Journal of Applied Sciences

ISSN 1812-5654

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Journal of Applied Sciences 11 (16): 2974-2983, 2011
ISSN 1812-5654 / DOI: 10.3923/jas.2011.2974.2983

Studies on the Effect of L-Alanine on the Structural, Optical and Thermal Properties of Potassium Acid Phthalate Crystals

Ferdousi Akhtar and Jiban Podder
Department of Physics, Bangladesh University of Engineering and Technology, Dhaka, Bangladesh

Abstract: Potassium acid phthalate (KAP) crystals are promising materials as good monochromator for the qualitative and quantitative X-ray analysis of light elements like Fe, Al, Mg, F, Si, etc. in a long and middle range. KAP crystal exhibits a rare blend of ionic and molecular properties and has wide application by virtue of their polar nature. KAP is a non centrosymmetric molecular ionic crystal. L-alanine is an efficient organic non Linear Optical (NLO) compound under the amino acid group. L-alanine doped semi organic material like KAP may be the fundamental building block to develop many complex crystals with improved NLO properties. In this paper an attempt has been made to grow large size optically transparent L-alanine doped KAP crystals by slow evaporation solution growth technique and to see the effects of L-alanine into the pure KAP crystals. The chemical composition of the grown crystals was determined by Energy Dispersive X-ray (EDX) and Fourier Transform Infrared (FTIR) Spectroscopy. The structure of pure and L-alanine doped KAP crystals have been examined by powder X-ray diffraction (XRD) study. Optical properties of the grown crystals were studied using UV-visible specrtroscopy. Using Thermogravimetry (TG) and Differential Thermal Analysis (DTA), the decomposition temperature was obtained. Powder XRD study on grown crystals showed that they belong to an orthorhombic system. The transmission in the visible region and the thermal stability of the crystal was found to increase with the doping concentration of L-alanine into the KAP crystal. Optically transparent, large size and thermally stable L-alanine doped KAP crystals were grown successfully in a laboratory for useful application in opto-electronic devices.

Key words: Energy dispersive X-ray spectroscopy, fourier transform infra red spectroscopy, X-ray diffraction, differential thermal analysis

INTRODUCTION

Potassium acid phthalate (KAP), K (C_6 H_4 COOH. COO) is well known material for its application in the production of crystal analyzers for long-wave X-ray spectrometers (Benedict *et al*., 2003; Krishnan *et al*., 2008a). KAP crystal possesses piezo-electric, pyro-electric, elastic and non-linear optical properties (Destro *et al*., 1988; Meera *et al*., 2004; Misoguti *et al*., 1996). It exhibits excellent cleavage and crystallized into the orthorhombic form with four molecules per unit cell and the unit cell parameters are; a = 6.320 Å, b = 12.343 Å, c = 5.784 Å, $\alpha = \beta = \gamma = 90°$. Single crystals of KAP exhibit a rare blend of ionic and molecular properties and have wide potential application by virtue of their polar nature. The non-linear susceptibility of KAP originates from the contribution of polarizable aromatic rings of phthalate ions (Uthayarani *et al*., 2008).

Amino acid family crystals are playing an important role in the field of non-linear optical organic molecular crystal. Among them L-alanine (LA), with chemical formula (CH_3 CH NH_2 COOH) is the smallest, naturally occurring chiral amino acid with a non-reactive hydrophobic methyl group (-CH_3) as a side chain. LA has the zwitterionic form (+NH_3-C_2H_4-COO-) both in crystal and in aqueous solution over a wide range of pH, which favors crystal hardness for device application (Nicoud and Twieg, 1986).

Recently, several new complexes incorporating the amino acid L-alanine have been crystallized and their structural, optical and thermal properties have also been investigated by Kajzar *et al*. (1995), Kejalakshmy and Srinivasan (2003), Aggarwal *et al*. (2003) and Srinivasan (2004). The growth of pure L-alanine crystals was reported by Vijayan *et al*. (2006) and found higher damage threshold than Potassium dihydrogen phosphate (KDP). It was reported that addition of bimetallic impurities influences the growth kinetics of KDP from aqueous solutions (Begum and Podder, 2009; Claude *et al*., 2006b). The properties of ammonium di

