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Effect of cobalt, magnesium, lithium and nikel dopants on solution grown KDP crystals

A.Claude[1]*, K.B.Rajesh[1], N.Vijayan[2]

[1]PG Department of Physics, Government Arts College, Dharmapuri - 636 705, (INDIA)

[2]National Physical Laboratory, New Delhi - 110 012, (INDIA)

E-mail: albertclaude@yahoo.com

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ABSTRACT

KDP is a versatile NLO material grown by low temperature solution growth. It is used in many solid-state electronic applications. Single crystals of KDP and (Co, Mg, Li, Ni) doped KDP were grown by the slow evaporation technique. The grown crystals were confirmed by powder XRD technique. The solubility studies indicated that the impurity level at 1 mol% changes the metastable zonewidth and the induction period gets reduced. It was observed that when the (Co, Mg, Li, Ni) dopants were added at 1 mol %, the crystallinity of the material was found to increase. FTIR investigations indicated that the impurities played an important role in the spectral characteristics of the material. High Resolution XRD revealed the comparative crystalline nature of the doped crystals.

KEYWORDS

Doping;
Growth from solutions.

INTRODUCTION

Crystal Growth from solution is a very important process used in many applications from the laboratory to the industry. Potassium di-hydrogen phosphate (KDP) having important applications in electro-optics and harmonic generation was grown by evaporation technique at room temperature. The KDP crystals were doped with an optimal quantity (1 mol %) of dopants like Co^{3+}, Mg^{2+}, Li^{2+}, Ni^{3+}. Many studies on the growth kinetics of KDP with different impurities were reported[1-3], and the changes of the crystal morphology and supersaturation[4] were discussed earlier. In this paper the effects in adding various dopants with KDP and the changes in the morphology and structure are investigated.

CRYSTAL GROWTH

Crystals of KDP and doped KDP were grown by solution growth employing evaporation technique at room temperature (30°C). The saturated solution of KDP mixed with 1 mol % each of the various dopants were taken in beakers (borosil, 500ml) and left to crystallize. Care was taken to provide an atmospheric ambient devoid of gusts of air currents and irregular exhausts. After 10-15 days the spontaneously nucleated crystals were grown to optimal sizes ranging from 10 x 5 x 5 mm^3 to 40 x 20 x 20 mm^3. Various soluble dopants like Cobalt, Magnesium, Lithium and Nikel were added at 1 mol% by weight where the subsequent changes in the morphology were visibly observed. Certain dopants like Cobalt produced a faint pink colouration and Nikel produced light green colouration in the grown crystals.

SOLUBILITY STUDIES

The solubility (Figure 1) of KDP in the pure state and that of KDP with dopants were studied. Solubility of KDP in its undoped state was found to be 28 grams per 100ml of the solvent (double distilled water). The various dopants were taken in 1mol % by weight of KDP and their solubility were studied independently. By adding various dopants it was observed that the solvent was able to accommodate a marginally increased amount of solute for saturation at the same temperature.

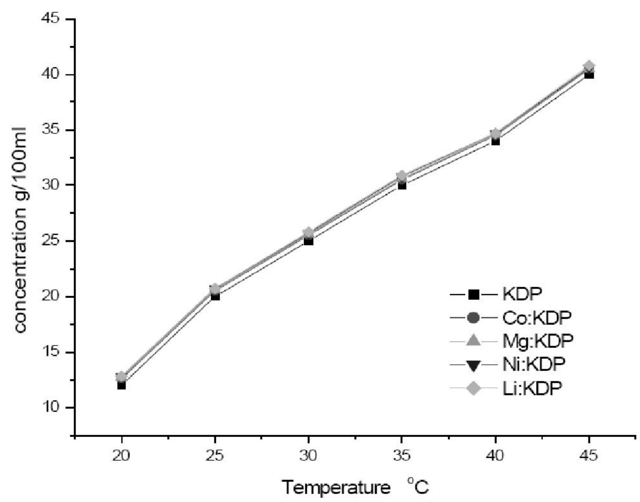

Figure 1 : Solubility studies on pure and doped KDP

METASTABLE ZONEWIDTH

The metastable zone width is the measure of stability of a solution in its supersaturated region where the largest width implies the substance having higher stability. 100 ml of the saturated solution was kept in the cryostat and the temperature reduced at 5°C per hour while the solution was stirred continuously. The temperature of formation of the first speck was found which corresponds to the width of the metastable zone. The metastable zone width of KDP was found to be the maximum in the lower temperature gradients than the higher gradients (Figure 2). Induction period i.e., the formation of the first speck of nuclei of pure KDP and with different dopants were studied (Figure 3). It was found that the induction period corresponding to concentration 1.1 was 300 sec and 1.5 was 62 sec respectively. When KDP was doped with Magnesium the formation of the initial nuclei was the fastest where Cobalt doping was observed to be the slowest.

