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Growth, optical, thermal, mechanical and dielectric studies of potassium sulphate crystals doped with urea

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ABSTRACT

Single crystals of pure and urea doped potassium sulphate were grown by slow evaporation technique. Single crystal XRD analysis confirms orthorhombic crystal structure. Powder XRD pattern confirms that the grown crystals posses high crystalline nature. Vibration spectrum reveals the symmetries of molecular vibrations. The TGA, DTA shows that the materials have very good thermal stability, The UV-Vis spectrum shows the transmitting ability of the crystal in the entire visible region. The dielectric constant and dielectric loss were calculated by varying frequencies at different temperature. The microhardness test reveals that the crystals possess very good mechanical strength.

Key words: refractive index, dielectric constant, thermal stability

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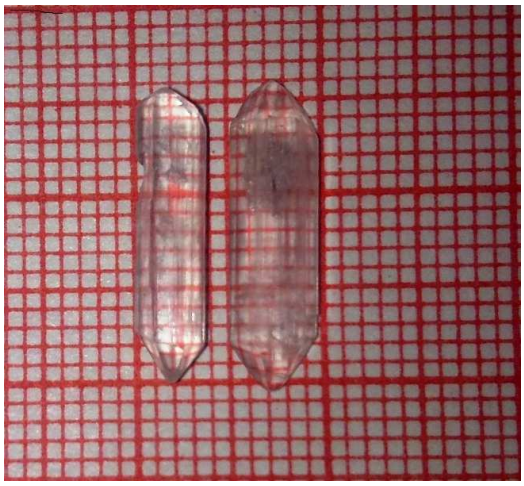
INTRODUCTION

Potassium sulphate K_2SO_4 belongs to the orthorhombic system with space group Pmcn and lattice parameters a=5.763Å, b=10.071Å and c=7.476Å [1]. The substance transforms upon heating at 587˚C in to a hexagonal structure with a=5.921Å and c=8.182Å [2] and is called as α- K_2SO_4. The orthorhombic form is called as β- K_2SO_4.

Urea $(NH_2)_2CO$ is an organic compound and belongs to the tetragonal system with the space group 42M similar to that of KDP [3]. Some novel properties of urea are its transparency extending to 200nm, large birefringence, high optical damage threshold and large nonlinear optical coefficients [4-6]. In the last decade numerous applications of the nonlinear optical (NLO) crystals have been discussed in the field of science and technology. But recent interest is focused on the development of the properties of the new semi-organic (NLO) materials. Semi-organic materials possesses the advantage of both organic and inorganic materials in terms of high thermal and mechanical stability as well as broad optical frequency range, higher SHG and high damage threshold[7-9]. The investigation of doping effect with urea in different concentration is the target of this article and we report the studies on solubility, growth, XRD, optical transmittance properties, mechanical strength, vibration and thermal properties of the grown pure and urea doped potassium sulphate crystals.

2.1. *Synthesis*
Recrystallised salts of (analar reagent grade) potassium sulphate (K_2SO_4), urea (NH_2CONH_2), and de-ionized water were used in the present crystal growth experiment. Saturated aqueous solutions were prepared at room temperature

following the known solubility data. The solubility of potassium sulphate and urea in de-ionized water (100ml) at room temperatures were 14gm and 165gm respectively. A mother solution of 600ml at room temperature (29˚C) was prepared using recrystallised salts of K_2SO_4 and deionised water were stirred well using a magnetic stirrer. Urea of 5mole% and 10mol% were added in two beakers of mother solution(200ml) and the remaining solution was used as standard. The solutions were mixed for about 5 hours using a magnetic stirrer with 500rpm to ensure homogeneous temperature and concentration through out the volume of the solution. The pH value of the solutions were found to be 7. The saturated solutions were filtered with whattmann filter paper and then covered with perforated transparent polythene paper and left undisturbed for slow evaporation. The solvent evaporates slowly leading to supersaturation which in turn initiate nucleation and the crystal grows. Good quality single crystals were grown in 32 days with size up to 17mm x 5mm x 2.85mm for 10mol% urea doped potassium sulphate crystals (10mol% UKS) and 8mm x 3mm x 2.5mm for 5mol% urea doped potassium sulphate crystals (5mol% UKS) and are shown in figure 1a and 1.b respectively..



