Available online at http://www.journalcra.com

International Journal of Current Research
Vol. 7, Issue, 07, pp.18401-18405, July, 2015

INTERNATIONAL JOURNAL OF CURRENT RESEARCH

ISSN: 0975-833X

RESEARCH ARTICLE

STUDIES OF MAGNESIUM CHLORIDE AND RHODAMINE-B DOPED L-HISTIDINE ACETATE CRYSTALS GROWN BY SOLUTION METHOD

[1]Shanmugam, P., [1,*]Pari, S., [1]Kathiravan, V., [2]Madhavan, J. and [3]Selvarajan, P.

[1]Department of Physics, National College, Tiruchirapalli, India
[2]Department of Physics, Loyola College, Chennai, India
[3]Deparment of Physics, Adriana College of Arts and Science, Tiruchendur, India

ARTICLE INFO

Article History:
Received 16th April, 2015
Received in revised form
21st May, 2015
Accepted 10th June, 2015
Published online 31st July, 2015

Key words:
L-histidine acetate;
Doping; Bulk crystals;
Growth from solutions;
XRD; Spectroscopy;
NLO; SHG.

ABSTRACT

Salts of magnesium chloride and rhodamine-B doped L-histidine acetate (LHA) were synthesized and single bulk crystals were grown at room temperature (30 °C) by solution method. The grown crystals are observed to be stable, non-hygroscopic, transparent and all the crystals are colourless except rhodamine-B doped L-histidine acetate. Rhodamine-B doped LHA crystals are slightly pink in colour and it reveal the incorporation of Rhodamine-B into the host LHA crystal. By XRD method, it is found that the crystal structure of the doped LHA crystals has not been altered. The relative second harmonic generation (SHG) efficiency was estimated by powder Kurtz-Perry technique. The grown crystals were excited with UV light to get the photoluminescence light output at different wavelengths. Microhardness values have been evaluated by Vickers hardness test. Dielectric parameters such as dielectric constant and dielectric loss of the samples were measured at different frequencies at room temperature. The optical band gap and the transparency of the samples have been determined by UV-visible transmittance studies.

Citation: Shanmugam, P., Pari, S., Kathiravan, V., Madhavan, J. and Selvarajan, P. 2015. "Studies of magnesium chloride and Rhodamine-B doped L-histidine acetate crystals grown by solution method", *International Journal of Current Research*, 7, (7), 18401-18405.

INTRODUCTION

Amino acids and their complexes have been subjected to many studies by several researchers and a series of amino acids such as glycine, L-alanine, L-histidine, L-threonine etc have been considered for NLO and other applications (Marder *et al.*, 1991; Eimerl, 1989; Marcy *et al.*, 1955; Rodrigues *et al.*, 2003 and Lucia Rose *et al.*, 2011). Histidine is an essential aromatic amino acid for infants, adult humans and mammals and it consists of an imidazole functional group. The imidazole side chain of histidine is a common coordinating ligand in metalloproteins and is a part of catalytic sites in certain enzymes. L-histidine is an alpha amino acid important for growth and repair of tissues and it is necessary for the maintenance of myelin sheaths, which protect nerve cells, and the production of red and white blood cells (Madden *et al.*, 1972). L-histidine acts as an antioxidant protecting against radiation damage by helping to remove heavy metals from the body.

L-histidine combines with many organic and inorganic salts to form novel NLO materials (Silva *et al.*, 2004; Marchewka *et al.*, 2003; Espinosa *et al.*, 1997 and Ratajczak *et al.*, 2000). Mostad *et al.* synthesized and solved the crystal structure of L-histidine acetate (Mostad *et al.*, 1995). It has been reported that doping NLO crystals like L-histidine acetate with organic and inorganic impurities can alter various physic-chemical properties (Praveen Kumar *et al.*, 2008; Krishnan *et al.*, 2008; Goma *et al.*, 2006 and Kumaresan *et al.*, 2008). In this work, L-histidine acetate crystals are doped with magnesium chloride and rhodamine-B to modify the properties of the host crystals. Solution method was adopted to grow the crystals of magnesium chloride and rhodamine-B doped L-histidine acetate and the harvested crystals were subjected to various studies.

