Growth and Characterization of Pure and Zinc Doped L – Alanine Alaninium Nitrate Single Crystals

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Abstract - Single crystals of pure and zinc doped L–alanine alaninium nitrate (LAAN) have been successfully grown by slow evaporation method. The grown crystals have been subjected to single X-ray diffraction studies to find the cell parameters. To improve the physicochemical properties of the LAAN crystal, 2 mol % of zinc dopant was added. ICP studies confirm the presence of zinc in the grown zinc doped LAAN crystal. The structural and optical properties of the grown crystals were characterized by FT-IR and UV-VIS –NIR studies. The band gaps of the pure and doped LAAN crystals were found to be 4.56 eV and 4.2 eV respectively. Vickers micro hardness test was also carried out to elucidate the mechanical behavior of the grown crystals. Dielectric studies of pure and doped LAAN single crystals were carried out. TG and DTA studies were carried out to determine the thermal stability of the pure and doped LAAN crystals. The SHG study depicts the nonlinear optical efficiency of the crystals.

Keywords: Crystal growth; slow evaporation; x-ray diffraction; FT-IR; UV-VIS-NIR; Micro hardness.

I. INTRODUCTION

Materials that possess optical nonlinearities have been studied extensively for their possible applications in various fields like telecommunication, optical computing, optical data storage and optical information processing. The generation of coherent blue light through second harmonic generation (SHG) from near infra-red (NIR) laser sources are an important technological problem that has attracted much attention in the last few years. Potential application lies in the fields of high-density data storage, high-resolution printing and spectroscopy [1-2]. The organic nonlinear optical materials have good nonlinear optical susceptibilities but low laser damage threshold value in comparison with inorganic counterparts. Among organic crystals for nonlinear optics (NLO) applications, amino acids display specific features of interest, such as (i) molecular chirality, which secures centric crystallographic structures, (ii) absence of strongly conjugated bonds, leading to wide transparency ranges in the visible and UV spectral region and (iii) zwitterionic nature of the molecule, which favors crystals hardness [3,4]. These versatile behaviors of amino acid based organic crystal attract the researchers towards crystal growth of NLO crystal. The amino acid L-alanine is an efficient organic NLO material under the amino acid family. Several new complexes incorporating the amino acid L-alanine have been crystallized and their structural, optical and thermal properties have been investigated [5-7]. Recently optical, spectral and second harmonic generation studies were carried out on L-Alanine based materials [8-11]. Dispersion of the linear and nonlinear optical susceptibilities of L-alanine single crystals were reported [12].

In the present work, pure and zinc doped L-alanine alaninium nitrate crystals were successfully grown by slow evaporation technique. Single crystal X-ray diffraction study has been carried out to confirm the grown pure and doped L-alanine alaninium nitrate crystals. ICP studies have been carried out to confirm the presence of zinc in the grown crystal. FT-IR, UV-VIS-NIR, microhardness, dielectric analysis, TGA and DTA analysis were studied for grown pure and doped crystals. The second harmonic generation (SHG) studies have been carried out for the grown pure and doped crystals.

II. MATERIALS AND METHODS

2.1 EXPERIMENTAL PROCEDURE

L-alanine alaninium nitrate (LAAN) salt was synthesized by taking L-Alanine and nitric acid in 2:1 molar ratio. The reactants were dissolved in double distilled water to prepare saturated solution. The saturated solution was filtered and allowed to evaporate at room temperature under optimized conditions. Seed crystals were obtained in a period of one month. Good quality crystals were obtained by successively recrystallization method. The same procedure was applied to grow the zinc doped crystals by adding 2 mol % of zinc sulphate to the LAAN solution. Good quality crystals were obtained in a period of one month. The incorporation of dopant into the pure solution has improved the growth rate and the quality of the crystals. The grown crystal was further studied by various characterization techniques. The photographs of the as grown pure and zinc doped crystals are shown in Figure 1.

