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Research Article

SYNTHESIS AND CHARACTERIZATION OF LANTHANUM CHLORIDE DOPED L-ARGININE HYDROCHLORIDE SINGLE CRYSTAL: FOR OPTOELECTRONICS APPLICATIONS

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ABSTRACT. Amino acid derivative crystals exhibit good nonlinear and electroptics properties. L-arginine hydrochloride doped by lanthanum chloride single crystals were successfully synthesized and grown by using slow evaporation solution growth method at room temperature. The single crystal XRD analysis revealed that both 1 and 2 mol% $LaCl_3$ doped LAHCl crystals were crystallized monoclinic system with $P2_1$ space group. The EDX result confirmed that the presence lanthanum and chloride in LAHCl crystal. The UV-Vis-NIR spectral studies revealed that the crystals were transparent in the wavelength rage between 235-1100 nm and the band gap energy of pure and doped samples is found to be 5.27 eV. The SHG efficiency of the grown crystals confirmed that the NLO behavior of green color emission to offer frequency doubling process for optoelectronics application.

Keywords: *Doping, Crystal Growth, Slow evaporation, Second Harmonic Generation*

INTRODUCTION

Crystal growth is an essential part of materials science and engineering. Fundamental aspects of crystal growth as well as systematic description of crystals had been derived from early crystallization experiments in the 18th and the 19th century. The preparation of crystals in laboratories for technical applications is called crystal growth [1, 2]. The methods of growing single crystals may be classified into three main types based on their phase transformation such as melt, vapour and solution growth methods. Among them slow evaporation solution growth method is currently widely used for growing single crystals because it is simplest, cost effective method [3]. Crystals possessing NLO properties are capable of producing higher values of the original frequency and find applications in optical modulation, fiber optic communication and optoelectronics [4, 5]. Therefore there is a need to produce high efficiency single crystals of NLO material. Currently, Researchers has given much attention in crystal growth on semi-organic crystals which enhance the nonlinear optical properties. Due to the familiar properties such as good mechanical strength, high optical transmittance, large damage threshold and chemical stability [6, 7]. That means, the organic NLO crystals with aromatic rings have attracted much attention because of their wide transparency range, high damage threshold, fast optical response time, and large nonlinear susceptibilities compared to inorganic crystal while inorganic crystals have better mechanical, high degree of chemical inertness and thermal properties [8]. Mainly in the outlook of those applications, organic amino acid crystals are fascinating because they have a paired donor carboxylic (COOH) group and proton acceptor (NH2) group recognized as a zwitterion, which creates hydrogen bonds. This form of dipolar nature of amino acids demonstrates to be a perfect candidate for those applications [6]. L-arginine is an α -amino acid and such types of crystalline materials are mostly used as a laser frequency doubler and electro-optic modulator [9]. Following this synthesis and characterization of series of amino acid single crystals such as L-arginine phosphate [10], L-Arginine Acetate [11], L-arginine monohydrochloridemonohydrate [12] and L-arginine hydrochloride [13] were reported. L-arginine hydrochloride is one of the most semi-organic NLO materials which crystallize non-centrosymmetric space group which is the basic criteria for a material to exhibit SHG. Even so L-arginine hydrochloride is commonly reported lanthanum chloride doped L-arginine hydrochloride is rarely reported. The dopants or additives can affect the crystalline perfection which may in turn influence the physical properties depending on the degree of doping and as per the accommodating capability of the host crystal. In the presence of dopants many of the useful physical properties like optical transparency, second harmonic generation (SHG) etc. get enhance[14, 15]. In the present work, the author reports lanthanum chloride doped L-arginine hydrochloride single crystals were grown by slow evaporation solution method and the results of structural, optical, second harmonic generation (SHG) and composition studies of the grown crystals were reported.

EXPERIMENTAL PROCEDURES

Crystal Growth

Firstly, L-arginine and hydrochloric acid where taken in an equimolar ratio. A calculated amount of L-arginine was dissolving by distilled water in a beaker and placed on a magnetic hot palate regulated at 40 °C then hydrochloric acid was added. The solution was stirred continuously using a magnetic stirrer for four hours to get homogenous supersaturated solution. Then the solution was filtered by Whitman filter paper into a 300 ml beaker. Then the filtered solution was taken in a beaker, which was tightly covered by perforated sheet so that the rate of evaporation could be minimized and kept in a dust free environment. To obtain Lanthanum chloride doped L-arginine hydrochloric 1 and 2 mol% of $LaCl_3$ were added in two beakers of similarly prepared one equimolar solution of L-arginine hydrochloride. After a period of 30 days, optically transparent crystals were harvested for undoped, 1 and 2 mol% $LaCl_3$ doped L-arginine hydrochloric acid respectively (Fig. 1).

