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Effect of Rare Earth Element Erbium and Transition Element Cobolt on L-Valinium Picrate Single Crystal

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ABSTRACT

L-Valinium Picrate, Rare earth element Erbium doped L-Valinium Picrate and soft transition element Cobolt doped L-Valinium Picrate were synthesized and grown as single crystals by slow evaporation method. The cell dimensions were obtained by single-crystal X-ray diffraction study. Optical properties, such as UV–visible–NIR absorption and second harmonic generation conversion efficiency were investigated to explore the optical characteristics of the grown crystals. Microhardness, Thermal and dielectric studies of the compound were also carried out.

1. Introduction

Recently, materials possessing non linear optical properties, especially those exhibiting second harmonic generation (SHG) have received considerable attention due to their wide range of technical applications. A novel class of SHG active compounds based on hydrogen bonded salts of inorganic oxyacids and polarizable organic cations seems to be very promising [1] because of the higher SHG efficiency and better physicochemical properties compared to the traditional classes (inorganic or organic salts) of SHG active materials. In the recent years, complexes of amino acids with inorganic acids and salts are promising materials for optical SHG, as they tend to combine the advantages of organic amino acid with that of inorganic acid [2-4]. A series of these compounds, such as L-argenine phosphate, L-argenine hydrobromide,L-argeninehydrochloride, L-hystidine dinitrate, L- hystidine tetrafluoroborate, L-threonine acetate, L-alanine maleate, L-Proline tartrate, L-Proline Picrate, L-cystine hydrochloride have been reported [5-11]. In this paper, we are presenting a report on synthesis and growth of L-Valinium Picrate, rare earth element, Erbium doped L-Valinium Picrate, soft transition element Cobolt doped L-Valinium Picrate and the grown crystals were subjected to various characterization studies.

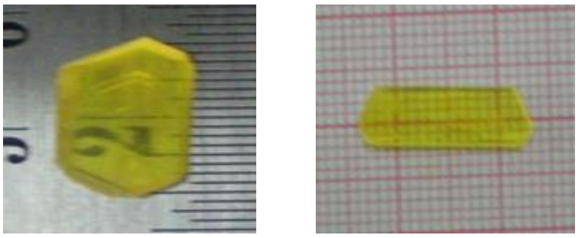
2. Experimental

2.1 *Crystal Growth*

Commercially available AR grade L-Proline (Loba chemie) and Picric acid were mixed in equimolar ratio and dissolved in the mixed solvent of double distilled water and acetone in 1:1 ratio to synthesize L-Valinium Picrate (LVP) source material. The synthesized salt was purified by repeated recrystallisation process and used for growing pure LVP. Rare earth element Erbium doped LVP crystals and transition element Cobolt doped LVP crystal, were grown from mixed solvents of water and acetone in the ratio of 1:1 using the well known solvent evaporation technique with 2 mol %, 5 mol % and 10 mol % of Cobolt (II) nitrate hexahydrate and Erbium Nitrate added to the Pure LVP saturated solutions.

Optical quality crystals were collected in a period of 30 to 45 days. From the physical observations of the grown crystals the 5 mol % Erbium doped LVP (Er5 : LVP), and 10 mol % Cobolt doped LVP (Co10 : LVP) crystals have good transparency and morphology and are shown in figure 1.

Pure LVP



Er5 : LVP Co10 : LVP

Figure 1. As grown pure LVP and doped LVP crystals.

2.2 *Characterization*

The grown single crystals of pure LVP, Er5 : LVP, and Co10:LVPwer subjected X-ray diffraction studyusing a Bruker AXS Kappa APEX II single crystal CCD diffractometer equipped with graphite monochromated MoKα (λ = 0.7107 Å). Energy dispersive and X-ray study (EDAX) was carried out using EDAX - AMETEK tester for the grown samples to analyze the percentage of dopants in the crystal. HIOKI 3532–50 LCR HITESTER was used for the dielectric study.