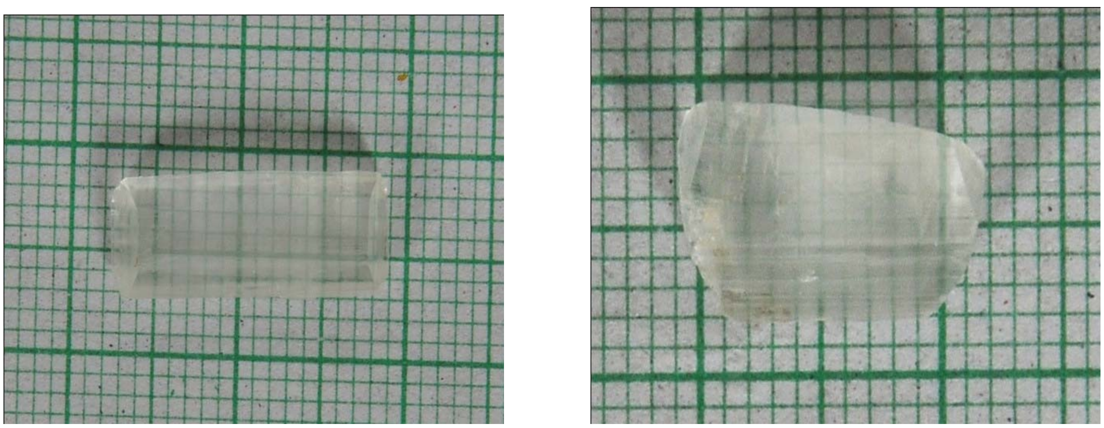


Figure.1. Photographs of pure and doped LAAN crystals.

III. RESULTS AND DISCUSSION

3.1 Single X-ray diffraction studies

Single crystal X-ray diffraction studies of pure and zinc doped LAAN crystal was carried out using MESSRS ENRAF NONIUS CAD4-F single X-ray diffractometer. Both the pure and doped LAAN crystals crystallize into the monoclinic crystal system with the space group $P2_{1.}$ The lattice parameter values of the pure LAAN crystal are well matched with the reported literature [13]. The lattice parameter values of doped LAAN crystals were show slight variations. These variations may be due to the incorporation of zinc in the LAAN crystal lattice. The lattice parameters of the pure and doped crystals are shown in Table 1.

Table 1: Lattice parameter values for pure and doped LAAN Crystals

Lattice parameters	Pure LAAN	LAAN-Zinc doped	Pure LAAN(reported)
Empirical formula	CH_3CHNH_2COOH	CH_3CHNH_2COOH + Zn	CH_3CHNH_2COOH
Crystal System	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1$	$P2_1$	$P2_1$
a (Å)	7.837	7.813	7.846
b (Å)	5.438	5.397	5.431
c (Å)	12.812	12.799	12.806
α^o	90.00	90.00	90.00
β^o	94.27	93.67	94.65
γ^o	90.00	90.00	90.00

Volume ($Å^3$)	546	429.2	543.8

3.2 ICP studies

10 mg of fine powder of the doped LAAN crystal was dissolved in 20 ml of doubled water and sample was prepared. The prepared sample was subjected to ICP analysis. The exact weight percentage of the zinc present in the doped crystal is found to be 0.7 % out of 2% of added dopant. It is seen that the amount of dopant incorporated into the doped crystal is less than the concentration of the dopant in the corresponding solution.

3.3 UV – VIS – NIR Analysis

The absorption spectra of pure and doped LAAN crystals were recorded using UV-VIS-NIR spectrophotometer in the range 250 nm - 2250 nm using lambda35 UV spectrophotometer. The absorption spectra of pure and doped LAAN crystals are shown in fig 2. The lower cut of wavelength for pure LAAN crystal is 245.5 nm and the lower cut of wavelength for doped LAAN crystal is 240.5 nm.

The good transmission property of the pure and doped LAAN crystals in the entire visible region suggests its suitability for second harmonic generation [14, 15]. The wide range of transparency suggests that the LAAN and zinc doped LAAN crystals are good candidates for nonlinear optical applications. The doped crystal has better transparency window compared to the pure crystal.

