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Growth and Characterization Of Pure And Rare Earth Doped Nonlinear Optical Single Crystal: Allylthiourea Cadmium Chloride (ATCC)

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Abstract: ***Nonlinear optical (NLO) single crystals of pure and Lanthanum (La^{3+}) doped Allylthiourea Cadmium Chloride (ATCC) crystals were grown from aqueous solution by slow solvent evaporation technique at room temperature. Grown crystals were confirmed by single crystal X-ray diffraction (XRD) and Energy dispersive X-ray analysis (EDAX). The crystals were characterized using Optical absorption (UV-Vis-NIR), Fourier Transform Infrared (FT-IR) spectral studies and Thermal analysis. The NLO activity of the grown crystals was also measured using Kurtz and Perry powder technique. The experimental data confirmed the second harmonic generation (SHG) efficiencies of the pure and La^{3+} doped ATCC crystals to be nearly 1.8 and 2.28 times higher than that of ureaThese instructions provide you guidelines for preparing papers for International Journal of Science & Research (IJSR). Use this document as a template and as an instruction set. Please submit your manuscript by IJSR Online Submission Module.***

Keywords: crystal growth, organometallic compounds, nonlinear optical crystals, slow evaporation

1. Introduction

With the introduction of the double radical model, scientists working in the field of nonlinear optical materials have developed a series of novel metal organic compounds. This model encourages the inclusion of organic conjugated molecular groups in the distorted polyhedron of co-ordination complex. These complexes have considerable high NLO coefficient (contrast to inorganic material), stable physicochemical properties and better mechanical intention (contrast to organic materials). Under the guidance of this theory, scientists have developed and reported few interesting complexes of allylthiourea along with the complexes of thiourea and thiocyanate [1-4]. The structure radical of the organometallic complex, especially in allylthiourea is no longer planar as the benzyl ring, hence the anisotropy of the crystal is reduced as compared with the organic crystals [4]. A comparatively high optical nonlinearity in these complexes comes from the distortion of the tetrahedron, which is composed of three allylthiourea ($C_4H_8N_2S$, AT) and one Cl combining with Cd. In this context, with allylthiourea acting as a ligand, scientists have developed tri-allylthiourea cadmium chloride (ATCC), tri-allylthiourea zinc chloride (ATZC) and tri- allylthiourea mercury bromide (ATMB) [5-7]. Tri-allylthiourea mercury bromide (ATMB) is an interesting organometallic complex material designed and synthesized by Hou Wenbo et al [4]. A relatively large susceptibility in ATMB comes from the distorted tetrahedron arrangement in its structure. The complex cation $[HgBr(AT)_3]^+$ forms a distorted tetrahedron using metal ion Hg^{2+} as a centre ion to connect with Br and three sulphur atoms in the allylthiourea molecules. The distorted tetrahedron arrangement increases the asymmetric structure and thereby contributes to the enhanced NLO activity. The same has been confirmed in the other complexes of allylthiourea and they possess higher SHG efficiency than both KDP and urea [6-8].

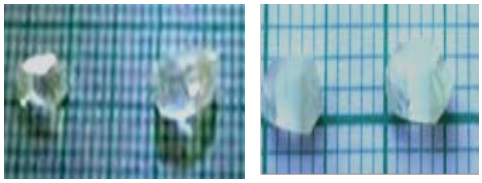
The present article deals with the growth of pure and La^{3+} doped allylthiourea cadmium chloride (ATCC) crystals grown from aqueous solution by slow solvent evaporation technique. The grown crystals were confirmed by single crystal XRD, FT-IR and EDAX analysis. The grown crystals were also characterized by optical absorption and Thermo gravimetric/Differential thermal gravimetric (TG-DTG) techniques. The NLO properties of the grown samples were investigated by Kurtz and Perry powder technique.