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The samples of size approximately 4 x 4 x 3 mm^3 were prepared from all the crystals and mounted between copper electrodes. In order to ensure good electrical contact between the crystal and the electrodes, the crystal faces were coated with silver paint. The dielectric measurements were carried out in a frequency range 100 Hz – 5 MHz and temperature range 35 – 95 ºC. The thermo gravimetric and differential thermal analyses (TG – DTA) response curves were drawn for pure and doped LVP sample in the temperature range from 20 to 800 °C using the instrument NETZSCH STA 409C at the heating rate of 10 K/min. in nitrogen atmosphere.

The optical transmission spectra were recorded using Shimadzu model - 1601 in the wavelength range of 300– 900 nm. The study of NLO conversion efficiency was carried out by the powder technique of Kurtz and Perry. The crystals were ground into fine powder and tightly packed in a micro capillary tube. It was mounted in the path of the laser beam. A Q-switched flash lamp pumped Nd:YAG laser of power 3.2 mJ with a wavelength of 1064 nm, pulse duration of 8 ns, a repetition rate of 10 Hz and a spot size of 1 mm diameter was used for SHG test. Vickers hardness study was made on the as grown crystal using Leica- Reichert Polyvar2 model hardness tester fitted with a diamond indenter.

3. Results and discussion

3.1 Single Crystal X-Ray Diffraction

Unit cell parameters of the grown LVP, Er5 : LVP, and Co10 : LVP single crystals are listed in Table1. The observed values of LVP agree well with the reported values [10, 11]. It was observed that volume of the Er5 : LVP and Co10 : LVP crystals are reduced since the rare earth metal ions Er and Co occupies the void spaces of pure LVP crystalline matrix and there will be a local compressive strain in the lattice. LVP and doped LVP belongs to monoclinic system, space group P2$_1$ which is recognized as non centro symmetric, thus satisfying one the basic and essential material requirements for the SHG activity of the crystal.

Table 1. Comparison of Single Crystal X-ray data of pure LVP and doped LVP crystals.

Parameters	Pure LVP	Er doped LVP	Co doped LVP
a (Å)	10.902	10.831	10.875
b (Å)	5.352	5.342	5.338
c (Å)	12.472	12.454	12.444
V (Å3)	686	682	682.32
System	Monoclinic	Monoclinic	Monoclinic
β(°)	109.11	108.76	109.17
Space group	P2$_1$	P2$_1$	P2$_1$

Table 2. EDAX analysis of doped LVP crystals.

Elements	Er doped LVP		Co doped LVP	
	Wt.%	At.%	Wt.%	At.%
C	32.08	37.9	38.81	46.01
N	23.16	23.47	17.22	17.51
O	43.39	38.50	40.38	35.93
Elements	Nd : 01.73	Nd : 00.17	Nb : 3.59	Nb : 0.55

3.2 EDAX Analysis

In order to analyze quantitatively the presence of dopants in the crystal, EDAX study was carried out for the grown samples and the percentage of dopant present in the LVP were confirmed and tabulated in Table 2. From EDAX analysis, it is observed that the amount of dopant atoms entered into the LVP lattice is very less.

3.3 Dielectric Studies

The variation of dielectric constant and dielectric loss as a function of frequency were determined for pure and doped crystals and are shown in the figures 2(a) and 2(b). It is found that the dielectric constants of LVP and doped LVP crystals are high at lower frequencies and they decrease with increase in frequency. This may be attributed to space charge polarization due to charged lattice defects. The trend of the dielectric constants of LVP and doped LVP crystals are almost the same. But at fixed frequency, the dielectric constants of doped LVP crystals are less than that of pure one. In accordance with Miller rule, the lower value of dielectric constant is a suitable parameter for the enhancement of SHG coefficient [12].

From the dielectric study, it is observed that the pure LVP crystal has high dielectric constant compared to that of the doped crystal. It shows that the pure LVP has higher polarization than that of the doped LVP crystals. This may be attributed that the polarization in one molecule is not well transported to neighboring molecules in the presence of dopants [13]. The characteristic of low dielectric loss at high frequencies for these samples suggest that the pure and doped crystals possess enhanced quality with lesser defects [14]. For a particular frequency, the dielectric loss of doped LVP is slightly lesser than that of pure, which indicates that the dopant enhances the optical quality of LVP and reduces the defects.

