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INVESTIGATION ON INFLUENCE OF CADMIUM IONS IN THE GROWTH, STRUCTURAL, OPTICAL, MECHANICAL AND NLO PROPERTIES OF L-ASCORBIC ACID SINGLE CRYSTAL

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Abstract:

L-Ascorbic acid (LA) and cadmium Nitrate doped L-Ascorbic acid (LACD) crystals are grown from aqueous solution at room temperature in slow evaporation technique. Single crystal X-ray diffraction analysis reveals that both the pure LA and LACD crystals belong to monoclinic system with the space group P21.The presence of functional are identified by FT-IR spectrum. UV-VIS-NIR spectral studies were carried out to analyze the optical absorption of the grown crystals and confirmed that absorption is almost negligible in the visible and UV regions for both pure and doped crystals. Mechanical behavior of the grown crystals was observed by Vickers micro hardness studies. EDAX analysis confirmed the presence of elements in the crystal. Thermal stability of the grown crystal was investigated using TG/DTA. NLO properties have been confirmed by Kurtz powder technique. The laser damage threshold value was measured by using Q-switched ND: YAG laser.

Keywords: organic single crystal, slow evaporation technique, X-ray diffraction, FTIR, Thermal analysis, Second Harmonic generation, Laser damage threshold.

1. INTRODUCTION

A variety of applications are possible with nonlinear optical materials including frequency conversion, light modulation, optical memory storage, second harmonic generation, and optical switching [1-2]. Developments of new and better nonlinear optical (NLO) materials are of much importance because of its extended applications. Organic NLO crystals have attracted many researchers because they have higher optical non-linearity, lower cut off Wavelength, low cost and flexibility. The researchers have identified amino acid based nonlinear optical crystals with better linear and nonlinear optical properties. The wider choice of materials, improved high non-linearity, low transformation temperature, fast response and high transparency make these systems more demanding than any other systems [3-4]. Amino acids are interesting because they have a donor carboxylic acid (COOH) and acceptor amino (NH_2) functional groups in them. These two functional groups form strong chemical bond called covalent bonds. Hydrogen bonds have employed in the possible generation of non-Centro symmetric structures, which is a prerequisite for an effective second harmonic generation (SHG) crystal [5-7]. The necessity for suitable crystal size, superior NLO, thermal, mechanical, and optical properties in optoelectronic and SHG applications has led to ongoing efforts to alter the

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properties of crystal by adding various impurities and/or changing growth settings. Our present work reports the growth and study of pure L-Ascorbic acid (LA) and Cd-doped (1 mol %) L-Ascorbic acid (LACD) single crystals. These were grown from aqueous solution by adopting the slow evaporation of solvent technique. These crystals were subjected to single crystal XRD study, Fourier transform infrared (FT-IR) spectroscopy; ultraviolet, visible and near infrared (UV–Vis-NIR) spectroscopy, Micro hardness and SHG efficiency measurement.

2. EXPERIMENTAL METHODS

Commercially available organic chemical of L-Ascorbic acid (LA) (AR grade) were used for the crystallization. The crystallization process was carried out by adding LA in 50 ml of distilled water with constant stirring. A saturated solution of LA was prepared at the room temperature. The solution was stirred well for 6 h using magnetic stirrer to attain homogeneity throughout the entire volume of the solution. Suspended impurities were removed by filtering the solution. The clear filtrated the solution was allowed to evaporate at room temperature approximately 32^0C. In a span of fifteen days, well-defined bright yellow single crystals of LA with an average dimension of 5 ×4×1 mm^3 were obtained. The grown LA crystals are shown in Fig. 2. In the same way to grow LACD single crystal. 1mol % of cadmium nitrate was added to the saturated solution of LA. The solution was allowed to evaporate at room temperature. After 15 days, well-defined single crystals of Cd doped L-ascorbic acid single crystal were obtained. The grown crystal of LACD shown in fig. 2 (a).

