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Effect of Chromium (II) Doping on Structural, Optical and Mechanical Properties of L-Alanine Strontium Chloride Single Crystal

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ABSTRACT

In the present course of work we synthesize L-Alanine stronitium chloride trihydrate salt by solution technique. After that pure L-alanine strontium chloride trihydrate ($LASRT_{2.}$ $3H_2O$) and chromium doped $LASRT_2.3$ H_2O single crystal were grown by slow evaporation solution technique (SEST). The synthesized salt is used to grow single crystal of $LASRT_2.3H_2O$ and the grown crystal is subjected to single crystal XRD for the structure determination and confirmation of the lattices parameter of title compound.. The calculated amount of chromium chloride is mixed in the solution to grow 1 mol %, 2 mol % $CrCl_2$ doped crystal. After a span of 25 days crystals were harvested. The grown crystals were crushed in to fine powder and subjected to powder XRD for structure analysis and refinement of cell parameters. A small but significant change in cell parameter confirms that the Cr ions have incorporated in the interstitial site. After that the synthesized salt is used for growing Cr doped LASRT single crystal Using powder XRD data, presence of mechanical strain was calculated using W-H analysis. FTIR spectra were recorded to confirm the presence of functional group. The grown crystals were also subjected to UV-Vis spectroscopy. Significant enhancement optical transmission of the compounds was observed. Hardness was measured by subjecting the grown crystal to Vicker Micro hardness tester. Significant enhancement in second harmonic generation efficiency is observed with the variation in doping concentration.

Keyword:L-Alanine strontium chloride trihydrate, Hardness no., Slow evaporation solution technique (SEST), Powder XRD, UV-Vis spectroscopy,

I.INTRODUCTION

In the coming era of technology, Photonics and non-linear optics have vast requirement of various optical storage data and high speed transmission devices. The design and development of such devices has attracted the young scientist and researchers to used photonic transmission instead of electronic transition. In literature, L-alanine strontium chloride tri-hydrate single crystal has been reported as one excellent NLO material which exhibit many potential features. It has also been observed that these important properties like optical transparency, thermal stability, mechanical hardness and second harmonic generation efficiency of the single crystal can be enhanced or improved by addition of some suitable dopants. It has also been observed that doping also affect the extent of crystalline perfection and also there physical properties. Hence, it becomes important to study the role or influence of extent of suitable dopants [1]. Kushwaha et al reported the enhancement of crystal perfection, Second harmonic generation, optical transparency, laser damage threshold by doping of magneese chloride [2,3]. Bright et al has also reported the effect of metal dopants like K^+ and Zn^{2+} on L-alanine cadiumiun chloride monohydrate. Chromium is reported as a photo refractive element and have the tendency on alter or enhance the optical properties of single crystals [4,5]. Anuj Krishna et al [6] has successfully reported the detailed investigation on chromium doped L-Alanine cadmium chloride monohydrate single crystal. In the present work, pure and chromium doped L-alanine strontium chloride tri-hydrate single crystals were grown by slow evaporation solution technique (SEST). We mainly focus on analyzing the effect of metal chromium doping in L-alanine strontium chloride tri-hydrate single crystal on structural, optical, mechanical, thermal and second harmonic generation efficiency.

II. EXPERIMENTAL DETAILS

2.1 Synthesis of salt

L-alanine strontium chloride tri-hydrate salt was synthesize by taking L-alanine (CDH) and strontium chloride (CDH) in 1:1equavimolar ratio as starting material. The calculated amount of both these salt were taken and dissolved in doubly distilled water with the help of magnetic stirrer. The solution was continuously stirred till the solution becomes transparent and saturated. The saturated solution was filtered with the help whattman filter paper having pores size 0.01 micro meters in a well cleaned beaker. The beaker is covered with a plane paper sheet having many pin holes in it so that constant evaporation can take place. The beaker is kept at a constant temperature in a oven set at 45^o C. After 5-6 days, salt was synthesized and taken out from the beaker.

