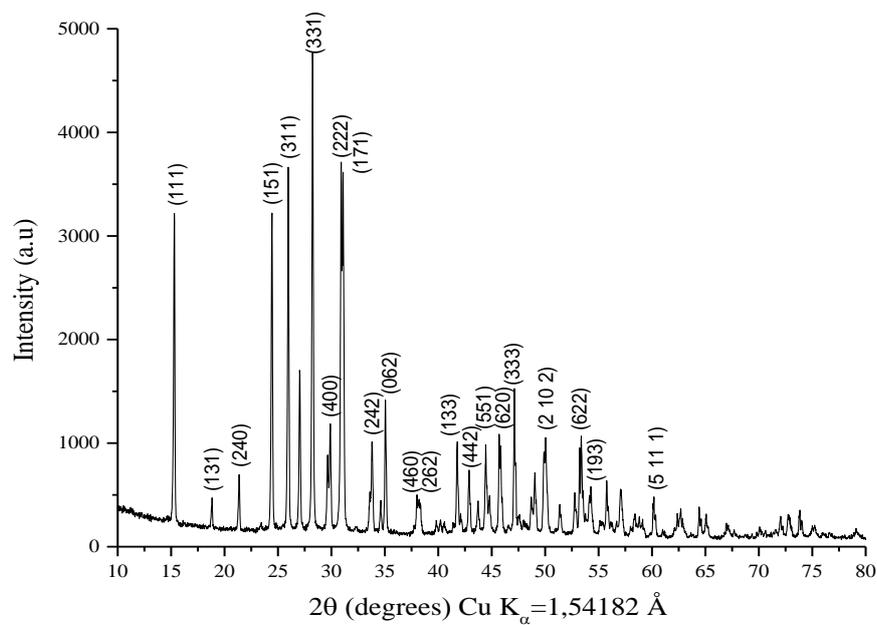


Figure 2 - XRD pattern of AgGaGeS₄ polycrystalline sample

b. Crystal Growth

Crystal growth was performed from the previously synthesized polycrystals. A single crystal seed, extracted from a large grain of the same polycrystal, was placed at the bottom of a specially designed quartz growth ampoule. The AGGS polycrystal was ground into powder and placed into the quartz ampoule. It was then evacuated, sealed, and placed into the Bridgman-Stockbarger furnace. The growth was performed at the rate of 0.4 mm.h⁻¹ with a temperature gradient of 12K.cm⁻¹ around the melting point. At the end, the obtained single crystal, orange in color, was 28 mm in diameter and 70 mm in length. A sample extracted from this ingot is shown on the Figure 3, left. Inhomogeneity in color and refractive indexes can be observed inside this crystal.

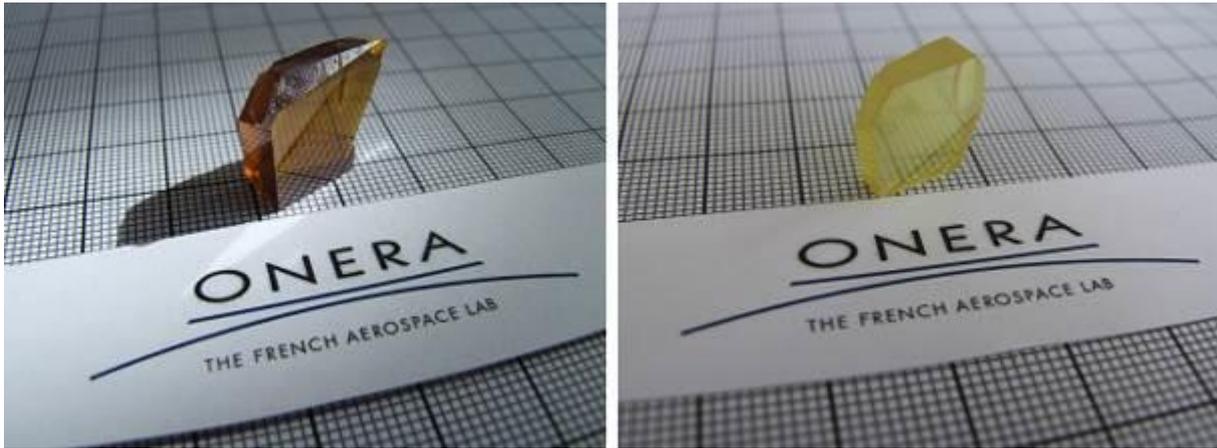


Figure 3 - Picture of a polished as-grown (left) and post-treated (right) AgGaGeS₄ single crystal.