2. Materials And Methods

Pure ATCC was synthesized by taking cadmium chloride ($CdCl_2$) and allylthiourea (AT) (AR grade with ≥ 99.8 % purity) as raw materials. They were thoroughly mixed in the double distilled water in the molar ratio 1:3 according to the following reaction:

$$CdCl_2 + 3CH_2{=}CHCH_2NHCSNH_2 \rightarrow CdCl_2(CH_2{=}CHCH_2NHCSNH_2)_3$$

$CdCl_2$ and AT were mixed together at 60 ˚C. The solution of ATCC was prepared and few drops of dilute HCl were added to adjust the pH value to 3 - 4. The solution was continuously stirred for few hours and the condition of supersaturation was achieved. After attaining the supersaturation, the solution was filtered and then allowed to evaporate at room temperature. The same procedure was repeated for the growth of La^{3+} doped ATCC crystals by substituting 2% of Cd by 2% of La^{3+} (AR grade with ≥ 99.8 % purity). The growth period ranged between 40- 50 days. The photographs of the pure and doped ATCC crystals are shown in Fig. 1(a&b).



(a) (b)

Figure 1: Photographs of (a) pure and (b) La^{3+} doped ATCC single crystals.

The single crystal X-ray analysis of pure and La^{3+} doped ATCC crystals was carried out using ENRAF NONIUS CAD4-F diffractometer. The structures were solved by direct method and refined by the full matrix least squares technique using the SHELXL program. The second harmonic efficiencies of the powdered samples were studied using Nd-YAG Q-switched laser with first harmonic output of 1064 nm and urea was taken as the reference material. The FT-IR studies were carried with freshly crushed samples mixed with KBr in the ratio 1:10 and palletized using a hydraulic press. The FT-IR spectra were recorded using BRUKER IFS–66 V spectrometer. The optical absorption spectra of the samples were taken using VARIAN CARY 5000 spectrophotometer. The EDAX analysis of the samples was performed using the instrument VEGA3 SBH. The TG/DTG analysis was carried out using the instrument NETZSCH STA 449F3 at a heating rate of 10K/min in nitrogen atmosphere.

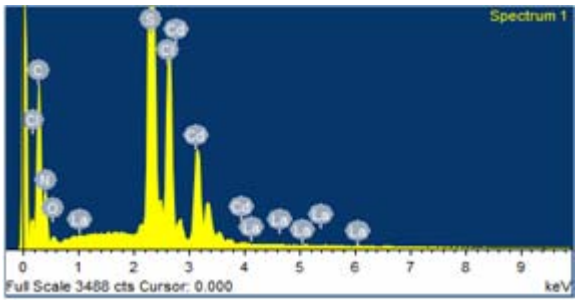
3. Results And Discussion

3.1 X-ray diffraction (XRD) analysis

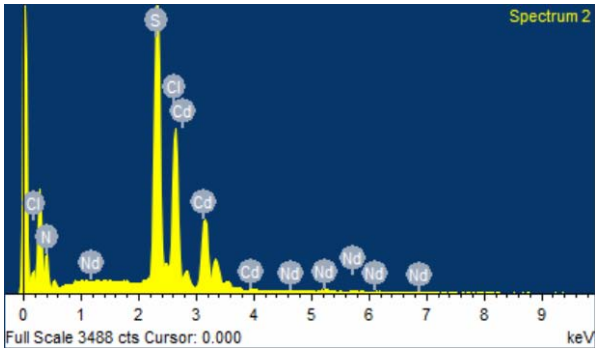
The experimental XRD data is in good agreement with the reported data [4]. Although the systems are the same for the pure and doped ones, there were slight variations in the unit cell parameters and are shown in Table 1.

3.2 EDAX Test

The exact weight percentages of La^{3+} present in the doped crystals was determined using EDAX analysis (Fig. 2a&b). The results show that only 0.54 % of La^{3+} was present in the doped sample out of 2 % of the dopant.



(a)



(b)

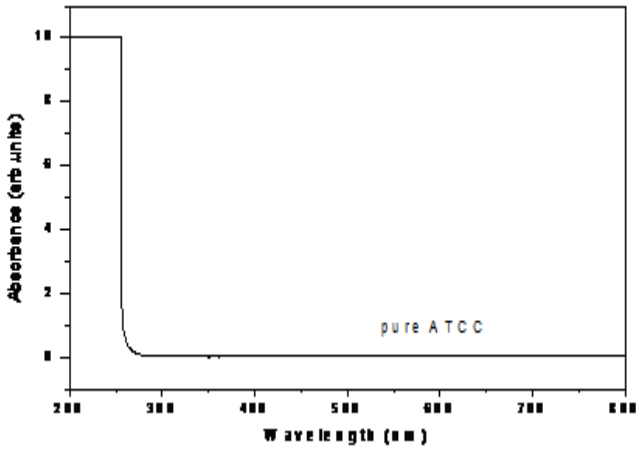
Figure 2: EDAX spectra of (a) pure and (b) La^{3+} doped ATCC single crystals.

