

Effect of divalent metal ions on the structure, optical and mechanical properties of KAP single crystals

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ABSTRACT

Single crystals of potassium acid phthalate (KAP), Nickel Doped KAP (NiKAP) and Cobalt doped KAP (Co KAP) have been grown from aqueous solutions by solvent evaporation method. The effect of these metal ions on surface morphology, structure, optical and mechanical properties have been studied. Single crystal XRD studies of these crystals confirm that both the added impurities have modified the structure of the KAP crystals in a similar manner. The presence of dopants in the crystal lattice have been further confirmed by FTIR analysis. The stoichiometric composition of both the doped crystals have been studied using EDAX analysis. Optical absorbance was carried out for all the crystals. The absorbance in the visible region observed in both the doped crystals was assigned to their d-d transitions. Micro hardness of the pure and doped crystals were found using Vickers's Hardness Technique.

Key words: Solution growth, KAP, Impurities, Semi-organic.

INTRODUCTION

The importance of Non-linear optical (NLO) materials is that they are required in the field of opto-electronics for frequency conversion, optical modulation and optical switching. To date, several thousand non-linear crystals and their related isomorphs have been developed. But characteristics such as transparency, phase matching, high optical quality, and availability in bulk form are necessary for them to serve as good NLO materials. Organic NLO materials have been studied extensively for second harmonic generation, but the growth of these crystals and also cutting and polishing is difficult. Hence much attention has been given to semi-organic NLO materials. The advantage of semi-organic materials is that the crystals can be grown from aqueous solutions and they can be easily cut and polished. The phthalic acid derivatives, when grown into crystals are potential candidates for NLO and electro-optic applications. Potassium acid phthalate (KAP) is one of the important NLO crystals in the phthalic acid family. KAP crystal is

an orthorhombic system, space group = $Pca2_1$ with unit cell parameters $a = 9.609\text{\AA}$, $b = 13.857\text{\AA}$, $c = 6.446\text{\AA}$ ^{1,2}. It has one perfect (0 1 0) cleavage plane and its cleavage faces find applications as substrates in epitaxial techniques. Hence, KAP crystals, besides application in soft X-ray spectroscopy, are used as substrates for the growth of highly oriented films of conjugated polymers with high non-linear optical susceptibility³. For a long time researchers have been interested in the influence of impurities on crystal growth kinetics and crystal morphology. This is due to the fact that additives can change the crystallization process drastically. It has been reported that organic additives, differing in their chemical behaviour, affect growth rates of different faces of KAP and KDP crystals^{4,5}. The surface morphology in the presence of inorganic impurities has also been reported⁶⁻⁹.

Since KAP itself is a semi-organic material having the combined nature of both organic and inorganic materials, impurities of both classes are expected to have significant influence. The effect of

trivalent metal ions like Fe^{3+} and Cr^{3+} ions on the structure, optical and electro-optical properties of KAP crystals were studied and reported¹⁰. The structure of cobalt and nickel doped KAP was reported earlier^{11,12}. In this present work, influence of divalent metal ions such as cobalt (Co^{2+}) and nickel (Ni^{2+}) on the morphology and optical properties of KAP crystals is carried out and reported.

Crystal Growth

Pure KAP crystal

All the chemicals used for the present experiment were of analar grade, supplied by E-Merck. Saturated solutions of KAP was prepared in double distilled water and was filtered using whatman filter paper. The filtered solution was transferred into a crystallization dish of 100 mm diameter and 50 mm height. The dish was covered with perforated covers. Tiny crystals were seen within 2 days. Crystallization completed in about 3 weeks. Pure KAP crystals grown from slow evaporation technique are shown in fig(1a).