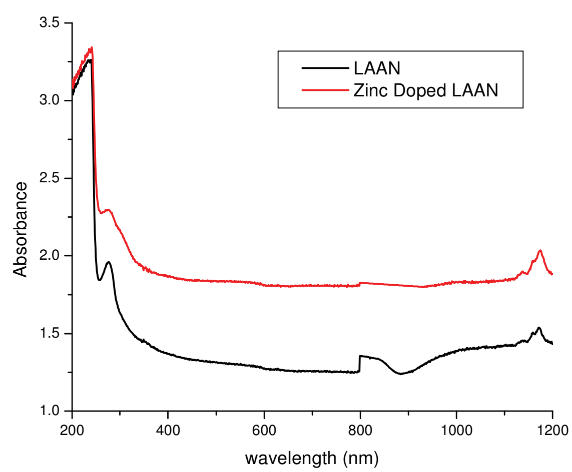


Figure. 2.UV-VIS-NIR spectra of pure and Zinc doped LAAN crystals.

3.4 Determination of optical band gap

The dependence of optical absorption coefficient with the photon energy helps to study the band structure and the type of transition of electron [16]. The optical absorption coefficient (α) was calculated from the transmittance using the following relation.

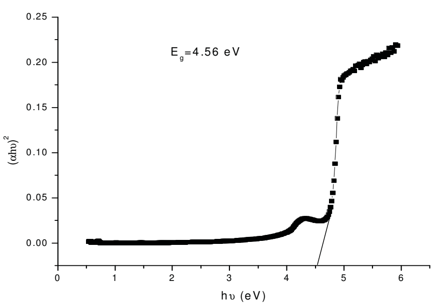
$$\alpha = \frac{1}{t}\log\left(\frac{1}{T}\right)$$

Where T is the transmittance and t is the thickness of the crystal.

Owing to the direct band gap, the crystal under study has an absorption coefficient (α) obeying the following relation for high photon energies (hν):

$$\alpha = \frac{A(h\nu - E_g)^{1/2}}{h\nu}$$

Where E_g is optical band gap of the crystal and A is a constant. The plot of variation of $(\alpha h\nu)^2$ versus hν is shown in fig 3 and 4. E_g is evaluated by the extrapolation of the linear part [17]. The band gap of the pure and zinc doped crystals were found to be 4.56 eV and 4.2 eV respectively.



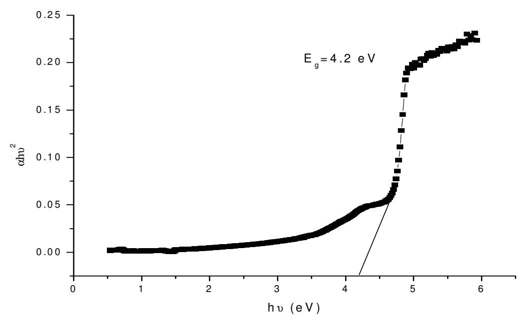


Fig .3.Tauc plot of pure LAAN crystal

Fig.4. Tauc plot of zinc doped LAAN crystal

3.5 Fourier Transform – Infra Red (FT-IR) spectra

The FT-IR spectra studies were to analyze the presence of functional groups in synthesized compound. The FT-IR spectra of pure and doped LAAN crystal were recorded at room temperature in the range of $600 cm^{-1}$ - $4000 cm^{-1}$ by employing BRUKKER IFS 66V FT-IR spectrometer, using KBr pellet method. The FT-IR spectra of pure and doped LAAN crystals are shown in Fig.5 and 6.

The C-H symmetric stretching vibrations were observed at $2594 cm^{-1}$ and $2590 cm^{-1}$ in pure and doped LAAN crystals. The C-C stretching vibration was observed for both of the pure and doped LAAN crystals at $2108 cm^{-1}$. The band observed around $1583 cm^{-1}$ and $1582 cm^{-1}$corresponds to (C=O) stretching vibrations of pure and doped LAAN crystals. The COO – symmetric stretching vibration was observed in pure LAAN crystal at $1451 cm^{-1}$ and doped LAAN crystal at $1450 cm^{-1}$.

The CH_2 twist stretching was observed for both of the pure and doped LAAN crystals at $1355 cm^{-1}$. The band observed around $1231 cm^{-1}$ and $1232 cm^{-1}$ corresponds to C-O structure vibration of pure and doped LAAN crystals. The C-N stretching vibrations were observed in pure LAAN at $1107 cm^{-1}$ and doped LAAN crystal at $1109 cm^{-1}$. The C-H bending vibrations were observed at $768 cm^{-1}$ for pure LAAN and doped LAAN crystals. It shows that addition of zinc dopant do not show any significant from the pure LAAN crystal spectrum. The observed vibrational wave numbers together with pure LAAN and doped LAAN crystals are shown in Table 2.

