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Structural and photoluminescence studies of Eu^{3+} doped L-Tartaric single crystal through evaporation technique

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HIGHLIGHTS

- Eu^{3+} doped LTA single crystals were synthesized by evaporation method.
- XRD & HRXRD confirms prepared sample is good crystalline material.
- SHG efficiency of Eu^{3+} doped LTA single crystal is 1.2 times that of pure KDP crystal.

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ABSTRACT

Europium doped L-Tartaric acid; a non-linear optical single crystal was grown by slow evaporation solution growth method. The grown crystal was characterized by XRD for phase analysis, HRXRD for crystalline perfection, functional group by FTIR spectroscopy and powder SHG measurement for getting an estimate of NLO efficiency. The emission spectrum of Eu^{3+} doped L-Tartaric acid obtained after excitation at 394 nm and corresponding excitation spectrum by monitoring at 615 nm emissions. The decay curve is recorded corresponding to the $^5D_0$ level of Eu^{3+} from tartaric acid doped with europium ions. The transparency of the crystal shows >90%, thermal analysis shows that the crystal to be thermally stable up to 189 °C and estimated atomic elemental composition in grown crystal with EDAX. L-Tartaric acid with chiral structure acts as a good host material for probing Eu^{3+} ions in synthesis of luminescent materials.

Introduction

The modern world is witnessing revolutionary advancements in the various aspects of science and technology. Every new day is suppressing its predecessor by some new achievements that require novel ideas leading towards the exploration of new materials for emerging fields, which were hitherto unknown [1]. Organic nonlinear materials are attracting a great deal of attention as they have large optical susceptibilities inherent ultra-fast response times and high optical thresholds for laser power as compared with inorganic materials. A number of such materials have been reported in the literature for their potential application [2,3]. Lanthanide doped non-linear optical (NLO) single crystals play a critical role in many technological applications. Due to the unique electronic structure of lanthanides, they have a wide variety of optical applications, including lasers, solar-energy converters and optical amplifiers. Hence, the search of new non-linear optical materials has been increased in recent times [4–7]. Many attempts were made to understand the interaction between rare earth and host materials electronic states and the influence in optical properties [8]. Many researchers are attracted towards new organic NLO materials possessing large dipole moment and with chiral structures. L-Tartaric acid (LTA) is chiral and its other complexes are known to possess good NLO properties [9–12]. In tartaric acid single proton ionization is easy, that Europium ions (Eu^{3+}) must be replacing the protons of carboxyl group and forming $(—COO)_3$:Eu^{3+} bindings [13,14].

In the present work, Eu^{3+} doped LTA single crystals are prepared by using slow evaporation method and characterized by using different techniques. The grown crystals were subjected to powder

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XRD to estimate the crystal structure and space group. The crystalline perfection was examined by HRXRD analysis. The functional groups are confirmed by FT-IR studies. The dopant of grown crystal was confirmed with EDAX and also analyzed the thermal stability. In addition to that the optical properties of the crystals are studied using second harmonic generation (SHG) efficiency. To the best of our knowledge no one reported the growth of LTA single crystals doped with rare earth ions.

Experimental study and characterizations

Crystal growth

LTA and Europium nitrate ($Eu(NO_3)_3$) were purchased from Merck Chemicals, India. All of the chemical reagents used in this experiment were analytical grade and used without further purification. Single crystals of Eu^{3+}:LTA were grown from aqueous solution by slow evaporation method. 0.1 mol% of solution has been prepared by using $Eu(NO_3)_3$ with double distilled water. The required amount of LTA acid are added and stirred continuously for 3 days. The prepared solution was filtered and kept undisturbed at constant temperature bath at 34 °C. Good quality crystals were obtained by spontaneous nucleation and within a span of 36 days, the crystals were harvested. Fig. 1 shows (a) bulk Eu^{3+} doped LTA crystal and (b) polished Eu^{3+} doped LTA single crystal.

Powder X-ray diffraction & EDAX analysis

Powder XRD measurements were carried out using a PW-1830 Philips Analytical X-ray diffractometer with nickel-filtered Cu Kα radiation (35 kV, 30 mA) at a scan rate 0.02° s^{-1} for the 2θ angular range of 10–70° at room temperature. The elemental analysis has been carried out by energy dispersive X-ray analysis (EDAX) using an FEI Quanta 200 instrument.

