# ภาคผนวก

ผลงานวิจัยของโครงการวิจัยนี้ได้รับการตีพิมพ์ในวารสารวิชาการนานาชาติ

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# Growth of Ferroelectric Tri-Glycine Sulphate Doped Potassium Dihydrogen Phosphate Single Crystal and Its Characterization

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*Potassium dihydrogen phosphate ($KH_2PO_4$, KDP) single crystals have been long studied due to their non-linear optical property. Also, these crystals can exhibit some ferroelectricity when applying an external electric field. In the absence of the external field, the remaining polarization is weak, and hence, the applications of KDP in the electronic industry are limited. In order to enhance the ferroelectricity of the KDP crystals, tri-glycine sulphate (TGS) was added to the KDP solution and then the doped crystals were grown using the slow evaporation method. The results show that the properties of TGS doped KDP crystals are similar to those of the pure KDP. However, the ferroelectricity of the TGS doped KDP has been improved by the small addition of the TGS. These reveal that the TGS molecules may disrupt the KDP lattice and hence, lead to the enhancement of the built-in polarization.*

**Keywords** Single crystal; X-ray diffraction; dielectric properties; ferroelectric properties

## Introduction

The nonlinear-optical properties of potassium dihydrogen phosphate (KDP) have been used in various applications such as electro-optic modulators, harmonic and parametric generators. Apart from such optical properties, this material also exhibit ferroelectricity with the ferroelectric phase transition at the temperature $T_c$ = 122 K [1–2]. However, the ferroelectric property of the KDP crystal is weak and thus unsuitable for commercial products. Many studies have been done to improve the ferroelectricity of pure KDP crystal, as well as the preparation technique for large-grain crystals [3–4]. Although some dopants have been added to improve the KDP crystals, tri-glycine sulphate ($(HCHNH_2COOH)_3.H_2SO_4$; TGS) has been doped for the ferroelectric enhancement [5–8] since it shows a typical second-order ferroelectric phase transition at $T_c$ 322 K [9–10]. Despite the improvement

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of the ferroelectricity, it is problematic to obtain large high-quality KDP crystals from the mixture between TGS and KDP solutions. In this work, the main research aim is to dope tri-glycine sulphate to the KDP crystals for the enhancement of the ferroelectric properties. The slow evaporation crystal-growth method, one of the solution-based methods, was thus used to grow large KDP crystals doped with tri-glycine sulphate. The grown crystals were then subjected to characterization.

## Experimental Procedure

The solution in this work was prepared using deionized water with the resistivity of 18.2 MΩ cm. The initial concentration of the solution was set close to KDP solubility in water. TGS with 5%mol was added to some solutions to grow the KDP crystals doped with TGS. After adding all the solutes in the water, the mixture was stirred for approximately 2 hours to dissolve all the ingredients in the DI water completely. In addition, the temperature of the solution was controlled in a water bath with an accuracy of ±0.1 K throughout the growing process. The temperature was decreased gradually to make the solution saturated, and hence, grow the KDP crystals. The temperature of the saturated solution was stabilized at about 313 K, within the ferroelectric phase. Crystals of pure KDP and KDP doped with TGS were purified by the recrystallization process in the deionized water three times. This recrystallization was done to remove other impurities and make the crystals clearer. In essence, the purification process was required to increase the quality of the crystals and avoid the alias result from the characterization process. The KDP and TGS crystals were successfully grown as shown in Fig. 1(a) and (b) respectively. In Fig. 1(c), the KDP crystal doped with TGS were harvested after 30–40 days of the growth process. No microbial contamination was observed in all the growth solutions throughout the long growing process.

