Optical Materials 36 (2014) 2007–2011

Contents lists available at ScienceDirect

Optical Materials

journal homepage: www.elsevier.com/locate/optmat

Growth and characterizations of $BaGa_4S_7$ crystal

Yifeng Guo, Yuqiao Zhou, Xinsong Lin, Weidong Chen, Ning Ye *

Key Laboratory of Optoelectronic Materials Chemistry and Physics, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou 350002, China

ARTICLE INFO

Article history:
Available online 10 January 2014

Keywords:
$BaGa_4S_7$
Mid-IR
Excess sulfur
Dual temperature
Thermal conductivity
Laser damage threshold

ABSTRACT

The nonlinear optical (NLO) $BaGa_4S_7$ polycrystalline materials with stoichiometric composition were synthesized from BaS, Ga, and S via solid-state reactions in the dual temperature zone rocking furnace with excess sulfur, and crystal $BaGa_4S_7$ for the mid-infrared (IR) was grown with Bridgman–Stockbarger technique. The ultraviolet (UV) and IR optical absorption edges of crystal $BaGa_4S_7$ were found to be at 350 nm and 13.7 μm, respectively. Its thermal conductivities at 50 °C were 1.45 W/(m K), 1.58 W/(m K) and 1.68 W/(m K) along *a*-, *b*- and *c*-directions, respectively. The laser damage threshold of a single crystal was about 7.1 J/cm^2 at 2.1 μm, and 26.2 J/cm^2 at 9.58 μm. The idler non-critical phase-matching OPO wavelength was between 6 and 10 μm when the pumped wavelength was varied around 2.2 μm.

1. Introduction

Because of the increasing demands in both military and civil applications, the generation of high-power tunable lasers in the range of 3–20 μm, especially in band II (3–5 μm) and band III (8–14 μm) of three atmospheric transparent windows, has become the focus of infrared (IR) laser technology recently [1–4]. However, it is particularly difficult to have suitable nonlinear optical (NLO) materials working in those two bands, which should have high NLO coefficients and high laser damage threshold simultaneously. Foe example, $A^{II}B^{IV}C_2^{V}$ and $A^{I}B^{III}\,C_2^{VI}$ chalcopyrite semiconductors with high NLO coefficients, such as $AgGaS_2$ (AGS) and $ZnGeP_2$ (ZGP), are well-known commercial available materials for mid-IR nonlinear optics, but they have relatively low laser-induced damage thresholds due to their narrow band gaps, which limits their applications in optical parametric oscillator (OPO) and high power laser output [5,6]. Recently, a new family of ternary chalcogenides containing Li element, such as $LiGaS_2$ (LGS) and $LiInS_2$ (LIS), was found to have a higher laser-induced damage threshold than chalcopyrite semiconductor due to their wider band gap [7,8]. The theoretical calculation also indicated that the lighter cation could effectively widen the crystal band gap, which then could improve the optical damage threshold [9]. Therefore, a non-centrosymmetric compound $BaGa_4S_7$ (BGS), a chalcogenide compound containing alkaline or alkaline-earth element, was selected to investigate new NLO materials in this study. BGS had been synthesized by Eisenmann et al. in 1983 [10] and its single-crystal structure was reported as $Pmn2_1$. Because of its similar structure to those of Li-contained chalcogenides, BGS might have a wide band gap and large NLO coefficients. Previously, we had grown single crystals of BGS via the Bridgman-Stockbarger technique and confirmed the SHG effect through the Kurtz powder test [11]. It was found that the bandgap was at 350 nm (3.54 eV) and the transparency extended up to 13.7 μm at the 0-level. From optical measurements of second harmonic generation on powders, the NLO coefficient d_{33} was determined to be 12.6 pm/V, the laser damage threshold of a single crystal reached to about 1.2 J/cm^2 at 1.064 μm, and the Vickers-hardness value of the crystal was 327.5 HV5, which is equivalent to Mohs' hardness of about 5. Recently, BGS and its selenide analogue, BGSe, were both grown via the Bridgman–Stockbarger method with large sizes that were sufficient to measure the dispersion of refractive indexes [12], which was a prerequisite to predict the phase-matching properties for down conversion of 1064 nm radiation into the mid-IR. For example, the calculated phase-matching properties for down-conversion processes, experimental measurements of the transparency, nonlinear coefficients and the damage threshold at 1064 nm (3.7 J/cm^2) of BGS [13], and optical parametric oscillation in the mid IR based on BGS pumped at 1064 nm had been reported [14].