2.2 Crystal growth

The synthesized salt was taken and dissolved in doubly distilled water to make a saturated solution. The solution was filtered in order to remove the suspended impurity. The solution was divided in equally four beakers. The calculated amount of chromium chloride was added to three beakers labeled as 1 mol %, 2 mol %, 5 mol%. The solution contained in each beaker is again stirred for 5-6 hours to make it completely dissolved and becomes homogenous. The solution is filtered and kept at constant temperature with a provision of constant evaporation. After a span of 22-24 day good quality single crystals of pure and chromium doped L-alanine strontium chloride trihydrate were harvested and were taken out from the mother solution. The grown crystals are shown in the figure1.

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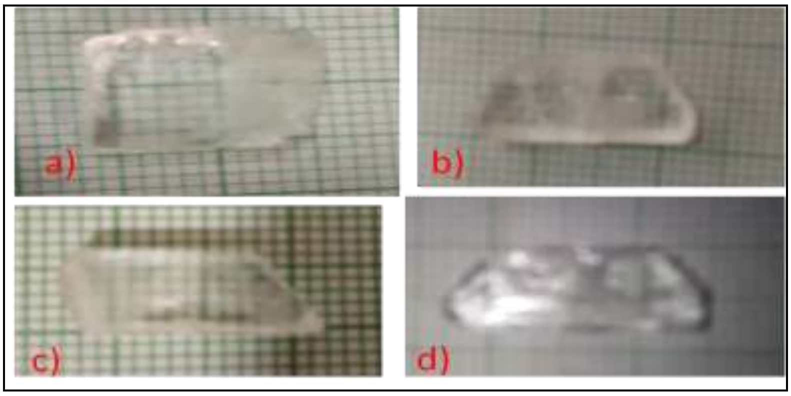


Figure 1: Photograph of (a) Pure LASRT (b) 1 mol % Cr doped
(c) 2 mol % Cr doped and (d) 5 mol % doped LASRT crystal

2.3 XRD analysis

Figure a) shows the pure $LASRT_2$ crystals. First of all, the grown crystal was subjected to single crystal x-ray diffraction to confirm the crystal structure and lattices parameter. The crystal structure is monoclinic with space group $P2_1$. The unit cell parameters are found a=8.597, b= 7.069, c=8.725 and β=95.23. The observed data is solved is found to be in well agreement with the already reported data.

2.3.1 Powder XRD and mechanical strain

The grown crystals were crushed in to fine powder and subjected to powder X-ray analysis. The diffraction curves were recorded for pure and doped crystals as shown in the figure. All the peaks of diffraction curve were well indexed with checkcell software and no additional peak is observed. Absence of any other peak reveals that crystal has no additional phase. The cell parameters were refined with the help of checkcell software and small variation in parameters of doped specimen is observed.

Table : 1 Refined cell parameters of pure and Cr doped LASRT crystal

Sr. No	Refined Cell parameters			
	Pure LASRT	1 mol % Cr	2 mol % Cr	5 mol % Cr
1	a = 8.597	8.584	8.579	8.574
2	b = 7.069	7.058	7.051	7.047
3	c = 8.725	8.719	8.709	8.703
4	β = 95.23	95.03	95.02	95.02

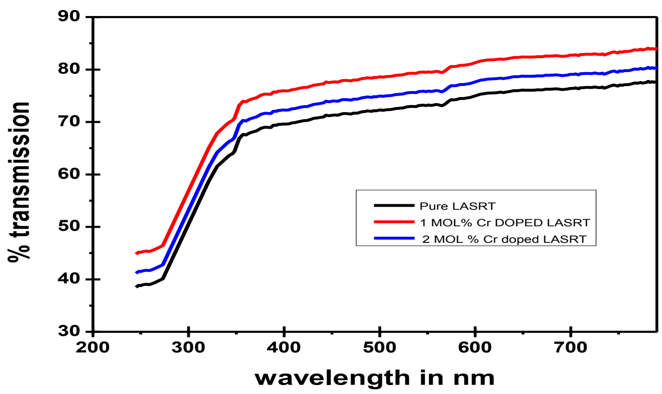
This indicates that the dopants atoms have been incorporated in the lattices site of the host crystal. This variation may be due to the variation in doping concentration. Further in order to calculate the mechanical strain present in the crystals, the XRD curve were carefully analyzed and FWHM were determined for each peak from XRD curve. Using W-H analysis, mechanical strain present in each crystal were calculated and found equal to. The successive decrease in the value of mechanical strain indicates that hardness of material increases and thus mechanical stability increases.