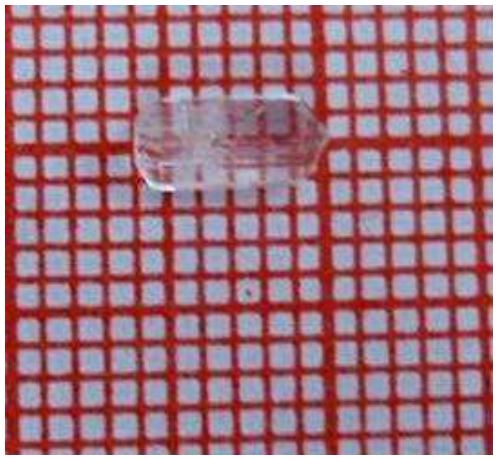


FIG. 1 .a.10mol% UKS **1.b. 5mol% UKS Crystal**

2.2 Solubility

In solution growth technique the size of a crystal depends on the quantity of the material available in the solution which is decided by the solubility of the material in that solvent. The solubility of the synthesized material was determined by adding water maintained at constant temperature to a known quantity of the material till the material was completely dissolved. Using this technique, we evaluate the magnitude of the solubility of urea doped potassium sulphate crystals at various temperatures between 25ºC and 45ºC which is shown in fig 2. Potassium sulphate crystals have a positive temperature coefficient of solubility. Thus slow cooling of aqueous solution of urea doped potassium sulphate crystal could be attempted to grow bulk crystals [10].

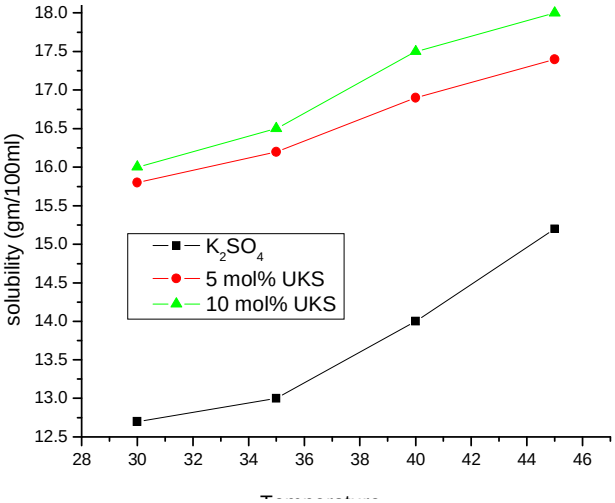


Figure 2 Solubility curve of pure and urea doped Potassium Sulphate Crystals

2.3. Analyzing techniques

The grown crystals were confirmed by single crystal x-ray diffraction analysis using ENRAF NONIUS CAD4 diffractometer. Powder x-ray diffraction (XRD) was recorded using XPERT PRO diffractometer with CuKα radiation (λ=1.5405 Å). The crystals were characterized by SPECTRUM ONE CPU 32 spectrophotometer, using KBr pellet technique. The optical properties of the grown crystals were studied using LAMDA 35 spectrophotometer in the wavelength region of 200nm to 1100nm. The dielectric study on UKS single crystals was carried out using the instrument, HIOKI3532-50 LCR HITESTER. Thermal stability and physiochemical changes of the sample were analyzed by recording the TG and DTA spectrum in the temperature range of 30ºC to 1000ºC in the nitrogen atmosphere at the heating rate of 10ºC/ min. Second Harmonic generation (SHG) test for the grown crystals was performed by the powder technique of Kurtz and Perry using a pulsed Nd:YAG laser (Model: YG501C, λ=1064nm). The microhardness measurement of the crystals was carried out by a REICHERT MD 4000E ultra microhardness tester with a diamond pyramidal indenter.

RESULTS AND DISCUSSION

3.1. Single crystal diffraction

Single crystal x-ray diffraction analysis for the grown crystals is carried out to confirm the crystalline nature and also to identify the unit cell parameters using ENRAF Nonius CAD4 single crystal x-ray diffractometer. It is observed that both pure and urea doped potassium sulphate crystals crystallize in the orthorhombic system with the space group Pmcn. The lattice parameters are tabulated below:

Lattice parameters	Potassium Sulphate	5 mol% UKS	10mol% UKS
a (Å)	5.765 (Å)	5.766 (Å)	5.768 (Å)
b (Å)	10.069 (Å)	10.04 (Å)	10.01 (Å)
c (Å)	7.475 (Å)	7.45 (Å)	7.44 (Å)
volume ($Å^3$)	433.90($Å^3$)	431.2($Å^3$)	429.5($Å^3$)

3.2. Powder X-ray diffraction

The grown single crystals of pure and urea doped potassium sulphate are subjected to powder Xray diffraction. The powder form of the above mentioned crystal is taken for the analysis using XPERT PRO diffractometer. The positions of the peaks are found to be in good harmony with the data available in JCPDS files and is presented in fig 3. In the case of urea doped potassium sulphate crystals, no new peaks are detected, rather a slight shift in the position of some peaks are observed. The sharp intense peaks on the patterns reveal that the cyrstallites are pure and dislocation free.