Corresponding Author: Jiban Podder, Department of Physics, Bangladesh University of Engineering and Technology, Dhaka-1000, Dhaka, Bangladesh Tel: +880-2-9665613, +88-01552423766 Fax: +880-28613046

hydrogen phosphate crystal were modified by the addition novel Ni, Mg (Claude *et al*., 2006a). It was also reported that the addition of some of the amino acids as dopant enhances the nonlinear optical (NLO) and ferroelectric properties of semi organic materials (Aggarwal *et al*., 2003; Vijayan *et al*., 2006). So L-alanine doped semi organic material (KAP) will be of special interest as a fundamental building block to develop many complex crystals with improved NLO properties. It was reported that the ferroelectric properties of KAP crystal exhibited by bimetallic impurities dopants Cu^{2+} and Zn^{2+} (Chithambaram *et al*., 2010) and electro-optics properties are improved by the addition of trivalent ions Fe^{3+} and Cr^{3+} (Kejalakshmy and Srinivasan, 2004). The key factor that affect the transmission characteristics of the 90° bent photonic crystal waveguides was explained by Dekkiche and Naoum (2008) and Nasipuri *et al*. (2011) and they elucidate the reason for enhancement of crystal size by Microbes.

In this study, pure KAP crystals were grown by slow evaporation process at room temperature (30°C) and the effect of L-alanine as impurity with concentration ranging from 3000-10000 ppm (i.e., 0.3-1.0 mol %) on the structural, optical and thermal properties of KAP have been reported.

MATERIALS AND METHODS

Solubility study: The solubility of pure KAP and L-alanine doped KAP in double distilled water was determined in the temperature range 30-50°C insteps of 5°C using a constant temperature bath of accuracy ±0.01°C. Five hundred milliliter of the saturated solution of pure KAP salt was prepared gravimetrically at 30°C. This solution was stirred well for six hours constantly using magnetic stirrer and then filtered using Whatmann filter paper. This solution was taken in five different beakers of 100 mL and L-alanine was added to each four beaker as 0.3, 0.5, 0.7 and 1 mol%. After making supersaturated solution of KAP, the 5 mL of the solution was pipetted out and poured into a 10 mL beaker of known weight. The solvent was completely evaporated by warming the solution at 50°C. The amount of the salt present in 5 mL of the solution was measured by subtracting the empty beaker's weight. From this the amount of the salt present in 100 mL of the solution was found out. In the same way, the amount of the salt dissolved in 100 mL at 35, 40, 45 and 50°C was determined. Figure 3 shows the solubility curves of pure and doped KAP salt. It is observed from the solubility graph that the solubility of pure and doped KAP in water increases as the temperature increases and decreases with doping concentration increase. From this solubility data it can state that the KAP material has positive temperature coefficient. Table 1 shows some physical properties of KAP.

Table 1: Some physical properties of potassium acid phthalate ($C_8H_5KO_4$)

Physical property	Values
Form	Powder
Color	Colorless
Molecular formula	$C_8H_5KO_4$
Molecular weight	204.23 g mol^{-1}
Crystal system	Orthorhombic
Density	1.64 g mL^{-1}
Cell dimension	a = 9.749 Å b = 12.905 Å c = 6.647 Å

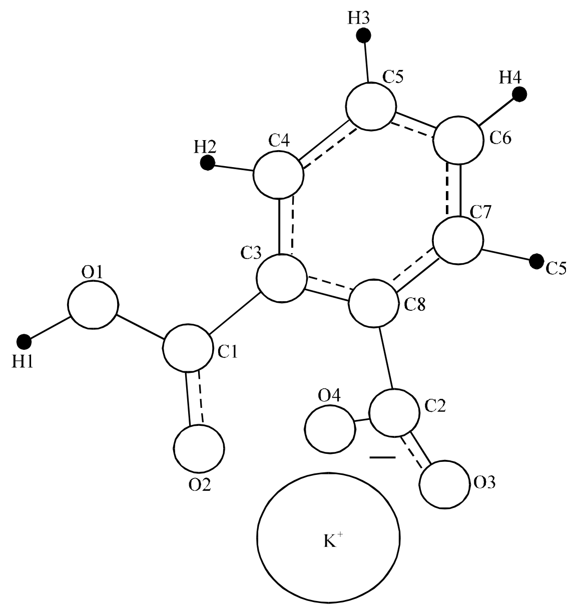

Fig. 1: Molecular structure of KAP crystal

Crystal growth: The pure KAP (AR grade) and L-alanine (AR grade chemical from SIGMA) doped KAP crystals were grown using a good quality seed crystal at room temperature (30°C) by solvent evaporation method. For the preparation of seed crystals saturated solution of KAP was prepared first and then kept in a petri dish covered with a perforated polyethylene and allowed to grow seed crystals within 4-5 days. The pH of the solution was ranged from 3.93 to 3.97. The purity of the crystals was improved by successive recrystallization process. The growth period takes 25-30 days for bigger size. The grown crystals were found color-less and transparent. The molecular structure of KAP crystal is shown in Fig. 1 and 2 show the photographs of pure and doped KAP crystals.

