Effect of rare-earth doping on the structural and optical properties of the Ag₃AsS₃ crystals

O. V. Smitiukh¹ · O. V. Marchuk¹ · Y. M. Kogut¹ · V. O. Yukhymchuk² · N. V. Mazur² · G. L. Myronchuk³ · S. M. Ponedelyk³ · O. I. Cherniushok⁴ · T. O. Parashchuk⁴ · O. Y. Khyzhun⁵ · K. T. Wojciechowski⁴ · A. O. Fedorchuk⁶

Received: 24 November 2021 / Accepted: 28 December 2021 / Published online: 21 March 2022 © The Author(s), under exclusive licence to Springer Science+Business Media, LLC, part of Springer Nature 2022

Abstract
Non-linear optical (NLO) materials allow the production of the coherent laser beam in the difficult frequency ranges of the electromagnetic spectrum. Aiming to explore new classes of the NLO materials with high optical performance in the infrared region, in this work, we investigated the effect of the rare earth doping (Pr, Eu, Yb) on the crystal structure and optical properties of the Ag₃AsS₃ crystals. The performed analysis of the XRD patterns indicates that the rare earth elements are located in the Ag sites of the crystal lattice. As a result, the second harmonic generation intensity, which determines the effectiveness of the NLO materials, increases with the increase of rare earth dopant content up to 1.0%. Using the absorption analysis and Raman spectroscopy, we show that the increase in the SHG intensity can be related to the slight decrease of the bandgap, as well as with the increased electron–phonon interaction in rare-earth-doped Ag₃AsS₃ crystals. Considering the discovered enhancement of the SHG intensity, accompanied by the low melting temperature, this work offers rare-earth-doped Ag₃AsS₃ crystals as potential candidates for the non-linear optical applications for the infrared frequency range.

Keywords Proustite · Rare-earth doping · Non-linear optical materials · Second harmonic generation · Raman spectroscopy
1 Introduction

Second-order nonlinear optical (NLO) materials are of great interest for the development of the new coherent and tunable laser applications, which role is becoming significant in many fields, including medicine, material science, civil industries, etc. (Lin et al. 2020; Chung and Kanatzidis 2013; Guo et al. 2017; Mutailipu et al. 2019; Wu and Pan 2018). Although technologies for the construction of such lasers are highly investigated nowadays, commercially available wavelength ranges with high efficiency are still limited (Duarte 2013).

Based on the transparent bands, the nonlinear optical crystals can be divided into three main categories: ultraviolet, visible, and infrared. The currently available nonlinear optical materials, such as β-BaB₂O₄ (β-BBO) (Chen et al. 1985), LiB₃O₅ (LBO) (Jiang et al. 1989), LiNbO₃ (LN) (Boyd et al. 2004), KH₂PO₄ (KDP) (Smith 1977), and KTiOPO₄ (KTP) (Hoffman et al. 1986), are well applicable for ultraviolet and visible regions. Despite that metal oxide NLO crystals have been developed for the visible and UV regions, nowadays great interest is focused on the IR spectral range of 2 – 25 µm, the so-called fingerprint region for organic and inorganic molecules. In this region, it is possible to detect hazardous and dangerous materials such as chemical warfare agents, pollutants, biohazards, explosives, and trace gases for homeland security, environmental monitoring, and industrial process controls (Chung and Kanatzidis 2013). Therefore, the development of novel nonlinear optical crystals for the infrared range is a great challenge.

The practical applications of the infrared nonlinear optical materials require few basic conditions, i.e. broad infrared transparent region, large nonlinear optical coefficient, high laser-induced damage threshold, large bandgap, moderated birefringence, and high thermal stability (Ohmer and Pandey 1998). Over the past decades, many chalcogenides, pnictides, and oxides have shown promising properties for the development of IR nonlinear optical materials. Among a variety of materials, the wide bandgap metal chalcogenides are the most promising for nonlinear optical applications operating in the IR region of the electromagnetic spectrum (Chung and Kanatzidis 2013; Abudurusuli et al. 2021; Fedorchuk et al. 2018; Cherniushok et al. 2021a).

