Synthesis and Evaluation of New Semi-Organic Non-Linear Optical L-Glutamic Acid Manganese Chloride (LGAMC) Crystal for Frequency Conversion Applications

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Abstract

In this Work, L-Glutamic acid manganese chloride (LGAMC) semi-organic nonlinear optical crystal has been grown by slow evaporation technique. Crystal structure and essential functional groups of LGAMC crystal were confirmed by single crystal XRD and FTIR analyses. Thermal stability and surface trait were determined by using TG/DTand SEM analyses. Linear optical studies revealed the lower cut-off wavelength at 244 nm in transparency UV-Visible region. Mechanical behavior of the crystal was analyzed by microhardness test which indicates that the hard category material. From photoluminescence spectrum, a sharp emission peak was observed at 532 nm which demonstrates that the grown crystal has good nonlinear optical behavior. The SHG efficiency of LGAMC crystal was found to be 1.3 times superior than well-known reference KDP crystal.

Introduction

Recently, nonlinear optical crystal materials are technologically important because of their applications such as data storage device, frequency converters, optoelectronics, optical communication and lasers [1-3]. Organic nonlinear optical crystals like L-valinium picrate, L-Valine and L-valinium succinate, triphenyl methane, etc., were displayed good nonlinear optical properties which indicates that the wide attention in the field of frequency conversion application [4, 6]. Moreover, inorganic counterparts such as KBBF (Potassium Fluoro Borate Beryllate), BCB (Barium Calcium Borate) crystals showed the large thermal and mechanical stability, high transmittance properties in UV and visible region and low nonlinear efficiency [7, 8].

Now a days, amino acid families are discovered an important class of nonlinear optical semi-organic crystal of organic material combined with mechanical and thermal properties of inorganic materials [9-12]. Furthermore, Amino acids-based complexes as were reported as a potential candidate crystal for frequency conversion applications. Among them, L-arginine complexes have been examined as very good nonlinear optical materials [13-20].

Also, Amino acid complex are more suitable for synthesis of nonlinear optical crystal because of their dipolar nature which contains donor (COOH and acceptor (NH₂) group recognized as Zwitterions are responsible for hydrogen bonding in the system [21]. Amino acid based semi-organic NLO complexes such as L-Glutamic acid Hydrochloride [22], L-Histidine Hydrochloride [23], L-Glutamic Hydrobromide [24] revealed better thermal, mechanical stability and high transparency in visible region. Among these materials, L-Glutamic acid is an interesting and suitable molecule phase NLO material because of its high transparency in the ultra violet region [25].

L-glutamic acid belongs to acidic carboxyl group and it is an active chromophore to reveal the NLO property [26]. In this point of view, we report the synthesis of amino acids of semi-organic NLO crystal L-Glutamic acid manganese chloride (LGAMC) crystal by solution growth growth method through the slow
evaporation technique at ambient room temperature. Structural, optical, thermal and mechanical properties of the grown LGAMC crystal were analyzed, which showed the very suitable candidate crystal material for frequency conversion applications.

**Experimental**

2.1. Synthesis of LGAMC crystal

Commercially accessible L-glutamic acid salt (AR grade with 99.8% of purity) and manganese chloride (AR grade with 99.9% of purity) were taken 1:1 equimolar ratio and mixed with Millipore water as solvent at ambient room temperature. Figure 1 show the molecular reaction scheme of LGAMC.

\[ \text{HO}_2\text{CCH}_2\text{CH}_2\text{CH(NH}_2\text{)CO}_2\text{H} + \text{MnCl}_2 \rightarrow \text{Mn}[\text{HO}_2\text{CCH}_2\text{CH(NH}_2\text{)CO}_2\text{H}]\text{Cl}_2 \]

L-Glutamic acid + Manganese chloride → L-Glutamic acid Manganese chloride

2.2. Growth of LGAMC crystal

L-Glutamic acid was first dissolved in double distilled water, subsequently manganese chloride was added slowly to the above solution and stirred continuously for 6 hrs to get the homogeneous solution. After that, the resulting solution was filtered twice to confine the fast evaporation by using good quality perforated polythene sheet. It’s kept at room temperature in a dust free compartment for slow evaporation. Optically good transparent tiny crystals with 9 x 2 x 2 mm^3 dimension were harvested within a period of 100 days. Figure 2 shows the LGAMC crystal has needle shape with good transparency and their growth conditions are given in Table 1.

| Technique                        | Slow evaporation          |
|----------------------------------|---------------------------|
| Solvent                          | Double distilled water    |
| L-Glutamic acid & manganese chloride | 1:1 molar ratio           |
| Temperature                      | Room temperature          |
| Period of crystal grown          | 100 days                  |
| Size                             | 9x2x2 mm^3                |