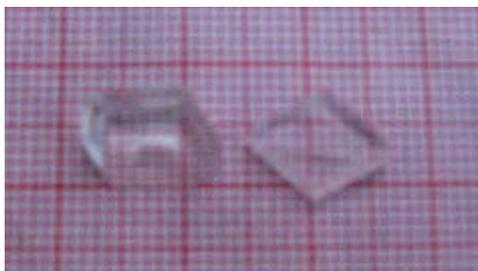


Fig. -1a: KAP crystal grown from slow evaporation technique

Co^{2+} doped KAP crystals

Cobalt doped KAP crystals were grown by dissolving 0.02M - 0.1M CoCl_2 in KAP solution and the solution was filtered and transferred into a crystallization dish of 100 mm diameter and 50 mm height. The dish was covered with perforated covers. Tiny crystals were seen within 2 days. It was observed that for lower concentrations such as 0.02M and 0.04M crystals of pink colour and colorless were observed in the same dish. For the concentration of 0.1M CoCl_2 , pink crystal of

dimension 20mmx15mmx5mm was observed. At this concentration, when the size of the crystal was big, 2 or 3 crystals only formed. But when more no. of crystal was formed, the size reduced. Few cobalt doped KAP crystals are shown in the Fig (1b).

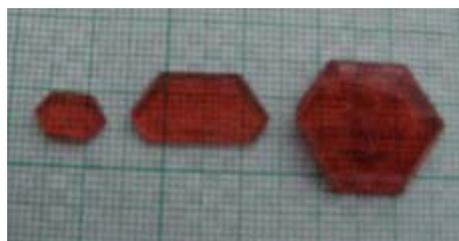


Fig. -1b: Cobalt doped KAP crystals

Ni^{2+} doped KAP crystals

For nickel doping, nickel was taken in the form of NiCl_2 . But the crystals formed were not of good size. Hence NiSO_4 was used. The concentration of nickel was also varied from 0.02M - 0.1M. It was observed that for the concentration 0.08M NiSO_4 , crystals of 15mmx12mmx4mm size was obtained [Fig(1c)]. For other concentrations crystals of smaller size were obtained.

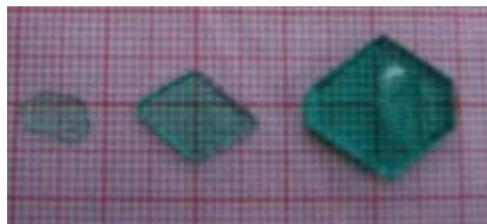


Fig. - 1c: Nickel doped KAP crystals

Characterization

The grown crystals were characterized by single crystal XRD, FTIR spectroscopy, UV-Visible spectroscopy, EDAX, AAS, thermal analysis, dielectric studies, birefringence, SHG, hardness and etching studies.

Single crystal XRD study

Single crystal XRD was carried out in ENRAF Nonius CAD4 diffractometer using a MoK_α radiation. KAP, cobalt and nickel doped KAP specimens of

dimensions 0.17x0.21x0.33 mm³ cut from the as grown crystals were used. Least square refinement of 25 reflections were done in the range 20 – 30°. Results of single crystal X-ray diffraction is given in table 1. The lattice parameters of the pure and doped KAP crystals were found to be in good

agreement with reported values [5,11,12]. The schematic morphology diagrams for the pure and doped KAP crystals are shown in fig 2a, 2b and 2c. There is significant departure from that of pure KAP^[13].

Table -1: Single crystal X-ray diffraction data

Pure KAP		Co: KAP		Ni: KAP	
Observed	Reported	Observed	Reported	Observed	Reported
a=9.620Å	a=9.60 Å	a=10.39 Å	a=10.38 Å	a=10.40 Å	a=10.434Å
b=13.260Å	b=13.857Å	b=6.838Å	b=6.862Å	b=6.864Å	b=6.85 Å
c=6.46 Å	c=6.446Å	c=29.311Å	c=29.309Å	c=29.447Å	c=29.44 Å
β=90°	β=90°	β=98.221°	β=97.804°	β=98.10°	b=98.068°