Searching for new promising nonlinear optical materials we came to the proustite crystals Ag₃AsS₃, which are known quite long ago as a natural silver mineral (K. S 2017). Beginning from the 1970s, Ag₃AsS₃ crystals are actively investigated as promising electronics materials as they are piezoelectric, pyroelectric, as well as thermo- and photosensitive semiconductors (Schönau and Redfern 2002). Also, the Ag₃AsS₃ crystals have been demonstrated nanosecond optical parametric oscillators (OPOs) (Anmann et al. 2003; Hanna et al. 1972, 2003). At low temperatures, they are semiconducting ferroelectrics, and at high temperatures, superionic conductors. In line with the aforementioned requirements to the NLO materials in the IR region, Ag₃AsS₃ is an acentric uniaxial crystal with large non-linear optical coefficients ($d_{31} = 30$ times $d_{36}$ in KDP, $d_{22} = 50$ times $d_{36}$ in KDP), large refractive indices (~ 3.0), a large negative birefringence ($n_o-n_e>0.2$) and high transparency over a wide range (0.6–13 µm) in the IR spectral region (Schönau and Redfern 2002; Bardsley et al. 1969; Gagor et al. 2009). Such crystals have low hardness (2–2.5 on Moss scale) (Nikogosyan 2005), therefore they are easy to process mechanically. The surfaces obtained by polishing the crystals are stable to non-aggressive atmospheric conditions (Hulme et al. 2004). Moreover, Ag₃AsS₃ exhibits a very low melting point (~ 480 °C) in comparison to other state-of-the-art NLO sulfides, e.g. AgGaS₂ (993 °C) (Chen et al. 2008), LiGaS₂ (1050 °C) (Isaenko et al. 2005) or AgGaGeS₄ (845 °C) (Rame et al. 2014).
This fact leads to the much lower vapor pressure of sulfur in the sealed quartz ampoules used for the crystal growth, and thus, it can be beneficial to grow a large stoichiometric Ag₃AsS₃ single crystal. On the other hand, such a low melting point makes this material very plausible for commercial production due to the much lower energy consumption required for material preparation. Despite many advantages of the Ag₃AsS₃ crystals, the material has one downside—its low laser damage threshold. Damage thresholds have been found for four laser wavelengths spanning the range 694 nm to 10.6 μm by using Q-switched lasers (Hanna et al. 1972).

Aiming to explore the potential of the Ag₃AsS₃ material for the fabrication of the non-linear optical crystals, in this work we investigated the effect of the rare-earth doping by Pr, Eu, and Yb on the crystal structure and optical characteristics of this compound. Although optical characteristics of proustite have been fairly extensively investigated, no studies on the effect of rare-earth alloying on their physical properties were found. The crystal structure of Ag₃AsS₃ is non-centrosymmetric and contains prismatic and octahedral voids. Therefore, we were able to successfully introduce the rare-earth elements into that voids in place of silver atoms. The main effect of such doping is related to the increase of the second harmonic generation intensity, which is the main requirement of the NLO materials. In the case of the 1% Yb doping of Ag₃AsS₃, the increase of the SHG intensity was almost 2 times, indicating the great potential of this material for practical applications.

2 Experimental details

2.1 Materials and synthesis

Alloys for the study were prepared by co-melting high-purity elements in quartz containers evacuated to the residual pressure of 10⁻² Pa. The total mass of the original batch for each sample was 2.0 g. The alloys were synthesized in an MP-30 programmable electric muffle furnace by heating to 550 °C at the rate of 24 °C/h (the melting point of Ag₃AsS₃ is 495 °C (Figs. S1, S2)), 10 h exposure, cooling to 200 °C at 6 °C/h. Homogenizing annealing at 200 °C for 500 h was followed by quenching into room temperature water without breaking the containers.

2.2 Powder XRD and scanning electron microscopy

The products were checked by X-ray powder diffraction (XRD) using a DRON 4-13 powder diffractometer (CuKα radiation, 10° ≤ 2θ ≤ 70°, step scan mode with a step size of 0.05° and counting time of 5 s per data point). The Powder Cell software has been used for the phase analysis of the synthesized alloys (Kraus and Nolze 2021).

For scanning electron microscopy SEM and EDXS analysis, samples were embedded in a conductive resin (Polyfast) and ground with SiC abrasive paper, and polished with a diamond suspension mixed with a water-free lubricant (semi-automatic system, EcoMet 250 pro, Buehler). The microstructure and chemical composition of annealed samples were analyzed by scanning electron microscopy with energy dispersive X-ray absorption spectroscopy (JEOL JSM-6460LV Scanning Electron Microscope) performed on the metallographic cross-section of samples.
2.3 Absorption, second harmonic generation and Raman spectroscopy

The spectral distribution of the absorption coefficient was studied on parallel-plane plates of 0.06–0.08 mm thickness with optical quality surfaces. Absorption spectra were measured at a spectrometer combining an MDR-206 diffraction monochromator with silicon photodiode, in the range of 360–1100 nm (spectral resolution was 0.2 nm or better).

The second harmonic generation of obtained materials was investigated using the fundamental beam of a nanosecond Nd:YAG pulse laser at $\lambda = 1064$ nm, with maximum pulse energy 80 mJ, and a pulse repetition rate of 1–100 Hz. Energy values were gradually varied by the Glan polarizer, to the maximum power density of 100 J/m$^2$. The incident fundamental radiation was measured with a Ge detector, and its second harmonic generation SHG with a photomultiplier supplied with an interference filter for the 532 nm wavelength of the second harmonic. The intensity levels of the output signals of the original radiation and its SHG were monitored by a Tektronix oscilloscope at a frequency of about 1 GHz. The SHG measurements were performed using the Kurtz-Perry powder technique (Kurtz and Perry 2003). The conditions of the use of this method are detailed in Aramburu et al. (2014). It should be noted that the Kurtz-Perry method allows a relative estimation of the efficiency of non-linear optical transformations using only the powder of a studied crystal. This method makes it possible to explore new promising non-linear materials by approximating the powder particles as single crystals with average dimensions of 100 μm that are randomly oriented in space.

