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Investigation on the growth and properties of $(LA)_X(K_2SO_4)_{1-X}$ single crystals

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ABSTRACT

L–arginine potassium sulphate (LAPS) with different concentration of L-arginine and K_2SO_4 is grown successfully by slow evaporation method. The grown crystals were subjected to single crystal X-ray diffraction analysis, Fourier transform analysis, and UV-visible absorption measurement.SHG efficiency of the grown crystals were confirmed by Kurtz powder technique. The electrical parameters of the single crystals were determined by AC measurement for various frequencies. All the results are reported herein.

Keywords: Crystal growth, L–arginine potassium sulphate, Fourier transforms analysis, UV-visible absorption measurement, SHG efficiency.

INTRODUCTION

Within the last few years, the fast development of optoelectronic field imposes new and efficient nonlinear optical (NLO) materials for second harmonic generation in optical communication and optical data storage etc. A great deal of effort was put in the development of nonlinear optical (NLO) materials for second harmonic generation (SHG). The organic compounds with electron rich (donor) and deficient (acceptor) substituents provide an asymmetric charge distribution in the π electron system and show large nonlinear optical response. NLO crystals should meet several requirements, such as large phase – matchable nonlinear optical co-efficient, a wide optical and chemical stability and a high damage threshold [1]. Amino acids are interesting materials for NLO application as they contain proton donor carboxyl acid (-COO) group and the proton acceptor amino (NH_2) group . Especially some amino acids like arginine, lysine, L-alanine and γ-glycine are evidently showing NLO activity because they have a donor NH_2 group and acceptor COOH group with a possibility of charge transfer. The organic crystals exhibit higher second order nonlinear coefficient, but poor in thermal and mechanical behavior and it may not be suitable for many device applications [2-4]. To overcome this difficulty, optically active amino acids of crystalline solids are combined with inorganic host favorable for good thermal and mechanical properties with high nonlinear optical coefficient like L–histidine chloride monohydrate [5], L–alanine cadmium chloride [6] and L–asparagine monohydrate [7] are already reported. Most of the amino acids are combined with inorganic salt to produce high SHG efficiency crystals like, L-alanine cadmium chloride [8]. Radika et al [9] have reported the growth and characterization of glyscine potassium sulphate single crystals for optoelectroc applications. Hardness of triglycine sulphate crystal was enhanced with $NiSO_4$ doping [10]. Puhal raj et al [11] examined the effect of phosphate mixing in ZTS NLO crystals. They found that, 10mol % doping increases the SHG efficiency by 10 times than the pure ZTS crystals. L-valine zinc sulphate single crystals were grown by using slow evaporation technique [12]. In the present investigation on semiorganic crystal of L–arginine potassium sulphate (LAPS) with different concentration of L-arginine and K_2SO_4 is grown successfully and the crystals were subjected to various characterizations.

1.1 Growth of $(LA)_X(K_2SO_4)_{1-X}$ SINGLE CRYSTALS

$LA_x PS_{(1-x)}$ (x varies from 0 to 0.8 in steps of 0.2) was synthesized from L-arginine and potassium sulphate. They were taken in the different molar ratio (0.2:0.8 , 0.4:0.6, 0.6:0.4 and 0.8:0.2) and dissolved in double distilled water. The calculated amount of reactants was dissolved in double distilled water and the solution was continuously stirred for an hour maintaining the temperature of 50^o C and the condition of saturation was achieved. After attaining the saturation, the solution was allowed to evaporate at room temperature. Tiny crystalline materials were obtained within a period of 10 days by slow evaporation at room temperature. A recrystallization process was carried out in order to eliminate impurities in the $LA_x PS_{(1-x)}$ crystal. According to the solubility data shown in Figure 1, the supersaturated solution of $LA_x PS_{(1-x)}$ was prepared. The semitransparent, good quality crystals were collected between 30 – 40 days. The obtained $LA_x PS_{(1-x)}$ crystals are shown in Figure 2.