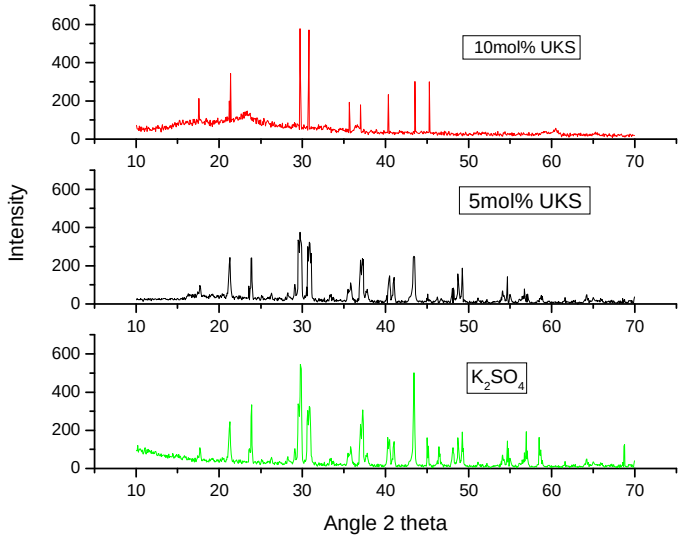


Figure 3. Powder Diffraction Spectrum of UKS single crystal

3.3 Optical transmission spectra

Transmission spectra are very important for any NLO materials, because a nonlinear optical material can be of any practical use if it has a wide transparency window. In the present study, we have recorded the UV-Vis NIR transmission spectrum in the range of 190nm-1100nm and is shown in fig 4. The instrument used in the analysis is LAMBDA-35 UV-Vis spectrophotometer. The crystals are transparent in the visible and infrared spectral regions. Optical transmittance is less and is about 20% for potassium sulphate crystal. Optical transmittance of about 100% is observed for 2mm plates of 5 and 10 mol% UKS crystals and is sufficiently good for SHG[11]. From the spectrum, it is seen that the UKS crystals have a lower cut-off wavelength of 384nm and the spectrum further indicates that the crystals have wide optical window from 385nm to 1100nm.

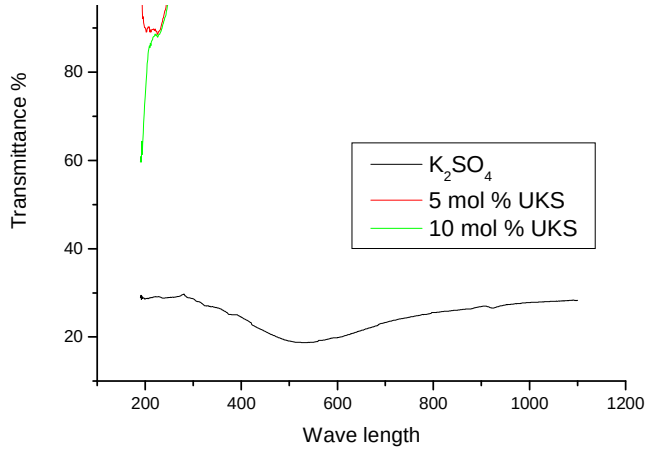


Figure 4. UV-Vis NIR Spectrum of UKS crystal

The measured transmittance (T) is used to calculate the absorption coefficient (α) using the formula:

$$\alpha = 2.303 \log (1/T) /t$$

where t is the thickness of the sample. The optical band gap (E_g) is evaluated from the transmission spectra and the optical absorption coefficient (α) near the absorption edge is given by [12]

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

where A is a constant, E_g the optical band gap, h the Planck's constant and υ the frequency of the incident photons. The band gap of the grown crystal is estimated by plotting $(\alpha h\upsilon)^2$ versus hυ as shown in Fig.5. and extrapolating the linear portion near the onset of absorption edge to the energy axis. From Fig.5.value of band gap is obtained as 1.2eV, 1.4eV, and1.6eV for 5mol%, 10mol% urea doped and pure potassium sulphate.