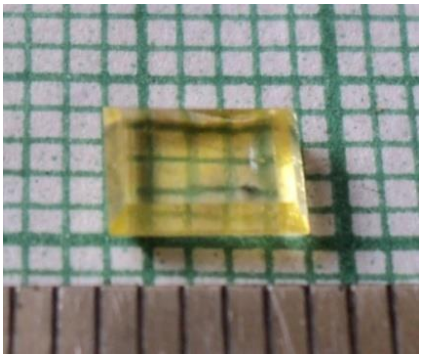

Fig.2 Grown pure LA single crystal

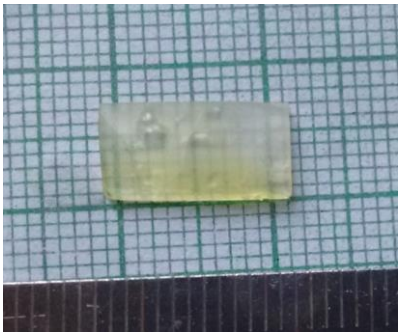

Fig.2 (a) Grown LACD single crystal

3. RESULTS AND DISCUSSION

3.1 Single crystal X-ray diffraction:

Single crystal X-ray diffraction studies of pure and Cadmium doped LA crystals were carried out using BRUKER AXS SMART APEXII, single X-ray diffractometer. The single crystal XRD data shows that both pure LA and LACD crystals belong to monoclinic crystal system with space group of P21. The lattice parameters of LA crystals are in good agreement with the reported values [8]. The observed lattice parameter value of the pure LA and LACD crystals were compared and are presented in Table 1. A marginal decrease

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in the lattice parameters and volume has been observed for the LACD crystal in comparison with the pure LA crystal.

Table 1: Lattice parameters of LA and LACD crystal

Cell parameters	LA	LACD
Unit cell dimension	a = 6.45Å	a = 6.43Å
	b = 6.40 Å	b = 6.37 Å
	c = 17.24 Å	c = 17.19 Å
	α= γ = 90°	α= γ = 90°
	β= 99.50º	β= 99.36º
Volume	V= 702 Å^3	V= 695 Å^3

3.2 FTIR- Spectrum analysis:

The FTIR analysis of LA and LACD was carried out to investigate the presence of functional group and vibrational modes. The spectrum was recorded in the region 4000-400cm^{-1} using SHIMADZU IR AFFINITY 1S spectrometer. The recorded spectrum is shown in Fig.3. The intense broadband between 3200cm^{-1} and 3530cm^{-1} is due to O-H stretching. The broadening is due to hydrogen bonding. The C=O stretching was observed at 1759cm^{-1}. The peak at 1660cm^{-1} is due to C=C stretching. The absorption peak at 1484 cm^{-1} is due to O-H in-plane bending and C-O stretching. . The in-plane bending and out of plane bending vibration of LA are observed at 1327cm^{-1} and 866cm^{-1}. The band absorbed at 748cm^{-1} and 551cm^{-1} are due to C-H stretching. The LACD crystal spectrum shows the shift in the values of wave number in peaks, which conforms the presence of cadmium ions in the crystals. [9-11].

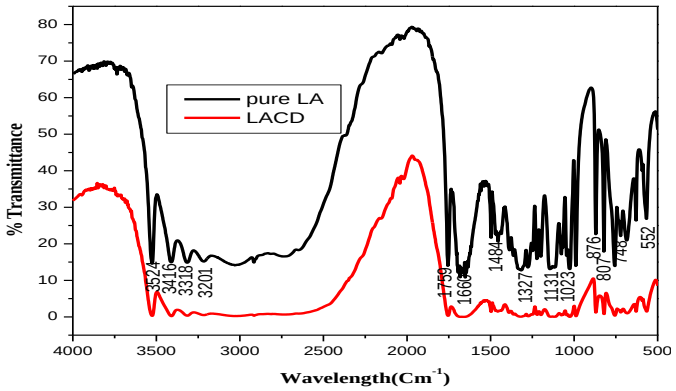

Fig.3 FTIR Spectrum of grown LA and LACD Single crystal

3.3 UV-VIS absorption spectral analysis:

The optical absorption spectra of LA and LACD single crystal was studied using SHIMADZU SPECTROMETER UV-1800 in the range of 200nm-1100nm. The recorded absorption spectrum is shown in Fig. 4. The UV cutoff wavelength of LA and LACD is observed at 306 and 298 nm respectively. The lower cut off wavelength and wide