2.4 FTIR spectroscopy

The presence of function group in pure and doped LASRT single crystals was confirmed from the recorded FTIR spectroscopy. All the peaks were assigned to different functional group. No additional functional group was observed due to chromium doping. However, small variation in transmitted intensity is observed which may be due to incorporation of chromium ion at the interstitial site of the crystal lattices. No significant variation in the peaks was observed due to chromium doping.

2.4 Optical analysis

Optical transparency is the prime requirement of an optical crystal for its use in device fabrication. So those crystals having high optical transmission and less absorption in wide wavelength range are highly preferred.



In this regard, we made an attempt to analyze the optical quality of doped LASRT crystals and hence compare with the result of pure LASRT crystal as published in our earlier publication [6]. For this, the crystals were cut and polished to get uniform thickness and to remove the surface impurities. Transmission spectrum of 1 mol%, 2 mol% and 5 mol% doped LASRT crystal were recorded in wavelength ranging from 200 to 800 nm as shown in Figure.

From the curves it is clear that that there is large transmission for all the doped crystals in the entire range from 200 nm to 1200 nm in the region of the spectrum which is needed for crystal to be used for nonlinear optical applications. For 1 mol% Cr^{2+} doped LASRT crystal the transmittance was found to be slightly higher than undoped crystal which may be better crystalline perfection and may be due reduction in number of vacancies and reduces the trans-mission quality [1,9,10]. For 2 mol% Cr^{2+} doped LASRT crystal optical quality is significantly reduced with increasing absorption which may due to deformation of lattice with increasing chromium

2.5 SHG efficiency by Kurtz method

SHG efficiency of pure as well as Cr^{2+} LASRT crystals was measured by Kurtz-powder test. The influence of Cr^{2+} doping on LASRT on the SHG efficiency is estimated by plotting a graph between doping concentration and output signal as shown in figure 3. From this figure, it may be understood that SHG efficiency increases for 1 mol % and 2 mol % and is found maximum for 2 mol % doping. This result also favors the result of UV-Vis study in which it has clearly been explained that small concentration of Cr^{2+} doping minimize/eliminate the vacancy type defects from the crystal and as a result it reduces the probability of trapping of SHG photon.

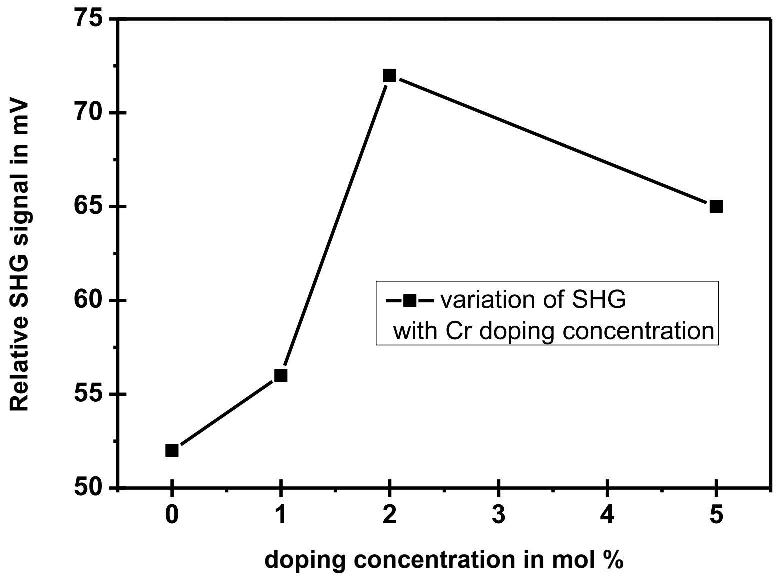
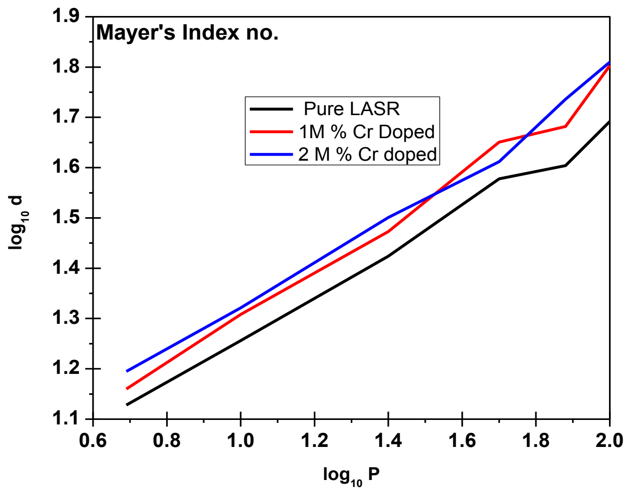