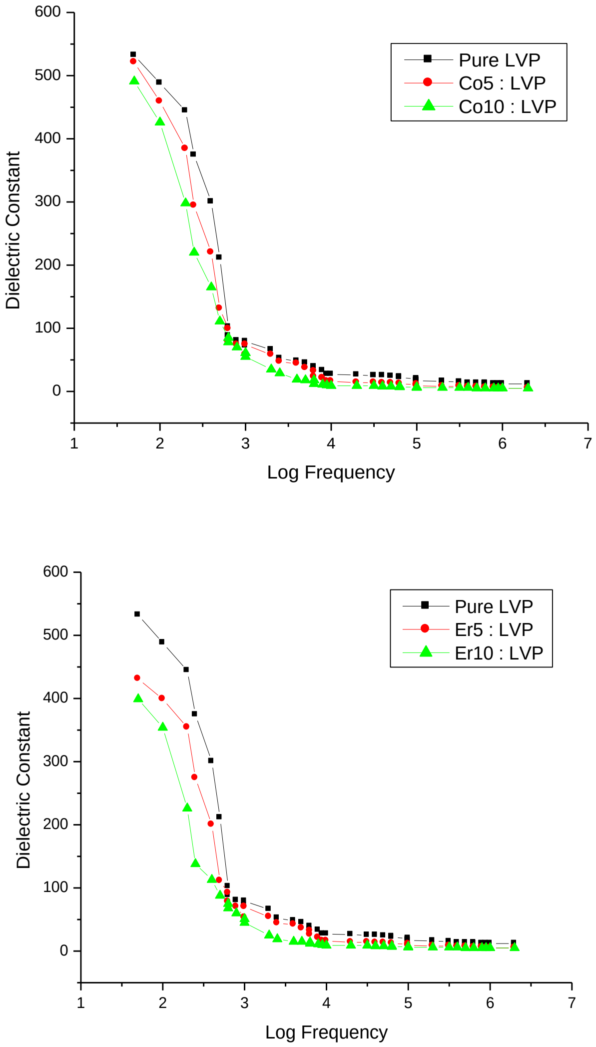


Figure 2. (a). Dielectric Constant vs. Log frequency for pure and doped LVP crystals.