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transparency is the important properties for NLO application. The absorption coefficient (α) was calculated from the absorption (T) spectrum using the following relation [12].

$$\alpha = (2.303/t) * \text{absorbance} \quad (1)$$

where‘t’ is the thickness of the sample. The optical band gap (Eg) was estimated using the relation [13].

$$(\alpha h\nu) = A\,(Eg - h\nu)^n \quad (2)$$

Where n is called the power factor of transition mode. The value of n for direct allowed, indirect allowed, direct forbidden and indirect forbidden transition are n = ½, 2, 3/2 and 3 respectively. By plotted the curve between $(\alpha h\nu)^n$ and photon energy(hv) for all power coefficient values (n= ½,2,3/2,3) for the present sample. Fig.5 Shows a linear behavior, which can be, consider as an evidence of the indirect transition. The optical band gap value was obtained by extrapolating the linear part of curve $(\alpha h\gamma)^{1/2}$ as a function of incident photon energy hγ known as Tauc plot. The calculated indirect optical band gap of the grown crystal is found to be 4.10eVand 4.16eV for LA and LACD respectively. The absorption percentage is also slightly reduced by the addition of cadmium. It is an important requirement for a crystal in exhibiting laser and device applications [14-15].

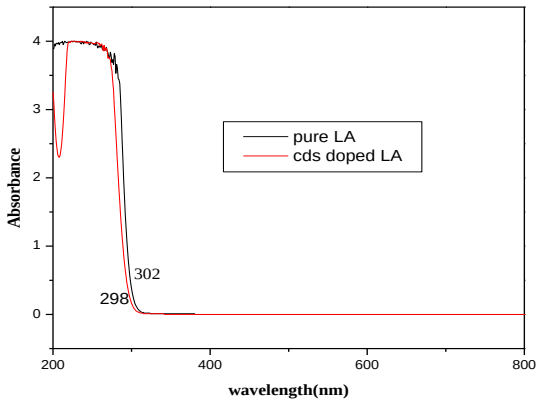

Fig.4 UV absorption spectrum of LA and LACD

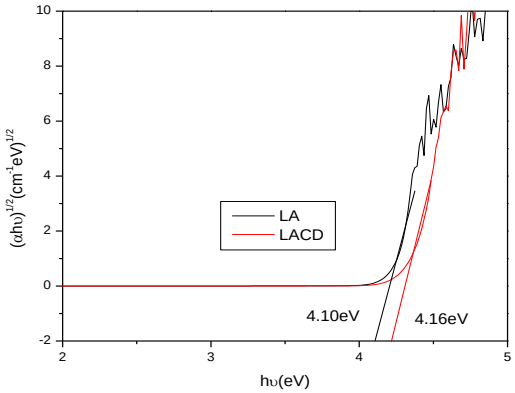

Fig.5 Band gap spectrum of LA and LACD

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3.4 Vickers Micro hardness:

The Vickers micro hardness measurements were carried out on pure LA and LACD crystal using SHIMADZU HMV - 2000 micro hardness tester. Mechanical properties are one of the important features for device fabrication. Hardness is the resistance offered by a material against the plastic deformation caused by scratching or indentation. The hardness of the material, Hv is determined by the relation

$$Hv = 1.8544\ (P/d^2)\ (Kg/mm^2) \quad (3)$$

Where P is the applied load in kg and d the diagonal length of indentation impression in mm. Fig.6. Shows the variations of hardness number with the applied load. The micro hardness (Hv) values increases with load for both pure LA and LACD. From the results, it is observed that the value of hardness of the LACD crystal is higher than the hardness value of pure LA single crystals for all loads. The hardness value of the material increases with the increase of applied load. Such a phenomenon was referred to as reverse indentation size effect (RISE).This increase in the hardness value of doped sample can be attributed to the incorporation of the impurity in the lattice of the LACD crystal. The Mayer index number was calculated from Mayer's law, which relates the load and indentation diagonal length. Consider as

$$P = k_1 d^n \quad (4)$$

$$\log P = \log k_1 + n \log d \quad (5)$$

Where k is the material constant and n is the work-hardening coefficient. According to Onitsch, $1.0 \leq n \leq 1.6$ for hard materials and $n \geq 1.6$ soft materials [16]. The plot between log P and log d is shown in Fig.7. It is a straight line, which is in good agreement with Mayer's law. The work hardening coefficient of grown LA and LACD crystal was determined by the least – squares fit method. The n value of grown crystal was found to be 2.06 and 2.14. Hence it is concluded that the LA and LACD belongs to soft material category.