Experimental

Synthesis

Analar Reagent (AR) grade of L-histidine and acetic acid in the molar ratio of 1:1 were used for synthesis of L-histidine acetate (LHA) salt. The calculated amounts of L-histidine and

---

***Corresponding author: Pari, S.,**
Department of Physics, National College, Tiruchirapalli, India

acetic acid were dissolved in double distilled water and stirred well using a magnetic stirrer for about 3 hours. The solution was heated until the synthesized salt of L-histidine acetate salt was obtained. To obtain magnesium choride doped LHA sample, 10 wt% of magnesium chloride was added to the solution of LHA and for getting rhodamine-B doped LHA salt, 10 wt% of rhodamine-B was added to the solution of LHA.

Growth of single crystals

Pure (undoped), magnesium chloride and rhodamine-B doped L-histidine acetate crystals were grown by solution method with slow solvent evaporation technique. Saturated solutions of the synthesized salts were prepared separately and the solutions were constantly stirred for about 2 hours using a magnetic stirrer and were filtered using 4 micro Whatmann filter papers. Then the filtered solutions were kept in borosil beakers covered with porous papers and kept in a dust-free atmosphere. The crystals were harvested after a period of about 30 days and the harvested crystals are displayed in the Figure 1. The grown crystals are observed to transparent and hygroscopic. The morphology of LHA crystals were observed to be modified when they are doped with magnesium chloride and rhodamine-B.

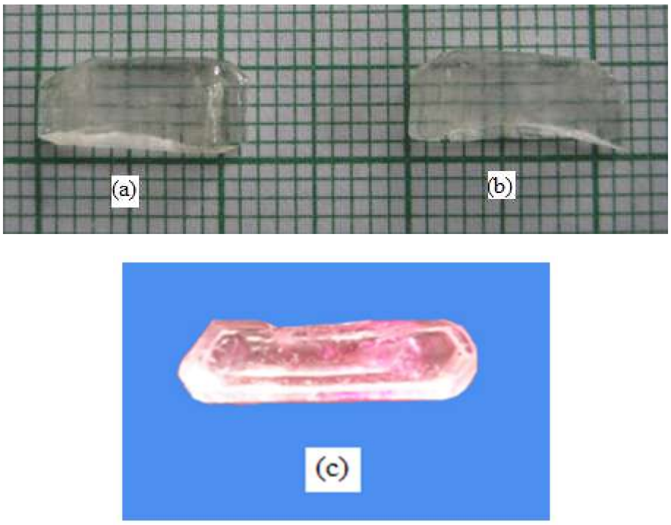

Figure 1. Grown crystals of (a) undoped , (b) magnesium chloride doped and (c) rhodamine-B doped L-histidineacetate crystals

Analyzing techniques

The grown single crystals were subjected by single crystal XRD studies using an ENRAF NONIUS CAD4 diffractometer with MoK_α radiation (λ=0.71073 Å). Second Harmonic Generation (SHG) test for the grown pure, magnesium chloride and rhodamine-B doped LHA crystals was performed by the powder technique of Kurtz and Perry (Kurtz and Perry, 1968) using a pulsed Nd: YAG laser (Model: YG501C, λ=1064 nm). Pulse energy of 4 mJ/pulse, pulse width of 10 ns and repetition rate of 10 Hz were used. The grown crystals were ground to powder of grain size 300- 400 μm and the input laser beam was passed through IR reflector and directed on the powdered sample packed in a capillary tube. Mirocrystalline material of KDP was used as reference in this experiment. A Varian Cary 5E UV-Visible-NIR spectrophotometer was used for spectral transmission studies. A crystal thickness of about 1.5 mm was used for transmission studies. Microhardness hardness study of the grown crystals was carried out using Leitz Weitzler hardness tester fitted with a diamond indenter. Smooth, flat surface was selected and subjected to this study on the (001) plane of the samples. Indentations were made for various loads from 25 g to 100 g. Several trials of indentation were carried out on the prominent face and the average diagonal lengths were measured for an indentation time of 10 seconds. The Vickers microhardness number was calculated using the relation $Hv = 1.8544\ p/d^2\ \mathrm{kg/mm^2}$ where p is the applied load and d is the diagonal length of the indentation impression (Lucia Rose *et al*., 2011). The photoluminescence spectra were recorded for the grown crystals in the range of 260–700 nm with the excitation wavelength of 240 nm using a Perkin-Elmer photoluminescence spectrometer (Model: LS45). The measurements of dielectric constant and dielectric loss for the grown crystals were carried out using an LCR meter (Agilent 4284A) at various frequencies in the range 10^2 - 10^6 Hz at 30°. For the good ohmic contact, opposite faces of the sample crystal were coated with good quality silver paint.