Raman spectroscopy was used to determine the effect of various amounts of rare-earth dopants on the vibrational spectra and to investigate the structure flawlessness of the synthesized materials. Raman scattering spectra were recorded at room temperature in the back-scattering geometry with an MDR-23 single-stage spectrometer equipped with a CCD detector (Andor) using $\lambda_{\text{exc}} = 671$ nm (diode-pumped solid-state laser, CNI Laser). To prevent sample damage during the investigation, laser power density was selected as minimum suitable for the reliable recording of the spectra.

3 Result and discussion

3.1 Phase analysis and crystal structure features

The sample quality was verified by powder X-ray diffraction. Obtained diffraction patterns are plotted in Fig. 1b–d.

The XRD patterns were analyzed using the Rietveld method. Models of the crystal structure of the phases presented in the sample, together with instrumental and background information, were used to generate the theoretical diffraction pattern that was compared to the recorded pattern. According to the $hkl$ indexes, and their intensities, the structure of rare-earth-doped $\text{Ag}_3\text{AsS}_3$ samples (Fig. 1a) belongs to the trigonal structure system ($hR42$, S.G. $R\bar{3}c$, No. 161). The analysis of the diffraction patterns indicates that rare-earth doping with the amount of $\leq 1\%$ has virtually no effect on the crystal structure of $\text{Ag}_3\text{AsS}_3$. Only the sample with 1% Pr atoms exhibits minor differences from the original pattern. To further analyze the effect of the rare earth metals on the crystal structure, we also estimated the lattice constant for all samples. The results of the estimation are shown in Table 1.
The lattice parameters of the alloying compositions are slightly increasing compared to the undoped $\text{Ag}_3\text{AsS}_3$ (Table 1). On the one hand, this feature can indicate that the doping atoms occupy the sites which belong to the Ag positions. On the other hand, the atoms of silver, due to small atomic radii, can leave their sites and migrate through the lattice volume (Heep et al. 2017). This can be a reason for a rather small change of the lattice parameter for doped samples.

![Crystal structure of $\text{Ag}_3\text{AsS}_3$](image)

**Fig. 1** Crystal structure of $\text{Ag}_3\text{AsS}_3$ (a), powder XRD patterns (Cu Kα radiation) of rare-earth doped $\text{Ag}_3\text{AsS}_3$ samples with: Praseodymium (b), Europium (c) and Ytterbium (d)

| Composition  | $a$, Å  | $c$, Å  | $V$, Å$^3$  |
|--------------|--------|--------|-------------|
| $\text{Ag}_3\text{AsS}_3$ | 10.819(5) | 8.704(4) | 882.27(7) |
| $\text{Ag}_3\text{AsS}_3$:0.4% Pr | 10.824(7) | 8.705(7) | 883.22(4) |
| $\text{Ag}_3\text{AsS}_3$:0.7% Pr | 10.819(5) | 8.700(4) | 881.88(5) |
| $\text{Ag}_3\text{AsS}_3$:1.0% Pr | 10.821(4) | 8.701(3) | 882.27(2) |
| $\text{Ag}_3\text{AsS}_3$:0.4% Eu | 10.828(4) | 8.708(3) | 884.1(3) |
| $\text{Ag}_3\text{AsS}_3$:0.7% Eu | 10.824(5) | 8.703(4) | 883.02(3) |
| $\text{Ag}_3\text{AsS}_3$:1.0% Eu | 10.834(7) | 8.703(4) | 884.23(1) |
| $\text{Ag}_3\text{AsS}_3$:0.4% Yb | 10.825(4) | 8.704(4) | 883.22(2) |
| $\text{Ag}_3\text{AsS}_3$:0.7% Yb | 10.827(5) | 8.710(4) | 884.23(1) |
| $\text{Ag}_3\text{AsS}_3$:1.0% Yb | 10.823(9) | 8.702(7) | 882.84(1) |
To understand the influence of rare earth metals on the Ag₃AsS₃ crystal structure and to identify the mechanism of their doping we performed a detailed analysis of proustite crystal chemistry. Arsenic atoms in the structure of the Ag₃AsS₃ compound (hR42, S.G. R₃c, No. 161) (Bindi et al. 2010) occupy trigonal-prismatic voids (Fig. 2a) where they are significantly shifted to the base of the prism. The interatomic distances As–S from arsenic atom to sulfur atoms at the opposite base of the prism, as well as to S atoms centering the side faces of the prism, exceed the sum of the corresponding ionic radii. This observation holds true even if arsenic atom were perfectly in the center of the trigonal prism (Fig. 2b).