In this contribution, we will report the growth the Bridgman–Stockbarger technique, the optical properties, the thermal properties of BGS crystal with and the measurements of its laser damage threshold at the mid-IR region.

2. Experimental procedure

2.1. Polycrystal synthesis and crystal growth

Polycrystalline BGS samples were synthesized in a dual temperature zone rocking furnace as shown in Fig. 1. A stoichiometric mixture of Ba compound (analytical grade), Ga (analytical grade) and S (analytical grade, excess of at 5%) were evacuated to a

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* Corresponding author. Tel.: +86 591 83776076; fax: +86 591 83750713.
E-mail address: nye@fjirsm.ac.cn (N. Ye).

0925-3467/$ - see front matter © 2014 Published by Elsevier B.V.
http://dx.doi.org/10.1016/j.optmat.2013.12.028

residual pressure of 3×10^{-4} Pa and sealed in a quartz ampule, which then was placed in the rocking furnace, specifically to leave the two third of the quartz ampule with the starting materials in the high temperature zone. The low-temperature end was not heated, but the high-temperature end of the furnace was angled downward, slowly heated to 1115 °C, which was above the melting point, in 72 h, and then held for about 5 h. The curve of the temperature gradient was shown in Fig. 1a. Sequentially, the low-temperature end was slowly heated to 1115 °C in 30 h to have the temperature homogenous over the whole heating area (Fig. 1c). Then the furnace was rocked in every 2 h for one day in order to get a homogenous melt. The high-temperature end was lowered to have the melt flown to the bottom of the quartz ampule. Finally, both of the heating zones were cooled to the room temperature in 10 h.

BGS single crystals were grown with a Bridgman-Stockbarger technique through spontaneous nucleation from BGS polycrystalline materials in a vertical furnace with an axial temperature gradient as described in Ref. [11].

2.2. Crystal Characterization

X-ray powder diffraction data were obtained on a Rigaku DMAX2500 $^{\text{diffractometer}}$ by using Cu Kα radiation. Single-crystal X-ray diffraction data were collected at room temperature on a Rigaku Mercury CCD diffractometer with graphite monochromated Mo Kα radiation (λ = 0.71073 Å).

The X-ray powder diffraction data were collected on a Panalytical X'pert Pro MPD diffractometer using graphite-monochromated Cu-Kα radiation in the 2θ range of 10–60 with a step size of 0.02°.

Laser damage testing at 2.1 μm was performed by using a repetitively *Q*-switched Dy/Ho:YAG laser with 30 ns pulse width at 1 Hz pulse frequency as the damage-inducing source. A lens with a focal length of 50 mm was used to focus the beam at 20 mm before the polished surface of the crystal sample. Laser damage testing at 9.58 μm was performed by using T5J200A tunable CO_2 laser with about 100 ns pulse width at 1 Hz pulse frequency as the damage-inducing source. Multi-spectrum ZnSe lens was used to focus the beam *t* 15–30 mm before the polished surface of the crystal sample. The beam was periodically re-characterized during the damage testing to ensure the constant beam quality. Surface damage was detected audibly under a microscope.

The thermal diffusivities from room temperature to 250 °C were measured with a heating rate of 10 K min^{-1} on a NETZSCH LFA 457 NanoFlash and two 10 × 10 × 2 mm samples with their surfaces perpendicular respectively to *a*, *b* and *c* orientations.