RESULTS AND DISCUSSION

Determination of crystal structure

The crystal structure of the grown crystals was found by single crystal X-ray diffraction studies. The instrument used to carry out single crystal XRD studies was a single X-ray diffractometer Bruker-Nonius MACH3/CAD4). The obtained crystallographic data are provided in the Table 1. The crystal structure of the all the three samples is found to be triclinic. It is noticed from the results that there is no change of crystal structure and there is a slight alteration in the lattice parameters when LHA is doped with magnesium chloride and rhodamine-B. The dopants seem to be occupying the interstitials of lattice of doped LHA crystals and slight changes in the values of unit cell parameters are observed in this work.

Table 1. Lattice constants for pure and doped LHA crystals

Sample	Unit cell constants
Pure LHA crystal	a = 8.521(2) Å b = 9.058(1) Å c =9.023(2) Å α = 60.20(1)°, β= 86.55(2)° γ =85.97(2)°
LHA crystal + 10 wt % of magnesium chloride	a = 8.629(4) Å b = 9.102(2) Å c = 9.028(1) Å α = 60.28(2)°, β= 87.02(3)° γ =85.12(2)°
LHA crystal + 10 wt% of rhodamine-B	a =8.517(3) Å b = 8.995(3) Å c = 9.198 (4) Å α = 59.12(4)°, β= 85.48(3)° γ =86.24(1)°

Optical transmittance

Optical transmittance and other optical constants are determined from the UV-visible spectra and they are assisted in understanding electronic structure of the samples. UV-Visible transmittance spectra of pure and doped LHA crystals were recorded in the range 200-1100 nm covering the near UV, visible, near infrared region. UV-visible-NIR transmittance spectra of the samples are displayed in the Figure 2. From the results, it is noticed that pure and magnesium chloride doped LHA crystals have high transmittance in the entire visible-NIR region of the spectra and rhodamine-B doped LHA crystal has an absorption at 390 nm and this is due to pink colouration of the crystal. A sharp fall in the transmittance is observed at 254 nm for all the three samples and this is due to fundamental absorption. The band gap value is found to be 4.88 eV and this is same for undoped and doped LHA samples. It is observed that the transmittance values are reduced when LHA are doped with magnesium chloride and rhodamine-B.

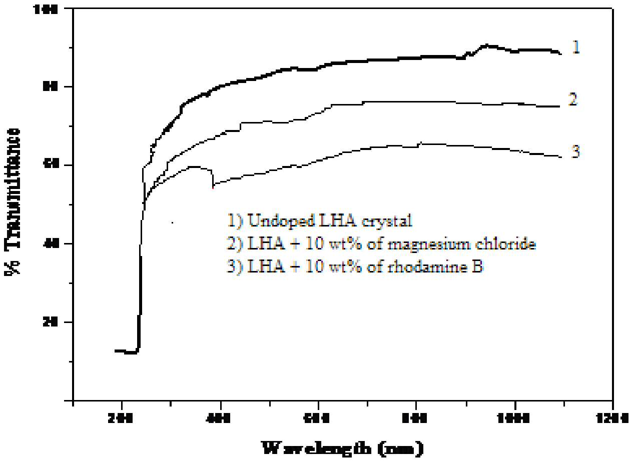

Figure 2. Optical transmittance spectra for pure and doped LHA crystals

Mechanical properties

The Mechanical properties of the grown crystals have been studied using LEITZ microhardness tester, fitted with a Vickerss diamond pyramidal indenter. A well polished crystal has been placed on the platform of Vickers microhardness tester and the loads of different magnitudes have been applied in a fixed interval of time.