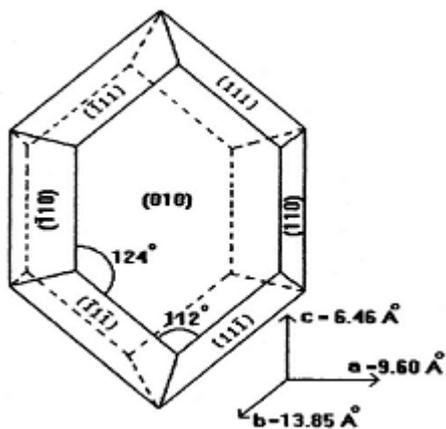


Fig. - 2a: Pure KAP crystal

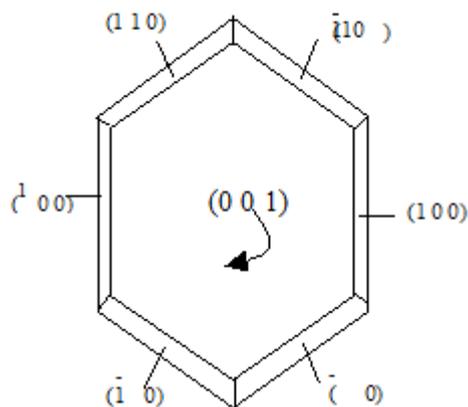


Fig. - 2b: Co : KAP CRYSTAL

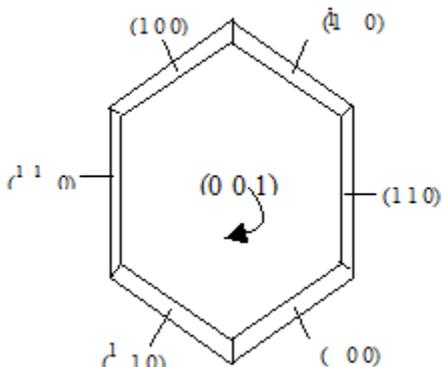


Fig. - 2c: Ni : KAP CRYSTAL

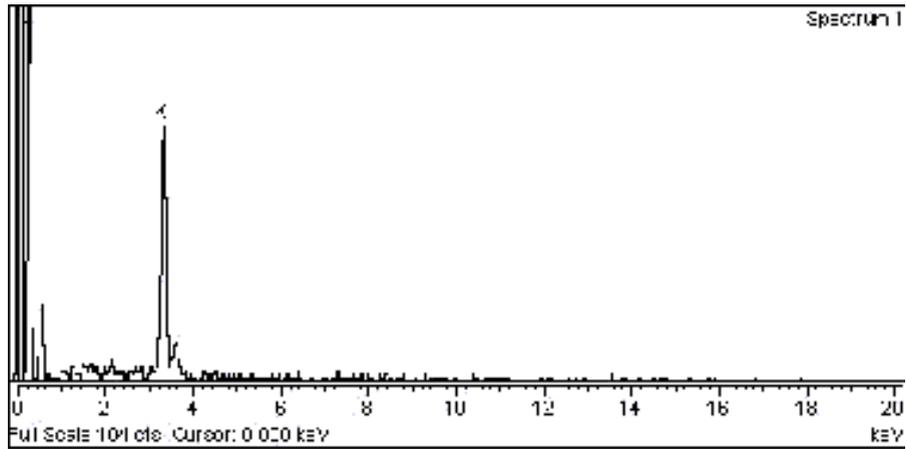


Fig. - 3: EDAX spectra of KAP

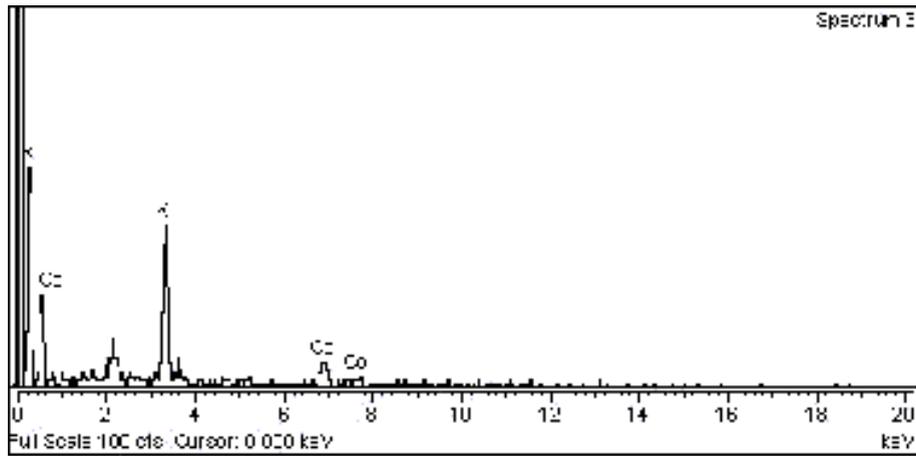


Fig. - 3b : EDAX spectra of Co:KAP

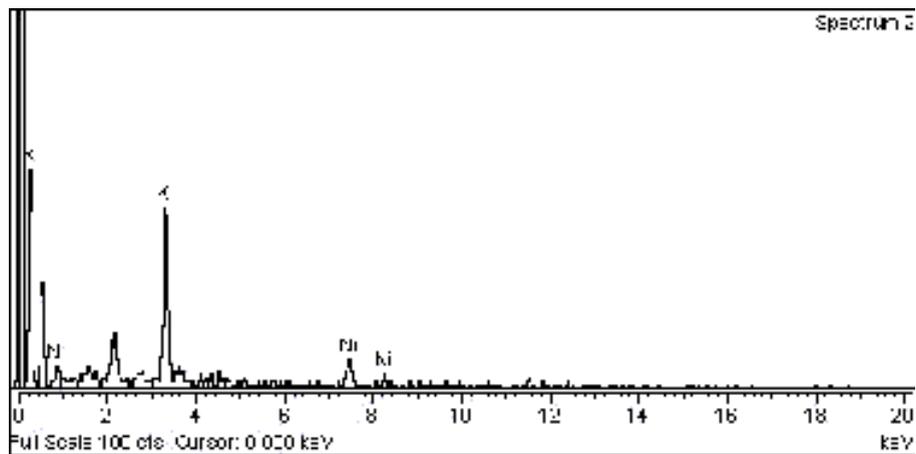


Fig. - 3c : EDAX spectra of Ni:KAP

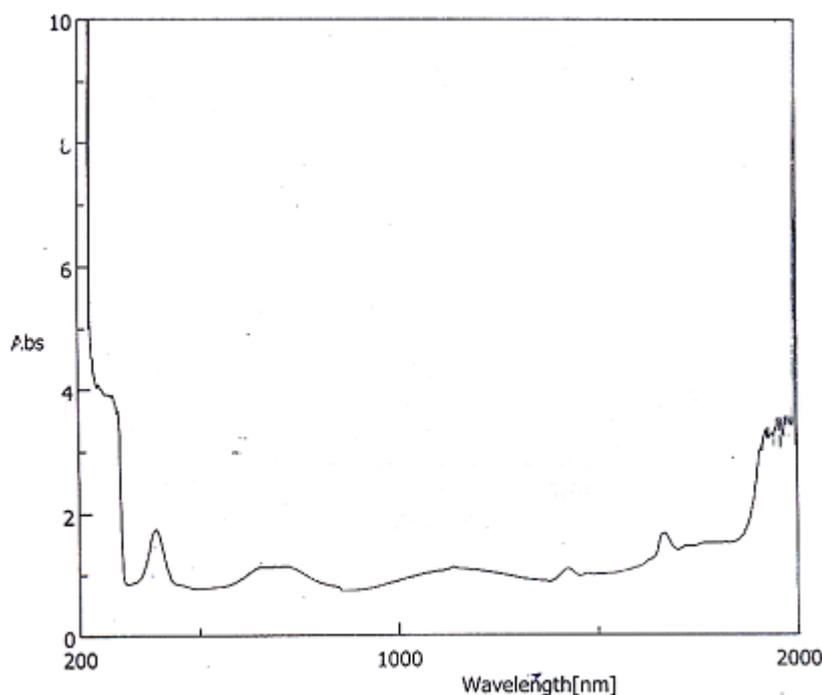
Table - 2

	Element	weight (%)	Atomic (%)
Pure KAP	KK	100%	100%
Co:KAP	KK	96.06	96.99
	Cok	3.94	3.01
Ni:KAP	KK	95.79	96.73
	NiK	4.21	3.27

Energy Dispersive Analysis by X-ray Diffraction (EDAX) and Atomic Absorption Spectroscopic analysis (AAS)

The energy dispersive X-ray diffraction was carried out in IWCA 200 system connected to a LEO – stereo scan 440 scanning electron microscope. EDAX spectra of KAP, Co: KAP, Ni: KAP are shown in Fig.3a, 3b and 3c respectively. The atomic percentage of metals in each crystal is indicated in