## Results and Discussion

### *X-ray Diffraction Analysis*

The $CuK\alpha$ source was used to generate the X-ray radiation. The powder X-ray diffraction (PXRD) patterns of pure KDP, pure TGS and the KDP doped with TGS were examined at room temperature using a Bruker powder X-ray diffractometer. The PXRD spectra are shown in Fig. 3. Well defined Bragg peaks are obtained at specific $2\theta$ values in the XRD pattern. This showed that the samples were a well-grown crystal using the slow evaporation technique. The pattern of the TGS doped KDP sample is different to that of the pure TGS but similar to that of the pure KDP. However, some different peaks can be observed from the spectra as depicted in Fig. 3. This confirms that the TGS doped KDP sample has a crystal

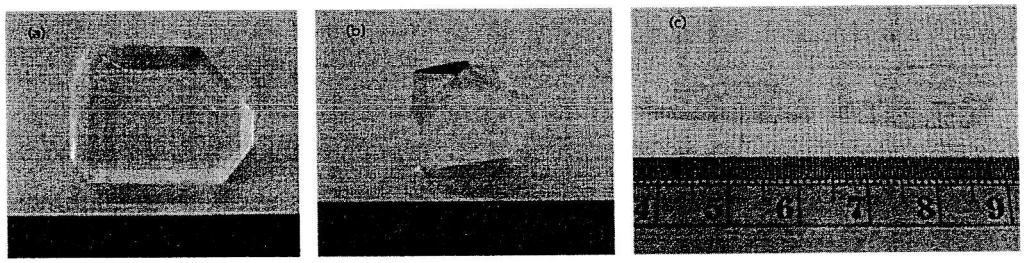


**Figure 1.** (a) KDP, (b) TGS and (c) TGS doped KDP crystals. (Color figure available online.)

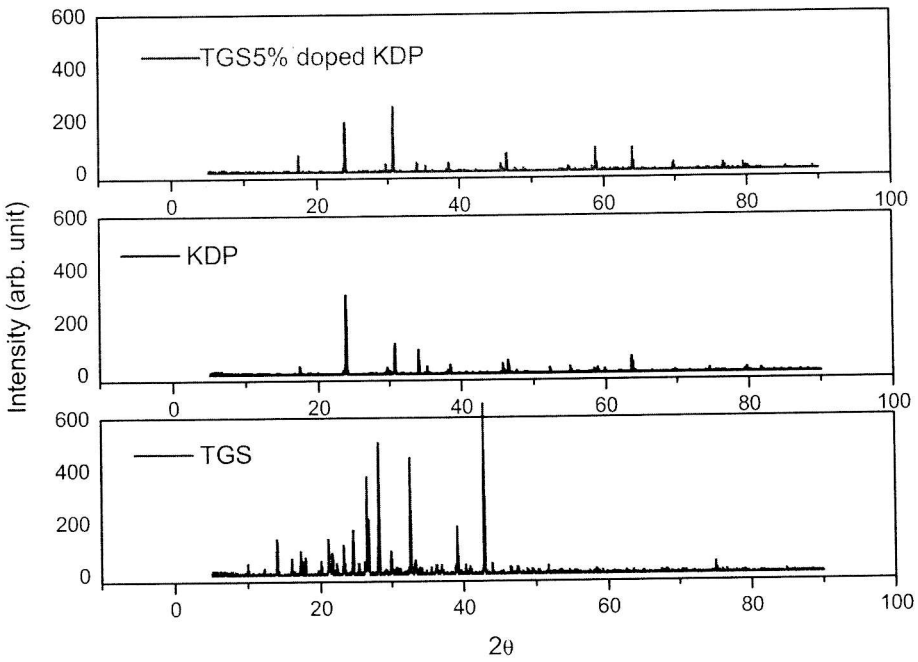


**Figure 2.** X-ray diffraction pattern of KDP and TGS doped KDP single crystals. (Color figure available online.)

structure similar to that of the pure KDP, the slight variation may reveal the interaction between TGS molecules and the KDP lattice. Also, this result shows that the small amount of TGS (~5%mol) did not have a strong influence on the KDP lattice, and hence the TGS doped KDP is likely to have the orthorhombic structure.