Characterization: The pure and doped KAP crystals were characterized by Energy Dispersive X-ray Spectroscopy

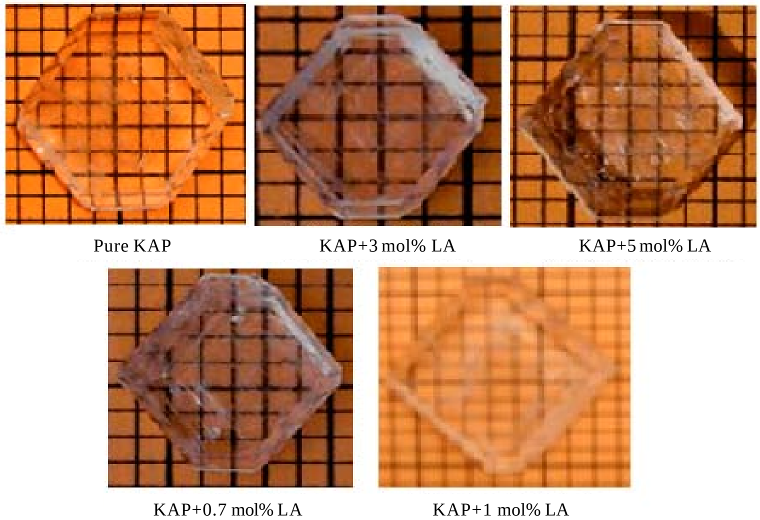

Fig. 2: Solution grown pure and doped KAP crystals

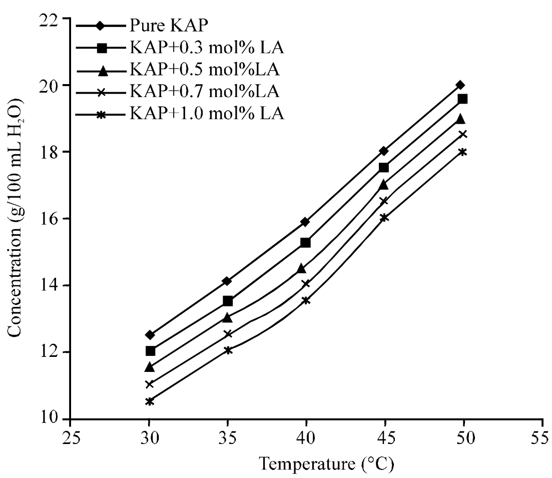

Fig. 3: Solubility curves of pure and doped KAP materials

(EDX), Powder X-ray Diffraction (XRD), Fourier Transform Infrared Spectroscopy (FTIR), Optical Transmission Spectrum, Thermo Gravimetric Analysis (TGA) and Differential Thermal Analysis (DTA).

In order to confirm the presence of L-alanine into KAP, crystals were subjected to EDX. EDX patterns were recorded using JEOL-6360 Scanning Electron Microscope. The recorded EDX spectra are shown in Fig. 4-6. Powder XRD was recorded using a Philips X pert PRO X-ray diffractometer with CuKα (λ = 1.5418Å) radiation. The XRD spectrum is shown in Fig. 7. The lattice parameters were calculated from the XRD data and tabulated in

Table 2: Unit cell parameters of pure and L-alnine doped KAP crystals

Materials	Crystal system	Unit cell parameters
Pure KAP	Orthorhombic	a = 9.749Å, b = 12.905Å, c = 6.647Å α = β = γ = 90°, V = 836.265 Å^3
KAP+0.3 mol% LA	Orthorhombic	a = 9.774Å, b = 12.873Å, c = 6.663Å α = β = γ = 90°, V = 838.343 Å^3
KAP+0.5 mol% LA	Orthorhombic	a = 9.767Å, b = 12.849Å, c = 6.659Å α = β = γ = 90°, V = 835.278 Å^3
KAP+0.7 mol% LA	Orthorhombic	a = 9.768Å, b = 12.863Å, c = 6.656Å α = β = γ = 90°, V = 836.293 Å^3
KAP+1.0 mol% LA	Orthorhombic	a = 9.754Å, b = 12.869Å, c = 6.650Å α = β = γ = 90°, V = 834.757 Å^3