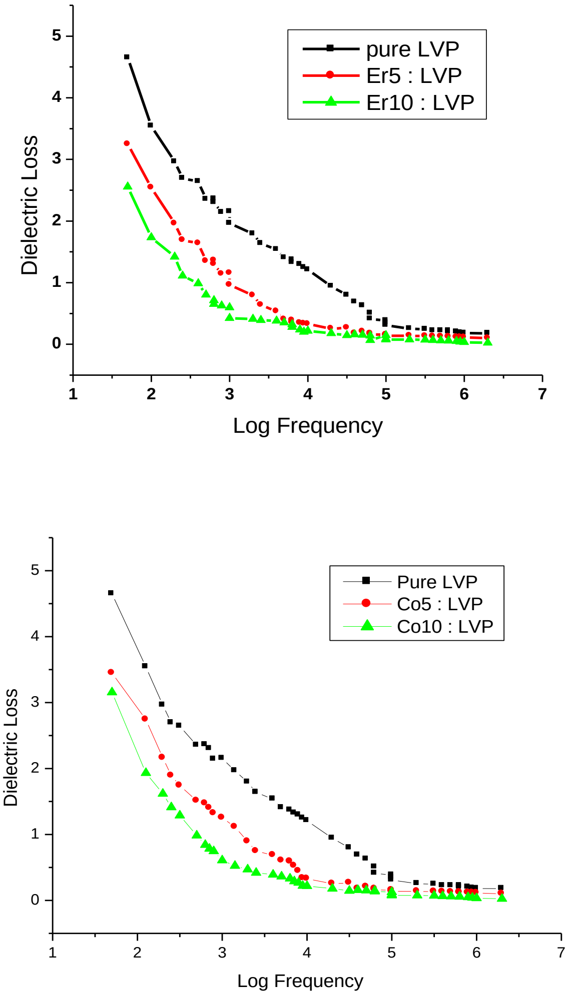
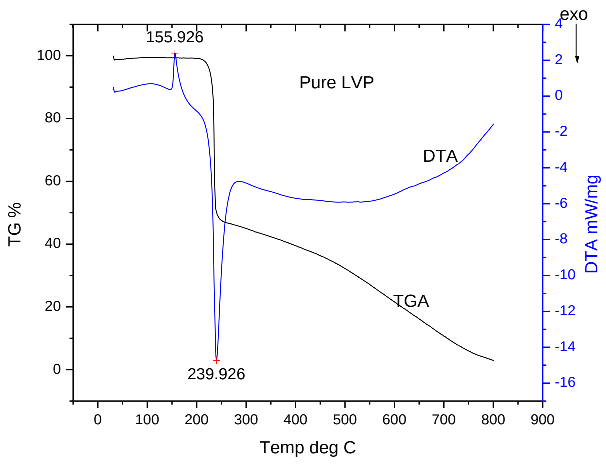
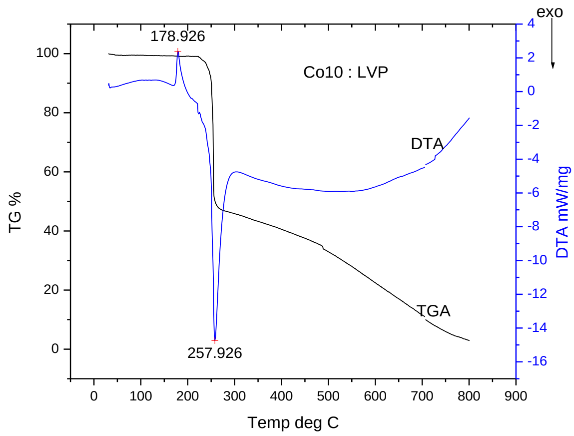


Figure 2 (b). Dielectric Loss vs. Log frequency for pure and doped LVP crystals.

3.4 Thermal Analyses

The TG - DTA curves of LVP and doped LVP samples exhibit nearly similar stage of decomposition between 100 and 900ºC as shown in figure 3.In order to study the influence of the dopant on thermal stability of LVP, the temperature corresponding to a peak maximum of first stage of phase transition in DTA trace is taken into account for comparison. The temperature on the first stage of transition for the LVP and doped LVP crystals are tabulated in Table 3. This shows that the doped crystal possess good thermal stability compared to pure crystal.





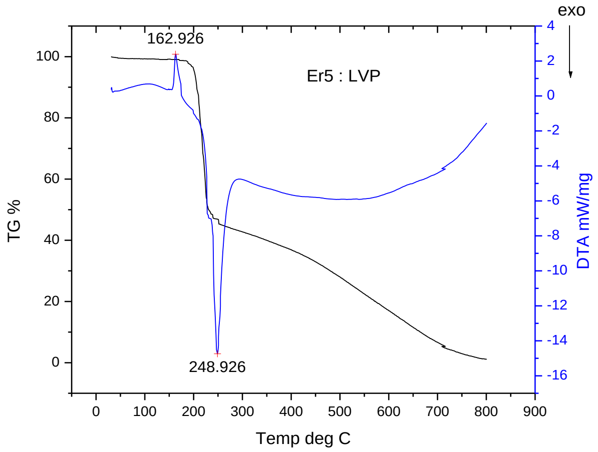


Figure 3. TG-DTA graph for pure and doped LVP samples.

Table 3. Thermal Analysis data for pure and doped LVP crystals.