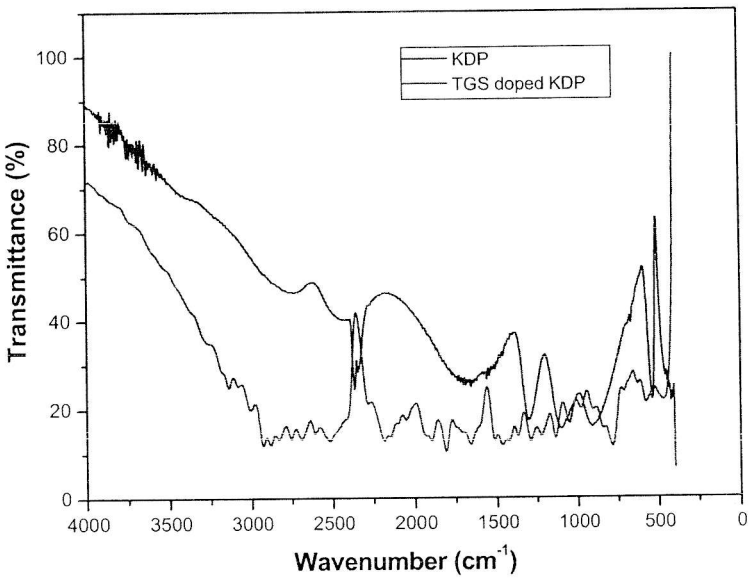


**Figure 3.** FT-IR of KDP and TGS 5% mol doped KDP single crystals.

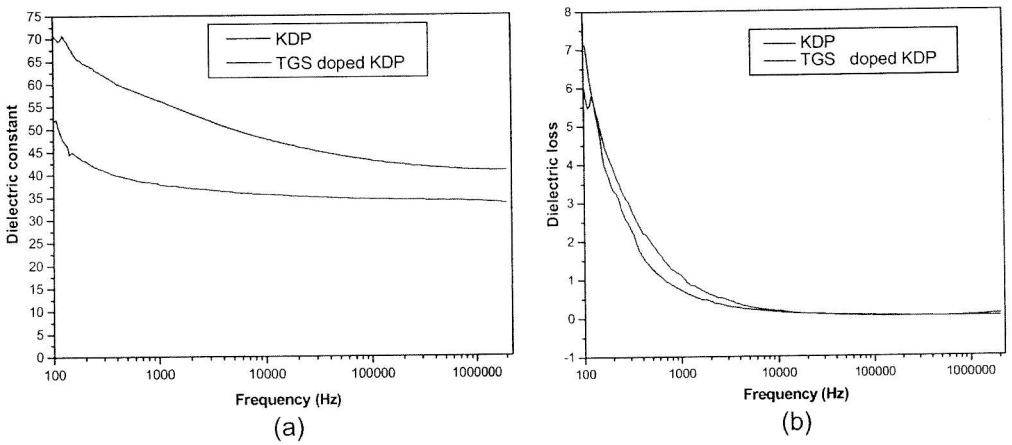


**Figure 4.** (a) Dielectric constant and (b) dielectric loss.

### *FI-IR Spectrum*

A BRUKER IFS 66V FT-IR spectrometer was used to investigate the FT-IR spectrum of the grown crystals. The KBr pellet technique was employed in the frequency range 400–4000 $cm^{-1}$. The FT-IR spectra of both pure KDP and TGS doped KDP are shown in Fig. 3. It is evident that the TGS molecules had some significant interactions with the KDP molecules since some of the IR absorption peaks change significantly. Although the samples were translucent under visible light, their transmittances under IR light decreased significantly. Especially, when adding TGS to the KDP sample, the IR transmission through the doped crystal is significantly lower than the pure KDP crystal. This may reveal that the TGS molecules have a strong influence on the vibration of the KDP lattice, and hence increase the absorbance of the doped crystal. This may show that TGS molecules were a substitutional dopant for the KDP lattice. However, IR light with a wavenumber of about 2300–2400 $cm^{-1}$ can be transmitted through the doped KDP sample, instead of being absorbed as it penetrated through the pure KDP sample. This may be because the large TGS molecules hinder the vibration mode corresponding to the phonons with a wavenumber within such range.