Table 2. In order to confirm the presence of functional groups in the crystal lattice, FTIR spectrum was recorded by KBr pellet technique using a Shimadzu FT-IR-8900 spectrometer in the wave number range 400-4000 cm^{-1}. The FTIR spectra of pure and doped KAP are shown in Fig. 8. The optical properties of the grown crystals were studied by the transmission spectra using Shimadzu UV-1601 visible spectrometer in the wavelength region from 200 to 1100 nm. The transparent crystals with 2 mm thickness samples were used and mounted in a standard manner so that equal area of samples was exposed to the radiation. The transmission spectra of pure and doped KAP crystals are shown in Fig. 9. Thermal analysis was conducted on pure and doped KAP crystals using simultaneous Thermo Gravimetric Analysis (TGA) and Differential Thermal Analysis (DTA) using thermal analyzer (model no. TG/DTA- 6300) from 30 to 700°C at the rate of 15°C min^{-1} in nitrogen atmosphere. The spectra of TGA and DTA of pure and doped KAP crystals are shown in Fig. 10 to 12.

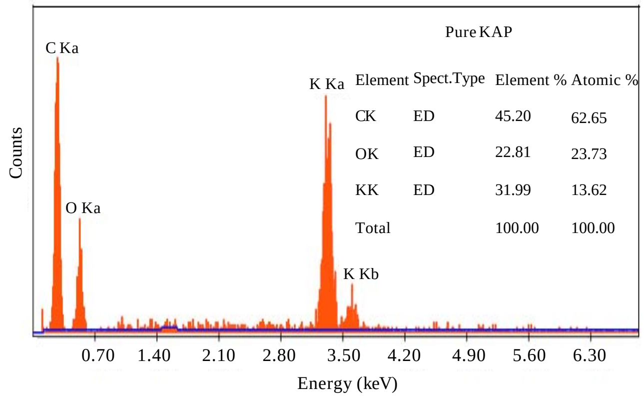

Fig. 4: EDX spectrum of pure KAP crystal

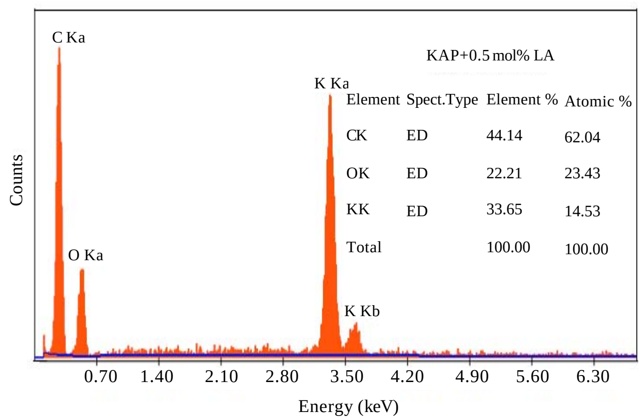

Fig. 5: EDX spectrum of pure KAP+ 0.5 mol% LA crystal

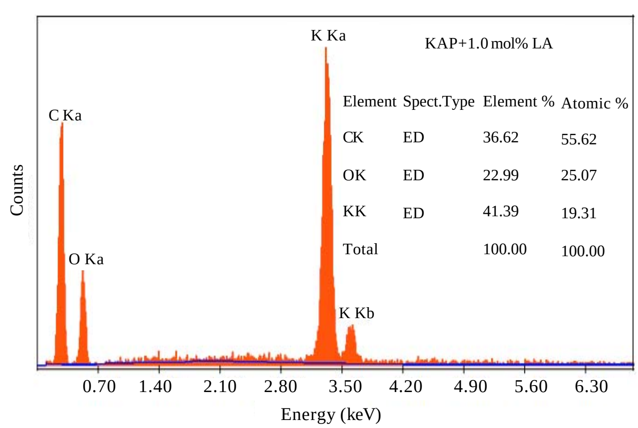

Fig. 6: EDX spectrum of pure KAP+1.0 mol% LA crystal

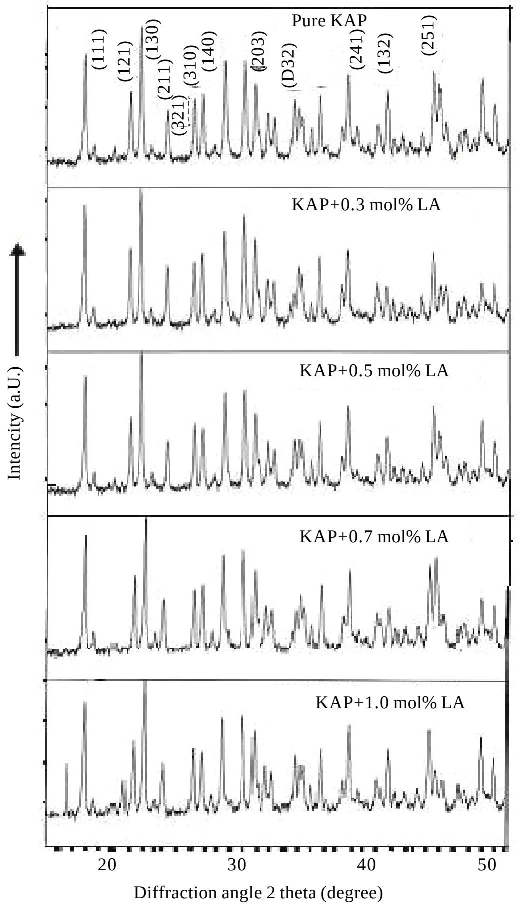

Fig. 7: XRD spectra of pure and doped KAP crystals

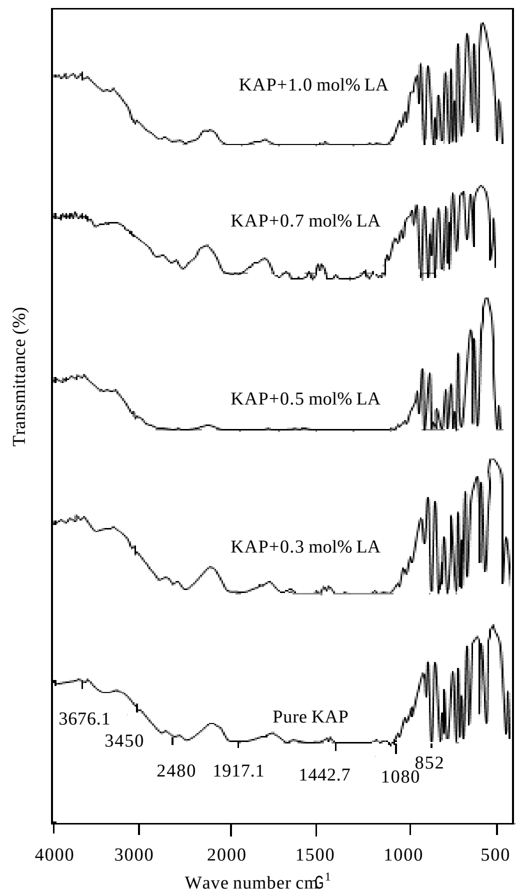

Fig. 8: FTIR spectra of pure and doped KAP crystals

RESULTS