Table 2: F T-IR Spectral Assignment of Pure and Doped LAAN Crystals

Pure LAAN	LAAN –Zinc doped	Assignment
2594	2590	C-H symmetric stretching
2108	2108	C-C stretching
1583	1582	(C=O) stretching
1451	1450	COO - symmetric stretching
1355	1355	CH_2 twist
1231	1232	C-O structure
1107	1109	C-N stretching
768	768	C-H bending

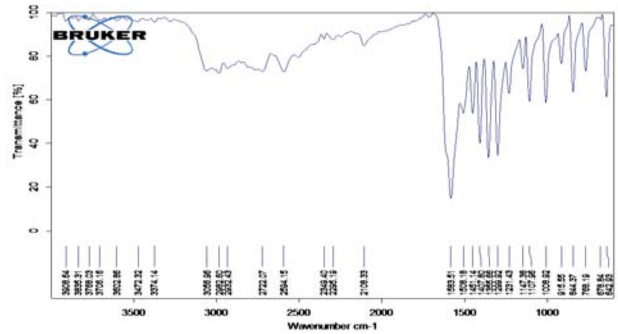


Figure. 5. The FT-IR Spectrum of pure LAAN crystal.

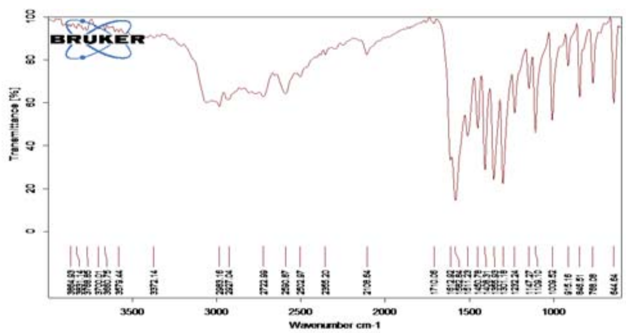


Figure.6.The FT-IR Spectrum of doped LAAN crystal.

3.6 Microhardness measurements

Microhardness studies of pure and doped LAAN crystals have been carried out using HMV SHIMADZU micro hardness tester, fitted with diamond Vickers pyramidal indenter by varying the applied load from 10 g to 100 g. The indentation time was kept as 5 s for all the loads. Figure 7 shows the variations of Vickers hardness number with applied load for (100) plane of the pure and doped crystals. The values of work hardening coefficient (n) of the pure and zinc doped crystals were found to be 1.1 and 1.4 respectively. According to Onitsch, n lies between 1 and 1.6 for hard materials and n is greater than 1.6 for soft materials [18]. Hence, it is concluded that the pure and doped LAAN crystals belong to hard material category.

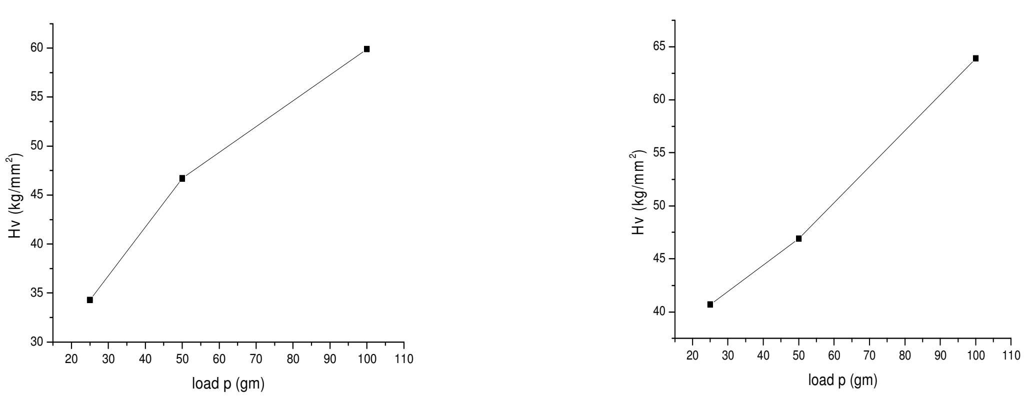


Figure.7. Variation of hardness number with applied load for the plane (100) of pure and doped LAAN crystals.