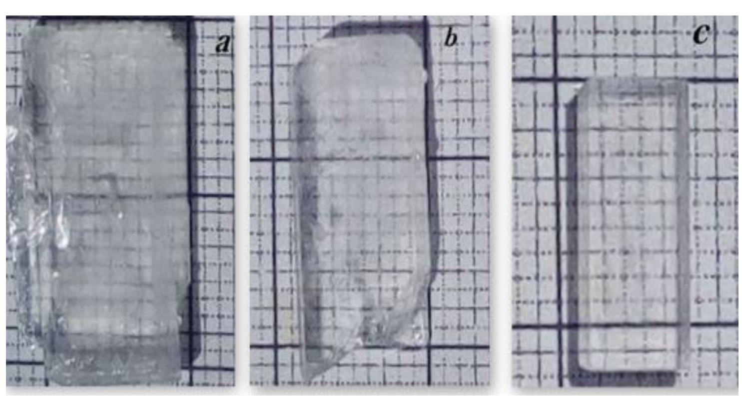

Fig.1. *Photo images of (a) undoped, (b) 1 mol% $LaCl_3$ doped and (c) 2 mol% $LaCl_3$ doped LAHCl single crystals respectively*

CHARACTERIZATION STUDIES

Single crystal X-ray diffraction studies

The grown single crystals of 1 and 2 mol% $LaCl_3$ doped LAHCl samples has been subjected to single crystal X-ray diffraction. The single crystal structures of 1 and 2 mol% of $LaCl_3$ doped LAHCl samples were examined by using a Bruker AXS Kappa APEXII single crystal CCD diffractometer equipped with graphite monochromated Mo Kα (λ = 0.07107 nm) radiation. The lattice parameters, crystal system, lattice angle and space groups of the grown single crystals are listed in the table 1. The lattice parameters are very close agreement with the corresponding reported value [12]. But there is a slight change in the lattice parameters of the doped crystals. It is may be due to lattice distortion by doping in the parent crystal. Hence, it is revealed that dopant can enter in the lattice of LAHCl without causing much distortion [16]. Both 1 and 2 mol% of $LaCl_3$ doped LAHCl crystals are satisfying one the basic and essential material requirements for the SHG activity of the crystal [17].

Table1. *Comparison of Single Crystal X-ray data of LAHCl and doped LAHCl crystals*

Parameters	Pure [12]	1mol% $LaCl_3$ +LAHCl	2mol% $LaCl_3$ +LAHCl
a(Å)	11.044	11.036	11.039
b(Å)	8.483	8.382	8.388
c(Å)	11.208	11.256	11.259
Crystal system	Monoclinic	Monoclinic	Monoclinic
β(^{0})	91.044	91.03	91.05
Space group	$P2_1$	$P2_1$	$P2_1$

Second Harmonic Generation (SHG) Test

The NLO properties of the grown crystals were tested by the Kurtz and Perry powder technique. For this analysis, a high intense Nd: YAG laser source of wavelength and energy 1064 nm and 8mJ/pluse respectively were used. The LAHCl doped by $LaCl_3$ samples, packed in a microcapillary tube in the form of very fine powder, was placed in the path of Nd-YAG laser beam [18]. KDP crystalline sample in the form of powder was used as a reference material and the beam voltage of the transmitted radiation was 12 mV. But the transmitted beam voltage through LAHCl doped by 1 and 2 mol% of $LaCl_3$ samples were measured as 15 and 18 mV respectively. The transmitted beam from the sample holder was observed in green color and the wavelength of the beam was 532 nm. The second harmonic generation is revealed by the emission of green light. Hence the SHG efficiency are 1.25 and 1.5 times greater than that of the standard KDP crystal respectively. From the results, it was observed that when LAHCl crystals were doped with $LaCl_3$, the values of SHG efficiency enhanced and found that $LaCl_3$ doped LAHCl crystals are the better candidates for optoelectronics applications [19].