Fourier transform infrared (FTIR) analysis: The FTIR spectra of pure and doped KAP crystals are shown in Fig. 8. The frequencies with their relative intensities obtained in pure and L-alanine doped KAP with different concentrations and their most probable assignments are presented in Table 3. The following vibration assignments showed the hydrogen bonding extends throughout the molecule of KAP. These hydrogen bonding results in the modification of stretching frequencies of O-H and the carboxyl groups. The asymmetric and symmetric stretching modes of C = O (with vertical double bond of oxygen on carbon) were observed at around 1650 cm^{-1}. C = C aromatic ring group appears around the frequency 1481 cm^{-1}. C-H aromatic stretching vibration appears between 1911 and 2025 cm^{-1}. Carboxylic O-H stretching vibration produced resolved multiple bands at 1443 cm^{-1}. Carbonyl group C = O presents in the range 1300-1385 cm^{-1}It was clearly illustrated that the strong hydrogen bonding interaction of C-H group and the corresponding C-H in plane and out of plane bands were observed as weak bands between 811 and 812 cm^{-1}. All these observations confirmed the presence of the functional groups in all grown crystals.

Powder X-ray diffraction analysis (XRD): The lattice parameters and cell volume of pure and doped KAP crystals are shown in Table 2. It was observed that the lattice parameters and cell volume of L-alanine doped KAP crystals slightly differ from those of pure KAP, which may be attributed to the presence of L-alanine in KAP crystals. The powder XRD analysis confirmed that the crystal structure of KAP is orthorhombic.

