Optics and Laser Technology 104 (2018) 83–89

Contents lists available at ScienceDirect

Optics and Laser Technology

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

Full length article

Novel report on SHG efficiency, Z-scan, laser damage threshold, photoluminescence, dielectric and surface microscopic studies of hybrid inorganic ammonium zinc sulphate hydrate single crystal

S.P. Ramteke [a,1], M.I. Baig [b], Mohd Shkir [c,d], S. Kalainathan [e], M.D. Shirsat [f], G.G. Muley [a], Mohd Anis [a,*,1]

[a] Department of Physics, Sant Gadge Baba Amravati University, Amravati 444602, Maharashtra, India
[b] Prof Ram Meghe College of Engineering and Management, Amravati 444701, Maharashtra, India
[c] Advanced Functional Materials & Optoelectronic Laboratory (AFMOL), Department of Physics, College of Science, King Khalid University, P.O. Box 9004, Abha 61413, Saudi Arabia
[d] Research Center for Advanced Materials Science (RCAMS), King Khalid University, P.O. Box 9004, Abha 61413, Saudi Arabia
[e] School of Advanced Sciences, Centre for Crystal Growth, VIT University, Vellore 632014, India
[f] RUSA Centre for Advanced Sensor Technology, Department of Physics, Dr. Babasaheb Ambedkar Marathwada University, Aurangabad 431005, Maharashtra, India

ARTICLE INFO

Article history:
Received 16 November 2017
Received in revised form 6 January 2018
Accepted 12 February 2018

Keywords:
Crystal growth
Inorganic materials
Dielectric studies
Optical studies
Microscopic studies

ABSTRACT

Hybrid inorganic nonlinear optical crystals find huge applications in laser assisted photonic devices therefore present communication firstly aims to investigate the dielectric, microscopic and linear-nonlinear optical properties of ammonium zinc sulphate hydrate (AZSH) crystal. The inorganic AZSH complex has been synthesized and $15 \times 10 \times 09$ mm^3 single crystal was grown by slow solvent evaporation method. The powder and single crystal X-ray diffraction technique has been employed to evaluate the crystalline phase and determine the structural parameters of AZSH crystal. The optical transparency of AZSH crystal has been examined within the wavelength rage of 200–1100 nm. The enhanced second harmonic generation efficiency of AZSH crystal is 2.53 times higher than standard KDP crystal. The laser damage threshold of AZSH crystal has been determined using the Nd:YAG laser operating at 1064 nm. The close and open aperture Z-scan studies have been performed to ascertain the nature of third order nonlinear optical (TONLO) refraction and absorption of AZSH crystal. The order of TONLO parameters n_2, β and χ^3 is found to be 10^{-9} cm^2/W, 10^{-4} cm/W, 10^{-4} esu respectively. The AZSH crystal is found to have violet colored luminescence emission centered at 370 nm. The dielectric constant and dielectric loss of AZSH crystal has been evaluated within 30 Hz to 1 MHz. The chemical etching technique has been imposed to examine the growth habitat and determine the etch pit density of AZSH crystal.

1. Introduction

In past few decades the development of new hybrid inorganic NLO crystals has been accelerated as they cater unique qualities such as wide transparency window ranging from far infrared to deep UV-region, huge mechanical stability, highly packed structural design, sufficient nonlinear response and large threshold to laser exposure which ultimately vitalize the credibility of these crystals for optoelectronics, photoemission spectroscopy, laser micromachining, semiconductor lithography, optical modulation, frequency shifting/conversion, optical switching and laser device applications [1–5]. The appealing technologically vital inorganic NLO crystals that are currently utilized in laser complied device applications at mass scale are MgO:$LiNbO_3$, $NH_4H_2PO_4$, $LiIO_3$, KH_2PO_4, KD_2PO_4, $CsLiB_6O_4$, $KNbO_3$, $KTiOAsO_4$, $CdGeAs_2$ [6,7]. Looking at the stimulating impetus of inorganic crystals across the globe attention of our group is focused to explore the unique class represented by the general formula $A_2B(XO_4)_2{\cdot}6H_2O$ where A corresponds to big univalent cations (K^+, NH_4^+, Rb^+, Cs^+, etc), B corresponds to smaller divalent cations (Ni^{2+}, Co^{2+}, Cu^{2+}, Mg^{2+}, Zn^{2+}, Fe^{2+}, etc) and X corresponds to the S, Se or Cr. El-Fadl et al. recently explored the structural, morphological and linear optical properties of potassium zinc sulfate hydrate (KZSH) and ammonium zinc sulfate hydrate (AZSH) single crystals [8]. However, from the application point of view the precise knowledge of second harmonic generation (SHG) efficiency, third order nonlinear optical parameters, laser damage threshold, luminescence, dielectric and microscopic surface properties are essential which are not reported in case of KZSH and AZSH crystals. In current investigation a novel report is put forth which deals to explore the most vital missing