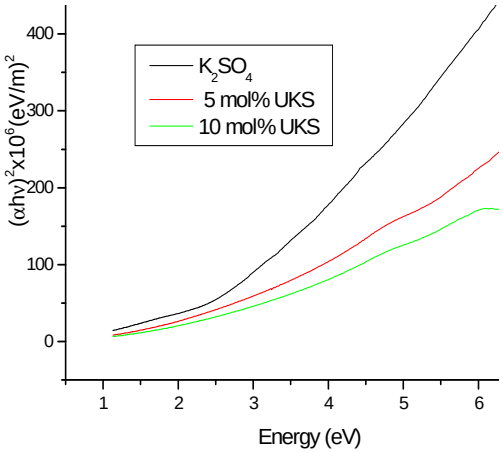


Figure 5 .Plot of energy versus $(\alpha h\upsilon)^2$

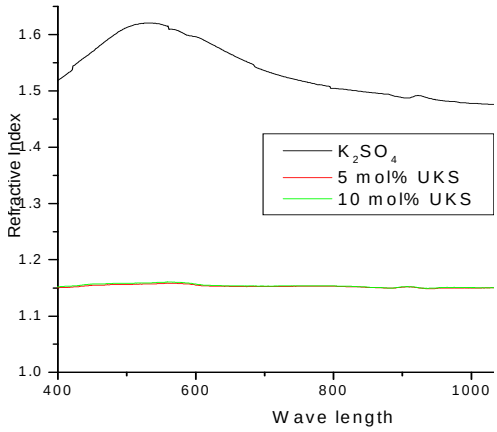


Fig6.wavelength versus refractive index

The reflectance R in terms of the absorption coefficient is given bythe relation[13]

$$R= \exp(-\alpha t)\pm\beta\sqrt{(\exp(-\alpha t)T-\exp(-3\alpha t)T+\exp(-2\ \alpha t)T^2)} / \exp(-\alpha t)+ \exp(-2\ \alpha t)T$$

The refractive index (n) can be determined from reflectance data using

$$n= - (R+1) \pm 2\sqrt{R} / (R-1)$$

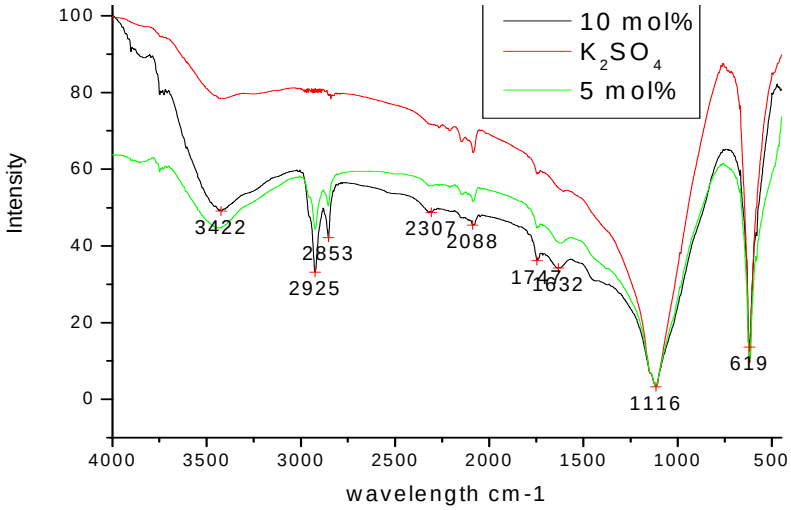


Fig.7. FTIR spectrum of urea potassium sulphates

Figure.6. shows the energy dependence of n in the range of 400-1100nm for the grown crystals. The refractive index increases and then decreases with increase in wavelength for pure potassium sulphate. The refractive index (n) is 1.149 at 1000nm for UKS crystals.

3.4. FTIR analysis.

The FTIR spectral analysis (fig 7) for the grown crystal is recorded in the range of 400-4000cm^{-1} using SPECTRUM ONE, CPU 32 spectrophotometer using the KBr pellet technique. The broadness of the peak from 2900 cm^{-1} to 3700 cm^{-1} is due to the intermolecular hydrogen bonding. The peak at 1632 cm^{-1} is due to C=O stretching of the urea compound. This is not present in the pure potassium sulphate crystal. The presence of sulphate ion is confirmed at 1115cm^{-1} and 619 cm^{-1}.

3.5. Dielectric Studies

The dielectric constant is one of the basic electrical properties of solids. The dielectric constant is the measure of how easily a material is polarized in an external electric field [14]. The dielectric study of the grown crystals are carried out using the instrument, HIOKI3532-50 LCR HITESTER. A sample having silver coating on the opposite faces is placed between the two copper electrodes and thus a parallel plate capacitor is formed [15]. The capacitance is measured in the frequency range of 100Hz to 5MHz. The dielectric constant is calculated using the relation $\varepsilon_r = Cd/A\ \varepsilon_0$ and is shown in fig8.