table 2. The level of Co and Ni doping in KAP is observed to be nearly equal. This reveals that KAP has nearly the same driving force to take in either Co or Ni in the same quantities in the crystal lattice. This appears to be true, because the

phthalate ion is not making any direct bonding interaction with either cobalt or nickel. This is also evident from the report^[11], who reported the X-ray crystal structures of nickel doped KAP crystal. In both the crystals, the phthalate ion is seen to interact with water present in the coordination sphere of the metals. Since cobalt can also accommodate six water molecules in its coordination sphere like nickel, Co:KAP crystal structure is also expected to be same as that of Ni:KAP. In line with our view, as discussed in the XRD analysis, the structure of Co:KAP is same as that of Ni:KAP. Hence within the lattice both cobalt and nickel in their crystals are expected to have same level of bonding interaction in order to provide the same crystal structure, with the same unit cell constants. The binding energy value close to 8 KeV for both cobalt and nickel illustrates two chemical status for both; it could be assigned to metals buried in the bulk portion of the crystal and those close to the surface. The atomic absorption spectroscopic studies were carried out to confirm the incorporation of Ni^{2+} and Co^{2+} dopants.

**Fig. - 4a: Absorption spectrum of Ni:KAP crystals**

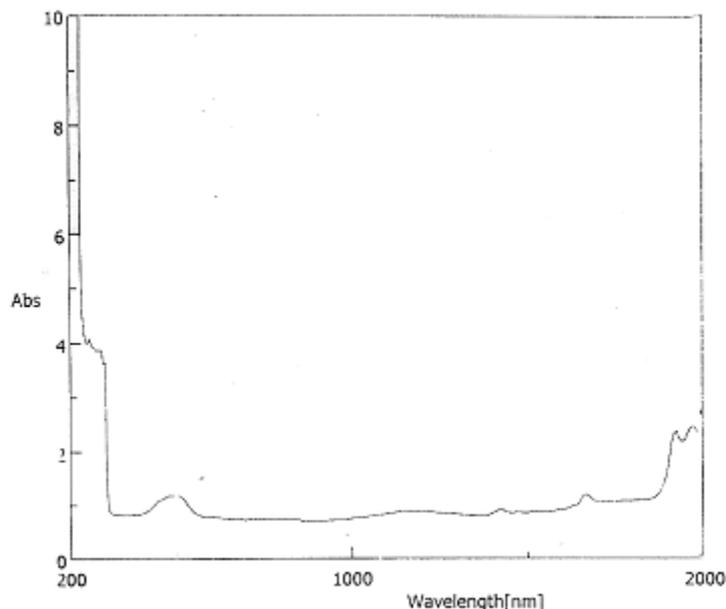


Fig. - 4b: Absorption spectrum of Co:KAP crystals

UV-Visible spectral analysis

Linear optical properties of the crystals were studied using a Shimadzu UV-Visible spectrophotometer. The UV-visible spectral analysis of KAP, cobalt doped and nickel doped KAP crystals were carried out covering the ultraviolet, visible and near IR regions. The plot of wavelength against absorbance for Co:KAP and Ni:KAP are presented in Fig. 4a and 4b respectively. There are absorption bands below 750 nm in all the spectra, which are assigned to overtones, and combination bands. In