Therefore, the structure of the Ag₃AsS₃ compound can be viewed as the packing of the structural groups [AsS₃]³⁻ that behave as separate anions. Their second coordination surrounding (SCS) (Fedorchuk et al. 2013) has the form of a rhombododecahedron (cuboctahedron with two additional atoms at the opposite quadrangular faces) which indicates close packing of these atom groups (Fig. 3).

Silver atoms within the SCS occupy octahedral voids (Fig. 4) where they are somewhat shifted to one of the corners. Due to the contact with five [AsS₃]³⁻ anions (Fig. 4b) the closest coordination surrounding of silver atoms is shaped like a flattened octahedron (Fig. 4c) where the cations lay between two opposite sulfur atoms (Fig. 4d). The distances from the prism center to sulfur atoms are commensurate with the RE–S distances in the corresponding compounds (Fig. 2b). Therefore, RE atoms as dopants statistically occupy the sites of silver atoms in the crystal lattice of the Ag₃AsS₃ compound.

The results of the SEM investigation are shown in Fig. 5. Backscattered electron (BSE) images show that studied Ag₃AsS₃-based materials are practically single-phase with a
small number of byproducts and pores on the grain boundaries. Performed EDXS analysis indicates that all samples mainly contain only a phase with the chemical composition close to Ag₃AsS₃ (Fig. 5c, d), however, trace amounts of inclusions of the Ag₃S phase on the grain boundaries are observed. Such types of inclusions are often observed for Cu- and Ag-based ternary chalcogenides, which typically crystallize with deficiency of these metals from stoichiometric composition (Cherniushok et al. 2021b). Figure 5c, d and f show the trace presence of rare-earth-rich phases, which can be connected with the exceeded solubility limit of RE sulfides in Ag₃AsS₃. Moreover, this observation is also in agreement with the claim that the RE dopants occupy the sites of silver atoms in the crystal lattice of the Ag₃AsS₃ compound, which can be a reason for the precipitation of the Ag₃S phase on the grain boundaries (Fig. 5).

### 3.2 Second harmonic generation

Due to the above-discussed non-centrosymmetry of the Ag₃AsS₃ crystal structure, its doping with rare-earth elements is of interest because of potential use in electro-optical and non-linear optical devices (Riccius and Siemsen 1974). Given this, second harmonic generation of the synthesized materials was investigated. The analysis of obtained experimental
results (Fig. 6) indicates that SHG intensity in these materials increases upon both Pr and Eu doping which is typical of multi-component chalcogenide crystals. Specifically, doping by 1 wt.% Pr and Eu increases SHG efficiency by about 18 and 24%, respectively. Ytterbium doping of proustite also leads to increased SHG, moreover, the effect is even more pronounced compared to the previous two cases. With increasing Yb doping from 0.4 to 0.7 wt.% the SHG intensity of proustite increases by 50 and 88%, respectively (Fig. 6c). However, further increase of Yb doping of Ag₃AsS₃ to 1 wt.% shows slight lower SHG intensity (from 88 to 75%) which is still substantially higher than undoped Ag₃AsS₃. All the above facts indicate that doping of Ag₃AsS₃ crystals with rare-earth elements like Pr, Eu, and Yb leads to increasing SHG intensity. Importantly, presented measurements reveal that such an effect on the SHG intensity depends on the position of the rare-earth element in the Periodic Table, i.e. the higher the atomic number of the dopant, the bigger the increase of the SHG intensity of Ag₃AsS₃. Presented experimental results lead us to conclude that the rare-earth-doped Ag₃AsS₃ crystals are promising non-linear optical materials for potential applications in the IR spectral range.

The increase of SHG intensity is primarily related to the non-linear microscopic hyperpolarization $\beta_{ijk}$, which can be described as:

$$\beta_{ijk} \approx \mu_i \mu_j \Delta \mu_k / E_g^3$$

Where $\mu_i$ and $\mu_j$ are the respective ground-state dipole moments; $\Delta \mu_k$ is the difference between the excited and ground states of the bands (Dovgii et al. 1991). Such a change in the band structure usually correlates with bandgap modification. Moreover, in the case of chalcogenides both, electrons and phonons, contribute to the total dipole moment $\mu = \mu_{el} + \mu_{ph}$. Taking into account the contribution of phonons, especially of anharmonic phonon sub-systems, as well as the energy resonances of intrinsic defects, the role of the phonon share may even be dominating (Skelton et al. 2016; Shvalya et al. 2017; Myronchuk et al. 2019). Consequently, even lower bandgap energy may result in lower SHG efficiency, and vice versa. To bring some insight to the origins of the increased SHG efficiency, we studied the absorption coefficient and Raman spectra for the investigated materials.