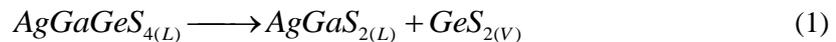
c. Post-growth treatment

A thermal annealing step was performed in order to improve the quality of the as-grown crystal. It was carried out under static vacuum at 873K for 250 h. After this step, the color was yellow and well more homogeneous than before (Figure 3, right).

3. Results and discussion

a. Chemical synthesis

The AgGaGeS₄ phase is formed in the solid solution AgGaS₂-GeS₂. Its stability range is included between 48 and 55 mol% of GeS₂ [4]. However, at high temperature, AgGaGeS₄ decomposes to form a GeS₂ vapor phase according to the reaction [5,6]:



According to our thermodynamic calculations (using the HSC Chemistry software) (Figure 4), which are in good agreement with experimental data obtained by Vasil'eva et al [5], GeS₂ volatility increases quickly above 1000 K (Figure 4). Indeed, vapor pressure of GeS₂ is about 0.7 bar around the melting point of AGGS (1123K) and about 5 bar at the synthesis temperature (1220 K). This vaporization can induce a deviation from the initial composition depending on the synthesis conditions, the amount of starting elements and the reactor volume. A small deviation from stoichiometry, keeping the composition in the range of pure AGGS phase formation, can induce structural defects such as germanium or sulfur vacancies in the crystal structure and so undesired optical absorptions reducing the optical quality of the crystal. However, if the GeS₂ vaporization leads to a melt composition below 48 mol% GeS₂, inclusions of AgGaS₂ appear in the material which became opaque and unusable for our applications. Our work focused on reducing the effect of the GeS₂ vaporization on melt stoichiometry in order to synthesize high quality AGGS polycrystals. Consequently, parameters such as ampoule volume, starting element amounts and synthesis temperature were optimized. Firstly, in this case, since vapor pressure only depends on temperature, the relative quantity of GeS₂ in the vapor phase can be reduced by decreasing the ampoule volume and/or increasing the reactants quantity taking into account the explosions hazards related to sulfur volatility. For the moment, we have tested 120 g of starting elements inside a 190 cm³ ampoule which was efficient to synthesized pure AgGaGeS₄ phase while avoiding ampoule explosion.

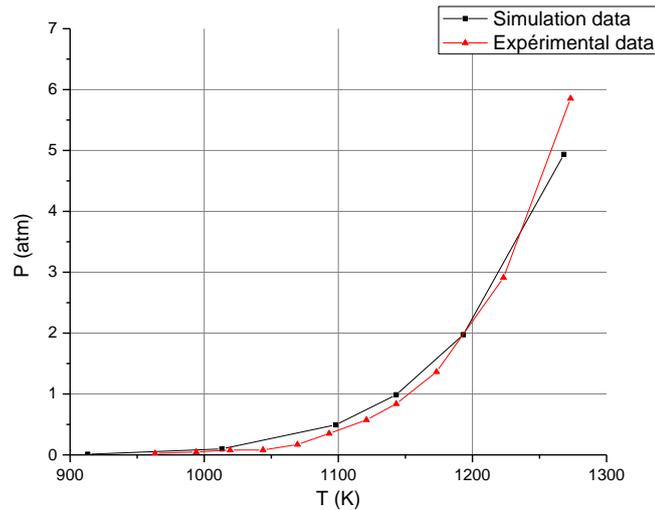


Figure 4 - Plot of calculated GeS₂ vapor pressure versus temperature and experimental data from ref [5].