UV-VIS studies: The Ultra Violet-Visible optical transmission spectra of pure and doped KAP crystals are shown in Fig. 9. This spectral study might be assisted in

Table 3: Comparison of vibrational frequencies obtained through FTIR studies of pure and doped KAP crystals

		L-alanine doped KAP (cm^{-1})			
Functional group	Pure KAP (cm^{-1})	0.3 mol%	0.5 mol%	0.7 mol%	1.0 mol%
O-H (hydrogen bonded)	3300	3325	3323	3325	3322
-C-H (aromatic stretching)	1917	1919	2025	1917	1911
Symmetrical C = O stretching	1650	1675	1650	1674	1720
C = O aromatic stretching					
C = C ring stretching	1535	1600	------	1545	1600
O-H in plane bending	1481	1485	------	1485	1485
-C = O carboxylate ion = O	1443	1443	------	1443	1450
Symmetric	1350	1325		1385	1300
C-COO stretching					
C-O stretching	1225	1220	------	1254	-------
= C-H out of plane bending	1150	1130		1151	1175
C-H out of plane bending	852	852	851	852	853
= C-H out of plane	811	------	812	-----	812
deformation	694	694	694	694	694
C-O wagging					
C = C-C out of plane ring deformation	679	679	679	679	679
deformation	582	582	582	582	582
C = C out of plane bending	409	409	413	409	409

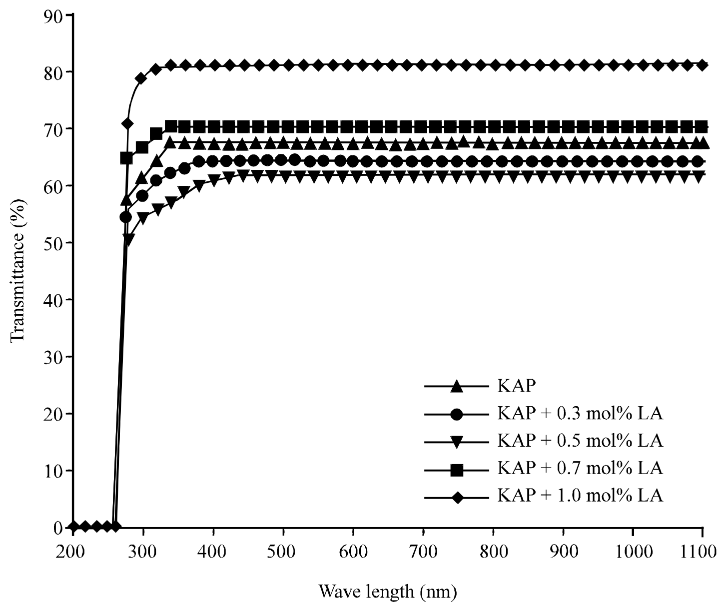

Fig. 9: UV-Visible transmissions of pure and doped KAP crystals

understanding electronic structure of the optical band gap of the crystals. It is clear from the Fig. 9 that the percentage of optical transmission increases with the increase of the concentration of L-alanine in KAP crystals. All of them have sufficient transmission in the entire visible and near IR (infrared) region. This is the most desirable property of materials possessing for nonlinear optical (NLO) activity. There is a strong absorption at 280 nm. Absorption in the near ultraviolet region arises from electronic transitions associated within the sample. Using the formula $E_g = hc/\lambda$, the band gap energy was found to be 4.42 eV. Hence, it could be concluded that the L-alanine doping play a key role in improving the optical quality of KAP crystals.

Thermo Gravimetric Analysis (TGA) and Differential Thermal Analysis (DTA): In this study, the effect of L-alanine doping on the thermal stability of KAP crystals was studied by employing TGA and DTA. Figure 10 indicated the thermo gram and differential thermal analysis for pure KAP crystal. The TGA trace showed the different stages of decomposition. The first stage of decomposition started at 281.0°C and at 302.5°C to be for the major stage of decomposition. It was observed that initially there is loss of water of hydration and then became anhydrous and remained in that form up to the end of the analysis. There is no weight loss below 281.0°C. The DTA curve of pure KAP showed an endothermic peak at 296.8°C. This