### 3.3 Absorption coefficient

As the introduction of rare-earths Pr, Eu, Yb into the crystal structure of proustite Ag₃AsS₃ may affect the bandgap energy, we evaluated this important parameter from the absorption
coefficient measurements. The bandgap was estimated from the spectral dependence of the absorption coefficient at the edge of the fundamental absorption (Fig. 7a–c) using Tauc’s method (Tauc 1974). The curve at the fundamental absorption edge fits the expression $(\alpha h) = f(h)$, where the degree $N$ can have values of $1/2$, $3/2$, 2, or 3, depending on the nature of the electron transition responsible for the absorption ($N=1/2$—direct permitted transitions, $N=3/2$—direct forbidden, $N=2$—indirect permitted, $N=3$—indirect forbidden transitions). Extrapolating the linear part of the spectrum onto the energy axis (Fig. 7, inserts b,d,f), we determined the bandgap energy of the studied materials as presented in Table 2.

The addition of rare-earth elements to the Ag$_3$AsS$_3$ matrix favors the decrease of the bandgap energy of the synthesized materials. At the same time, the amount of the decrease depends on the atomic number of the dopant which agrees well with refs. Lakshminarayana (2012), Makowska-Janusk et al. (2014), Piasecki et al. (2016). Within the approximation of strong bonding, the decrease of the bandgap energy upon the increase of the atomic

| Principal phase | Admixture | Doping, wt.% | $E_g$, eV |
|----------------|-----------|-------------|-----------|
| Ag$_3$AsS$_3$  | –         | –           | 2.16      |
| Ag$_3$AsS$_3$  | Pr        | 0.4         | 2.11      |
| Ag$_3$AsS$_3$  | Pr        | 0.7         | 2.09      |
| Ag$_3$AsS$_3$  | Pr        | 1.0         | 2.08      |
| Ag$_3$AsS$_3$  | Eu        | 0.4         | 2.10      |
| Ag$_3$AsS$_3$  | Eu        | 0.7         | 2.08      |
| Ag$_3$AsS$_3$  | Eu        | 1.0         | 2.07      |
| Ag$_3$AsS$_3$  | Yb        | 0.4         | 2.08      |
| Ag$_3$AsS$_3$  | Yb        | 0.7         | 2.07      |
| Ag$_3$AsS$_3$  | Yb        | 1.0         | 2.05      |
| Ag$_3$AsS$_3$  | Pr; Eu    | 0.2; 0.2    | 2.12      |
| Ag$_3$AsS$_3$  | Pr; Eu    | 0.3; 0.3    | 2.09      |
number is explained by the increase of the energy exchange integral. The higher the atomic number, the greater the size of the electron cloud and the degree of the overlap of the electron clouds of adjacent atoms, and the greater value of the energy exchange integral and corresponding width of permitted energy bands. Consequently, the $\text{Ag}_3\text{AsS}_3$ compound doped with dopants with a lower atomic number shows slightly lower values of the bandgap. Finally, we can conclude that the decrease of the bandgap energy roughly corresponds to the increase of the second harmonic generation coefficient for the investigated materials. Also, it should be noted that powder measurements of SHG in proustite should suffer from strong absorption part and the changes in absorption coefficient caused by doping (in a region where the various dopant curves are crossing) may well be responsible for quite minor changes in the SHG intensity observed in the present experiments. However, available facilities do not allow us the measurements of SHG with a pump at above 2 μm, in fact at wavelengths where the harmonic lies in the transparent region.

### 3.4 Raman spectroscopy

Raman spectra of the undoped $\text{Ag}_3\text{AsS}_3$ crystals and those doped with Pr or simultaneously doped with Pr and Eu are plotted in Fig. 8a, b. The additional doubly doped with Pr and Eu $\text{Ag}_3\text{AsS}_3$ samples were prepared to perform the comparative analysis of the Raman spectra.

As it was mentioned above and reported in ref. Byer et al. (2011), the crystal structure of $\text{Ag}_3\text{AsS}_3$ belongs to the trigonal symmetry, space group $R\overline{3}c$. Knowing the positions of atoms in the unit cell for the respective symmetry point group $C_{3v}$, we calculated symmetry types of all long-wave vibrations using theoretical group analysis: $\Gamma = 6A_1 \oplus 13E \oplus 7A_2 \oplus A_{2u} \oplus E_u$. The crystal compounds with the symmetry point group $C_{3v}$ can feature 19 optical modes $\Gamma_{\text{opt}} = 6A_1 \oplus 13E$, both in Raman and IR spectra, not counting possible splits of twice-degenerated symmetry modes E. Symmetry modes $A_2$ are silent and not represented in the vibrational spectra, and the $A_{2u}$ and $E_u$ modes correspond to acoustical vibrations.