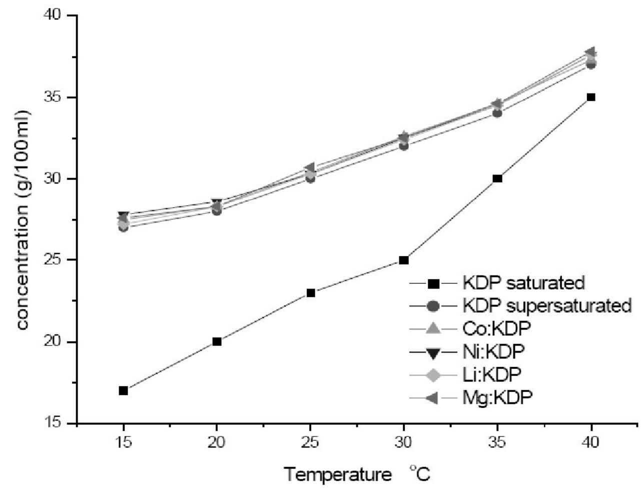

Figure 2 : Metastable zonewidth of pure and doped KDP

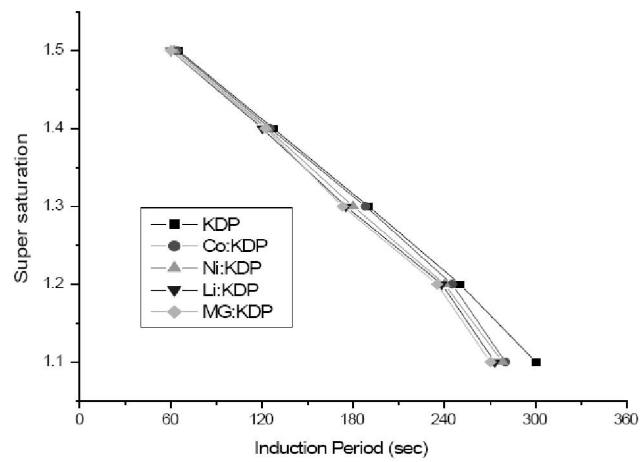

Figure 3 : Induction period of pure and doped KDP

X-RAY DIFFRACTION

XRD studies were carried out with the grown crystals in powdered form. The powder samples were loaded into a Rigaku X-Ray diffraction apparatus using CuKα radiation having $\lambda = 1.5405$ and analysed. Results were compared with the JCPDS database file number 35-0807 where the prominent peaks of the reported values coincided with the investigated patterns. The powder XRD pattern of KDP (Figure 4) as well as doped KDP (Figures 4a,4b,4c,4d,4e) had three prominent peaks at (200), (112), (321) respectively. The cell parameters were: a = 7.453 Å, c = 6.974 Å respectively.