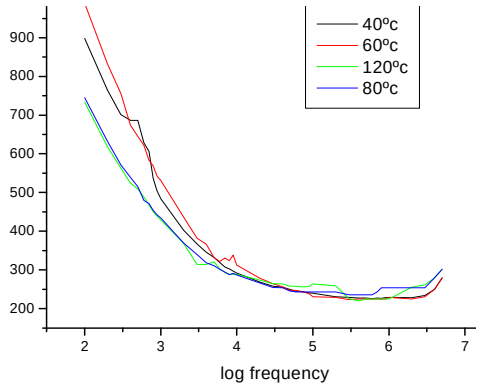


Figure 8.a. 5 mol% UKS

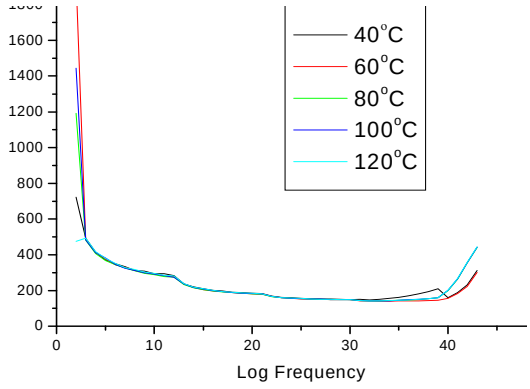


Figure 8.b. 10mol%UKS

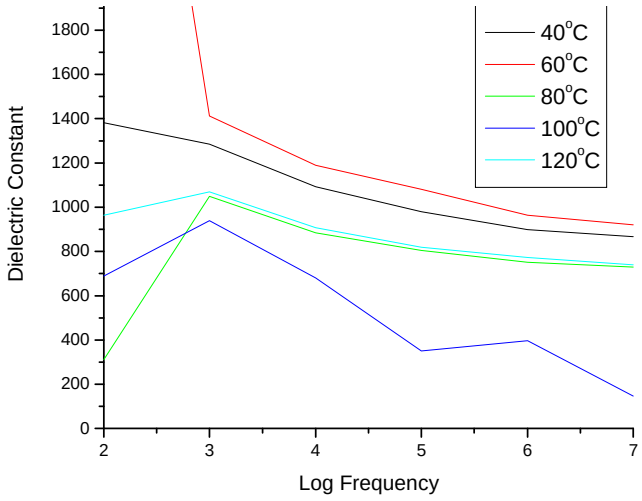


Figure 8.c. Potassium Sulphate

Fig. 8. Plot of Log frequency versus dielectric constant

The larger value of dielectric constant at lower frequency is due to the impedance of the motion of charge carriers at the electrodes. This results space charge and macroscopic distortion[16]. The dielectric constant is low at higher frequencies and is due to the fact that at higher frequencies the ionic and electronic polarizations are active [17]. According to Miller rule, the lower values of dielectric constant are a suitable parameter for the enhancement of SHG coefficient [18].

The dielectric loss versus log frequency is shown in fig 9. The dielectric loss values is found to be large at low frequencies and low at high frequencies. The low dielectric loss at higher frequency of the sample indicates that the crystals posses lesser number of electrically active defects[19] and this parameter is of vital importance for nonlinear optical materials in their applications.