### *Dielectric Properties*

The dielectric constant of the samples was measured using a Hewlett Packard 4194 A Impedance/Gain phase analyzer. Samples of known dimension were coated with silver on both parallel sides and then placed between the copper electrodes to form a parallel plate capacitor. An electric field was applied in the frequency range 100 Hz to 1.5 MHz to investigate the dielectric constant of the pure KDP and TGS doped KDP. As shown in Fig. 4(a) the dielectric constant decreased in the presence of 5%mol TGS in the KDP lattice. However, the dielectric constant becomes approximately unchanging between 1 kHz to 1 MHz. In contrast to the KDP crystal, the dielectric constant decreases significantly when the frequency increases from 1 kHz to 1 MHz. This may show that the electric dipole moments of the TGS doped KDP are weaker than those of the pure KDP. However, its dielectric relaxation time is likely to be smaller than that of the pure KDP, and hence the doped sample has a frequency response broader than the pure KDP. The graphs of the dielectric loss of the pure KDP and TGS doped KDP are shown in Fig. 4(b). The graph of the TGS doped KDP is similar to that

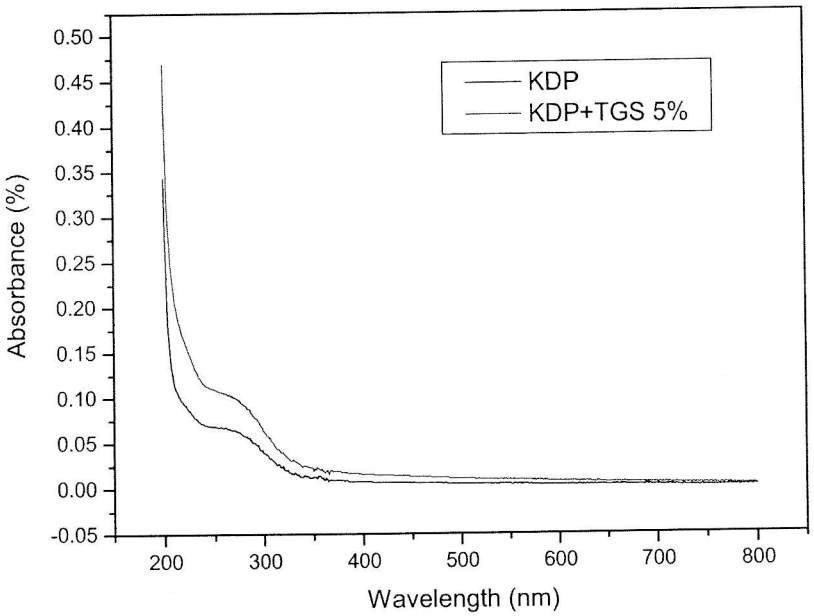


**Figure 5.** UV-vis spectra of KDP and TGS 5% mol doped KDP single crystals.

of the pure KDP. This reveals that the small amount of TGS did not have a strong influence on the dielectric loss of the KDP lattice since the TGS molecules did not increase the resistivity of the KDP lattice. However, the losses of the doped sample at frequencies lower than 10 kHz are slightly higher than those of the pure KDP. This is probably because the TGS molecules corrupted the KDP lattice, and hence led to the higher leakage current through the sample.

### *Optical Absorption Studies*

Optical absorption spectra were recorded using a Shimadzu (Model 1601) spectrophotometer. The spectra were recorded in the wavelength 200–800 nm. Figure 5 shows the optical absorption spectra of pure KDP and TGS doped KDP solutions. It was found that pure KDP solution has an absorption lower than TGS doped KDP. The UV cut offs of pure KDP and TGS doped KDP is 203 nm. This shows that doping the solution with TGS did not shift the