the visible region no absorbance is observed for KAP but in the spectrum of Co:KAP, there is an absorbance maximum close to 400nm. Similarly Ni:KAP shows broad absorbance maximum between 500-750nm. The absorbance in the visible region in both cobalt and nickel doped KAP is assigned to their d-d transitions. The absorbance in Co:KAP is assigned to $4T_{1g}(F) \rightarrow 4T_{1g}(P)$ transitions. It matches with the electronic transition in $[Co(H_2O)_6]^{2+}$.

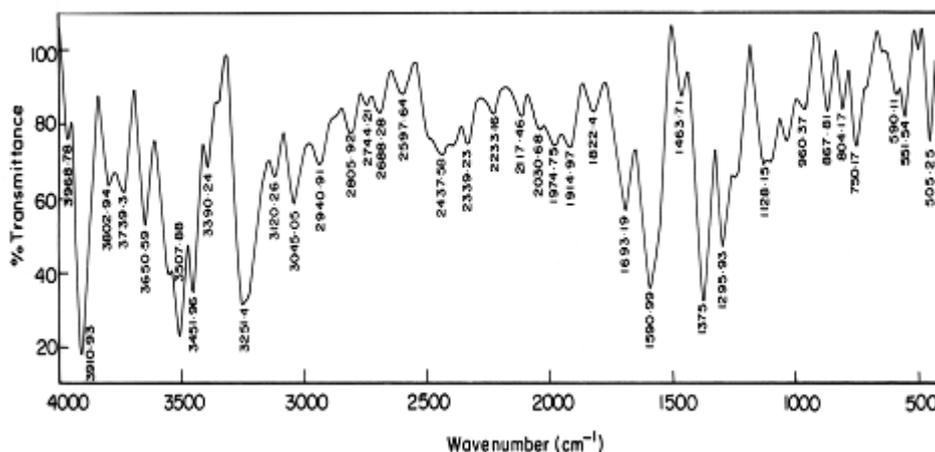


Fig. - 5a: FT-IR spectrum of pure KAP crystals

Hence this observation confirms the presence of six water molecules around cobalt in conjunction with XRD analysis as reported by^[12].

Generally $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ shows three absorption bands due to

- $3 A_{2g} \rightarrow 3 T_{2g}$ 1125 nm
- $3 A_{2g} \rightarrow 3 T_{1g}(F)$ 700 nm
- $3 A_{2g} \rightarrow 3 T_{1g}(P)$ 300 nm

transitions¹⁴. Similar absorption bands are also noted in the spectrum of Ni:KAP. Hence Ni might

also have six water molecules around its coordination sphere¹¹. The recorded spectrum of Co:KAP shows that the crystals show good transmission in the entire visible region. The lower cut-off lies below 300 nm in the ultraviolet (UV) region.

Fourier transform infrared analysis

The FTIR spectra of the samples were recorded in the range 400-4000 cm^{-1} employing a Perking-Elmer spectrometer by KBr pellet method. The middle FT-IR spectrum of KAP is shown in Fig (5a). In the higher energy region between 3100-

