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Investigations on growth and characterization of glycine admixture sodium molybdate crystals for nonlinear optical applications

K. Amarsingh Bhabu [a], S.R. Balaji [b], R. Sree Devi [c], T. Balu [c], G. Muralidharan [d], T.R. Rajasekaran [a,*]

[a] Department of Physics, Manonmaniam Sundaranar University, Tirunelveli 627 012, Tamil Nadu, India
[b] P.G. Department of Physics, V. O. Chidambaram College, Thoothukudi 628 008, Tamil Nadu, India
[c] Department of Physics, Aditanar College of Arts and Science, Tiruchendur 628 216, Tamil Nadu, India
[d] Department of Physics, Gandhigram Rural Institute-Deemed University, Dindigul 624 302, Tamil Nadu, India

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ABSTRACT

Single crystals of semi-organic nonlinear optical material tris-glycine sodium molybdate were grown by slow evaporation technique from aqueous solution at room temperature. Good optical quality crystals with dimensions of $2.3 \times 1 \times 0.5\ cm^3$ were obtained. Single crystal X-ray diffraction was used to measure the unit cell parameters and affirmed the crystal structure. Powder X-ray diffraction revealed that the crystallinity of the crystals grown. Fourier transform infrared spectra confirmed the complex formation of glycine and sodium molybdate. Ultra violet absorption studies indicate that the crystals were transparent in the entire visible range. Direct optical band gap and indirect optical band gap values of the grown crystals were calculated from the Tauc plot. Vickers microhardness test was performed to understand the mechanical strength of the crystals. Thermal stability and melting point of the grown crystal was identified from thermo gravimetric analysis and differential thermal analysis. The surface morphology of the grown crystals was studied using scanning electron microscope analysis. Chemical composition and purity of the crystal was corroborated by energy dispersive X-ray analysis. The nonlinear optical property of the crystal was measured by Kurtz and Perry powder technique using Nd:YAG laser operating at 1064 nm.

1. Introduction

Crystals are the back bone of today's technological development. Progress in crystal growth was highly demanded in view of its recent advancements in the field of semiconductors, polarizers, transducers, infrared detectors, ultrasonic amplifiers, ferrites, magnetic garnets, solid state lasers, nonlinear optic, piezoelectric, acousto-optic, photo sensitive materials and crystalline thin films for industrial applications. There are many techniques and ways to grow the crystals and the choice is decided by the physical and chemical properties of the material to be grown as in the crystalline form. Invention of lasers during 1960s played a vital role in the field of crystal growth. This led to an entirely new field, nonlinear optics and the discovery of various phenomena such as second harmonic generation and difference frequency generation [1]. Nonlinear optical (NLO) materials, structures and devices with enhanced figure of merit has been developed over the past few decades as a major force to help drive nonlinear optics from the laboratory to real applications. The emerging field of NLO research and applications still requires new material for a large variety of processes [2]. Nowadays, the most widely used NLO crystal for second harmonic generation of Nd:YAG laser was potassium dihydrogen phosphate (KDP). However, many problems associated with the use of KDP crystals in terms of changes in the refractive, optical damage and hygroscopic. Therefore, research for new NLO crystals becomes most important. Pristine forms are not always interesting. The addition of impurities which alter the optical and electrical properties of materials due to the creation of localized states and defects created by the doping [3]. Similarly creation of a new compound by mixing of two materials yields interesting properties which are not exhibited by the individual materials. In an attempt to discover new crystalline materials for industrial applications, in the present study, we have made an attempt to combine glycine with sodium molybdate to form tri-glycine sodium molybdate (TGSM) crystals.

Complexes of amino acids with inorganic salts are of interest as materials for second harmonic generation. In general, organic materials (amine group) show good efficiency for second harmonic generation. Glycine is the simplest amino acid. It has no asymmetric

* Corresponding author. Tel.: +91 9442327921; fax: +91 462 2334363.
E-mail address: trrpub1959@gmail.com (T.R. Rajasekaran).

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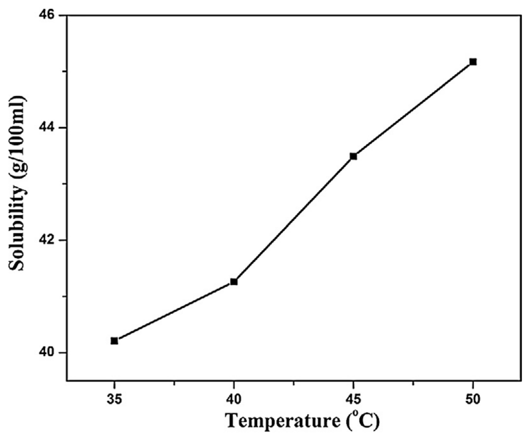

Fig. 1. Solubility of tri-glycine sodium molybdate.

carbon atom and it is optically inactive. It has three polymorphic crystalline forms α, β and γ. Glycine is ferroelastic, ferroelectric and it exhibits anti-ferroelectric behavior [4–6].