![Fig. 8](image_url)  

**Fig. 8** a Raman spectra of the undoped $\text{Ag}_3\text{AsS}_3$ crystals (curve 1) and Pr-doped crystals: 0.7 wt.%—curve 2; 1 wt.%—curve 3. b Raman spectra of the original (curve 1) $\text{Ag}_3\text{AsS}_3$ crystals and doped with: 0.3 wt.% Pr and 0.3 wt.% Eu—curve 2; 0.4 wt.% Pr and 0.3 wt.% Eu—curve 3
The experimental Raman spectra of undoped crystals contain 13 bands (Fig. 8a, b, curves 1). The attribution of each band to a certain vibration type is possible by comparison with the spectra and theoretical calculation in refs. Ewen et al. (1983), Riccius et al. (1975). The characteristic modes in Raman spectra of the Ag₃AsS₃ crystals are detected at 364 cm⁻¹ and 332 cm⁻¹. The former is assigned to the symmetrical stretching vibrations of As–S bonds, with a shoulder near 352 cm⁻¹ due to asymmetrical stretching vibrations, while the latter (332 cm⁻¹) is assigned to the symmetrical bending S–As–S, with a shoulder near 318 cm⁻¹ due to asymmetrical bending.

A particularity of Raman spectra of rare-earth-doped Ag₃AsS₃, especially heavily doped ones (~1%), is the occurrence of two more bands at 406 cm⁻¹ и 415 cm⁻¹ (Fig. 8, curves 3). It was shown in Byer et al. (2011), Ewen et al. (1983), Riccius et al. (1975) that Raman spectra of Ag₃AsS₃ do not feature first order bands with frequencies above 370 cm⁻¹. Therefore, three possible reasons were considered to explain the emergence of these two bands in the measured Raman spectra.

It is known that half-widths of photoluminescence bands in the samples with rare-earths are commensurate with Raman band half-widths. Therefore, spectra upon the excitation by a laser with another wavelength, 532 nm, were recorded to ascertain that Raman and not PL bands were observed in our case. Two additional bands at the same frequencies were detected confirming that these are Raman bands.

The occurrence in Raman spectra of additional bands that are usually present in IR spectra is possible upon weakening of the selection rules due to deviations in the crystal symmetry of the studied samples. It was shown earlier that the proustite structure is based on the complex packing of separate trigonal pyramids [AsS₃] and silver atoms. As and S atoms form the covalently bonded [AsS₃] pyramids that are stretched along the c axis of the third order. The opposite pyramids are connected by a glide plane. As rare-earth atoms in the growth process of proustite crystals occupy prismatic or octahedral voids present in the structure, the lattice violation will be negligible at their low concentrations, while at the same time may become substantial as their content increases. IR reflection spectra of Ag₃AsS₃ exhibit a wide band with weak reflectance in the region of 400 cm⁻¹ (Claudel et al. 1977) that might occur in Raman spectra upon weakening the selection rules. However, the IR band has a quite large half-width and one maximum, and our Raman spectra contain two bands that partially overlap.

Finally, the above-mentioned bands in Raman spectra may be the bands of the second order, namely the sums of the vibrational modes of the first order with the same symmetry. For instance, in curve 3 in Fig. 8b the band at 406 cm⁻¹ is the result of the addition of the vibrations at 361 and 43 cm⁻¹, and the band at 415 cm⁻¹, of the vibrations at 361 and 58 cm⁻¹. The occurrence of the bands at 406 and 415 cm⁻¹ only in the samples with high content of rare earth atoms indicates that their addition to Ag₃AsS₃ substantially intensifies electron–phonon interaction. Indeed, it is well known that the increase of the ratio of the intensities of the second-order bands compared to the intensities of the first-order bands indicates the increase of the magnitude of electron–phonon interaction (Yaremko et al. 2007). This result is agreed with the aforementioned reasons for the increased SHG efficiency for the rare earth doped Ag₃AsS₃ materials.
4 Conclusions

In this work, the effect of the doping by the rare-earth elements Pr, Eu, and Yb on the structure, as well as linear and non-linear optical properties of Ag$_3$AsS$_3$ crystals, were investigated aiming to explore their potential for the NLO applications in IR spectra. The analysis of the XRD patterns indicates that the rare earth elements occupy Ag sites in the structure and have rather a small effect on the crystal lattice. EDXS analysis showed that all samples contain the phase with the element composition close to Ag$_3$AsS$_3$, at the same time trace inclusions of other phases at the grain interfaces were observed. The latter is explained by exceeding the solid solubility limits of rare-earth elements in Ag$_3$AsS$_3$ and supports the assertion that Pr, Eu and Yb atoms occupy Ag sites in the structure.

Investigation of second harmonic generation indicates that SHG intensity in the studied materials increases with the dopant content in all cases except Yb. In the latter case, the SHG intensity firstly sharply increases and then slightly decreases. It was determined that such trends of the SHG intensity roughly correlate with the changes of the bandgap. We found that the introduction of rare-earth elements to the Ag$_3$AsS$_3$ matrix leads to a modest (0.01–0.03 eV) decrease of the bandgap energy of the synthesized materials. At the same time, its magnitude depends on the atomic number of the dopant, which can be explained within the approximation of strong bonding by the increase of the energy exchange integral with the atomic number of rare earth elements.