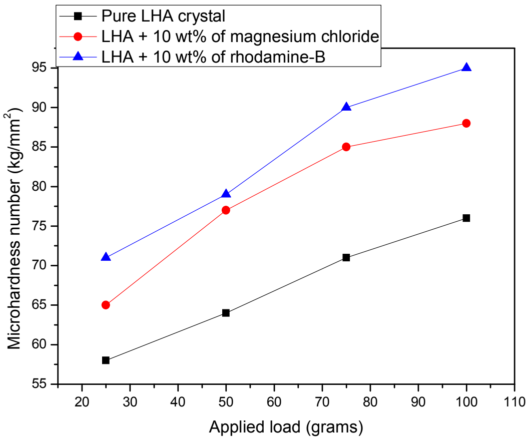

Figure 3. Load dependence of hardness for pure and doped L-histidineacetate crystals

The indentation time has been kept 10 seconds for all the loads. Vickers microhardness values have been calculated by using the formula Hv = 1.8544 p/d^2 kg/mm^2 where Hv is the Vickers microhardness number, p is the applied load in kg, d is the mean diagonal length of the indentation impression in mm and 1.8544 is a constant of a geometrical fraction for the diamond pyramid. A graph has been plotted between hardness number and applied load and it is shown in Figure 3. At lower loads there is an increase in the hardness with load, which can be attributed to the work hardening of the surface layers. At higher loads, the 'H_v' shows the tendency to saturate. Beyond the load of 100 gm significant cracking occurs which may be due to the release of internal stresses generated locally by indentation.

Measurement of photoluminescence

Photoluminescence (PL) in solids is the phenomenon in which electronic states of solids are excited by light of particular energy and the excitation energy is released as light. The photon energies reflect the variety of energy states that are present in the material. The photoluminescence spectra of magnesium chloride and rhodamine-B doped L-histidine acetate crystals are shown in the Figures 4 and 5.

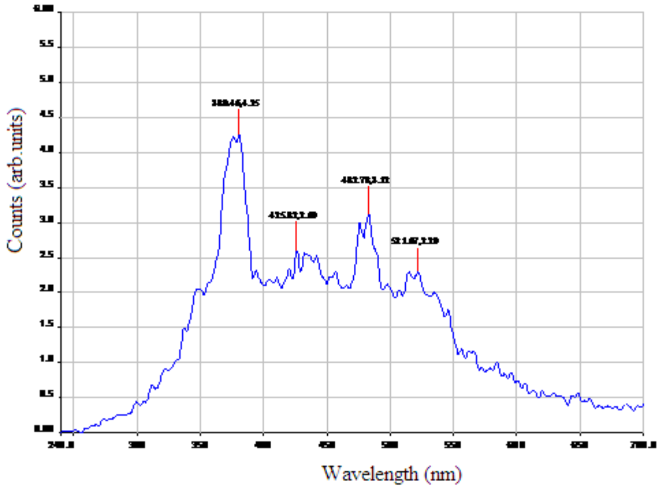

Figure 4. PL spectrum for magnesium chloride doped L-histidineacetate crystal

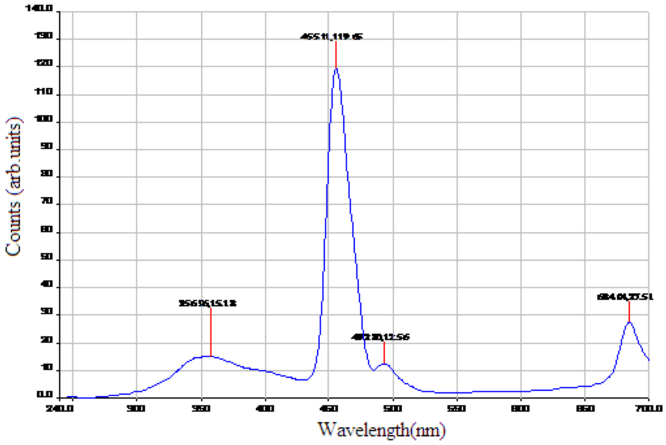

Figure 5. PL spectrum for rhodamine-B doped L-histidineacetate crystal

Figure 4 consists of four emission bands: a strong UV emission band at 382 nm, a strong blue band at 435 nm, and a weak blue band at 482 nm and a green band at 521 nm. The PL spectrum of rhodamine-B doped LHA crystal consists of four emission bands viz. a strong UV band at 356 nm, a strong blue band at 455 nm, a weak blue band at 482 and a red band at 684 nm. From the results, it is confirmed that the grown crystals are photo luminescent materials when they are excited with UV light of wavelength 240 nm.