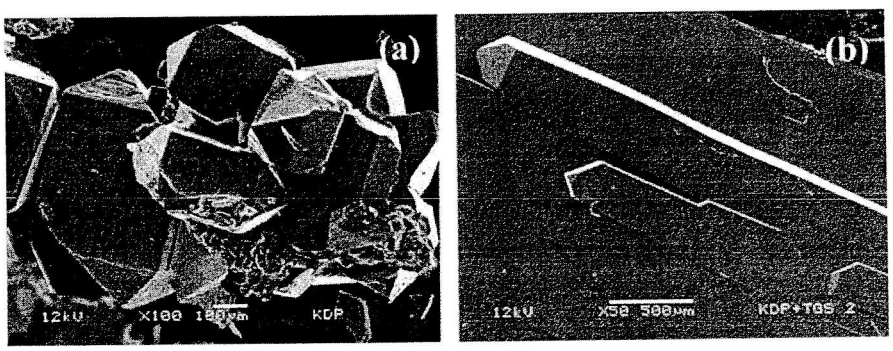


**Figure 6.** SEM of (a) KDP and (b) TGS 5% mol doped KDP single crystals.

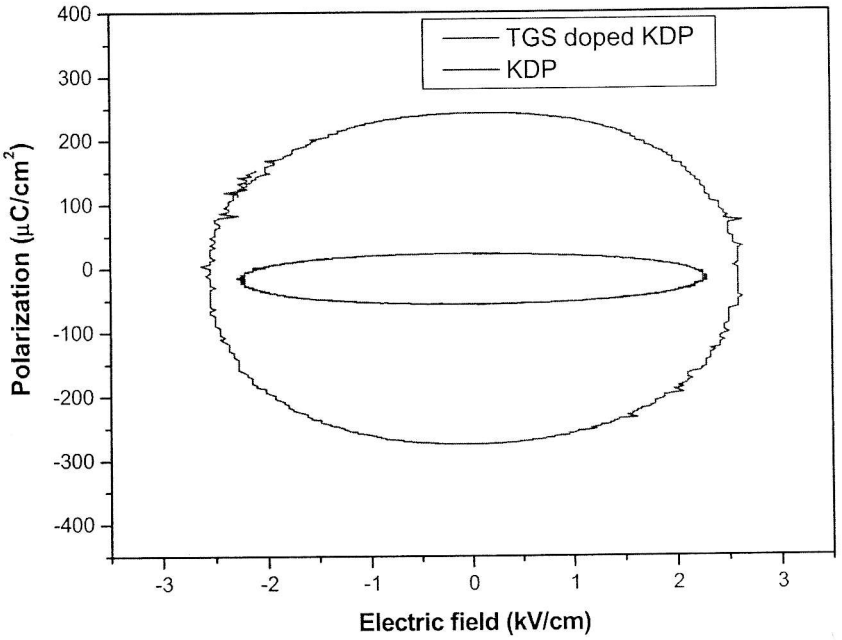


**Figure 7.** Hysteresis of KDP and TGS doped KDP single crystals.

UV cut off frequency. However, the percentage of absorption was increased due to TGS addition.

### *SEM Micrograph*

A scanning electron microscope (SEM) was used to determine the surface morphology of the grown crystals. The surface pictures of the pure KDP and TGS doped KDP crystals are illustrated in Fig. 6(a) and (b), respectively. The results show that the doped KDP has a smooth surface while the pure KDP has a rougher surface. This shows that the TGS molecules have an effect on the surface morphology. With fewer defects and imperfections, the TGS doped KDP crystal may have a more suitable surface for further fabrication processes.

### *Ferroelectricity*

A Sawyer-Tower circuit [11], using a RT66A ferroelectric test system, was operated at 273 K to measure the ferroelectric hysteresis of the crystals. The results of both pure KDP and TGS doped KDP are shown in Fig. 7. It is evident that the polarization of the doped crystal increases significantly. Without an external electric field, the polarization of the TGS doped KDP were approximately four times larger than that of the pure KDP. This reveals that the small addition TGS to the KDP lattice can promote the electric dipole moment in a KDP lattice. The TGS molecules may corrupt the lattice, and hence, the corrupted structure hinders the dipoles to move freely in the absence of the electric field. The aligned electric dipoles remain in the lattice architecture and produce a strong built-in polarization [12]. However, this stronger polarization may not be able to form the electric domain at 273 K.

As a result, the pure and doped KDP crystals did not show the ferroelectric property. Their polarization characteristics were similar to an ideal resistor.

## Conclusions

A TGS doped KDP crystal was grown successfully using the slow evaporation technique. In essence, the TGS molecules have an influence on the KDP lattice, especially the ferroelectricity. With a small addition of TGS to KDP the remaining polarization became significantly larger than that of the pure KDP, and hence, the ferroelectricity of the KDP could be enhanced. On the other hand, TGS molecules also have an influence on the optical property of the KDP lattice.

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