Crystals	Temperature corresponding to the first stage of phase transition
Pure LVP	156°C
Er5 : LVP	178°C
Co10 : LVP	210°C

3.5 Optical Transmission Study

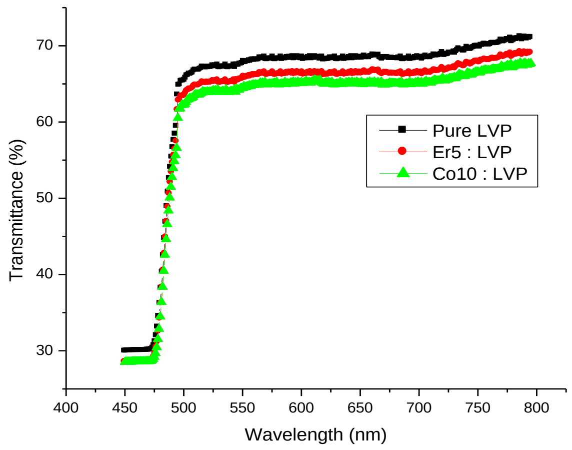


Figure 4. Optical transmission for pure and doped LVP crystals.

The figure 4 shows the optical transmission spectra of LVP and doped LVP crystals. The thickness of the samples used for this study was 1.5 mm. The lower cut off for LVP and doped LVP crystals are around 470 nm. This shows that doping the crystal with Erbium and Cobolt do not influence the lower cut-off value, but, the percentage of transmission is varied and is listed in Table 4.

3.6 Powder SHG Measurement

The study of NLO conversion efficiency was carried out by the powder technique of Kurtz and Perry [15]. Table 5 shows the second harmonic signal and SHG efficiency for pure and doped LVP crystals for an input energy of 3.2 mJ/pulse and is compared with standard KDP sample. The standard KDP sample gave a SHG signal of 15 mV/pulse for the same input energy. The results obtained by this method shows that SHG efficiency of doped LVP crystals are less than the pure LVP and this is due to ineffective transportation of polarization from one molecule to its neighbor in the presence of dopants. Since the second order non linear efficiency will vary with the particle size of powder sample [16], the care has been taken to maintain uniform particle size of source and the reference material.

Table 5. SHG efficiency for pure and doped LVP crystals.

Crystals	Second Harmonic Signal	SHG Efficiency with respect to KDP
Pure LVP	720 mV	48 times
Er5 : LVP	462 mV	31 times
Co10 : LVP	441 mV	29 times

3.7 Vicker's Microhardness Study

The good quality crystals are needed not only with good optical performance but also with good mechanical stability [17] for applications. In order to study the mechanical behavior of the grown LVP crystal, indentations was made on the cleaved (100) plane of pure LVP and doped LVP crystals with the applied load ranging from 5 to 100 g. The time of indentation was kept constant as 5 s for all indentations. The Vicker's hardness number was calculated using the relation [18],

$$H_V = \frac{1.854P}{d^2}\ kg/mm^2$$

where P is the applied load and d is the diagonal length. The Vicker's hardness for LVP and doped LVP crystals as a function of load are shown in figure 5. The hardness values of LVP were found to be lower than that of the doped LVP crystals. Vicker's hardness increases with increase of load till 70 g for Er5 : LVP and Co10 : LVP crystals but upto 50 g for pure LVP crystal. The Loads above 70 g for Er5:LVP, Co10:LVP crystals and 50 g for pure LVP developed multiple cracks around the indentation mark and hardness decreases with the further increase of load. The value of H_v increases on doping because dopant ions enters into the lattice and hinder the formation of dislocation. By plotting log P versus log d, the value of the work hardening coefficient (n) was found out and is given in the table 6. According to Onitsch, $1.0 \leq n \leq 1.6$ for hard materials and $n > 1.6$ for soft materials [19]. Hence it is concluded that LVP and doped LVP crystals are soft materials. In order to find the increase in strength that accompanies plastic deformation of the grown crystal, yield strength (σ_y) of the crystals was also calculated using the relation [20]

$$\sigma_y = \left(\frac{H_V}{3}\right)0.1^{n-2}\ \textbf{MPa}$$

where 'H_v' is the maximum hardness and 'n' is the work hardening coefficient. Yield strength for LVP is 0.07 MPa and for doped LVP crystals it is 0.08 MPa respectively.