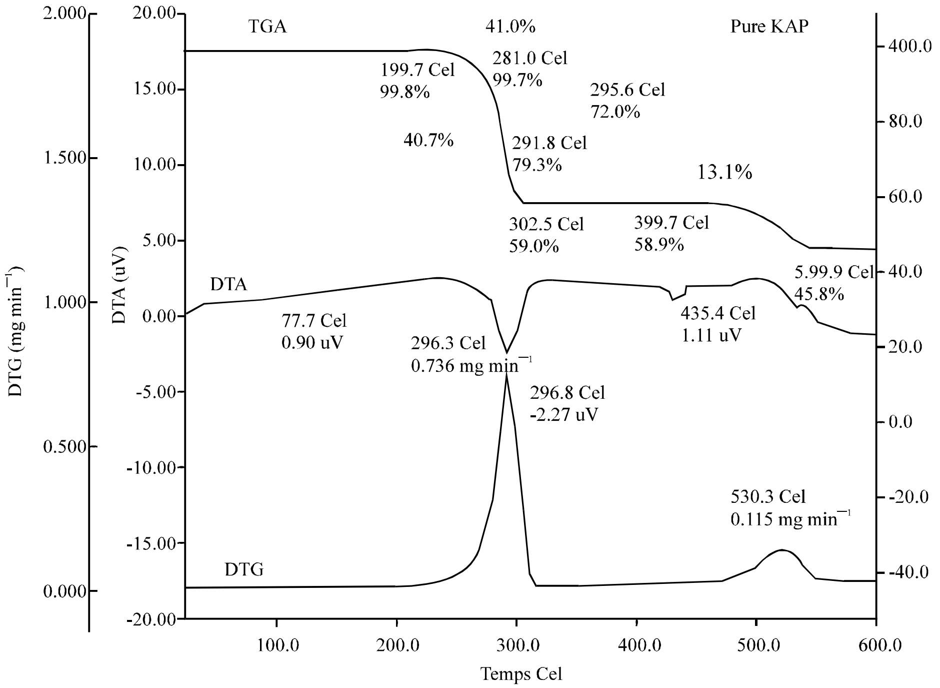

Fig. 10: TGA/DTA spectrum of pure KAP crystal

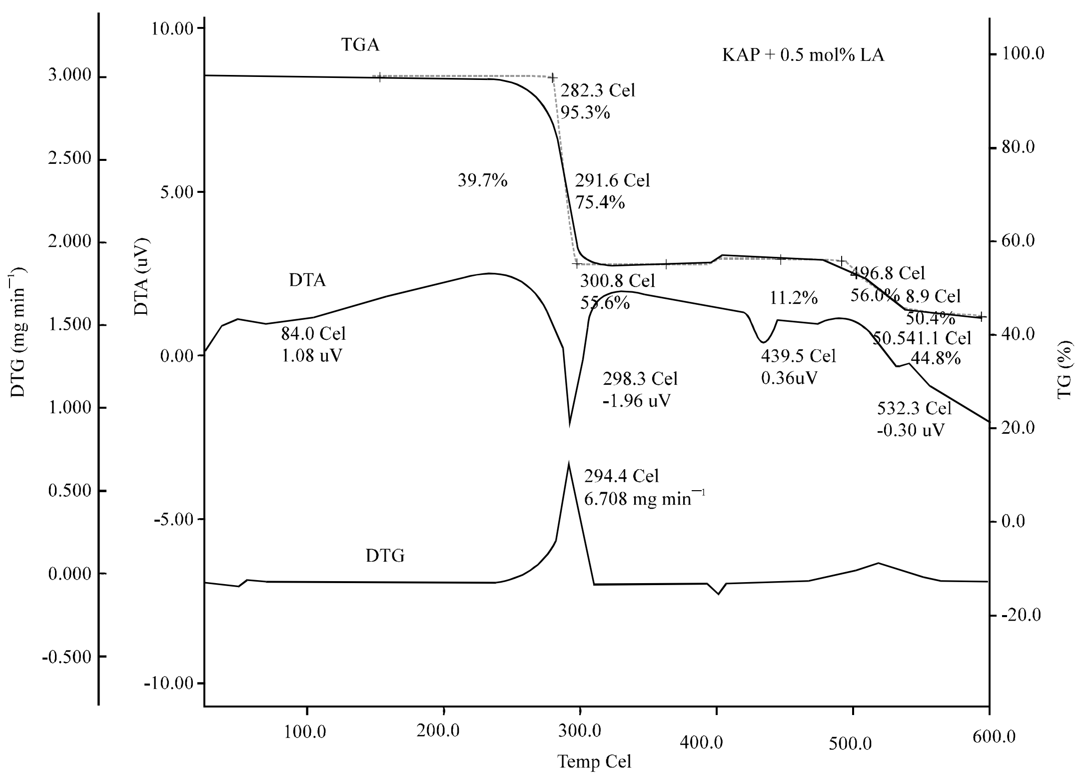

Fig. 11: TGA/DTA spectrum of KAP+0.5 mol% LA crystal

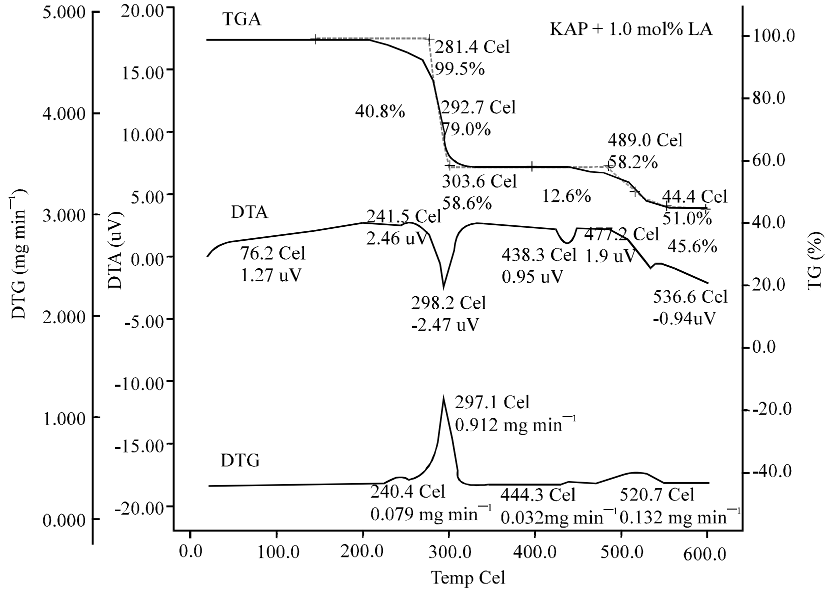

Fig. 12: TGA/DTA spectrum of KAP+1.0 mol% LA crystal

endothermic peak corresponded to the decomposition temperature of the crystal. The TGA/DTA curves for L-alanine (0.5 mol%) doped KAP are presented in Fig. 11. DTA/TGA curve of 1.0 mol% L-alanine doped KAP showed an endothermic peak at 298.2°C (Fig. 12). The major stage of decomposition started at 303.6°C. It was confirmed that there is no phase transition for pure and doped KAP crystals up to temperature range 30 to 201°C.

DISCUSSION

The solubility of KAP determined by the solution method agrees well with that reported in the literature (Vasudevan *et al*., 2009) and the addition of L-alanine impurities, the solubility of KAP has been slightly changed which is also agreed well with Parikh *et al.* (2010). Large size, transparent, pure and L-alanine doped KAP crystals were grown by slow evaporation technique within a period of 30 days. Energy dispersive X-ray spectroscopy confirmed the presence of L-alanine into the KAP crystals. The powder X-ray diffraction spectra showed a small shifting of the peak position and also the variation in the intensities, which indicated the incorporation of L-alanine into the KAP crystal. The same result was found in KAP by DL-alanine doping (Uthayarani *et al*., 2008) and in KDP by doping L-alanine (Parikh *et al*., 2010). In the FTIR spectra of pure and L-alanine doped KAP crystals, the shifting to higher energy due to L-alanine doping indicated the interaction of O-H grouping of KAP with COO group of L-alanine. But Uthayarani found the opposite to this result. The optical transmission of KAP crystals increased with impurities concentration and the result agreed with Uthayarani *et al.