Table 1

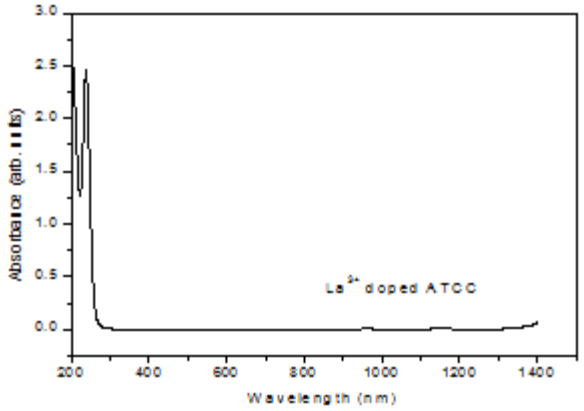
Lattice parameters	pure ATCC	La^{3+} doped ATCC
a (Å)	11.4795	11.4195
b (Å)	11.4795	11.4737
c (Å)	28.1351	28.1619
$\alpha = \beta$ (deg)	90	90
γ (deg)	120.0457	120
Space group	R_{3c}	R_{3c}
Crystal System	Trigonal	Trigonal
Volume $(A^0)^3$	3210.88	3195.53

3.3 Optical absorption studies

It is well known that an efficient NLO crystal has an optical transparency at lower cut-off wavelengths between 200 and 400 nm [9]. It is observed from the spectra that the pure and doped ATCC crystals have a wide transmission window (Fig. 3a&b). The UV cut off wavelengths of the pure and La^{3+} doped ATCC crystals are observed to be 273 nm and 303 nm respectively. In the entire visible region, the optical absorption spectra are flat and constant.



(a)

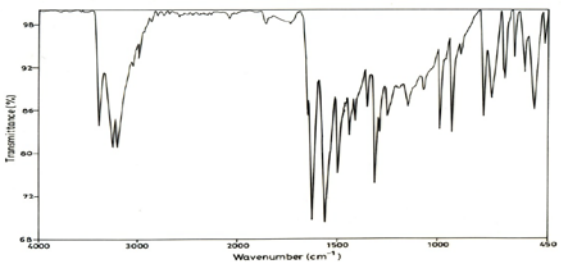


(b)

Figure 3: Optical absorption spectra of (a) pure and (b) La^{3+} doped ATCC single crystals.

3.3 FT-IR Studies

The functional groups of the crystals were confirmed by recording the FT-IR spectrum (Fig. 4a&b) using BRUKER IFS–66V spectrometer. The band observed in pure ATCC at 1561 cm^{-1} is due to the stretching ν (C=S), indicating the co-ordination of C=S group to Cd atom in the complex is now observed to be shifted to 1555.86 cm^{-1} when doped with La. In addition to this, the band observed at 767 cm^{-1} in pure ATCC, which is assigned to the bending vibration of C=S group is now observed to be shifted to 765.05 cm^{-1} due to the presence of La^{3+}dopant. This also supports the co-ordination of C=S to Cd/La atom in the complex. The sharp intense peak at 3395 cm^{-1} in pure ATCC is attributed to NH stretching of the substituted amide group. Generally, NH stretching occurs close to 3300 cm^{-1}, but here it is shifted to higher wave number due to resonance delocalization of nitrogen lone pair over C=S group. The asymmetric and symmetric vibrations of NH_2 group in pure ATCC are positioned between 3243 and 3051cm^{-1}, whereas as they are observed to be positioned between 3248.04 and 3051.65 cm^{-1} when doped with La. The fine structure observed in the lower energy portion of the intense peak in pure ATCC between 2600 and 3500 cm^{-1} is due to hydrogen bonding of NH_2 group overlapping with that due to olefinic CH stretching (2985 cm^{-1}) and alkyl CH_2 stretching (2867 and 2802 cm^{-1}). The same CH and CH_2 stretchings due to NH_2 group overlapping when doped with La are observed at 2984.41 and 2751.10 cm^{-1} respectively.