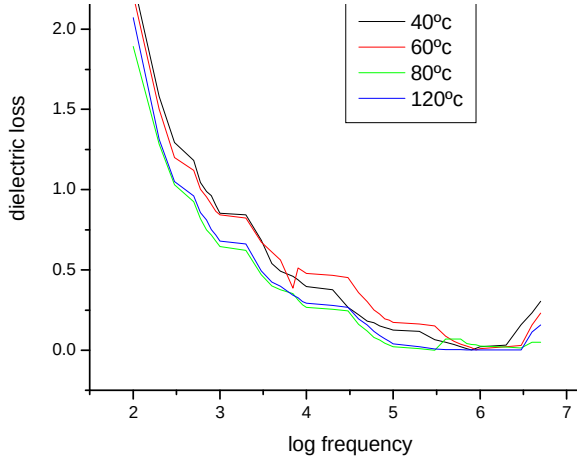


Figure 9.a. 5 mol% UKS

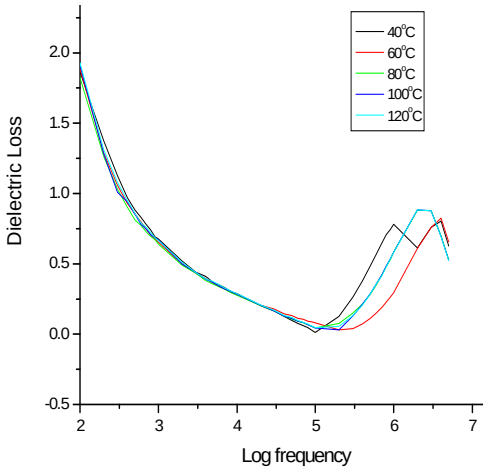


Figure 9.b. 10mol%UKS

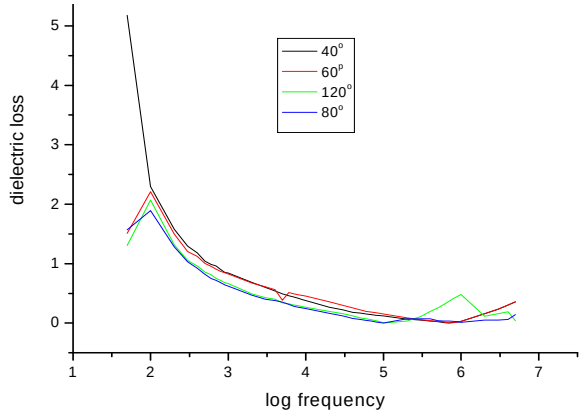


Figure9.C Potassium sulphate

Fig. 9. Plot of Log frequency versus dielectric loss

The AC conductivity (σ_{ac}) is calculated using the relation [20],

$\sigma_{ac} = \varepsilon_0 \varepsilon_r \omega \tan\delta$ where ε_0 is the permittivity of free space ($8.85*10^{-12}$ C^2 N^{-1} m^{-2}) and ω is the angular frequency ($\omega = 2 \pi f$). The plot of AC conductivity versus log frequency is shown in figure 10. The AC conductivity is low and almost constant at low frequency and increases at frequency above 1MHz.