The elastic stiffness constant is calculated using Wooster's empirical formula, given by

$$C_{11} = H_v^{7/4} \quad (6)$$

Which gives an idea about the tightness of bonding between the neighboring atoms. The calculated value of C_{11} indicates that the binding forces between ions are quite strong [17]. From the hardness value, the yield strength σ_v of a material is calculated using the relation.

$$\sigma_V = \frac{Hv}{2.9}\{1-(n-2)\}\left[\frac{12.5(n-2)}{1-(n-2)}\right]^{n-2} \quad (7)$$

The tensile strength (T) of the pure LA and LACD crystal have been calculated using the linear mathematical relation [18]

$$T = 0.2\ H_v + 6 \quad (8)$$

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The load dependent hardness parameters n, yield strength (σ_v), Tensile strength and stiffness constant are calculated for LA and LACD crystal are given in table 2. Hardness is important factor in selecting the processing (cutting, grinding, polishing) steps of bulk in fabrication devices based on the crystals.

Table.2 Mechanical parameters of LA and LACD crystals

Mechanical parameters	Values of LA	Values of LACD
Hardening co-efficient n	2.06	2.14
Yield Strength σ_v ($\times 10^{10}$Pa)	2.5	2.8
StiffnessConstantC_{11}($\times 10^3$GPa)	2.071	4.158
Tensile Strength T(GPa)	16.07	21.86

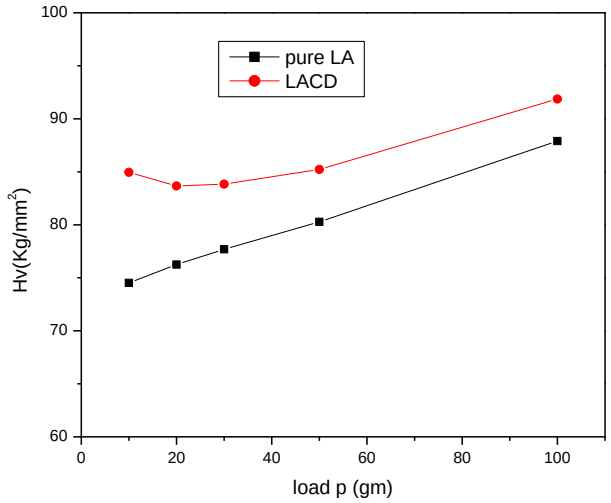

Fig.6 Hv Vs load p

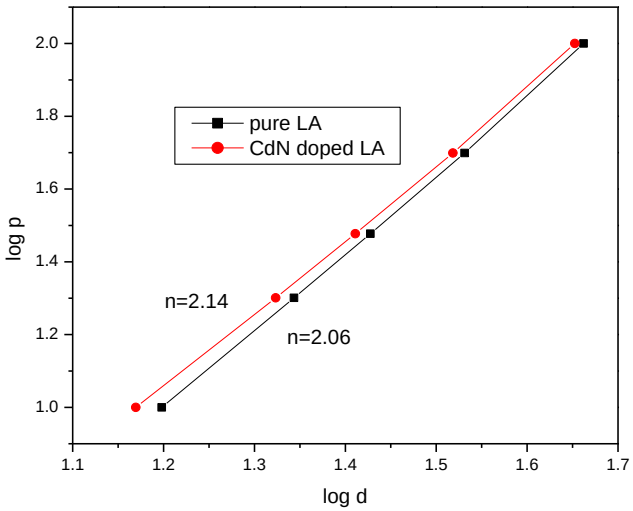

Fig.7 log P Vs log d

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3.5 SHG Efficiency Analysis:

The SHG efficiency of pure LA and LACD was determined by Kurtz's Perry technique [19]. The Q-switched mode locked the ND: YAG laser with fundamental output at 1,064 nm, repetition rate 10 Hz, and pulse energy 3.1 mJ. The output at the second harmonic wavelength 532 nm was monitored. The crystal was ground into a very fine powder and tightly packed in a micro capillary tube. Then it was mounted in the path of ND: YAG laser beam. Second harmonic radiation generated by the randomly oriented microcrystals was focused by a lens and detected by a photomultiplier tube. A sample of potassium dihydrogen phosphate (KDP) was used as a reference material for the measurement of SHG efficiency. The SHG conversion efficiency of LA and LACD is found to be 1.2 and 1.6 times that of KDP. This indicates that the SHG efficiency of LACD is higher than that of pure LA.

3.6 EDAX Analysis:

The grown LACD single crystal were analyzed by using energy dispersive X-ray (EDAX), it give the information about atomic percentage of element present in the sample. The EDAX spectrum of LACD shown in fig.8

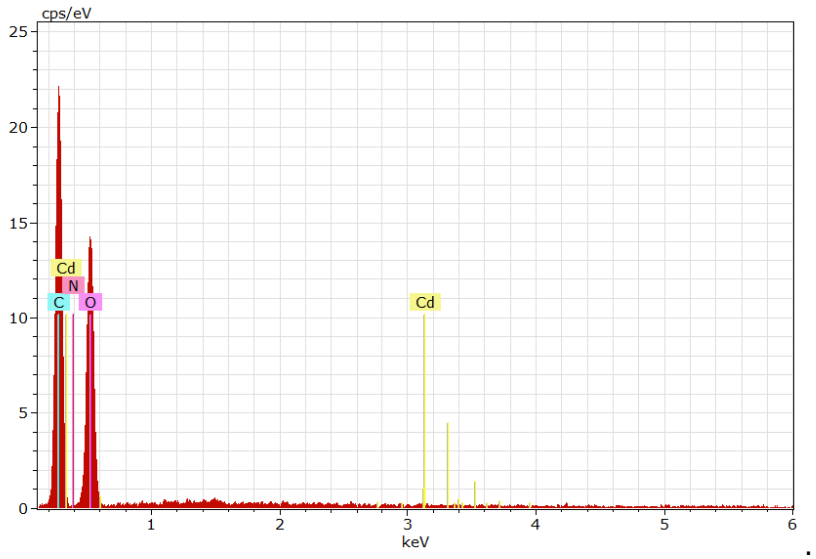

Fig.8 EDAX Spectrum of LACD crystal

The EDAX spectrum confirms that the cadmium ions are doped into L-Ascorbic acid. The amount of energy possessed for the corresponding carbon, oxygen and nitrogen peaks emitted by the electrons in k-shell and for corresponding cadmium peaks emitted by the electrons in the L-shell. The atomic percentage for C, O, N and Cd is 55.67%, 44.08%, 0.41%and 0.01%, which provides the presence of Cd-ions in the LA single crystal.

3.7 Thermal analysis

The TG–DTA spectrum of LA and LACD recorded within the temperature range from 30^{o}C to 400^{o}C are shown in Fig. 9 and fig.10. From TGA spectrum the grown LA and LACD

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crystal has found to be stable up to 193^{o}C and 194^{0}C. There is no big changes was observed in the thermal stability of LACD. The major weight loss of the grown crystals occurs in the range of 193^{0}C-240^{0}C. The sharp endothermic peak occurs in the DTA curve occurs which corresponds to the decomposition of grown LA and LACD. There is no weight loss around 100^{0}C in the grown crystals, which indicates that, the absence of water molecules. TG/DTA reveals that there is no phase transition before its melting point, which is the good agreement for the crystalline nature of the material.