UV-Vi-NIR Transmission studies

The UV-Vis-NIR transmission spectrums of the grown samples were studied by using Perkin Elmer Lambda 35 UV-VIS-NIR spectrophotometer in the wave length range of 200 – 1100 nm. The recorded spectrums of pure, 1 and 2 mol% of $LaCl_3$ doped LAHCl single crystals were shown in the fig. 2. From the spectrum observed that crystals were transparent in the wavelength range between 235-1100 nm. For optical device, the crystal should be highly transparent in the substantial region of wavelength. Hence, an efficient NLO crystal has optical transparency at lower cut-off wavelength between 200 and 400nm[20]. It shows that the transparency of the grown crystals were good in the entire UV-Visible region and it was evident that the crystals has a low cut-off wavelength at 235 nm which is appropriate for SHG laser radiation of 1064 nm for frequency doubling process and optoelectronic application [21, 22]. The absence of absorption of light in the visible region is an important property of all the amino acids. The percentage transmittances of 1 and 2 mol% of $LaCl_3$ doped LAHCl crystals are increased compared to pure LAHCl crystal. This may be suggested that the more number of point defects in LAHCl crystal that scatter as well as absorb incident light and reduced the output intensity[15]. The band gap energy was calculated using the formula $Eg = 1240/\lambda min$, where λmin is the cut-off wavelength of the light in nm[23] and it was found around 5.27 eV for pure and doped samples.

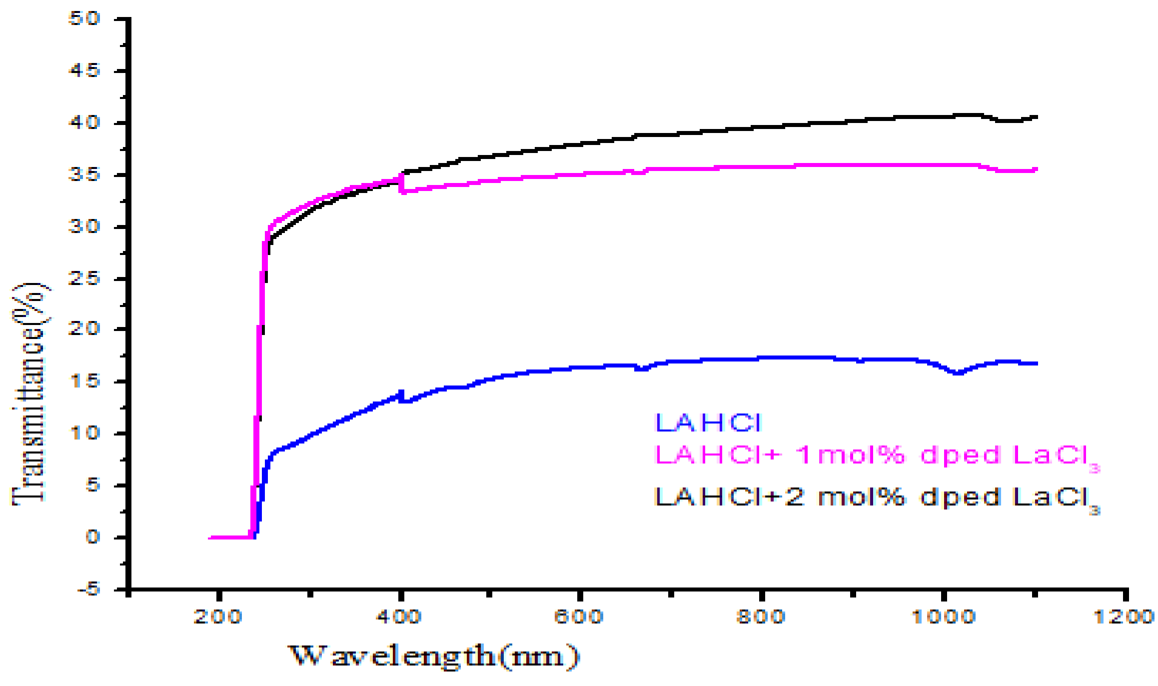

Fig.2. *Transmittance versus wavelength for pure, 1 and 2mol% of $LaCl_3$ doped LAHCl crystals*

Energy dispersive X-ray (EDX) analysis

Energy dispersive X-ray analysis is used to obtain information about the chemical composition of the grown crystal. In this study the chemical composition of the grown crystals are carried out by using JEOL-6390LV scanning electron microscope attached to EDX and it is shown Fig.3. The spectrum confirms that the presences of oxygen, lanthanum and chlorine in both 1 and 2mol% of $LaCl_3$ doped LAHCl crystal. The weight and atomic percentages of the elements are shown in table 2.