* Corresponding author.
E-mail addresses: loganees@yahoo.com, loganees@gmail.com (M. Anis).
[1] These authors contribute equally to this work.

https://doi.org/10.1016/j.optlastec.2018.02.018

properties of AZSH crystal by imposing structural, UV–visible, Kurtz-Perry test, Z-scan, laser damage threshold, photoluminescence, dielectric and chemical etching analysis to bring out the potential credibility of AZSH crystal for distinct NLO device applications.

2. Experimental procedure

2.1. Synthesis and crystal growth

In order to synthesize the AZSH complex the SDfine make ammonium chloride and zinc sulphate were dissolved in double distilled water in 1:1 M ratio and the mixture was allowed to stir on a constant speed for four hours to facilitate the homogeneous reaction of the reactants. The scheme of chemical reaction giving the product of AZSH is given below,

$$ZnSO_4 \cdot 6H_2O + (NH_4)_2SO_4 \xrightarrow{H_2O} (NH_4)_2ZnSO_4 \cdot 6H_2O \ (AZSH)$$

The mixture solution was filtered through the membrane filter paper using the vacuum pump. The filtrate was transferred in the clean rinsed beaker and it was placed in the vibration free constant water bath maintained at 35 °C. As the slow evaporation process begins the nucleation of seed crystal was observed and single crystals of appreciable size with well-defined faces were obtained within the period of two weeks. The as grown AZSH complex crystal of dimension 15 × 10 × 09 mm^3 is shown in Fig. 1a. The purity of AZSH material was achieved by repetitive recrystallization process.

2.2. Characterization techniques

The properties of AZSH crystal has been evaluated by different techniques as discussed: (a) Single crystal X-ray diffraction (XRD) analysis was performed by using Enraf Nonius CAD4 single crystal X-ray diffractometer, (b) powder XRD pattern analysis was recorded using the Bruker Advanced D8 powder X-ray diffractometer and indexing was done using the powderX software constraining the 2θ error limit to 0.01°, (c) Linear optical study was examined within 200–1100 nm using the Shimadzu UV-1061 spectrophotometer, (d) SHG efficiency was determined using the Nd:YAG laser (Q-switched mode, 1064 nm, 10 Hz, 6 ns), (e) Z-scan analysis was performed using the CW He-Ne laser operating at 632.8 nm and the optical resolution of components utilized in Z-scan setup is focal length of focusing lens = 20 cm, optical path distance = 113 cm, beam waist radius (ω_a) = 1 mm, aperture radius (r_a) = 1.5 mm, beam intensity at the focus (Io) = 2.3375 KW/m^2, (f) LDT was determined using the Nd:YAG laser (1064 nm, 10 ns, 10 Hz), (g) dielectric studies were carried out within frequency range of 30 Hz to 1 MHz using the HIOKI 3532 LCR cubemeter, (h) photoluminescence nature was examined using the Hitachi F-7000 fluorescence spectrophotometer with analysis method emission and excitation slit width = 1 nm, scan speed = 240 nm/min, delay = 0 s, response time = 0.1 s, (i) optical microscope Carl Zeiss was used to capture the microimage of crystal surface in reflection mode at resolution of 100 μm.