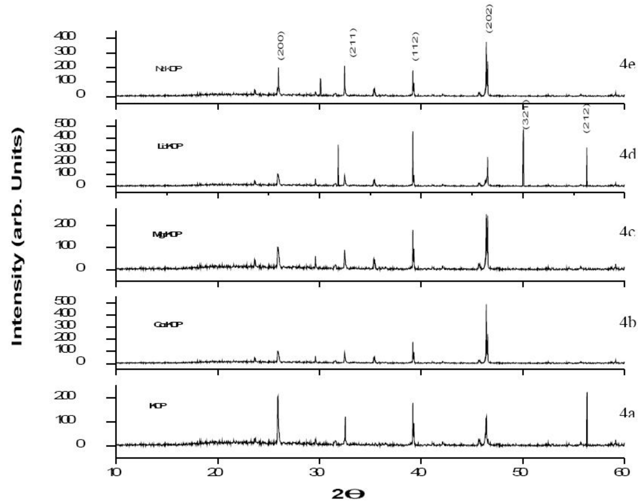

Figure 4 : Powder XRD patterns of pure and doped KDP crystal

FTIR ANALYSIS

FTIR spectra of the KDP (Figure 5a) and doped KDP were done on a Perkin-Elmer 781 spectrophotometer in the regions 400-4000cm^{-1} using a KBr pellet. Many useful observations[5] were observed in the group frequency regions (4000-1300cm^{-1}) and the fingerprint region (1300-650cm^{-1}). The intermediate frequency range, 2500–1540 cm^{-1} (*unsaturated* region) contains triple bond frequencies which appear from 2500 to 2000 cm^{-1} and double bond frequencies from 2000 to 1540 cm^{-1}. In the region between 1300 and 650 cm^{-1} there are single bond stretching frequencies and bending vibrations (skeletal frequencies) of polyatomic systems involving motions of bonds linking a substituent group to the molecule. Some of the most useful applications of infrared spectroscopy are in the area of coordination and organometallic chemistry which describes the change in the symmetry of a ligand upon coordination. For example, when small molecules (e.g. N2, O2 and H2) are linked to transition metal ions a symmetry change occurs which has a strong influence on the infrared spectra. These metal–ligand vibrations appear in the low frequency region (600–100 cm^{-1}) and provide direct information about the structure of the coordination sphere and the nature of the metal–ligand bond. Metal–ligand vibrations are also metal sensitive and are shifted by changing the metal or its oxidation state which is applicable only to isostructural metal complexes.

Thus the lower regions 667–100 cm^{-1} contain the bending vibrations of carbon, nitrogen, oxygen and fluorine with atoms heavier than mass 19. The observed frequencies for the diatomic molecule O_2 was at 1661cm^{-1}. Orthophosphate ion, PO_4^{3-} having T_d point group symmetry, showed vibration modes at 478 cm^{-1} in all the samples of undoped and doped KDP irrespective of the dopants included. Cobalt doping (figure 5b) on KDP gave rise to a metal-ligand vibration peak at 535 cm^{-1} and a wide oxygen double bond stretching at 1720 cm $^{-1}$. Dopants like Mg (Figure 5c) had absorption peaks due to vibration at 762 cm^{-1}, Ni^{3+} at 487cm^{-1} and strong absorption bands for lattice water (antisymmetric and symmetric OH strechings) at 3452 cm^{-1} were also detected. It was observed in Ni^{3+} doped KDP (Figure 5d) an additional absorbance peak was detected at 3246 cm^{-1} which implies that the inclusion of Nikel reduced the transparency of the doped crystal at that region. Lithium doping gave rise to a wide vibration peak (Figure 5e) observed at 472 cm^{-1}, and OH bond interaction at 2857 cm^{-1}. The absorption band was much more prominent in the Nikel Magnesium bimetallic crystal (Figure 5f) which had an increased absorbance at 3231 cm^{-1}. The rest of the dopants were not seen to appreciably modify the FTIR spectrum.

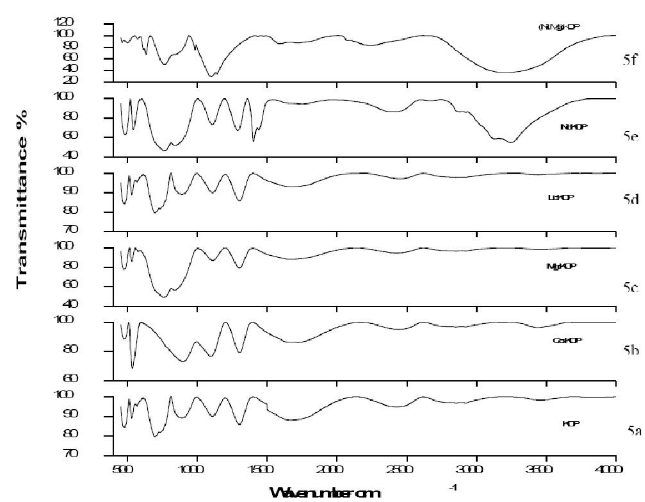

Figure 5 : FTIR spectrum of KDP and doped KDP crystals

HIGH RESOLUTION XRD INVESTIGATIONS

The high-resolution diffraction curves recorded for specific diffracting planes which are mentioned in the curved brackets with the multicrystal X-ray diffractometer[6] in symmetrical Bragg geometry. A well-collimated and monochromated MoKα_1 beam obtained from a set of three plane (111) Si monochromator crystals set in dispersive (+,-,-) configuration has been used as the exploring X-ray beam. The specimen crystal is aligned in the (+,-,-,+) configuration. Due to dispersive configuration, though the lattice constant of the monochromator crystal(s) and the specimen are different, the unwanted dispersion broadening in the diffraction curve of the specimen crystal is insignificant.

Pure KDP crystal (Figure 6) had a single diffraction peak FWHM at 11”. Wheras Nikel doped KDP crystal (Figure 7) had the diffraction peak at 10”, which indicates that the crystal with Nikel dopant seems to have increased the order of crystallinity in KDP. Except the diffraction curve of Co doped KDP (Figure 8) all the curves are having single peaks. This diffraction curve shows that though the quality of this crystal is very good, the specimen contains one *very low* angle boundary. The solid line in the figure is obtained by the convolution of two peaks shown with dotted line. The solid line is well fitted with the experimental points represented by the filled circles. This indicates that the specimen contains an additional peak, which is 12 arc sec away from the main peak. This peak corresponds to a *very low* angle boundary with tilt angle (angle between the two crystal regions on both sides of the boundary) of 12 arc sec. The half width of the main peak and the low angle boundary are respectively 9 and 34 arc sec, which shows that the crystalline quality of the specimen is reasonably good.