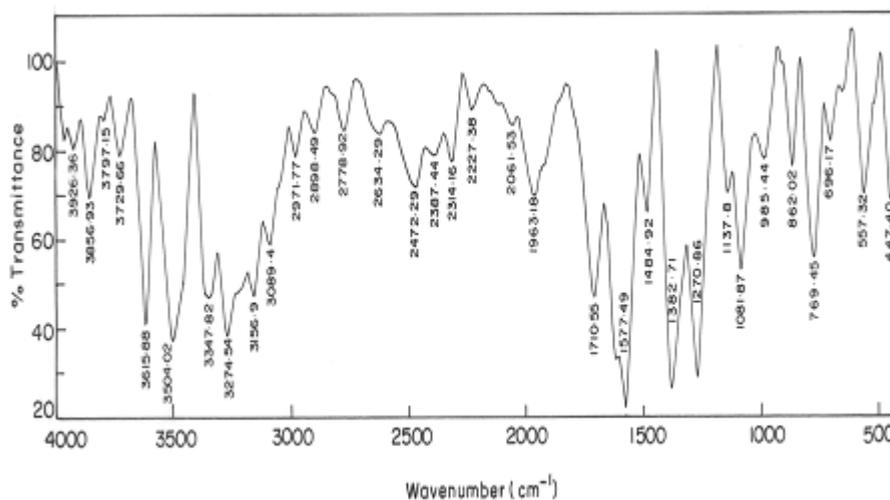


Fig. - 5b: FT-IR spectrum of Ni²⁺ doped KAP crystals

4000 cm^{-1} , there are resolved peaks due to O-H stretch of COOH group of potassium acid phthalate and water. The aromatic C-H stretching vibration appears just above 3000 cm^{-1} . The bands between 2500 cm^{-1} and 3000 cm^{-1} are the additional fine structure bands due to hydrogen bonding interaction of COOH group. The peaks between 2000 cm^{-1} and 2500 cm^{-1} are due to overtones and combination

bands. The C=O stretch appears to be partly resolved at 1685.48 cm^{-1} . The asymmetric and symmetric C-O-O stretching vibrations appear at 1587.13 cm^{-1} and 1373.07 cm^{-1} . The aromatic ring C-H bend occurs at 761.7 cm^{-1} . The aromatic ring skeletal vibrations are not well resolved due to its overlapping with asymmetric C-O-O stretching vibrations.

Table - 3: Infrared group vibrations

	C=O	C00 (assy)	C00 (symm)
KAP	1685.48	1587.13	1373.07
Co:KAP	1693.19	1590.79	1375.00
Ni:KAP	1710.00	1577.49	1382.71

The middle FT-IR spectrum of Co(II) doped KAP is shown in Fig. 5b. The spectrum carries characteristic features as that of Fig.5b, but in addition there is significant shift in the position of C=O stretching vibration and C-O-O symmetric and asymmetric stretching modes as shown in Table 3. This observation clearly indicates coordination of C-O-O grouping to the Co (II). Since the O-H

stretching vibrations in the higher energy region are clearly distinct, the COOH group is to be bonded to cobalt without deprotonation. It is also evident from the molecular packing diagram of the unit cell¹².

The middle FT-IR spectrum of Ni:KAP is shown in Fig. 5c. It also carries features same as Fig. 11 and 12. Similar to Co (II) doped KAP, this crystal also shows bonding of the carboxyl group to nickel as there is distinct shifting of peak positions due to C=O and carboxyl groupings as shown in Table 3. The C=O stretching appears at 1685.48 cm⁻¹, for the parent KAP. But it is shifted to 1693.19 cm⁻¹ and 1710 cm⁻¹ for Co (II) and Ni (II) doped crystals respectively. Hence this shifting is a clear indication

for the coordination of C-O-O with the metal. In the absence of metal coordination there is much electron delocalization in the C-O-O grouping, and hence the strength of C=O group gets decreased. But when the carboxyl group is bonded to Co (II) the strength of C=O bond is increased due to less electron delocalization and hence the C=O stretching frequencies of both the metal containing crystals are shifted to higher values.