3. Results and discussion

The single crystal XRD data reveals that the title crystal belongs to the monoclinic crystal system oriented with the space group $P2_1/a$. The unit cell parameters of AZSH crystal are a = 9.235 (±0.013) Å, b = 12.516 (±0.007) Å, c = 6.248 (±0.002) Å, β = 106.89° and the volume V = 690.025 (±1.1) $Å^3$. These values match well with the reported data in ICDD PDF card No. 04-007-5463 confirming the formation of AZSH crystal. The powder XRD technique has

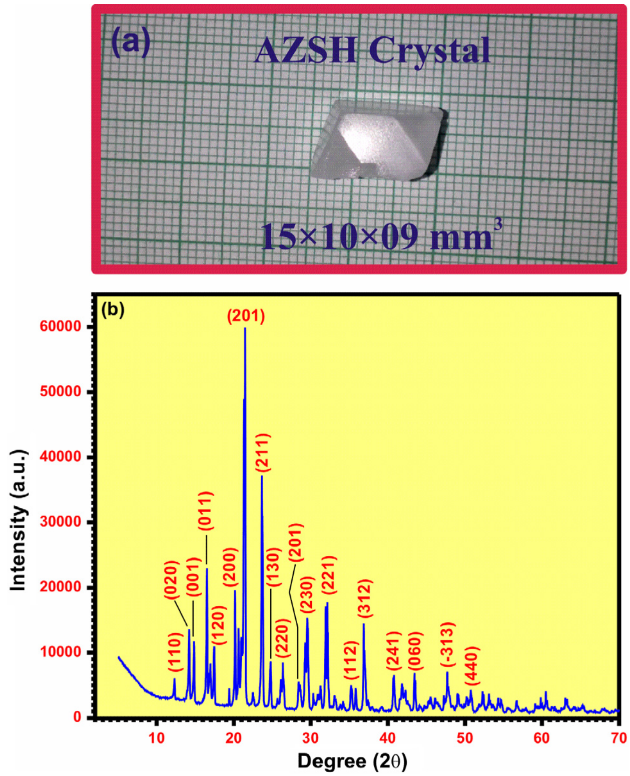

Fig. 1. (a) AZSH single crystal. (b) PXRD pattern of AZSH.

been employed to examine the crystalline phase and purity of the AZSH crystal. The recorded PXRD pattern is shown in Fig. 1b. It is worth mentioning that the PXRD pattern and indexing match very well with reported PXRD pattern [8]. The sharpness/broadening of diffraction peaks give determinant clue about the crystalline quality of material [9]. In present study the AZSH crystal material offers sharp, narrow and high intensity diffraction peaks which are ideal feature of material exhibiting good crystalline nature and lesser density of defects and grain boundaries [10,11]. The crystals with lesser defect centers are eventually desirable for device fabrication.

Thus the intrinsic and extrinsic factors that dwells the property of linear optical transmittance in crystal is governed by the electronic transition facilitated by the interaction of electromagnetic signal with material composition (atoms, ions, electrons) [12–14] while the limit of transmittance is determined by molecular anisotropy along the crystal plane and internal scattering/absorption from defects (grain boundaries, voids, cracks, bubbles, impurities, solvent inclusions) [15,16]. The designing of polarizer and lenses demand high quality and optically homogeneous crystal hence in order to testify that the optical transmittance of 1.5 mm thickness AZSH crystal has been recorded within 200–1100 nm as shown in Fig. 2a. It reveals that the AZSH crystal attributes the maximum transmittance up to 67% throughout the visible region. Interestingly the title crystal does not show any transition within visible region which might have been expressed due to lesser density of scattering centers in crystal medium [17] also the presence of Zn^{2+} ion offers high optical transparency in visible region owing to closed d^{10} shell electrons [18–20]. Thus wide operative wavelength range of AZSH crystal suggest its prime utility for designing components for transmission of 2nd/3rd harmonic signals derived from Nd:YAG laser [21] and UV-tunable lasers [22].

The most fundamental and essential condition for crystal to generate the SHG is to acquire the acentric symmetry and the Kurtz-Perry powder test [23] is the most reliable tool to determine the exact magnitude of the SHG efficiency of the given crystal. In