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Studies of Cerium Doped L-Alanine Alaninium Nitrate NLO Crystal

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Highlights:
- **Cut off wavelength is 250 nm**
- **Visible spectrum has an absorption peak at 668 nm**
- **Melting point of the cerium doped LAAN crystal is 278.97 ^{o}C**

Abstract: ***Cerium-doped l–alanine alaninium nitrate, a nonlinear optical single crystal, was grown by solution growth method and characterized in view of finding changes in its properties. The crystal structure and space group were confirmed by single crystal X-ray diffraction and linear, nonlinear optical properties were studied by UV-Vis-NIR and SHG analysis respectively. The surface hardness and thermal studies were performed by Vicker's microhardness tester and TG/DTA analysis in order to reveal the stability of the grown crystal. Moreover, the incorporation of the cerium element due to the doping of ammonium cerium nitrate into the parent compound l-alanine alaninium nitrate was identified by EDAX analysis.***

Keywords: Crystal growth; X-ray diffraction; Nonlinear optical crystals; Recrystallization; Harmonic generation

1. Introduction

Noncentrosymmetric materials play an important role in the field of nonlinear optics, which includes many illusions of interesting effects and applications in the field of laser technology [1]. Most of the amino acids crystallize in noncentrosymmetric crystal structure and particularly l-alanine has chiral symmetry. L-alanine alaninium nitrate crystals doped by lanthanum oxide [2] and zinc [3] were grown and reported with few favorable changes in nonlinear and thermal properties. Nitric acid is a strong oxidizing agent and the dopant ammonium cerium nitrate compound is also a specialized oxidizing agent in organic synthesis. In general properties of a material can be changed due to the addition of foreign elements substitutionally or interstitially into the parent compound. Because of this reason, a research attempt was made to grow cerium doped l-alanine alaninium nitrate semiorganic crystal and it was subjected to characterization to find the changes in its nonlinear, mechanical and thermal properties.

2. Growth of Material

Single crystals of cerium doped l-alanine alaninium nitrate (LAAN) were grown by slow evaporation of saturated aqueous solutions at room temperature. Aqueous solution containing l-alanine and nitric acid in 2:1 molar ratio respectively and 1mol% of ammonium cerium nitrate was prepared in a glass beaker. The solution was allowed to stir continuously for 3 hours by using distilled water as a solvent to get a good homogeneity of the mixers. The resulting solution was filtered through a qualitative filter paper into a clean dry beaker to remove suspended impurities and allowed to crystallize. The beaker was covered with perforated polythene paper in order to minimize the rate of evaporation and then placed upon a vibration less table. The pH value of the prepared solution was 3. The purity of the synthesized salt was further improved by the successive recrystallization process. Fig.1 shows the grown crystals at room temperature.

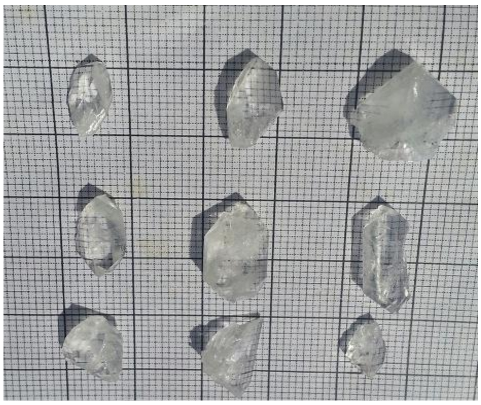

Figure 1: Photograph of cerium doped LAAN crystal

3. Experimental Methods

The cerium doped LAAN crystals were subjected to characterization in order to find optical properties, thermal and mechanical stability after confirming its crystal structure by single crystal X-ray diffraction. The single crystal X-ray diffraction was carried out using a Bruker AXS Kappa APEX II single crystal CCD diffractometer equipped with graphite-monochromated MoKα (λ= 0.7107Å) radiation. The UV-visible spectral analysis gives useful information about electronic transitions in the compound [4]. Because of wide optical applications of NLO materials, the transmission range and cut off wavelength are very important parameters, especially for crystals used in second harmonic generation (SHG). The UV-Vis-NIR transmission spectrum was recorded in the range of 200 to 1100 nm using Perkin-Elmer Lambda 35 UV-VIS spectrometer for 3 mm thickness crystal. The Second Harmonic generation is used as an important tool to evaluate qualitatively the bulk homogeneity of the samples under investigation [5]. It was analyzed using Kurtz-Perry powder technique and compared with the standard KDP crystal as a reference. A high intense Nd: YAG laser source of wavelength 1064 nm and energy 16.5 mJ/pulse was used for this. The input pulse and pulse width was 1mV/pulse and 10 ns respectively. Then laser radiation was allowed to pass through the sample taken in a microcapillary tube in powder form. Both the reference and test samples had been prepared into a uniform particle size of 150 microns. Thermal properties such as melting point and dissociation temperature of the crystal were studied by Thermogravimetric analysis (TGA) and Differential thermal analysis (DTA). These were carried out between 30 °C and 990 °C in a nitrogen atmosphere at a heating rate of 10 °C/min using SDT Q600 V20.9 Build 20 TG/DTA instrument by a stepwise isothermal method. Since mechanical properties are more essential for any kind of nonlinear optical photonic device applications, the crystal was subjected to microhardness testing using HMV2T Vicker's Microhardness tester. The Vicker's microhardness values were calculated from the standard formula $H_v = 1.8544\ P/d^2$ kg/mm^2 and measured the corresponding indentation length. Elemental analysis was performed by employing the energy dispersive X-ray analysis (EDAX) technique using the Jeol6390LV model scanning electron microscope instrument in the range of 0–10 keV.