**Characterization**

Crystal structure of LGAMC was analyzed by using P analytical X’pert-PRO powder X-ray diffractometer. Molecular structure and cell parameters values of grown LGAMC crystal were determined by ENRAF
Results And Discussion

4.1. Single Crystal X-Ray Diffraction

LGAMC crystal belongs to orthorhombic crystal system with lattice parameter \( a = 5.20\text{Å}, b = 6.99\text{Å}, c = 17.58\text{Å} \) and volume \( = 547.23\text{Å}^3 \) were confirmed by single crystal XRD analysis. Figure 3 shows the packing structure of LGAMC crystal and three dimensional ORTEP diagram of LGAMC crystal has shown in Figure 4.

4.2 Powder X-Ray Diffraction Analysis

In order to understand the crystalline nature of the LGAMC crystal was examined by the powder XRD analysis. Figure 5 shows the XRD pattern was recorded in the range from \( 10^\circ \) to \( 80^\circ \) at the scan rate of \( 2^\circ/\text{min} \) with \( \lambda = 1.5490 \times 10^{-10} \text{m} \) radiation. The fine defined Bragg peaks at specific \( 2\theta \) angles confirmed the admirable crystalline nature of the L-Glutamic acid manganese chloride (LGAMC) crystal.

4.3 FT-IR Analysis

Functional groups of the obtain compound of LGAMC crystal was identified by using the FT-IR analysis. Figure 6 shows the FT-IR spectrum was recorded in the range of \( 4000 – 400 \text{ cm}^{-1} \). The sharp absorption peak was observed at \( 544 \text{ cm}^{-1} \) assigned to COO-waging. The presence of COO\(^-\) reveals that plane deformation and it was confirmed from the peak at \( 714 \text{ cm}^{-1} \). The peak observed at \( 806 \text{ cm}^{-1} \) corresponds to O-H implanted formation. The O-H bending vibration was observed at \( 942 \text{ cm}^{-1} \). The C-H and O-H bending modes of vibration are observed at \( 1517 \text{ cm}^{-1} \) and \( 1635 \text{ cm}^{-1} \) respectively. The peak of O-H stretching modes of vibration is assigned at \( 2653 \text{ cm}^{-1} \) and \( 2741 \text{ cm}^{-1} \). The obtained peaks with corresponding wave number are given in the Table 2.

Table 2 FT-IR functional group assignments of the grown LGAMC crystal
| Wavenumber (cm\(^{-1}\)) | Assignments         |
|--------------------------|----------------------|
| 544                      | COO-Waging           |
| 714                      | COO-plane deformation|
| 806                      | O-H plane deformation|
| 942                      | O-H Bending          |
| 1517                     | C-H Bending          |
| 1635                     | N-H Bending          |
| 2653                     | O-H Stretching       |
| 2741                     | O-H Stretching       |

4.4 Optical Transmittance Studies

The optical transmittance spectrum is essential characterization because the crystal may be used for
device application based on the transparent region. The UV-Vis-NIR transmission spectrum of the LGAMC
crystal was recorded from 200 nm to 800 nm as shown in the Figure 7. The LGAMC crystal possesses
good transparency about 96 % and having lower cutoff wavelength at 244 nm. Lower cutoff wavelength
value with high transparency region of LGAMC implies that it is suitable for frequency conversion
applications and fabrication of optoelectronic devices.

4.6 Microhardness Studies

The mechanical property of L-Glutamic acid manganese chloride crystal was examined by using the
Vickers diamond pyramid indenter. The hardness of the material is a measure of its resistance to local
defection \cite{27}. Vicker's microhardness number (H\(_{\nu}\)) was calculated using the following relation.

\[
H_{\nu} = 1.8544 \left( \frac{P}{d^2} \right) \left( \frac{Kg}{(mm)^2} \right) \quad (1)
\]

Where, ‘P’ is the applied load (kg), ‘d’ is the mean diagonal length of the indentation (mm).

A graph was plotted between the hardness numbers (H\(_{\nu}\)) and the applied load (P) as shown in Figure 8.
From the graph, it is observed that the hardness value increases with the increasing load. The variation of
microhardness values with the applied loads were varied from 25 to 100 g. Meyer’s law\cite{28} relates to load
and size of indentation.

\[
P = ad^n \quad (2)
\]

\[
\log P = \log a + n \log d \quad (3)
\]
Where P is the applied load, d is the diagonal length of impression, 'a' is the constant for a given material. The work hardening coefficient (n) was estimated by plotting the graph between log P and log 'd' as shown in Figure 9. By applying the least squares fit method, the value of 'n' was calculated as 1.18. According to Onitsch [29], the value of work hardening coefficient ‘n’ could be 1 and 1.6 which implies hard materials and more than 1.6 indicates materials category. Therefore, the grown LGAMC crystal belongs to hard category material.