Additional bands at ~406 and ~415 cm$^{-1}$ were detected in Raman spectra of Ag$_3$AsS$_3$ doped with a high content (1%) of rare earth elements. Their occurrence in the spectra is related to the increased magnitude of electron–phonon interaction in rare-earth-doped Ag$_3$AsS$_3$ crystals, which clarifies the reason for the increased SHG intensity observed for the investigated materials. Finally, in the present work, we show the large potential of the rare-earth-doped Ag$_3$AsS$_3$ crystals for the non-linear optical applications in the infrared range, for instance, the conversion of IR to visible light.

Supplementary Information The online version contains supplementary material available at https://doi.org/10.1007/s11082-022-03542-w.

Acknowledgements This work was partially supported by the subsidy of the Ministry of Education and Science for the AGH University of Science and Technology in Krakow (Project No 16.16.160.557).

Funding Funding was provided by Swansea University (Grant Nos. ID0E4EAE5148, ID0E4EAE51488).

Data availability The data that supports the findings of this study are available within the article [and its supplementary material].

Declarations

Conflict of interest The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

References

Abudurusuli, A., Li, J., Pan, S.: A review on the recently developed promising infrared nonlinear optical materials. Dalt. Trans. 50, 3155–3160 (2021). https://doi.org/10.1039/D1DT00054C
Heep, B.K., Weldert, K.S., Krysiak, Y., Day, T.W., Zeier, W.G., Kolb, U., Snyder, G.J., Tremel, W.: High electron mobility and disorder induced by silver ion migration lead to good thermoelectric performance in the argyrodite Ag8SiSe6. Chem. Mater. 29, 4833–4839 (2017). https://doi.org/10.1021/acs.chemmater.7b00767

Hoffman, H.J., Perkins, P.E., Stone, R.E., Driscoll, T.A.: Efficient second-harmonic generation in KTP crystals. JOSA B 3(5), 683–686 (1986). https://doi.org/10.1364/JOSAB.3.000683

Hulme, K.F., Jones, O., Davies, P.H., Hobden, M.V.: Synthetic proustite (Ag3AsS3): a new crystal for optical mixing. Appl. Phys. Lett. 10, 133 (2004). https://doi.org/10.1063/1.1754880

Isaenko, L., Vasilyeva, I., Merkulov, A., Yelisseyev, A., Lobanov, S.: Growth of new nonlinear crystals LiMX (M=Al, In, Ga; X=S, Se, Te) for the mid-IR optics. J. Cryst. Growth. 275, 217–223 (2005). https://doi.org/10.1016/J.JCRYSGRO.2004.10.089

Jiang, A., Wu, B., Chen, C., You, G., Li, R., Lin, S., Wu, Y.: New nonlinear-optical crystal: LiB3O5. JOSA B 6(4), 616–621 (1989). https://doi.org/10.1364/JOSAB.6.000616

Kharbish, S.: Spectral-structural characteristics of the extremely scarce silver arsenic sulfosalts, proustite, smithite, trechmannite and xanthoconite: μ-Raman spectroscopy evidence. Spectrochim. Acta. A. Mol. Biomol. Spectrosc. 177, 104–110 (2017). https://doi.org/10.1016/J.SAA.2017.01.038

Kraus, W., Nolze G.: PowderCell for windows download - free powder pattern calculation program, PowderCell Wind. - Free Powder Pattern Calc. Progr. (n.d.). https://powdercell-for-windows.software.informer.com/ (accessed October 7, 2021)

Kurtz, S.K., Perry, T.T.: A powder technique for the evaluation of nonlinear optical materials. J. Appl. Phys. 39, 3798 (2003). https://doi.org/10.1063/1.1656857

Lakshminarayana, M.P.G.: Photovoltaic, photoelectric and optical spectra of novel AgxGaxGe1-xSe2 (0.167 > x > 0.333) quaternary single crystals, Photovoltaic, Photoelectr. Opt. Spectra Nov. AgxGaxGe1-xSe2 (0.167 > x > 0.333) Quat. Single Cryst. (2012) 837–841. http://isp.kiev.ua/images/Institute/depo6/Rada02/Thesis Garvilyuk.pdf (accessed September 10, 2021)

Lin, H., Wei, W.B., Chen, H., Wu, X.T., Zhu, Q.L.: Rational design of infrared nonlinear optical chalcogenides by chemical substitution. Coord. Chem. Rev. 406, 213150 (2020). https://doi.org/10.1016/J.CCR.2019.213150