4. Results and Discussions

The compound cerium doped LAAN crystal crystallizes monoclinic structure with the space group of $P2_1$ and the unit cell parameters determined are a=7.844(3) Å, b= 5.436(2) Å, c= 12.810(3) Å, β=94.62° and V= 546.218 Å^3. When the crystallographic parameters are compared with the existing report, the result is highly agreed with them [6]. In the UV-Visible-NIR spectrum shown in the Fig.2, a steady transmittance throughout the visible region about 50 % and the lower cut off wavelength at 250 nm makes it suitable for frequency conversion device. Moreover there is a sharp absorption peak obtained at 668 nm, which may be due to the excitation of electron from the lower energy level [7]. The crystalline sample, packed in a microcapillary tube in the form of very fine powder, was placed in the path of Nd-YAG laser beam for finding its second harmonic efficiency. The beam voltage of the transmitted radiation was measured as 24 mV for pure KDP reference material, but it was 12 mV through the cerium doped LAAN sample. Hence the SHG efficiency is just half of that of the standard KDP crystal. The transmitted beam from the sample holder was observed in green color and the wavelength of the beam was 532 nm. From this observation, cerium doped L-Alanine alaninium nitrate is a material for frequency conversion in a nonlinear optical device.

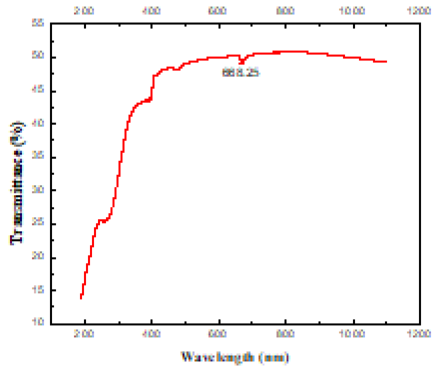

Figure 2: UV-VIS-NIR Transmittance spectrum of cerium doped LAAN crystal

The TG/DTA curves are shown in the Fig.3, which shows that the crystal is devoid of any physically adsorbed water on it due to no weight loss below the temperature 240 °C. At this temperature, the material begins to melt in associated with decomposition simultaneously and thereafter it dissociate completely at the temperature 278.97 °C, which is precisely observed in the thermogram. The DTA response curve too shows a sharp endothermic peak at 278.97 °C,

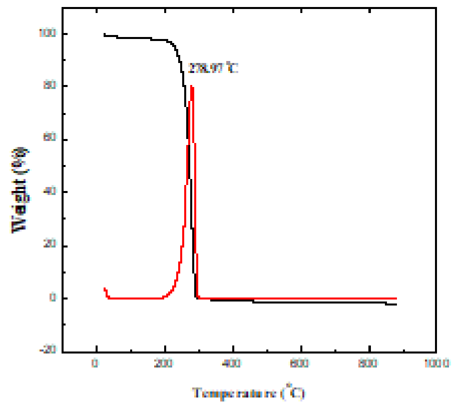

Figure 3: TG/DTA curves of cerium doped LAAN crystal

which corresponds to the melting point of the material. The melting point of this material is found to be 36 °C greater than the parent material [6]. This remarkable increase of thermal stability could be possible due to the incorporation of the rare earth element cerium into the parent material. From the thermogram, it is found that the material undergoes decomposition and melting simultaneously. Hence the nonlinear optical crystal cerium doped LAAN crystal is stable up to 240 °C and it can be utilized for any kind of photonic device application up to 240 °C.