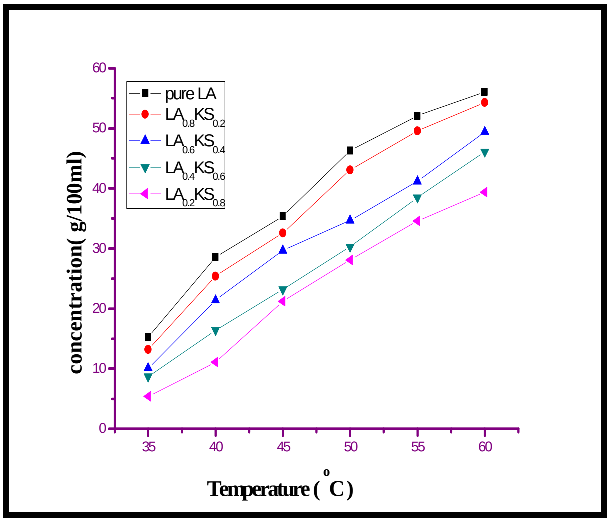


Figure1: Solubility curve of $LA_x PS_{(1-x)}$

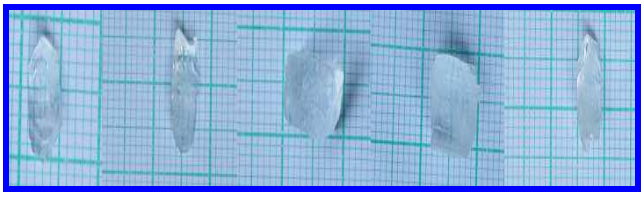


Figure 2: photograph of the grown crystals [From left]
Pure LA; $LA_{0.8}PS_{0.2}$; $LA_{0.6}PS_{0.4}$; $LA_{0.4}PS_{0.6}$; $LA_{0.2}PS_{0.8}$

2. CHARCTERIZATION

The single crystal X-ray data was collected using an automatic X-ray diffractometer (MESSRS ENRAF NONIUS, The Netherlands) with MoK_α (λ = 0.717 Å) radiation. The FT-IR spectrum was recorded in the range of 4000 – 450 cm^{-1} using BRUKER IFS 66V FT-IR SPECTROMETER. The optical absorption spectrum was recorded in the range of 200-800 nm using VARIAN CARY 5E UV-Vis-NIR SPECTROPHOTOMETER. The NLO efficiency of $LA_x PS_{(1-x)}$ crystals were evaluated by Kurtz and Perry powder technique [13]. Dielectric constant, dielectric loss and the AC conductivity of the $LA_x PS_{(1-x)}$ crystals were determined to an accuracy of ± 2 % using an LCR meter (Agilent 4284A) with four different frequencies (1 kHz, 10 kHz, 100 kHz and 1 MHz) at various temperature ranging from 30 – 150° C along a- direction.

2.1 Single crystal XRD Analysis

The single crystal XRD data of the pure LA and $LA_x PS_{(1-x)}$ single crystals are presented in Table 1. It is observed that, pure LA , $LA_{0.8}PS_{0.2}$ and $LA_{0.6}PS_{0.4}$ crystals belongs with monoclinic structure whereas $LA_{0.2}PS_{0.8}$ and $LA_{0.4}PS_{0.6}$ crystals belongs to orthorhombic structure which resembles the structure of K_2SO_4 with slight shift in diffraction peaks which may due to incorporation of LA in K_2SO_4 lattice. Thus by increasing the concentration of K_2SO_4, the crystal system of the mixed crystals change from monoclinic to orthorhombic structure.

2.2 FT-IR Analysis

The FT-IR spectrum was recorded in the range of 4000–450 cm^{-1} using BRUKER IFS 66V FT-IR SPECTROMETER. Figure 3 shows the FTIR transmission spectrum of the pure LA and LA $_x$ $PS_{(1-x)}$ crystals in the region 4000-450 cm^{-1}. The functional group frequencies present in the recorded spectra confirms the grown crystals.