Measurement of dielectric constant and dielectric loss

Every material has a unique set of electrical characteristics that are dependent on its dielectric or insulation properties. Accurate measurements of these properties can provide valuable information to ensure an intended application or maintain a proper manufacturing process. Dielectric constant measurements can be performed easier and faster than chemical or physical analysis techniques making them an excellent material analysis tool. The dielectric constant and the dielectric loss for different frequencies at room temperature are shown in Figures 6 and 7.

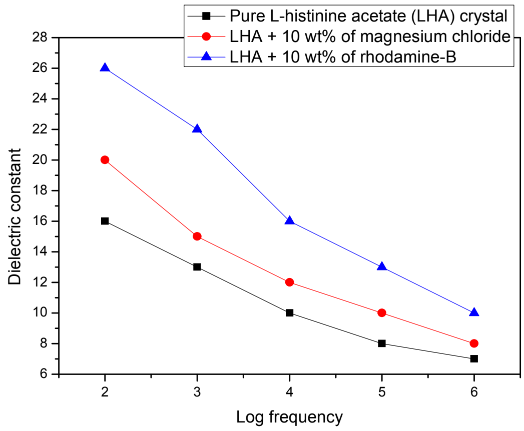

Figure 6. Frequency dependence of dielectric constant for pure, magnesium chloride and rhodamine-B doped L-histidineacetate crystals

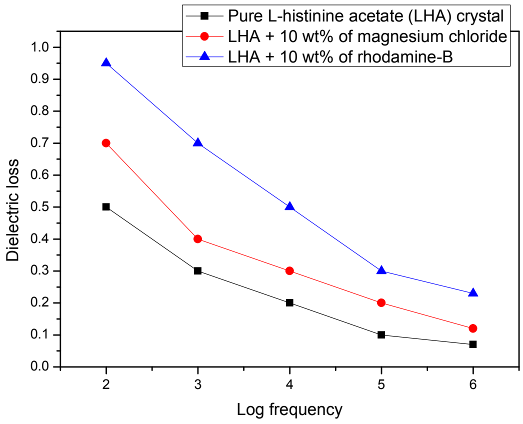

Figure 7. Frequency dependence of dielectric loss for pure, magnesium chloride and rhodamine-B doped L-histidineacetate crystals

The values of dielectric constant and dielectric loss decrease with increase in frequency. In general the variations in dielectric constant with frequency suggest the presence of higher space charge polarization of the material in the low frequency region and the decrease in polarization leads to the reduction in dielectric constant. The space charge polarization depends on the purity and perfection of the material and its influence is noticeable in the low frequency region. The orientational polarization can sometimes be seen in some materials even up to 10^{10} Hz. Ionic and electronic polarizations exist below 10^{13} Hz. At higher frequencies, the values of dielectric constant and loss are low because molecules of larger relaxation times may not be able to respond to these higher frequencies. The lower value of dielectric constant at high frequencies may be due to the loss of polarizations gradually and is important for these materials in the construction of photonic and NLO devices. It is also noticed that the values of dielectric loss decrease with increase in frequency for the samples and the low value of dielectric loss indicates that the grown crystals are of good quality dielectrics. Again the material with low dielectric constant will have less number of dipoles per unit volume. As a result it will have minimum loss as compared to the material with high dielectric constant. It suggests that the dielectric loss strongly depends on the frequency of the applied field, which is similar to the dielectric constant in the ionic system (Krishnan *et al*., 2009).