Vicker's microhardness of the crystal is shown in the Fig.4, in which hardness increases with the increase of load up to 100 gram and a fine crack developed in the crystal when it was subjected to 100 g. The maximum crack length formed on the crystal was measured as 43.67 µm from the center of the indentation. Microhardness value was calculated for every load applied on the crystal and the corresponding diagonal length of the indentation formed on the crystal was measured. The maximum hardness obtained in this material is 50.52 kg/mm^2. In order to find work hardening

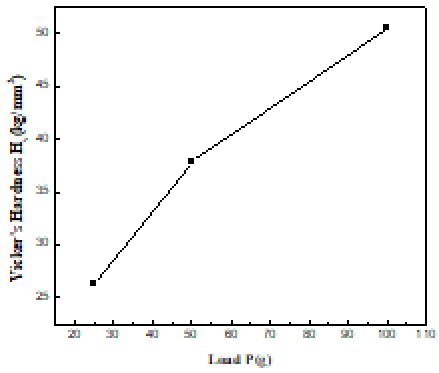

Figure 4: Hardness Vs load graph of cerium doped LAAN crystal

coefficient (n) of the grown crystal, a graph Fig.5 was drawn between the logarithmic values of the load and the diagonal length of the indentation. Using the Meyer's law $P = ad^n$, it was calculated as 3.45. Here, "a" is the constant for the given material. A crystal behave as a harder material if the coefficient "n" lies between 1 and 1.6, and it is soft material for above 1.6. As its value is more than 1.6, the grown crystal is suggested as a soft material. Using the mathematical expression $\sigma_y = (H_v/3)(0.1)^{n-2}$, yield strength of the grown cerium doped LAAN single crystal was calculated; where σ_y is the yield strength. It was calculated as 0.597 MPa from the relation and hence the grown crystal has low mechanical strength [8]. Fracture toughness K_c was calculated as 49502 $kg/m^{3/2}$ using the formula $K_c = P/\beta C^{3/2}$, where C is the crack length from the center of the indentation found and

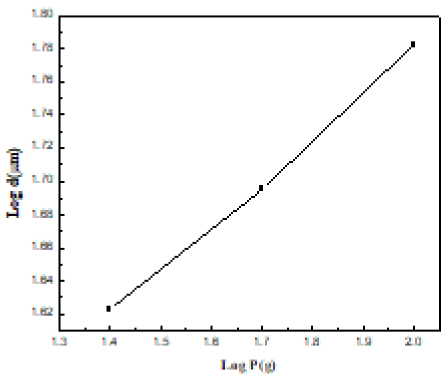

Figure 5: Log P and log d of cerium doped LAAN crystal

β (=7) is the geometrical constant for Vickers indenter. An important mechanical property of any crystal which is to be used for photonic device application is Brittleness. Using the expression $B_i = H_v/K_c$, it was calculated as 1020 $m^{-1/2}$. Elastic stiffness constant was also calculated from the microhardness by Wooster's empirical relation $C_{11} = (H_v)^{7/4}$[9] as 9.57x 10^{12}. The EDAX spectrum of the crystal is shown in Fig.6, in which the spectrum reveals the low incorporation of 'cerium' in addition to the presence of constituent elements oxygen, nitrogen and carbon.

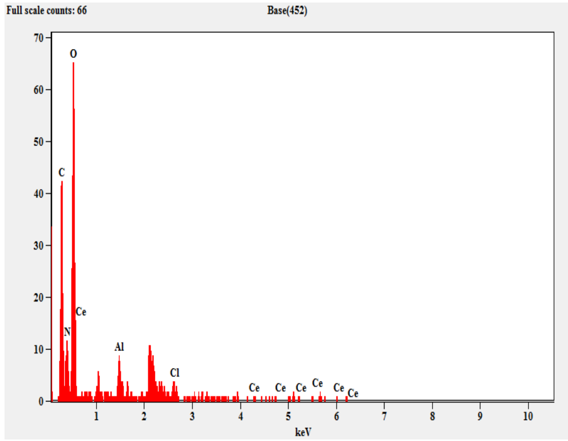

Figure 6: EDAX spectrum of cerium doped LAAN crystal

5. Conclusions

Cerium doped L-alanine alaninium nitrate crystal was characterized by optical, thermal and mechanical properties systematically. The lower cut off wavelength at 250 nm and 50 % transmittance in the entire visible region makes it suitable to be used for the nonlinear optical device. Its second harmonic efficiency is half of that of KDP crystal. But its remarkable change obtained towards higher thermal stability over than the parent compound makes still a better candidate for device application even though the crystal possesses somewhat less efficiency in nonlinear optical characteristics. Vicker's microhardness 50.52 kg/mm^2 at 100 g load and other related mechanical properties have been calculated and presented. The EDAX analysis confirms the incorporation of the element cerium. It might be occupied substitutionally in the array of the parent compound since its thermal and mechanical stability is moderately higher than the parent compound.

6. Acknowledgement

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