Table 1: **Lattice parameter for pure L-arginine (LA) and LA $_x$ $PS_{(1-x)}$ from single crystal XRD**

DATA	LA	$LA_{0.8}(PS)_{0.2}$	$LA_{0.6}(PS)_{0.4}$	$LA_{0.4}(PS)_{0.6}$	$LA_{0.2}PS_{0.8}$
a (Å)	9.695	9.642	9.573	5.741	5.758
b (Å)	16.080	16.05	15.985	9.987	10.032
c (Å)	5.590	5.610	5.643	7.432	7.453
α^o	90	90	90	90	90
β^o	98	97.6	97.1	90	90
γ^o	90	90	90	90	90
Crystal System	monoclinic	monoclinic	monoclinic	Orthorhombic	Orthorhombic

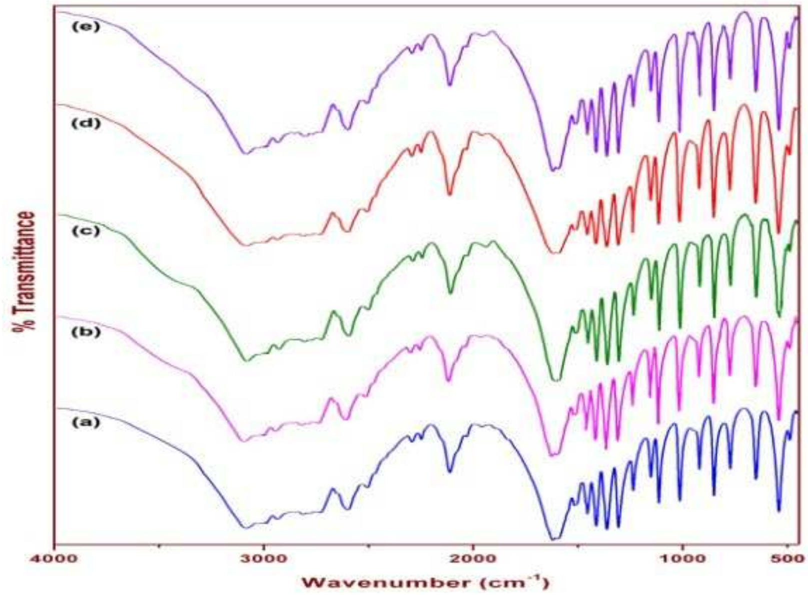


Figure 3: FT-IR spectra of pure LA and LA $_x$ $PS_{(1-x)}$ crystals

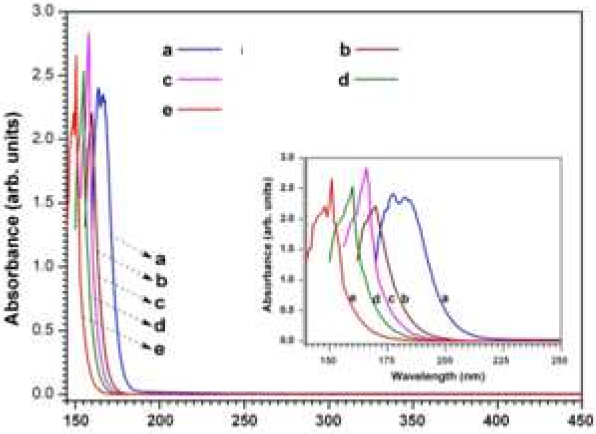


Figure 4: UV-Visible absorption spectrum of pure LA and LA $_x$ $PS_{(1-x)}$ crystals

2.3 Optical absorption spectrum Analysis

Figure 4 shows the optical absorption spectrum of pure LA and LA $_x$ $PS_{(1-x)}$ crystals in the wavelength range from 190 - 800 nm. Most of the absorption spectroscopy of organic compounds is based on transitions of n or π electrons to the π* excited state which takes place in the range 200–700 nm. In this point of view, the max absorption peak observed for pure LA at 228 nm, $LA_{0.8}PS_{0.2}$ at 224 nm, $LA_{0.6}PS_{0.4}$ at 219 nm, $LA_{0.4}PS_{0.6}$ at 205 nm and $LA_{0.2}PS_{0.8}$ at 201 nm can be assigned to n→π* transition. From figure, it is found that the shape and position of the absorption peaks of $LA_x PS_{(1-x)}$ has some significant blue shift from the pure LA. As it is clear from Figure 4, the concentration (from 0.2 mole to 0.8 mole) of K_2SO_4 in $LA_x PS_{(1-x)}$ has not affect the optical absorbance in the entire visible range, however there is a small significant variation in UV range.