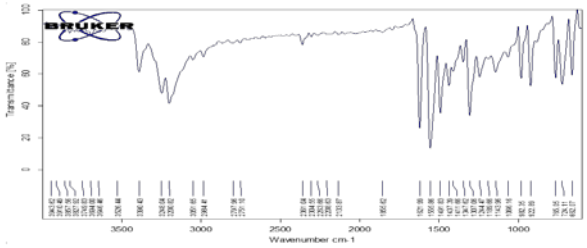
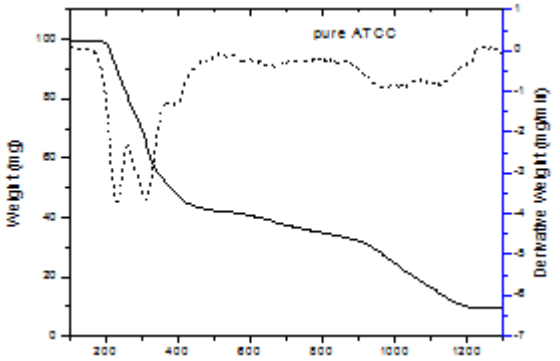


Figure 4: FT-IR spectra of (a) pure and (b) La^{3+} doped ATCC single crystals.

3.4 Thermal analysis

The thermogravimetric (TG) and the differential thermal gravimetric (DTG) traces of the pure and doped ATCC crystals are shown in Fig. 5a&b. The studies were carried out in the temperature range from room temperature to 1400 ˚C. Thermal analysis confirmed that the Pure and La^{3+} doped ATCC crystals are thermally stable up to 231˚C and 226.1 ˚C respectively.



(a)

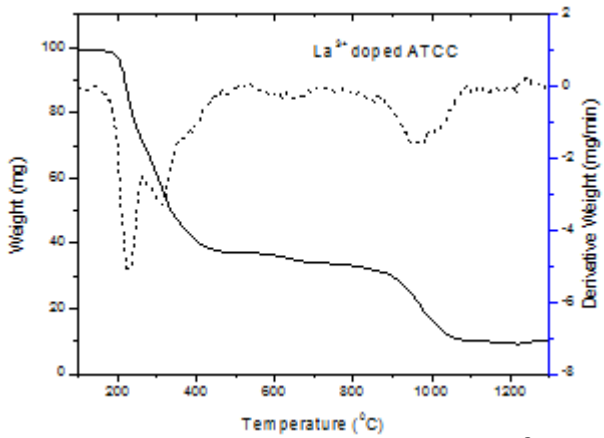


Figure 5: TG-DTG curves of (a) pure and (b) La^{3+} doped ATCC single crystals

3.5 Nonlinear optical (NLO) studies

For a laser input of 6.2 mJ, second harmonic signals of 532 nm were produced at 91.66 mW, 256.64 mW and 300.64 mW respectively for urea, pure and La^{3+} doped ATCC crystals. The experimental data confirmed second harmonic efficiencies of pure and La^{3+} doped ATCC crystals to be nearly 1.8, 2.28 times higher than that of urea. Thus the presence of dopants has slightly increased the SHG efficiency of the pure ATCC.

4. Conclusions

Good quality grade single crystals of pure and La^{3+} doped ATCC crystals were grown successfully by slow evaporation technique. The structure of the grown crystals and their compositions were confirmed by single crystal XRD and EDAX analysis. The presence of dopants has slightly enhanced the SHG efficiency of the pure ATCC. Thermal analysis confirmed that the pure and La^{3+} doped ATCC crystals are thermally stable up to°C231 and 226.1˚C respectively. The reasonably good optical, thermal property combined with SHG efficiency suggests that ATCC crystals with rare earth substitution are promising materials for photonics device fabrications.

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