Table 6. Maximum Hardness and Work hardening coefficient for pure and doped LVP.

Crystals	Maximum Hardness (H_v)	Work Hardening Coefficient (n)
Pure LVP	11.4	3.73
Er5 : LVP	13.4	3.08
Co10 : LVP	13.2	3.01

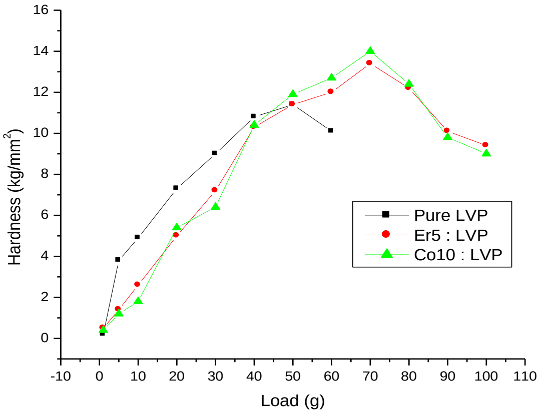


Figure 5. Microhardness measurement for pure and doped LVP crystals.

Elastic stiffness constant was calculated from the microhardness by Wooster's empirical relation $C_{11} = (H_v)^{7/4}$ [21]. Fracture toughness, K_c, is the resistance of a material to failure from fracture starting from a preexisting crack. It was calculated using the formula $K_c = P/\beta C^{3/2}$, where C is the crack length from the center of the indentation, P is the applied load and β (= 7) is the geometrical constant for Vicker's indenter [22]. Brittleness is an important property of the crystal which determines its fracture without any appreciable deformation. It is expressed in terms of brittleness index [23]. Brittleness index was calculated using the formula $B_i = H_v/K_c$ [24]. Elastic stiffness constant, fracture toughness and brittleness index for pure LVP, Er5: LVP and Co5 : LVP are tabulated in table 7.

Table 7. Elastic Stiffness, Fracture Toughness and Brittleness index for pure LVP, Er5 : LVP and Co5 : LVP crystals.

Crystals	Elastic Stiffness Constant (C_{11})	Fracture Toughness (K_c)	Brittleness Index (B_i)
Pure LVP	71.8×10^{12} pascal	16,233 kg $m^{-3/2}$	$6.77 \times 10^{-3} m^{-1/2}$
Er5 : LVP	76.24×10^{12} pascal	30,398 kg $m^{-3/2}$	$3.55 \times 10^{-3} m^{-1/2}$
Co10 : LVP	101.3×10^{12} pascal	24,390 kg $m^{-3/2}$	$5.74 \times 10^{-3} m^{-1/2}$

4. Conclusion

The experimental results of pure LVP, Cobolt doped LVP, rare earth element Erbium doped LVP can be summarized as follows.

1. Pure LVP, Cobolt doped LVP, Rare earth element Erbium doped LVP crystals were grown from mixed solvent of water and acetone in the ratio of 1:1 by the solvent evaporation method.
2. From the XRD analysis, it is observed that the pure LVP and doped LVP crystals retain the monoclinic structure and the calculated lattice parameter values are comparable with the reported values of LVP.
3. The presence of fewer amounts of Erbium and Cobolt as a dopant in LVP crystal was confirmed by EDAX analysis.

4. Optical transmission study shows that the grown Erbium and Cobolt doped LVP crystals have high transparency in the wavelength range from 470 nm to 800 nm.
5. The dielectric constant and dielectric loss of Cobolt and Erbium doped LVP crystals are found to be lesser than that of LVP. This shows that the doped crystals possess better optical quality with lesser defects compared to pure crystals.
6. The thermal studies of the samples suggest that the thermal stability is better for doped crystals.
7. Hardness study reveals that the LVP and doped LVP crystals are soft materials and higher hardness is obtained for doped LVP crystals than that of the LVP crystals.
8. Yield strength, elastic Stiffness, fracture toughness and brittleness index of the pure and doped LVP crystals were also reported.
9. The NLO efficiency for the doped LVP crystals is less than that of the pure LVP crystal.

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