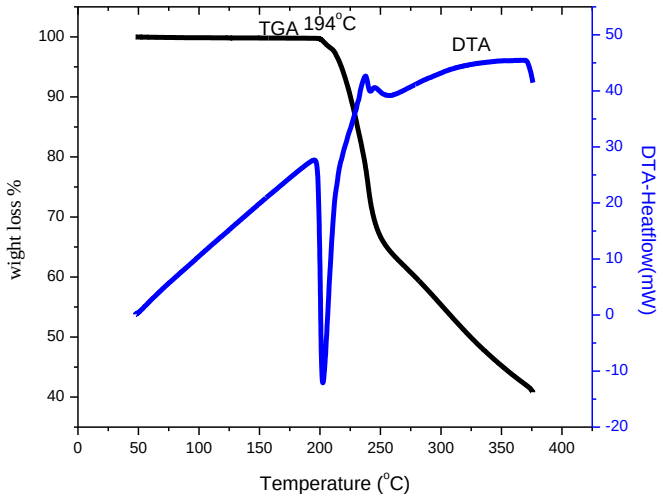

Fig.9 TG-DTA spectrum of LACD

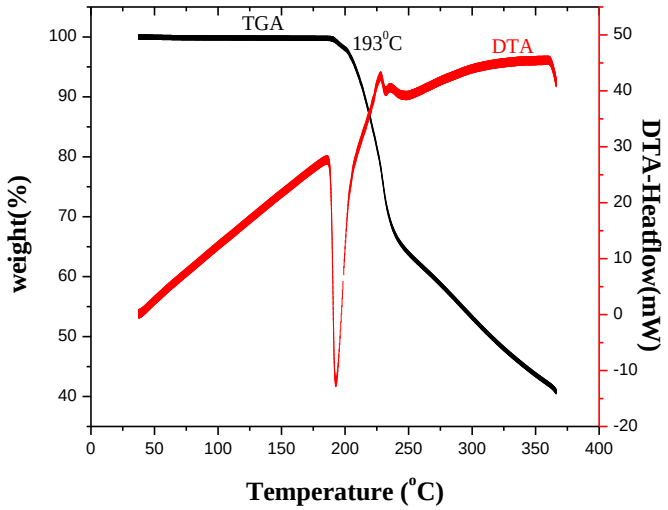

Fig.10. TG/DTA Spectrum of LA crystal

3.8 Laser Damage threshold measurements

The laser damage threshold measurement was carried out by using Q-Switched Nd: YAG laser of 1064nm laser beam with pulse width 10ns and 10Hz repetition rate as the source. The cut and polished grown crystal of LA and LACD was placed at the focus of a plano

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convex lens of focal length 30cm. The multiple short modes LDT measured was made on well-polished crystal. An attenuator was used to vary the laser pulses with a polarizer and a half wave plate. The laser damage threshold value was measured using combination of a phototube and an oscilloscope. The surface damage threshold of the crystal was calculated using the relation

$$\text{Power density } (P_d) = E/ \tau \pi r^2 \quad W/cm^2$$

Where E is the energy (mJ), τ the pulse width (ns), and r the radius of the spot (mm). When the intensity (in mJ) of the laser beam increases, initially a dot occurs on the surface of the grown crystal. This is followed with the crack and heavy damage occurs on grown single crystal. The laser induced surface damage threshold of LA and LACD single crystal is 1.8 GW/cm^2 and 1.87GW/cm^2. Form the result-doped crystal has higher LDT value than the LA crystal, which is due to addition of cadmium ions.

4. CONCLUSION

In summary, L-Ascorbic acid (LA) and cadmium nitrate -doped L-Ascorbic acid (LACD) single crystals were successfully grown via slow evaporation method. From SXRD, The change in the lattice parameter and Volume of LACD crystal compared to the LA crystal is due to the lattice distortion caused by Cd ions. The presence of functional group of the grown LA and LACD crystals are confirmed by FTIR spectrum. From the UV spectra, the lower cut off wavelength of grown LA and LACD crystal is 302nm and 298nm. The absorption is very low in the entire visible and the IR region makes it a potential candidate for laser applications. Vickers Micro hardness studies confirmed that the grown LA and LACD crystal belongs to soft material category. LA and LACD is thermally stable up to 193^{0}C and 194^{o}C.The SHG conversion efficiency of the LACD crystal is higher than the LA crystal by inclusion of cadmium ions. The presence of cadmium has been confirmed by the EDAX. From LDT, the value of laser damage threshold of grown LA and LACD crystal is 1.8GW/cm^2 and 1.87GW/cm^2.

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