Otherwise, the cooling rate is another important parameter to take into consideration during the process. Indeed, the percentage of GeS₂ in the vapor phase is respectively around 2.0 and 0.5 mol% GeS₂ at 1223 K (the synthesis temperature) and 1118 K (the crystallization point). Thus, a fast cooling rate can induced an important stoichiometric deviation in the final crystal because GeS_{2(v)} do not have time to react with the melt before crystallization. A cooling rate of 0.2 K.min⁻¹ was sufficient to promote vapor-melt reaction during cooling and totally consume the GeS₂ content in the vapor phase. Thus, by combining the optimization of these parameters (ampoule volume, reactant quantities, cooling rate), we have limited the effect of GeS₂ vaporization and, so, the stoichiometric deviation in the synthesized polycrystals (Figure 2) obtaining a pure AGGS orthorhombic phase (JCPDS 72-19123).

b. Crystal growth

The ratio between starting elements and ampoule volume has also to be optimized in the crystal growth step in order to avoid stoichiometry deviation during the crystallization process. However, another important parameter has to be taken into consideration: the supercooling of AGGS. Indeed, crystal growth from the melt without seed led to the growth of ingots composed by a mixture of AgGaGeS₄ and AgGaS₂ phases. Differential Thermal Analysis (DTA) were performed in order to explain these results and to study the supercooling amplitude. We measured a supercooling temperature value of 86K which is relatively high. Consequently, it could be responsible for a multi-nuclei formation observed on samples grown from the melt without seed. Indeed, the use of single crystal seed avoided the supercooling and decomposition effect by providing a starting nucleation point. This allowed to grow AGGS single crystals whose an extracted sample is shown on the Figure 3. Characterizations were performed on the annealed samples. The crystals had good homogeneity according to Electron Dispersive X ray Spectroscopy (EDS) analysis. The measured thermal conductivity value was 0.44 W.m⁻¹.K⁻¹. The crystal has a high transparency from about 0.5 to 11.5 μm (Figure 5) with an absorption coefficient below 0.1 cm⁻¹ in the 2-8 μm spectral range which indicates the good optical quality of our AGGS crystals.

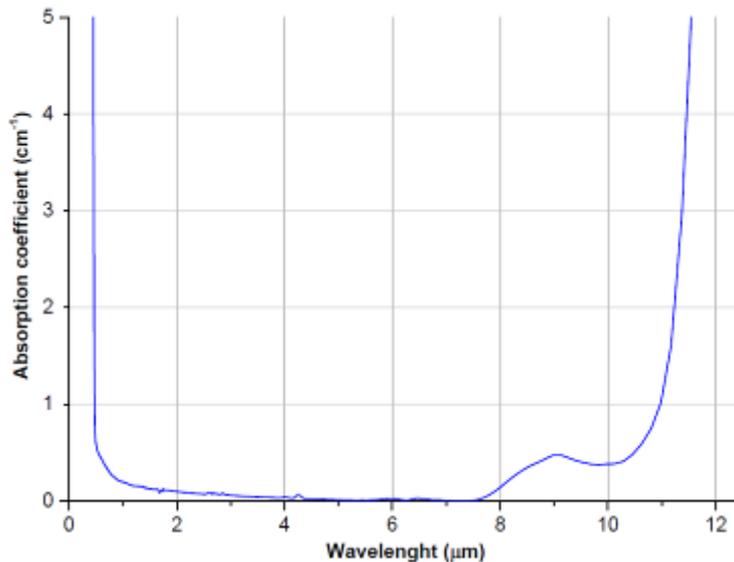


Figure 5 - Optical absorption of AGGS (thickness: 4.4 mm) in the 0.5-12.5 μm range.

4. Conclusion

The different steps of AGGS processing were described in this paper. The strong influence of GeS_2 vaporization on melt stoichiometry and crystal quality was outlined. Solutions to reduce the impact of this compound's volatility on stoichiometry were presented. With optimized experimental conditions, we have synthesized high quality AgGaGeS_4 polycrystals and, then, grown good optical quality single crystals by the Bridgman-Stockbarger method. These crystals have good homogeneity and the absorption loss coefficient was below 0.1 cm^{-1} in the 2-8 μm spectral range which makes it suitable for non linear optical applications. Laser experiments are currently in progress.

5. References

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