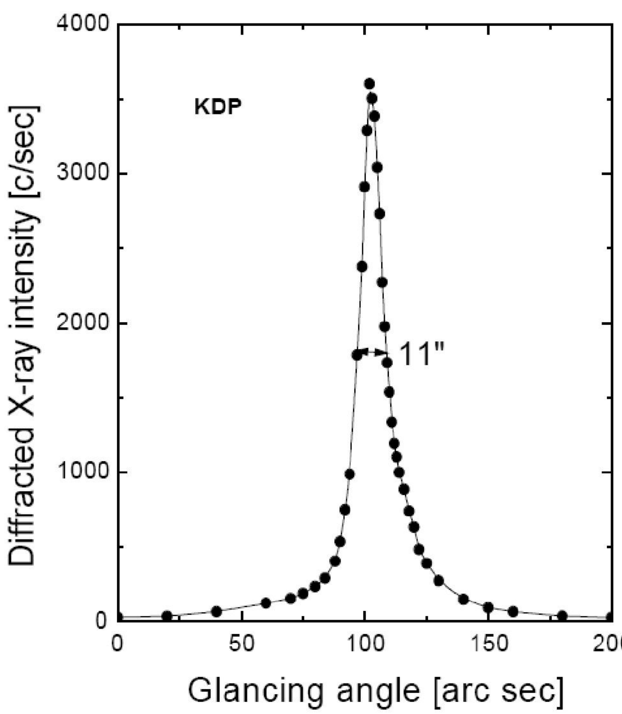

Figure 6 : High resolution XRD of pure KDP

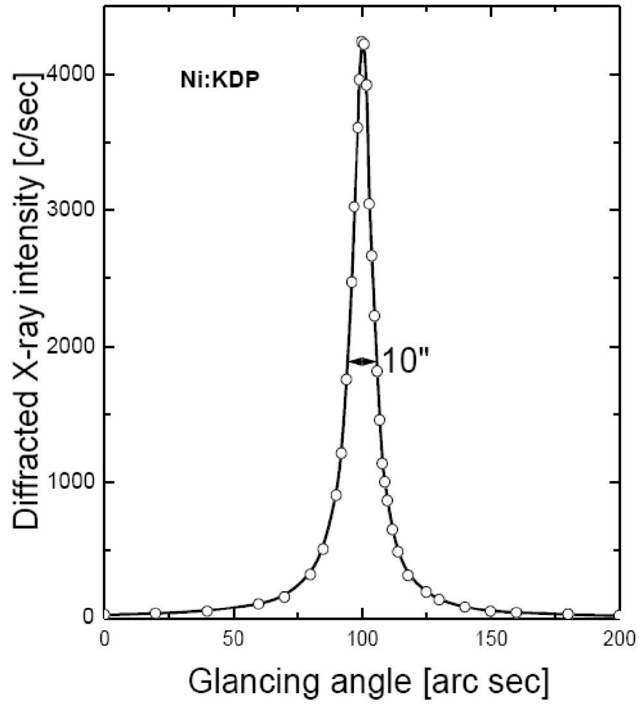

Figure 7 : High resolution XRD of nikel doped KDP

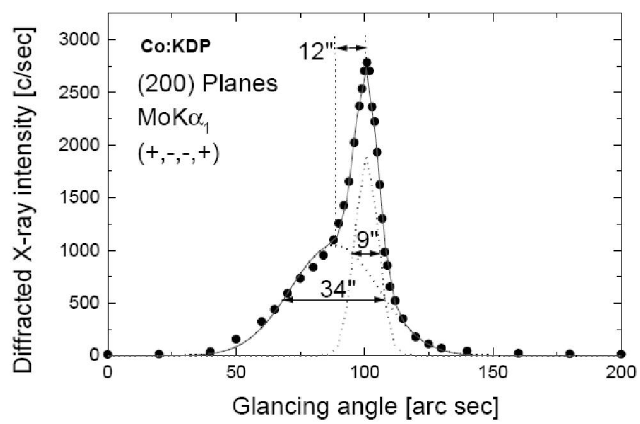

Figure 8 : High resolution XRD of cobalt doped KDP

CONCLUSION

The crystals grown doped with impurities in the form of dopants were found to have faster nucleation rates as investigated and decreased induction period where the crystallinity was also found to improve (as reported by HRXRD).

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