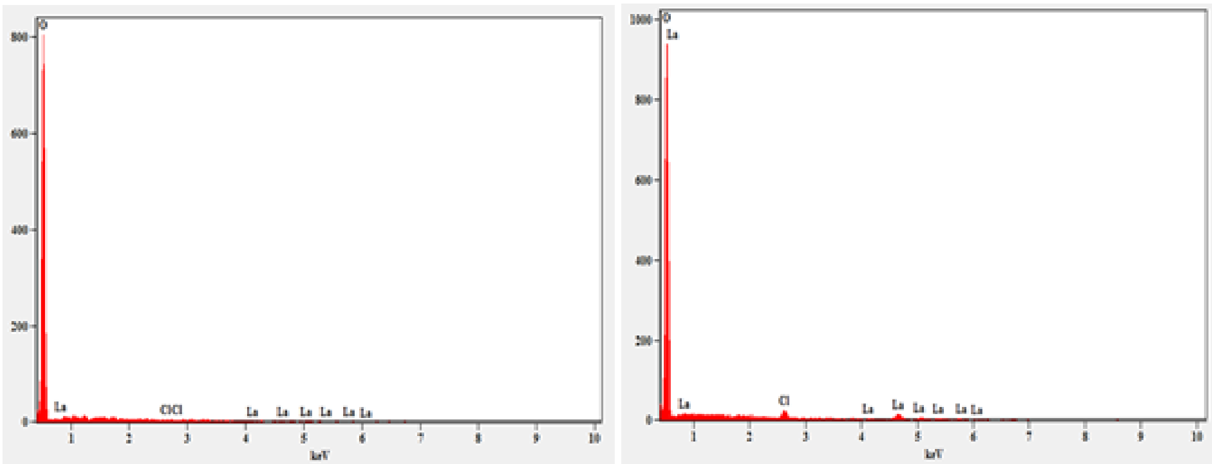

Fig.3. *EDX spectrum of 1 and 2mol% of $LaCl_3$ doped LAHCl crystals respectively.*

Table 2. *Energy dispersive X-ray analysis*

Elements	1mol% $LaCl_3$ +LAHCl		2mol% $LaCl_3$ +LAHCl	
	Weight%	Atomic%	Weight%	Atomic%
OK	89.72	89.28	82.4	83.3
ClK	0.28	0.12	2.45	1.8
LaL	7.25	8.3	10.8	9.6
LaM	2.75	2.3	4.35	5.3
Total	100	100	100	100

CONCLUSION

Optically good quality single crystals of pure and lanthanum chloride doped L-arginine hydrochloride have been grown by using slow evaporation solution growth method at room temperature using water as a solvent. The grown crystals where subjected to various characterization studies. From the single crystal XRD, it is observed that both 1 and 2 mol% of $LaCl_3$ doped LAHCl single crystals were retain monoclinic system and space group $P2_1$. The UV-Vis-NIR spectral studies revealed that Pure, 1 and 2 mol% of $LaCl_3$ doped LAHCl crystals has good transmittance in the entire UV–visible and IR region and the calculated band gap energy of pure and doped samples are found to be 5.27 eV. The EDX analysis of both 1 and 2 mol% of $LaCl_3$ doped LAHCl crystals confirms the presences of lanthanum and chlorine in theLAHCl single crystal. The SGH test for 1 and 2 mol% of $LaCl_3$ doped LAHCl crystals revealed an efficiency of 1.25 and 1.5 times greater than that of the standard KDP crystal respectively. Owing to wide optical transparency and relatively high SHG efficiency of $LaCl_3$ doped LAHCl crystals are a potential candidate for fabrication of optoelectronics devices and laser application.

Declaration of conflict of interest. The authors declared that there is no conflict of interest.

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