Vickers's Hardness studies

In order to study the mechanical properties, micro hardness measurements were carried out on the {010} face of both pure and doped crystals. Static indentation tests were made at room

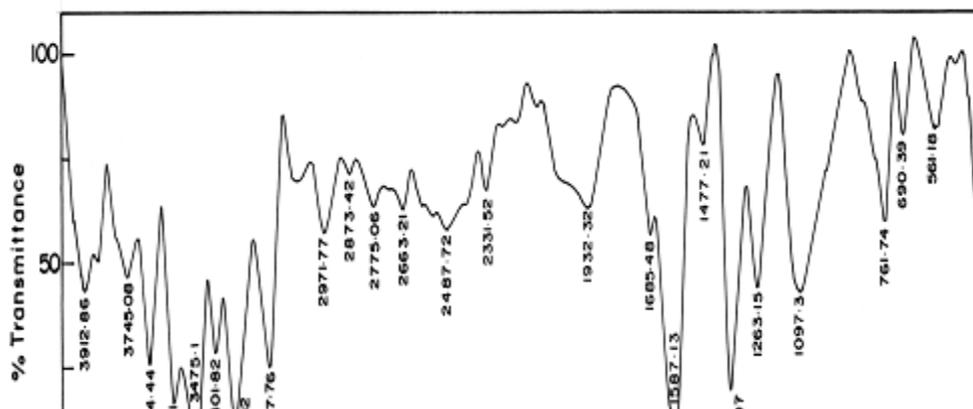


Fig. - 5c. FT-IR spectrum of Co²⁺:KAP crystals

temperature (300 K) using a Leitz Wetzlar hardness tester fitted with a Vickers's pyramidal indenter. Loads of different magnitude 5, 10, 35 and 50 g were applied over a fixed interval of time. Indentations were made at different sites on the crystal surface. Vickers's micro hardness values were calculated from the formula

$$H_v = 1.8544 (P/d^2) \text{ kg/mm}^2$$

where H_v is the Vickers's micro hardness number in kg/mm², P is the applied load in g and d is the average diagonal length in mm. In pure KAP it was observed that the hardness decreases at lower loads and saturates for a load of 50g. These

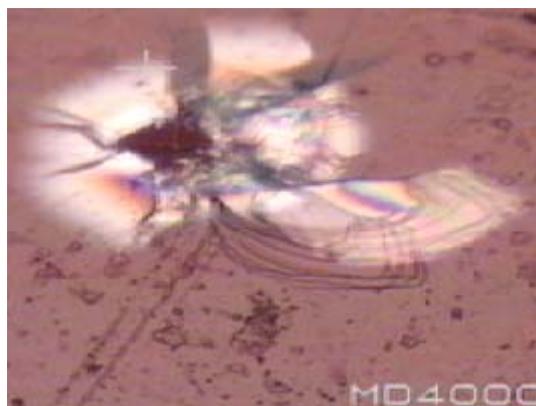


Fig. -6

results can be attributed to the work hardening of the surface layers. Above 50g load cracks were formed due to the release of internal stress generated locally by indentation. Metal ion doped KAP showed lower hardness values than the pure crystals, which may be due to the decrease in bond energy due to doping. The doped KAP crystals show cracking even at very low loads, as shown in the figure (6). The hardness values are
 H_v for Co: KAP = 93 kg/mm²
 H_v for Ni: KAP = 89.15 kg/mm²

CONCLUSIONS

The pure, cobalt doped and nickel doped crystals of KAP were grown by slow evaporation

method. The effect of these impurities on surface morphology, structure, optical, and mechanical properties have been studied. From the morphological studies, it is observed that there is significant effect of these impurities of the morphology. The crystallographic parameters were determined using single crystal XRD method. The presence of the dopants was confirmed by Atomic Absorption Spectroscopic studies and their nature inside the crystal studied using EDAX and FT-IR analysis. The above studies conclude that the impurities have gone into the crystal lattice and modified the morphology and structure of the KAP single crystals. The optical transmission is altered due to doping. Hardness of the material is decreased due to metal ion doping.

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