* (2008), Parikh *et al.* (2010), Krishnan *et al.* (2008b), Geetha *et al.* (2006) and Murugakoothan *et al.* (1999). Chithambaram *et al.* (2010) and Kejalakshmy and Srinivasan (2004) reported doped KAP crystals possessed very low absorption in the entire visible region by addition of bivalent and trivalent metal ions. In the present investigation, the effect of L-alanine on the thermal stability of KAP crystals was studied by TGA/DTA. The thermograms showed that the crystal became anhydrous presently than pure KAP which agreed with Vasudevan *et al.* (2009) but in case of KDP it happened opposite of this study. Since amino acid became unstable at lower temperatures, it weakens KDP crystal and as a result the dehydration process took place earlier and more rapidly with comparison to pure KDP.

CONCLUSIONS

The effect of amino acid (L-alanine) impurity on the growth of KAP from supersaturated solutions has been investigated experimentally by measuring structural, optical and thermal properties. The presence of L-alanine in KAP solution was found to increase the optical transmission and decomposition temperature. This phenomenon may be attributed due to zwitterionic nature of L-alanine molecule ($^{+}NH_3$-C_2H_4-COO^{-}). The enhancement of optical transmission of L-alanine doped KAP crystals highlights their prospects of application as NLO materials. Further studies viz., frequency response of the dielectric constant, tanδ, temperature dependant conductivity, resistivity, activation energy and Vicker's micro hardness are in progress and to be reported soon.

ACKNOWLEDGMENTS

The authors are thankful to Dr. Dilip Kumar Saha, CSO, for XRD measurements and Mr. Harinarayan Das, S.O. and Md. Al-Mamun, SO, Atomic Energy Centre, Dhaka, Bangladesh for EDX measurements.

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