2.4 NLO studies

The Nonlinear Optical property of the pure LA and $LA_xPS_{(1-x)}$ crystals were confirmed by Kurtz powder technique. The first harmonic output of 1064 nm from Nd: YAG laser was made to fall normally on the prepared crystal with pulse width of 8 ns, 10 Hz pulse rate and 6.5 mJ energy per pulse. The emission of green radiation from the crystals confirm the existence of second harmonic generation in the crystal. The output power from the pure LA and $LA_xPS_{(1-x)}$ crystals were compared to that of KDP crystal and the results are presented in Table 2.

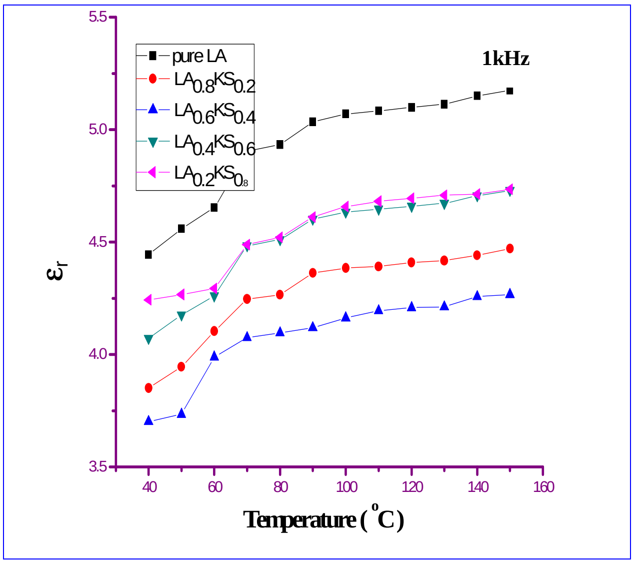
Table 2: SHG efficiency of pure LA and $LA_xPS_{(1-x)}$ crystals

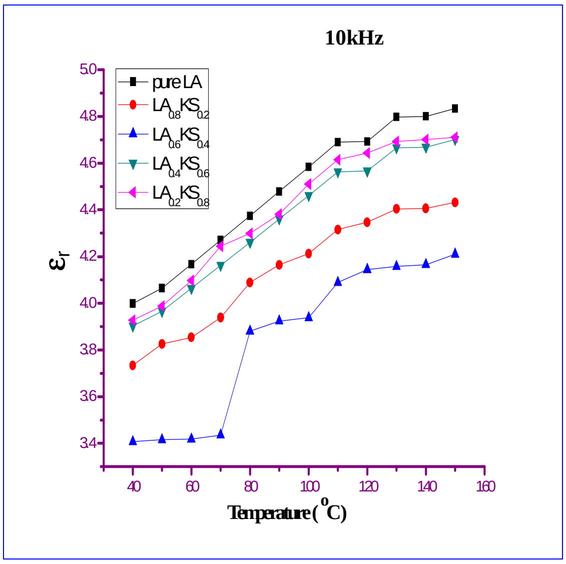
Sample name	Input power mJ	Output power mV	SHG efficiency (compared with KDP)
LA	6.5	102.3	1.93
$LA_{0.8}PS_{0.2}$	6.5	111.3	2.10
$LA_{0.6}PS_{0.4}$	6.5	155.5	2.93
$LA_{0.4}PS_{0.6}$	6.5	109.1	2.05
$LA_{0.2}PS_{0.8}$	6.5	58.6	1.105

The SHG efficiency of $LA_{0.8}PS_{0.2}$ and $LA_{0.6}PS_{0.4}$ crystals were higher than pure LA crystal. The maximum SHG efficiency obtained for $LA_{0.6}PS_{0.4}$ crystal which is 1.52 times greater than the pure LA crystal. Minimum SHG efficiency for $LA_{0.2}PS_{0.8}$ crystal favours formation of doped crystal than the mixed one. The good second harmonic generation efficiency indicates that the different concentration of K_2SO_4 in $LA_xPS_{(1-x)}$ crystals can be used for applications in nonlinear optical devices.