Figure 3: Variation of SHG efficiency with doping concentration.

This phenomena leads to significant increase in the SHG efficiency for low and moderate concentration of doping and crystal becomes more efficient for NLO applications as compared to pure LOMHCL [16]. The moderate concentration doping incorporated homogeneously in the crystal lattice at the interstitial site that causes the exploitation of electronic charge in the lattice around them [11, 17]. Due to interstitial incorporation of dopant atoms strain is developed in the crystal lattice. The strained lattice undergoes the strong electric-dipole-photon interaction due to the presence of electromagnetic laser radiation. At 5 mol % doping concentration, SHG efficiency decreases slightly due to agglomeration of Cr^{2+} ions as seen in the diffraction/rocking curve. In this case, it is necessary to explain that the dopant atoms do not contribute in the enhancement of SHG but generally lose their nature when they are not isolated. Hence, our results are also found in accordance with the already reported in case of Cr^{2+} doped LASRT single crystal [8].

2.6 Mechanical analysis

Mechanical stability is one of the prime requirementS of a single crystal for its use in any application. To measure the hardness and other elastic parameters Vicker micro Hardness technique was employed. In this technique a both sided flat surface crystal was taken for the analysis and indentation was measured by applying the load from 5 mg to 100 mg each time for 10 sec with dwelling rate of 20 mg /sec. Indentor impression were seen at lower value of applied load i.e. up to 10 mg and after that cracks were seen on the surface of the crystal with the help of optical microscope attached with the instrument. The variation of hardness no. with applied load for pure and doped crystals were plotted and shown in the figure. From the figure it is clear that for a particular crystal hardness no. increases and this enhancement also continue as the concentration of dopents increases. By using Mayer's Equation, $P = a.d^n$, log P v/s log d is plotted to calculate mayer index number or work hardening coefficient represented by 'n'. The slop of the line gives the value of work hardening coefficient which is found 1.12, 1. respectively for 1 mol%, 2 mol %. It is clear that there is slight increase in the work hardening coefficient which confirms that doping of Cr^{3+} ion increase the mechanical hardness. As a result, the Cr^{3+} doping in LASR crystal increases its use in photonic application.



III.CONCLUSIONS

Desirable quality pure and Cr^{3+} doped single crystals were grown successfully by slow evaporation solution technique. The compound was confirmed by single crystal XRD and unit cell dimensions were calculated. Powder XRD data was refined precisely by checkcell software which reveals that single phase in the grown crystal with an addition peak of Cr^{3+}. TGA/DTA analysis of the pure and doped specimen confirms the enhancement in the thermal stability with the incorporation of dopant in to crystal lattice. Optical study shows very small absorption and large transmittance which increases as the dopant concentration increase in the entire UV-Vis range.

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