Multicrystal X-ray diffractometry & FTIR spectroscopy

The crystalline perfection of the grown single crystals was characterized by HRXRD by employing a multicrystal X-ray diffractometer [15]. The well-collimated and monochromated Mo $K\alpha_1$ beam obtained from the three monochromator Si crystals set in dispersive (+, −, −) configuration has been used as the exploring X-ray beam. The specimen crystal is aligned in the (+, −, −, +) configuration. Because of dispersive configuration, though the lattice constant of the monochromator crystal(s) and the specimen are different, unwanted dispersion broadening in the diffraction curve (DC) of the specimen crystal is insignificant. The specimen can be rotated about the vertical axis, which is perpendicular to the plane of diffraction, with minimum angular interval of 0.4 arc sec. The DC was recorded by so-called ω scan method, wherein the detector was kept at the same angular position $2\theta_B$ with wide opening for its slit. FT-IR spectra were recorded using Perkin Elmer BX spectrometer in the range 400–4000 cm^{-1} using KBr pellets.

Photoluminescence studies

All luminescence measurements were carried out at room temperature by using an Edinburgh Instruments' FLSP 920 system, having a 450 W Xe lamp and a μs flash lamp (60 W) as excitation sources. Red sensitive PMT was used as the detector. Approximately 20 mg of sample was mixed with few drops of methanol, made into slurry and spread over a glass plate, which was then dried under ambient conditions prior to luminescence measurements. All emission spectra were corrected for the detector response and all excitation spectra for the lamp profile. All emission measurements were carried out with a spectral resolution of 3 nm. Lifetime measurements were carried out using a 60 W micro-second flash lamp.

Thermal analysis

The Thermal analysis (TG/DTA) of the samples were performed using SII Nanotechnology Inc., Japan, EXSTAR 6200 instrument at a constant heating rate of 10 °C/min over a temperature range of 40–950 °C using alumina powder (10 mg) as a reference material. The sample of about 26.3 mg was uniformly spread over the balance pan. The degradation of samples was carried out under nitrogen atmosphere at a flow rate of 400 ml/min.

UV–Vis spectra & SHG measurement

The optical transparency was checked by using a Perkin Elmer LAMBDA 35 UV–Vis spectrophotometer in the range 200–900 nm. The SHG behavior of powdered material was tested using Kurtz and Perry method (Kurtz & Perry, 1968), A KDP crystal was used as a reference. An Nd:YAG laser of fundamental wavelength 1064 nm, pulse width 10 ns, with a repetition rate of 10 Hz was used as a source. The laser radiation was made incident on the specimen sample and green output radiation from the specimen was detected by a photomultiplier tube coupled with a filter. SHG signals of the specimen crystal and the standard KDP were recorded. The signal from photomultiplier tube was used to assess the relative SHG efficiency of crystals.

Results and discussion

Powdered X-ray diffraction analysis

Fig. 2 shows the powder X-ray diffraction pattern of Eu^{3+} doped LTA single crystals. All the peaks observed in the XRD pattern are characteristic of LTA with monoclinic crystal structure with space group $P2_1$. The unit cell dimensions were calculated from the least square fit of the XRD peaks and are found to be $a = 6.201$ Å,

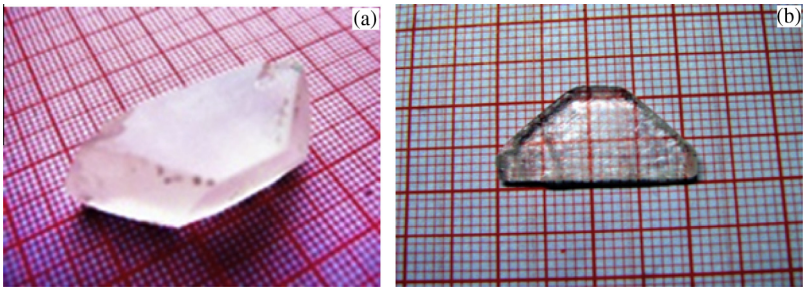

Fig. 1. (a) Bulk Eu^{3+} doped LTA crystal. (b) Polished Eu^{3+} doped LTA single crystal.