Makowska-Janusik, M., Kityk, I.V., Myronchuk, G., Zamurueva, O., Parasyuk, O.V.: Manifestation of intrinsic defects in the band structures of quaternary chalcogenide Ag2In2SiSe6 and Ag2In2GeSe6 crystals. CrystEngComm 16, 9534–9544 (2014). https://doi.org/10.1039/C4CE01005A

Mutalipu, M., Zhang, M., Yang, Z., Pan, S.: Targeting the next generation of deep-ultraviolet nonlinear optical materials: expanding from borates to borate fluorides to fluorooxoborates. Acc. Chem. Res. 52, 791–801 (2019). https://doi.org/10.1021/ACS.ACCOUNTS.8B00649

Myronchuk, G.L., Zamuruyeva, O.V., Parasyuk, O.V., Kityk, I.V., Czaja, P., Piasecki, M.: The effect of composition on photoconductivity and nonlinear optical properties in the acentric Ag2In2AB6 (A = Si, Ge, B = S, Se) crystals. Optik (stuttgart) 179, 948–956 (2019). https://doi.org/10.1016/J.OPTIK.2018.11.030

Nikogosyan, D.N.: Nonlinear optical crystals: a complete survey. Nonlinear Opt. Cryst. A Complete. Surv. pp. 1–427 (P. 374) (2005). https://doi.org/10.1007/B138685

Ohmer, M.C., Pandey, R.: Emergence of chalcopyrites as nonlinear optical materials. MRS Bull. 23, 16–22 (1998). https://doi.org/10.1557/S0883769400029031

Piasecki, M., Myronchuk, G.L., Zamurueva, O.V., Khyzhun, O.Y., Parasyuk, O.V., Fedorchuk, A.O., Albasam, A., El-Naggar, A.M., Kityk, I.V.: Huge operation by energy gap of novel narrow band gap Tl1−xBxIn1−xBxSe2 (B = Si, Ge): DFT, x-ray emission and photoconductivity studies. Mater. Res. Express. 3, 025902 (2016). https://doi.org/10.1088/2053-1591/3/2/025902

Rame, J., Viana, B., Clement, Q., Melkonian, J.M., Petit, J.: Control of melt decomposition for the growth of high quality AgGaGeS4 Single crystals for mid-IR laser applications. Cryst. Growth Des. 14, 5554–5560 (2014). https://doi.org/10.1021/CC500813Q

Riccius, H.D., Carey, P.R., Siimm, O.: Optical phonon modes in proustite (Ag3AsS3). Phys. Status Solidi 72, K99–K101 (1975). https://doi.org/10.1002/PSSB.222072171

Riccius, H.D., Siemsen K.J.: Proustite (Ag3AsS3) — An almost ideal nonlinear material, pp. 301–305. (1974) Doi: https://doi.org/10.1007/978-3-322-94774-1_50

Schöna, K.A., Redfern, S.A.T.: High-temperature phase transitions, dielectric relaxation, and ionic mobility of proustite, Ag3AsS3, and pyrargyrite, Ag3SbS3. J. Appl. Phys. 92, 7415 (2002). https://doi.org/10.1063/1.1520720

Shvalya, V., Oleaga, A., Salazar, A., Kohutych, A.A., Vysochanskii, Y.M.: Electron-phonon anharmonicity and low thermal conductivity in phosphorous chalcogenide ferroelectrics. Mater. Express. 7, 361–368 (2017). https://doi.org/10.1166/MEX.2017.1385
Skelton, J.M., Burton, L.A., Parker, S.C., Walsh, A., Kim, C.E., Soon, A., Buckeridge, J., Sokol, A.A., Catlow, C.R.A., Togo, A., Tanaka, I.: Anharmonicity in the high-temperature Cmcm phase of SnSe: soft modes and three-phonon interactions. Phys. Rev. Lett. 117, 075502-1–075502-6 (2016). https://doi.org/10.1103/PYHRSREVLETT.117.075502/FIGURES/2/THUMBNAI

Smith, W.L.: KDP and ADP transmission in the vacuum ultraviolet. Appl. Opt. 16(7), 1798–1798 (1977). https://doi.org/10.1364/AO.16.001798

Tauc, J.: Amorphous and Liquid Semiconductors. Springer, Boston (1974). https://doi.org/10.1007/978-1-4615-8705-7

Wu, K., Pan, S.: A review on structure-performance relationship toward the optimal design of infrared non-linear optical materials with balanced performances. Coord. Chem. Rev. 377, 191–208 (2018). https://doi.org/10.1016/J.CCR.2018.09.002

Yaremko, A.M., Yukhymchuk, V.O., Dzhagan, V.M., Valakh, M.Y., Azhniuk, Y.M., Baran, J., Ratajczak, H., Drozd, M.: Investigation of electron-phonon interaction in bulk and nanostructured semiconductors, (2007). http://dspace.nbuv.gov.ua/xmlui/handle/123456789/117861 (accessed September 10, 2021)

Publisher's Note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.