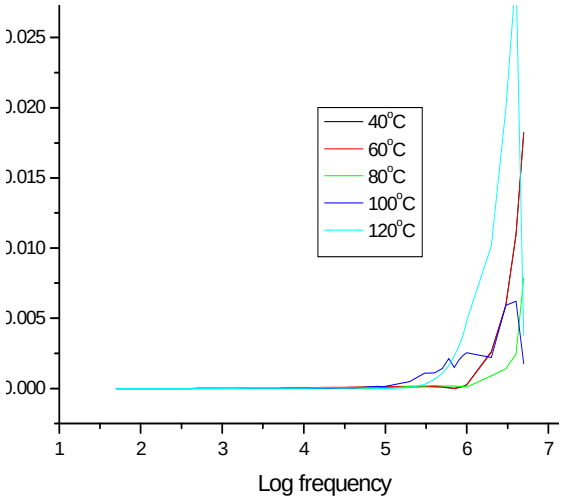


Figure 10.a. 5 mol% UKS

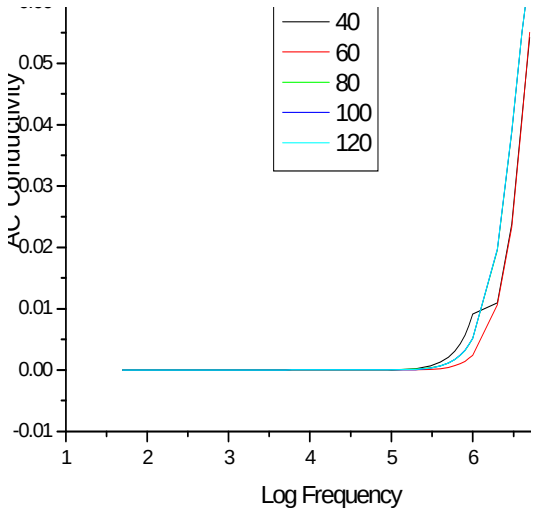


Figure 10.b. 10mol%UKS

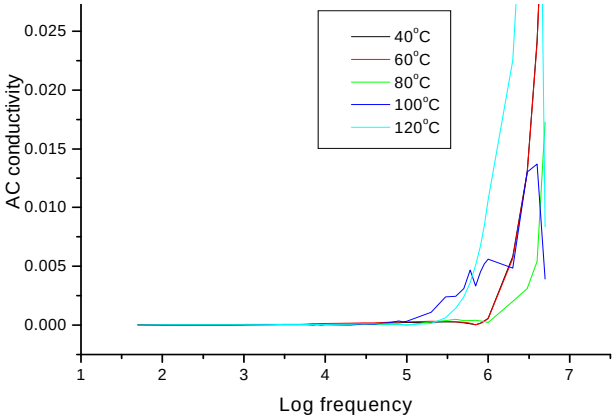
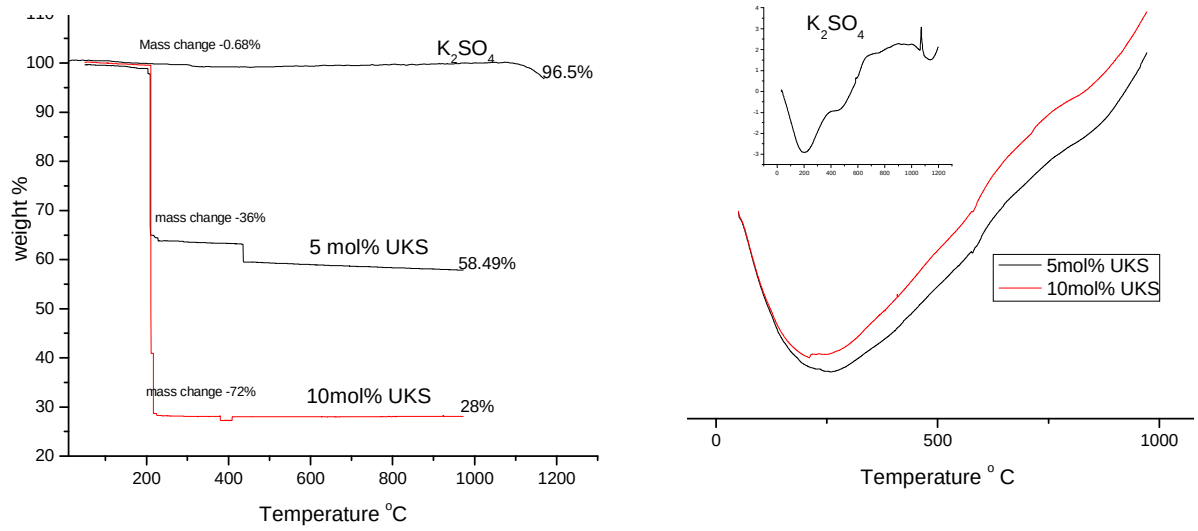


Figure10.C Potassium sulphate

Fig. 10. Plot of Log frequency versus AC conductivity

3.6. Thermal analysis

Differential thermogram analysis (DTA) and thermogravimetric analysis (TGA) give information regarding phase transition, water of crystallization and different stages of decomposition of the crystal system. We have carried out simultaneous TGA and DTA for the grown crystals in the temperature range of 30ºC to 1000ºC with a heating rate of 10K / min in the nitrogen atmosphere. The thermogram and differential thermogram are shown in fig.10. There is a continuous weight loss of 3.5% from 50°C to 1100°C leaving behind 96.6% residue for pure potassium sulphate crystal. The weight loss is due to the elimination of water molecule present in the crystal. But for UKS crystals, there is no weight loss up to 220ºC and it is due to the absence of water of crystallization in the molecular structure. A major weight loss of 36% and 72% for 5mol% and 10 mol% urea doped potassium sulphate crystals occur at 220°C which is due to the elimination of volatile substance like CO. This indicates the incorporation of urea compound in the crystal lattice of potassium sulphate. Further the crystal is thermally stable up to a temperature of 1000°C.



TG curves of potassium sulphate crystal **DTA curves of potassium sulphate crystal**

Fig 10.TG-DTA curves of potassium sulphate crystal

3.7. Second harmonic generation

The second harmonic generation behavior of the powdered material Is tested using the Kurtz and Perry [21] method. A high intensity Nd:YAG laser (λ=1064nm) with a pulse duration of 10 ns is passed through the powdered sample. The SHG behaviour is confirmed from the output of the laser beam having the green emission (λ=532nm) for 10mol% UKS crystal and it is absent for pure K_2SO_4 and 5mol% UKS crystals. The second harmonic signal of 0.08mJ is obtained for 10mol% urea doped potassium sulphate crystal. But the standard KDP crystal shows an SHG signal of 8.8mJ for the same input energy. Thus, it is observed that the SHG efficiency of the grown single crystal is 1/100 times that of the standard KDP crystal.