4.9 Second Harmonic Generation

NLO property (SHG efficiency) of LGAMC crystal was implemented by Kurtz and Perry technique [30]. The source of Q-switched Nd:YAG laser (wavelength 1064 nm) beam has been employed. The operating pulse of laser source was 0.70 mJ/pulse and pulse width of 6ns with the repetition rate 10 Hz. The grown single crystal of LGAMC was powdered with a uniform particle size and then packed in a micro capillary tube of uniform pore size and exposed to laser radiation. The second harmonic generation was confirmed by the emission of bright green light (λ=532nm) from the specimen. The observed SHG efficiency of the as grown LGAMC crystal was found to be 1.2 times greater than that of reference KDP.

4.7 Fluorescence Studies

Photoluminescence study is a contact less, non-destructive method of probing the electronic structure of materials [31]. Figure 10 shows the emitted spectrum was measured in the range of 280-900 nm. A high sharp intense peak in the spectrum was observed at 532 nm which concludes that the LGAMC exhibits bright green emission fluorescence [32]. The band gap energy at this wavelength was calculated using the formula,

\[ E_g = \frac{hc}{\lambda_e} \quad (4) \]

Where, the parameters of h, c, \( \lambda \) are constants and \( \lambda \) is the wavelength of fluorescence. The band gap for LGAMC was estimated to be 2.32eV [33].The wide band gap of LGAMC has large transmittance window and low absorption which confirms that this material suitable for nonlinear optical applications.

4.8 TG/DTA analysis

Thermal analysis is used for determining the thermal stability and behavior of the sample with temperature [34]. Thermo Gravimetric (TG) and Differential Thermal (DT) analyses were carried out for the LGAMC crystal using a STA differential thermal analyzer. The sample was tested in the temperature range of 50- 500° C with an inert nitrogen atmosphere at a heating rate of 20°C/min. The obtained TGA and DTA curve is shown in Figure 11. Two peaks were observed from DTA analysis, one exothermic peak was obtained at 105°C due to the presence of chlorine in the sample which may decompose and another peak endothermic observed at 217.8°C because of L-Glutamic acid gets melted. Also, the corresponding weight loss observed from TGA curve was around 5%. The sample has residual 30% which may due to
manganese. Hence, the grown sample was thermally stable around 217.8°C. TG/DTA analysis indicates that good crystalline nature of the LGAMC crystal.

4.9 SEM analysis

The scanning electron microscope was subjected to analyze surface morphology, grain size and composition of the crystal in the crystal surface. The different magnification of SEM images of the LGAMC crystal was shown in Figure 12. The crystalline surface shows the regular and linear pattern structure of layered by layer surface and fine particles presented.

Conclusion

Optically good transparent semi-organic crystal of L-GLutamic acid Manganese chloride was successfully grown by slow evaporation method at room temperature. Lattice parameter, crystal system were confirmed by single crystal X-ray diffraction. A good crystalline nature of LGAMC was confirmed by powder XRD analysis. Functional groups of the grown crystal were identified by FT-IR analysis. Lower cut-off wavelength was found to be 244nm in the UV region by UV-Vis-NIR spectral analyzer. The smooth surface morphology was investigated by SEM analysis. Mechanical properties were determined by Vickers microhardness test. LGAMC material exhibits green fluorescence emission at 532.01nm. Thermal property of LGAMC was examined by DTA/TGA analysis. SHG efficiency of the grown LGAMC crystal is found to be 1.2 time that of KDP. Hence, as grown LGAMC crystal is conventionally use to another inorganic KDP material.

Declarations

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Figures
Figure 1

Reaction scheme of LGAMC

Figure 2

Photograph of as-grown LGAMC crystal
Figure 3

Packing structure of LGAMC crystal

Figure 4
Packing structure of 3D ORTEP diagram of grown crystal

Figure 5

Powder X-ray diffraction analysis of LGAMC crystal

Figure 6

FT-IR spectrum of LGAMC crystal
Figure 7

Transmission spectrum of LGAMC crystal

Figure 8

Plot of Load P vs Hardness (Hv) of LGAMC crystal
Figure 9

Plot of log 'P' vs log 'd' of LGAMC crystal

Figure 10

Emission spectrum of LGAMC crystal
Figure 11

TGA-DTA graph of LGAMC crystal
Figure 12

SEM images of LGAMC indifferent magnification