3.7 Dielectric studies

The dielectric studies of pure and doped LAAN crystals were carried out using the HIOKI 3532-50 LCR HITESTER instrument. The capacitance values for both pure and doped crystals are found for frequencies varying from 50 HZ to 5 MHZ. Fig.8 and 9 show the plot of dielectric constant and dielectric loss pure and doped LAAN crystal as a function of log frequency for different temperatures (313 K, 323 K and 348 K). As the frequency increases, the dielectric constant and dielectric loss in all the three temperature range are found to decrease exponentially and attains constant values at higher frequencies. The higher value of dielectric constant at low frequencies may be attributed to space change polarization. The low dielectric constant and dielectric loss with high frequency implied that the sample posses good optical quality with lesser defects [19].

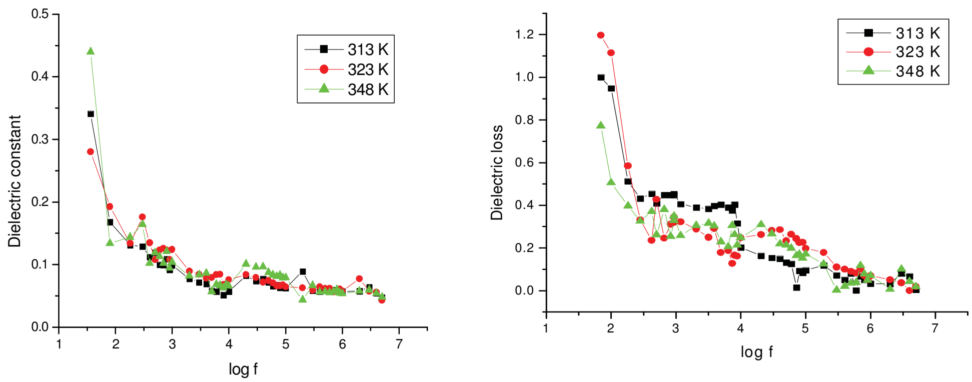


Fig.8. Variation of dielectric constant and dielectric loss with log frequency at different temperature for pure LAAN crystal.

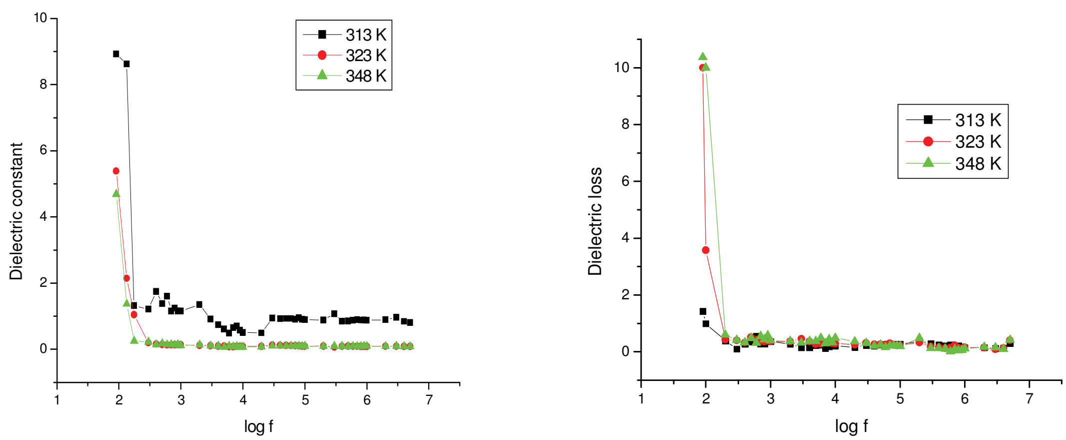


Fig.9. Variation of dielectric constant and dielectric loss with log frequency at different temperature for doped LAAN crystal.

3.8 Thermal studies

Single crystals of pure and doped LAAN crystals were subjected to thermo gravimetric analysis (TGA) and differential thermal analysis (DTA) simultaneously using NETSZCH STA 409° C, in nitrogen atmosphere. The sample was heated at a rate of 25° C/min. Figure 10 and 11 shows the resulting TGA and DTA traces of the pure and doped crystals. There is a sharp weight loss for pure and doped LAAN crystals absorbed at 245.8° C and 295° C. Below the onset of decomposition, no weight loss is observed and hence the pure and doped LAAN crystals are completely free from physically observed water or water of crystallization. The thermal studies indicate that the doped LAAN crystal is more stable than the pure LAAN crystal.