SHG efficiency

The analysis of second-order nonlinearity like second harmonic generation (SHG) of the grown crystals was performed by Kurtz powder method. The single crystals were powdered and were irradiated by an incident radiation (1064 nm) of pulse width 8 ns from a Q-switched quanta RAY GCR Nd: YAG laser. KDP was used for calibrating the SHG intensity. A concave mirror, collimated and focused onto the monochromator slit collected the SHG emitted from the crystal sample**.** The output power of the crystal was measured using a power meter and the error in the measured SHG was typically about 5-10%. The NLO property of the crystal was confirmed from the estimation of strong green radiation of the crystal. The obtained data of SHG efficiency of the grown crystals are summarized in Table 2.

Table 2. Relative SHG efficiency of pure and doped LHA crystals

Sample	Relative SHG efficiency (Ref.: KDP)
Pure LHA crystal	1.37
LHA crystal + 10 wt % of magnesium chloride	1.45
LHA crystal + 10 wt% of rhodamine-B	1.74

Conclusions

Pure, magnesium chloride and rhodamine-B doped L-histidine acetate crystals were grown by the slow solvent evaporation technique. The X-ray diffraction studies confirm the triclinic structure the grown crystals. Optical transmittance study shows that the grown crystals have wide transperency window from 200 to 1100 nm, which highlights the prospects of applications in the NLO devices. The powder relative SHG efficiency of the samples has been found by Kurtz powder technique. Vickers microhardness was calculated in order to understand the mechanical strength of the grown crystals. The measurements of dielectric constant and dielectric loss reveal that the grown crystals of this work have low dielectric constant and loss factor which leads to applications in electro-optic applications. The photoluminescence studies confirm that the samples are excellent photoluminescent materials.

REFERENCES

Eimerl, D. 1989. IEEE J. Quantum Electron QE 25, 179.

Espinosa, E., B. Wyncke, F. Brehat, X. Gerbaux, S. Veintemillas, E. Molins, 1997. *Infrared Physics Technol*. 38, 449.

Goma, S., C.M. Padma, C.K. Mahadevan, 2006. *Materials Lett*. 60, 3701.

Krishnan, C., P. Selvarajan, T.H. Freeda, 2008. J. *Crystal. Growth* 311, 141.

Krishnan, C., P. Selvarajan, T.H. Freeda, C.K. Mahadevn, 2009. *Physica B* 404, 289–294.

Kumaresan, P., S. Moorthy Babu, P.M. Anbarasan, 2008. *Mat. Res. Bull*. 43, 1716.

Kurtz, S.K., T.T. Perry, 1968. *J. Appl. Phys*. 39, 3798–3813.

Lucia Rose, A.S.J., P. Selvarajan, S. Perumal, 2011. *Materials Chemistry and Physics* 130, 950– 955.

Lucia Rose, S.J., P. Selvarajan, S. Perumal, 2011. *Mater. Chem. Phys*. 130, 950

Madden, J.J., E.L. McGandy, N.C. Seeman, 1972. *Acta. Cryst. B* 28, 2377.

Marchewka, M.K., S. Debrus, A. Pietraszko, A.J. Barnes, H. Ratajczak, 2003. *J. Mol. Struct*. 656, 265.

Marcy, H.O., M.J. Rosker, L.F. Warren, P.H. Cunningham, C.A. Thomas, Deloach, S.P. Velsko, L.A. Ebbers, J.H. Liao, M.G. Kanatzidis, 1995. *Opt. Lett*. 20, 252.

Marder, S.R., John E. Sohn, Galen D. Stucky, 1991. Materials for Nonlinear Optics, ACS Symposium series 455, ACS, Washington, DC.

Mostad, K.A. Nystol, Chr. Romming, S. Natarajan, Z. Kristallogr, 1995. 210, 352.

Praveen Kumar, P., V. Manivannan, S. Tamilselvan, S. Senthil, Victor Antony Raj, P. Sagayaraj, J. Madhavan, 2008. *Optics Communications* 281, 2989–2995.

Ratajczak, H., J. Barycki, A. Pietraszko, J. Baran, S. Debrus, M. May, J. Venturini, 2000. *J. Mol. Struct*. 526, 269.

Rodrigues, J.J. Jr, N.M. Barbosa Neto, D.T. Balogh, S.C. Zilio, L. Misoguti, C.R. 2003. *Mendonc, Optics Communications* 216, 233–237

Silva, M.R., A.M. Beja, J.A. Paixao, 2004. *J. Fluorine Chem*. 125, 696.

****