3. Results and discussion

3.1. Synthesis and crystal growth

It was well known that purity and quality of $BaGa_4S_7$ polycrystalline materials could play very important roles on the growth of high quality single crystal. However, it is difficult to control the impurity phase Ga_2S_3 and $BaGa_2S_4$ during the synthesis of $BaGa_4S_7$ to produce the high quality materials, and this contamination is not reversible by any post reproduction. For example, the XRD powder pattern (Fig. 2) of the sample synthesized in stoichiometric proportion showed the impurities of Ga_2S_3 and $BaGa_4S_7$, while the pattern of the sample synthesized with about 5% of excess sulfur was in a good agreement with the standard PDF, which indicated that the excess sulfur efficiently helped the formation of pure $BaGa_4S_7$ polycrystalline. However, extra sulfur led to the explosion of quartz ampule due to the high vapor pressure of sulfur.

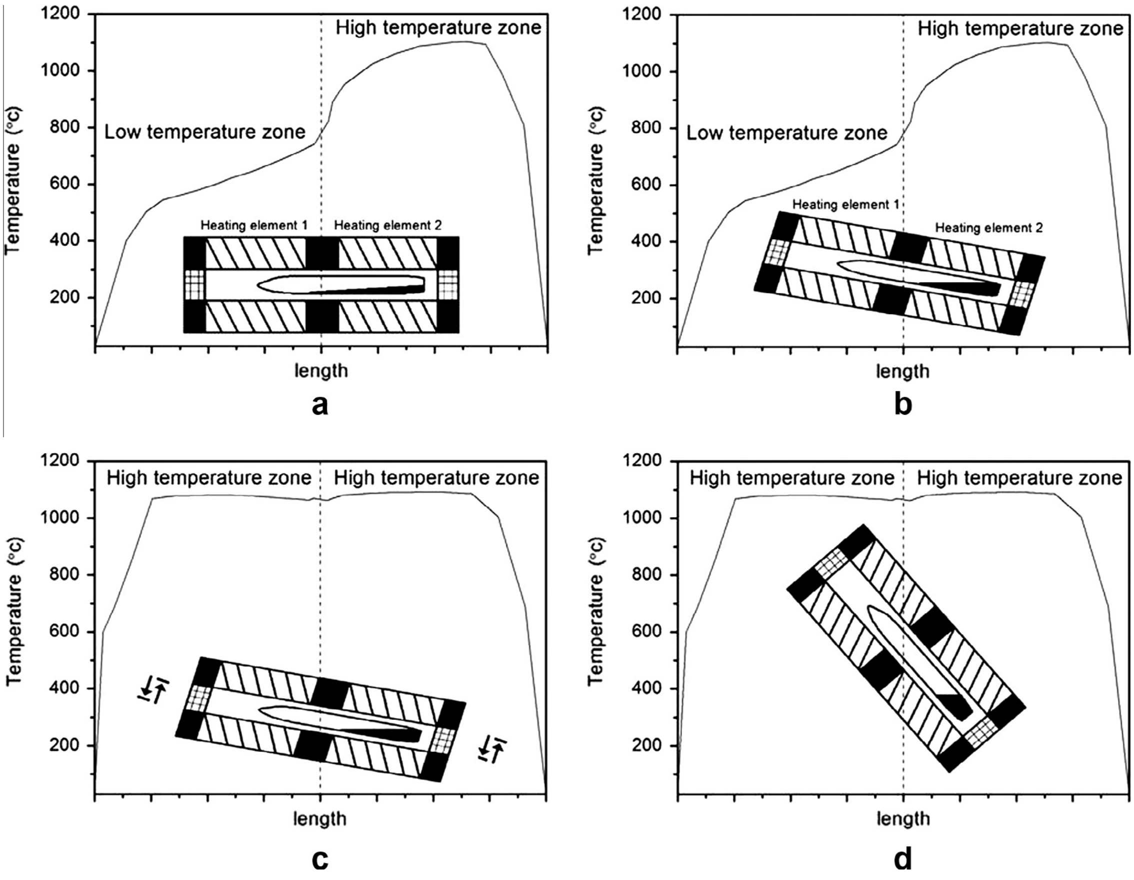

Fig. 1. Temperature distribution in the rocking furnace.