2.5 Electrical Studies

The electrical parameters, viz, dielectric constant, dielectric loss and AC electrical conductivities observed in the present study are increased with the increase in temperature for all the grown crystals. The ε_r and tan δ values were decreased whereas the σ_{ac} value increased with the increase in frequency of the AC applied for all the systems considered in the present study. The nature of decrease in ε_r and tanδ with frequency suggests that the crystals of this work seem to contain dipoles of continuously varying relaxation times. Since the dipoles of larger relaxation times are not able to respond to the higher frequencies, the dielectric constant and dielectric loss are low at higher frequencies [14,15]. The low value of dielectric loss at high frequency can be taken as a proof for the good optical quality of the crystal [16]. The application part of nonlinear optics demand high quality crystals with lesser defects.





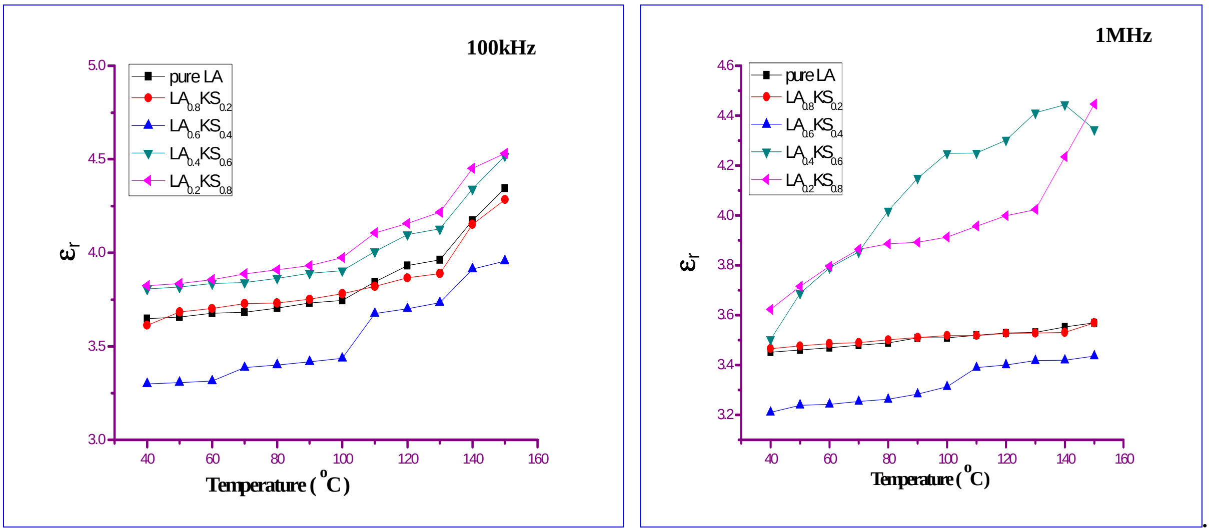


Figure 5 : Variation of dielectric constant with frequency

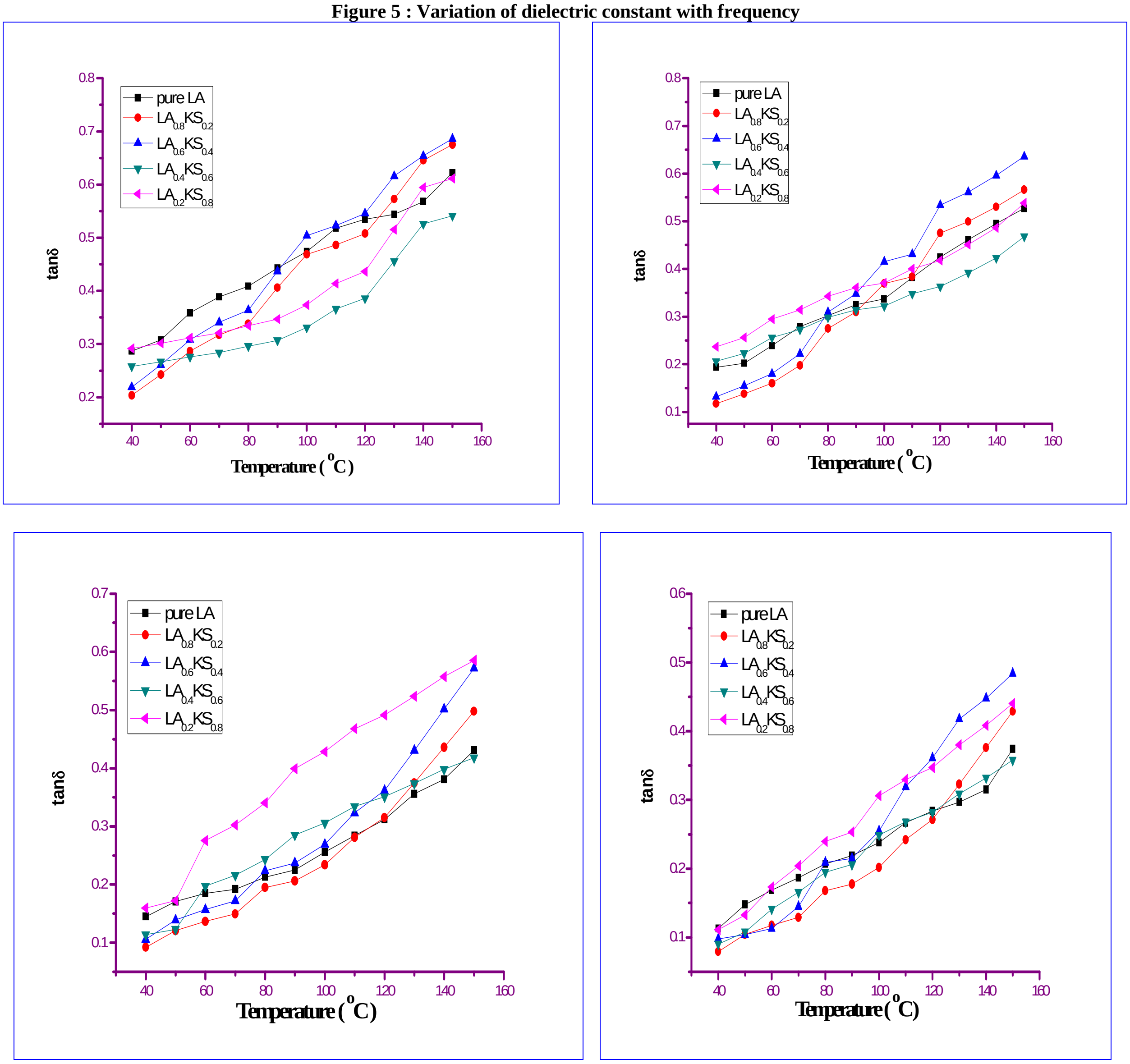


Figure 6 : Variation of dielectric loss factor with frequency

From the dielectric loss plots [Figures 4.14 - 4.17], the curves suggest that the dielectric loss strongly depends on the frequency of the applied field similar to that happens with the dielectric constant in the ionic system [17]. The characteristic of low dielectric loss with high frequency for the pure LA and LAPS crystals suggests that the crystals possess good optical quality with lesser defects and this parameter is of vital importance for nonlinear optical materials in their application [14].

CONCLUSION

Good quality pure LA and $LA_xPS_{(1-x)}$ crystals were grown from slow evaporation techniques. The single crystal XRD data revealed that, instead of forming a mixed system, at higher concentration of L-arginine, K_2SO_4 entered as a dopant and vice-versa. From the Uv-Vis analysis, we found that the concentration (from 0.2 mole to 0.8 mole) of K_2SO_4 in $LA_x PS_{(1-x)}$ has not affect the optical absorbance in the entire visible range, however there is a small significant variation in UV range. All the grown crystals exhibit NLO behavior. Minimum SHG efficiency for $LA_{0.2}PS_{0.8}$ crystal favours formation of doped crystal than the mixed one. The good second harmonic generation efficiency indicates that the different concentration of K_2SO_4 in $LA_xPS_{(1-x)}$ crystals can be used for various applications in nonlinear optical devices.

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