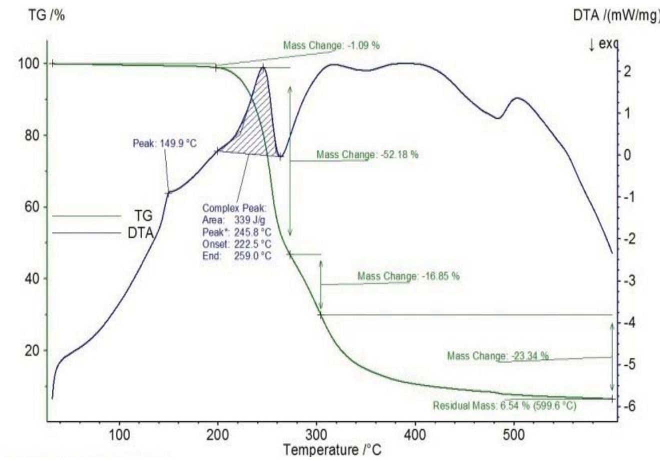


Fig. 10.TG-DTA curves of pure LAAN crystal.

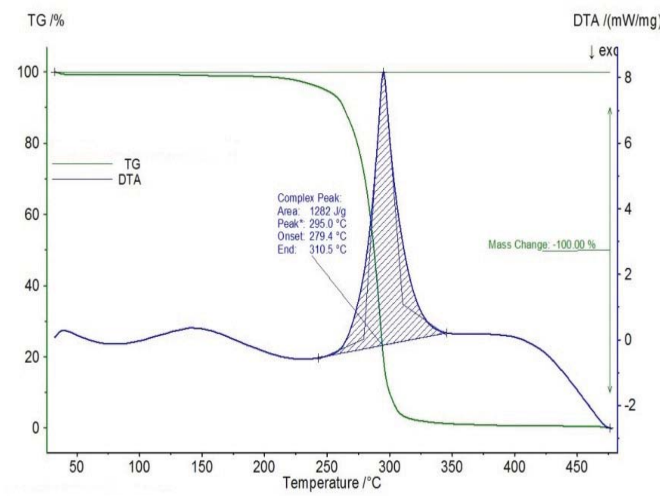


Fig. 11.TG-DTA curves of doped LAAN crystal.

3.9 NLO Studies

The nonlinear optical property of pure and zinc doped LAAN was confirmed by Kurtz and Perry powder technique [20]. The powdered crystal was exposed to a Q-Switched Nd:YAG laser beam of wavelength 1064 nm with pulse width of 8 ns and 10 Hz pulse rate. The NLO output for Pure LAAN and doped LAAN are 45 mJ and 63 mJ, while the reference KDP crystal gives the output of 21 mJ. Thus the SHG efficiencies of the grown pure and doped LAAN crystals were 2.14 and 3.0 times greater than that of reference KDP.

IV. CONCLUSION

Single crystals of pure, zinc doped L – alanine alaninium nitrate (LAAN) were grown by slow evaporation method. The grown crystals were characterized by single crystal XRD analysis, ICP studies, UV – VIS – NIR analysis, FT-IR analysis, Micro hardness study, Dielectric analysis, TGA and DTA studies and NLO studies. The XRD analysis confirms the crystalline nature of the materials. ICP studies confirm the presence of the dopant in the grown crystal. UV-VIS-NIR studies reveal that the pure and doped crystals possess wide transparency in the entire visible region. The band gap of the pure and doped LAAN crystals were found to be 4.56 eV and 4.2 eV respectively. The presences of various functional groups present in the pure and doped LAAN crystals has been confirmed by FT-IR analysis. Hardness test revealed that the grown pure and doped LAAN crystals are belonging to hard crystal category. The dielectric studies reveal that the dielectric constant decreases with log frequency, owing to its total transparency in the visible region. The thermal studies indicate that the doped LAAN crystal is more stable compared to the pure crystal. The SHG efficiency of the pure and Zinc doped LAAN crystals were 2.14 and 3 times greater than KDP crystal. Owing to all these properties doped LAAN crystal could be a promising material for NLO applications.

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