A survey of literature shows that the various combinations of sodium molybdate [7–11], like $NaTb(MoO_4)$, $LiNa(MoO_4)\cdot 2H_2O$, $Cs_2(MoO4)$-$Na_2(MoO_4)$-H_2O, $Na_2(MoO_4)$-$K_2(MoO_4)$-H_2O [12–15] can be obtained. To the best of our knowledge this is the first time the preparation, growth and the characterization of tri-glycine sodium molybdate has been attempted. We have also attempted to examine the second harmonic generation capabilities of the tri-glycine sodium molybdate crystals grown in the present work. Investigation on the growth and structural, optical, mechanical, thermal behavior, surface morphology and NLO properties of the grown crystal was carried out; the obtained results are also discussed.

2. Experimental procedure

The starting materials glycine (Merck) and sodium molybdate (Merck) were taken in the stoichiometric ratio 3:1. Estimated quantities of salts were dissolved in double distilled water and stirred well at room temperature using a magnetic stirrer. Tri-glycine sodium molybdate (TGSM) salt was synthesized according to the reaction:

$$\underset{\text{(glycine)}}{3[C_2H_5NO_2]} + \underset{\text{(sodium molybdate)}}{[Na_2(MoO_4)]} \rightarrow \underset{\text{(TGSM)}}{[Na_2Mo(C_2H_5NO_2)_3O_4]}$$

2.1. Solubility

TGSM was purified several times by recrystallization in deionized water. The solubility of pure TGSM in deionized water was assessed as a function of temperature in the range 35–50 °C. The saturated solution was kept in a constant temperature bath and allowed to reach the equilibrium at a chosen temperature and then the solubility was gravimetrically analyzed. The same process was repeated for different temperatures and the solubility curve was obtained. The solubility curve is shown in Fig. 1. The solubility increases linearly with increase of temperature.

2.2. Crystal growth

The growth of tri-glycine sodium molybdate single crystal was carried out by slow evaporation technique. Sodium molybdate and glycine were taken as raw material. TGSM solution was prepared at room temperature with water as a solvent. The solution was filtered using high quality Whatmann filter paper to remove the insoluble and unwanted impurities. The prepared solution was taken in a beaker and closed with perforated covers and kept in a clean and dust free atmosphere. Fine crystal of size $2.3 \times 1 \times 0.5\,cm^3$ was grown in a period of 30 days. The grown crystal of TGSM is shown in Fig. 2.

3. Results and discussion

3.1. X-ray diffraction studies

The grown crystals were crushed to a uniform fine powder and were subjected to powder X-ray diffraction using PANalytical X'pert pro powder diffractometer. The Cu Kα radiations (λ = 1.5406 Å) from a copper target were used. The fine powder was scanned in the reflection mode in the 2θ range 10–60° with four decimal accuracy. Fig. 3 represents the powder diffractogram and $(h\,k\,l)$ values of the TGSM crystals. The position of the peaks in the TGSM crystals was found to be in good agreement with the data of pure glycine available in JCPDS files (card no.: 502131) thereby confirming the incorporation of sodium molybdate in the grown crystal. Some planes, which are missing in the pure glycine pattern, are now occupied by sodium molybdate atoms. Hence new pattern was produced in addition of glycine with sodium molybdate. The prominent well-resolved Bragg's peak at specific 2θ angle reveals the high crystalline nature of the crystal. No other secondary phases were found in the diffraction pattern, which shows the high crystalline nature of the TGSM crystal.

Single crystal X-ray diffraction analysis was carried out with the help of single crystal X-ray diffractometer CAD4/MACH 3. Single crystal X-ray diffraction suggests that the crystal belongs to triclinic

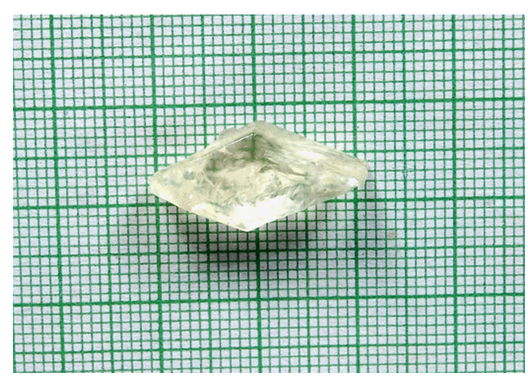

Fig. 2. Grown crystal of tri-glycine sodium molybdate.

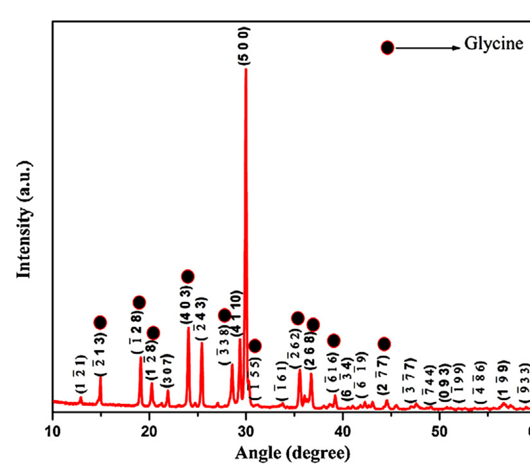

Fig. 3. Powder X-ray diffraction pattern of tri-glycine sodium molybdate.