3.8. Microhardness Studies

The mechanical strength of crystals are evaluated by mechanical characteristics. The fastest and simplest type of mechanical testing is hardness measurement. Among the different testing methods, the Vickers hardness test is more commonly used. Microhardnes measurements were made using a Leitz microhardness tester fitted with a diamond pyramidal indentor. Single crystals of pure and urea doped potassium sulphate crystals are subjected to microhardness on (001) orientation. The applied load are varied from 25 to 100 g for a constant indentation period of 10s. the Vicker's hardness number H_v is calculated using the relation

$$H_v = 1.8544P/d^2 \text{ Kg/mm}^2$$

where P is the indentor load in kg and d is the diagonal length of the impression in mm[22]. The variation of H_v with applied load is shown in Fig11a. It is evident from the plot that the microhardness of the crystal increases with increasing load. For loads above 200g cracks developed on the surface of the crystal and is due to tha release of internal stress generated locally by indentation.

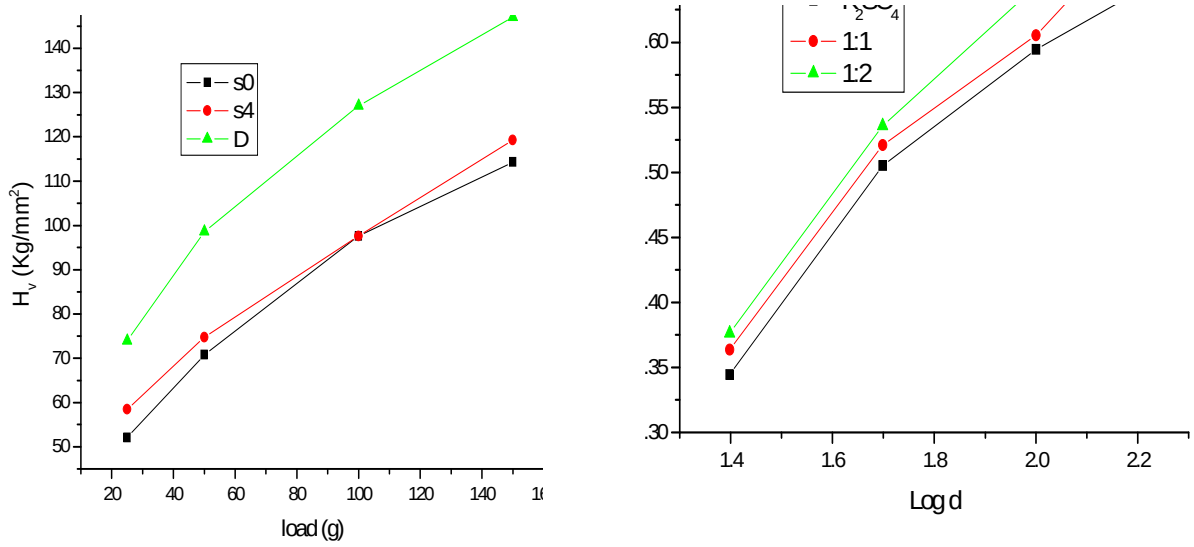


Figure 11a. Plot of microhardness number vs load b. Plot of log d vs log p

Mayer's law [23] relates load and size of indentation as P=a d^n where a and n are the constants. The plot of log d versus log p is drawn (fig 11.b) and from plots, the hardening coefficient (n) was determined. The `value of n is less than 1.6 for all the grown crystals. According to Onitsch, n should be below1.6 for hard materials and above 1.6 for softer ones[24]. Hence the grown crystals belong to hard materials.

CONCLUSION

Optical quality crystals of pure and urea doped potassium sulphate could be successfully grown by slow evaporation method. The grown crystals were characterized using single crystal X-Ray diffraction analysis, which shows that the UKS crystals belong to orthorhombic system. The presence of functional groups of UKS and the bond interaction between urea and potassium sulphate have been confirmed by FTIR analysis. Optical studies show that the UKS crystals have a wide transparency window in the entire visible region making it is an ideal candidate for NLO device applications. The optical band gap and refractive index were also calculated. The TG-DTA studies reveal that the crystal is thermally stable up to ~220ºC for UKS crystals and the mechanism responsible for weight loss is discussed. Low dielectric constant and dielectric loss at high frequency suggest that the sample possesses enhanced optical quality with lesser defects. From the mechanical measurements, it was observed that the hardness increases wjth increase of load. Hence it is concluded that optically good quality urea doped potassium sulphate single crystals with good thermal and mechanical stability can be grown by slow evaporation technique and is suitable for the fabrication of various optoelectronic devices.

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