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Crystal Growth of Novel Bimetallic Nickel, Magnesium (Ni^{3+} , Mg^{2+}) Potassium Di Hydrogen Phosphate by Solution Growth and their Characterizations

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Abstract: Potassium Di-hydrogen Phosphate (KDP), crystal is a good nonlinear optic material having Second Harmonic Generation property (SHG). These KDP crystal is grown with bimetallic dopants Nickel-Magnesium (Ni^{3+} , Mg^{2+}) to form Nickel-Magnesium Di-hydrogen Phosphate (NMKDP). The grown crystals were analysed for structural and optical characteristics and compared with pure KDP. FTIR analysis explains the inclusion of the metallic impurities which extends the transmission region visibly. High resolution XRD confirms the order of crystallinity of the material which is found to be superior in the pure form than the bimetallic form thereby conforming the inclusion of the bimetals. The conversion efficiency and verification of SHG generation of the grown crystals were also confirmed by Kurtz method.

Key words: Crystal growth, ADP, nonlinear materials, second harmonic generator, HXRD, properties

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 solution grown by slow evaporation technique at room temperature. Many studies on the growth kinetics of KDP with different impurities were reported earlier^[1-3], and the changes of the crystal morphology and supersaturation^[4] were also discussed. In this study the effects in adding bimetallic dopants Ni^{3+} , Mg^{2+} with KDP and the changes in the morphology and structure were investigated using many characterization techniques.

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 pure KDP and bimetallic KDP were taken and left to crystallize. Care was taken to provide an atmospheric ambient devoid of irregular air currents and exhausts. After 10 to 15 days the spontaneously nucleated crystals were grown to optimal sizes ranging from 10×5×5 mm³ to 40×20×20 mm³.

Crystals of pure and bimetallic Ni^{3+} and Mg^{2+} KDP were grown by solution growth technique Solubility^[4] studies of pure KDP and KDP with Nickel and Magnesium were studied. Solubility of KDP in its undoped state was

found to be 28 g per 100 mL of the solvent (double distilled water). By adding Nickel and Magnesium (Ni^{3+} , Mg^{2+}) it was observed that the solubility decreased marginally which is attributed to the impurities that were added^[5].

The stability of the solution in its supersaturated region is measured as metastable zone width where the largest width explains the substance having higher growth stability. Hundred milliliter of the saturated solution was kept in the cryostat and the temperature reduced at 5°C h⁻¹ while the solution was stirred continuously. The temperature of conception of the first speck was found. The metastable zone width of KDP was found to be the maximum in the lower temperature gradients than the higher gradients. With the addition of the bimetallic impurities (Ni^{3+} , Mg^{2+}) it was further noted that the metastable zone altered marginally due to the presence of dopants. It was devoid of spontaneous nucleation which explains that the solution was stable until complete crystal growth.

CHARACTERIZATION

Powder X-ray diffraction studies were carried out on the grown crystals. The powder samples were taken in a Rigaku X-Ray diffraction apparatus which used a CuK α radiations having $\lambda = 1.5405$ nm and analysed for available maxima. 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 (Fig. 1) as well as

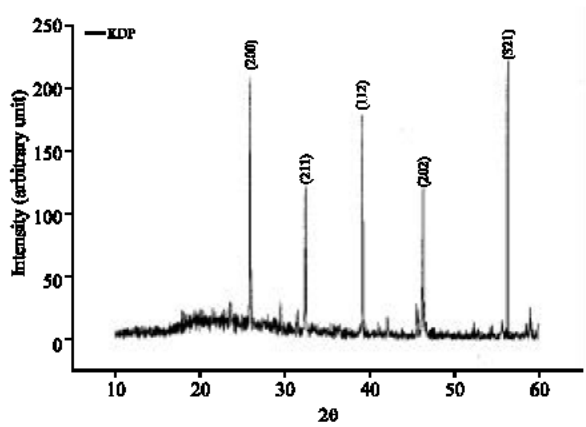


Fig. 1: Powder XRD of pure KDP crystal

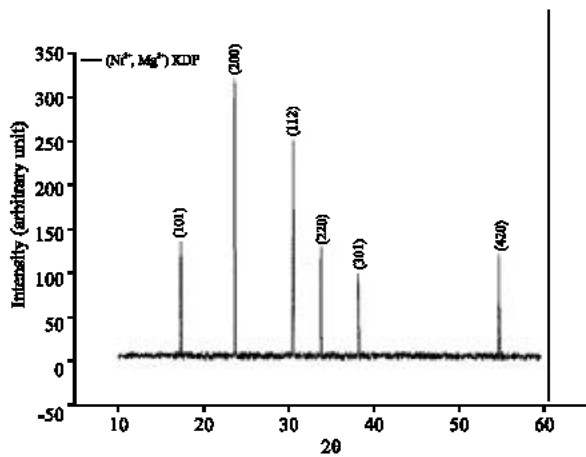


Fig. 2: Powder XRD of (Ni³⁺-Mg²⁺) KDP

bimetallic Nickel-Magnesium (Ni³⁺, Mg²⁺) KDP (Fig. 2) had three prominent peaks at 200, 112 and 321, respectively. The cell parameters were: a = b = 7.453 Å, c = 6.974 Å, respectively. The volume of the unit cell was calculated as 387.386 Å³.

FTIR INVESTIGATIONS

FTIR spectra of the KDP (Fig. 3) and bimetallic (Ni³⁺, Mg²⁺) KDP (Fig. 4) were done on a Perkin-Elmer 781 spectrophotometer in the regions 400 to 4000 cm⁻¹ using a KBr pellet. Many useful observations^[6] were observed. 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. 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

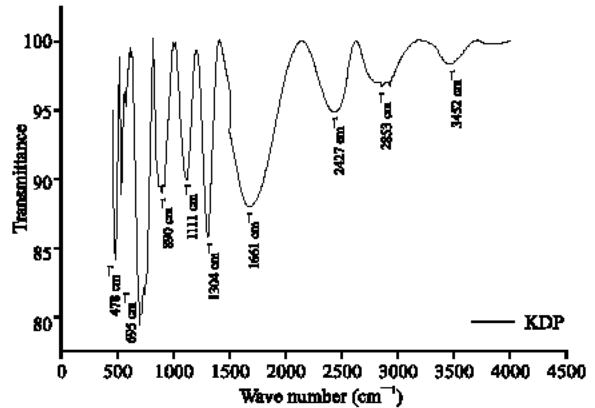


Fig. 3: FTIR spectrum of pure KDP crystal

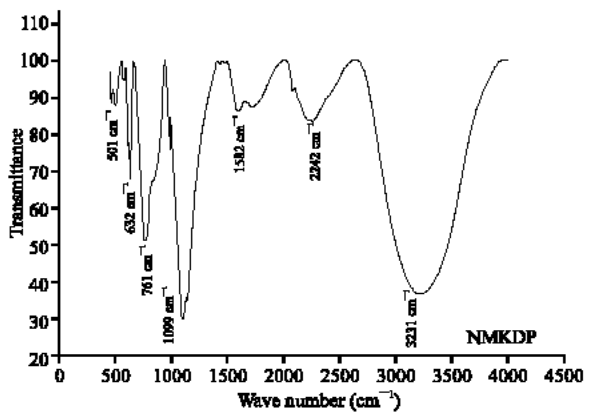


Fig. 4: FTIR spectrum of (Ni³⁺-Mg²⁺) KDP crystal

metal-ligand vibrations appear in the low frequency region (600 to 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.

Orthophosphate ion, PO₄³⁻ 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. The absorption band was much more prominent in the Nickel Magnesium bimetallic crystal (Fig. 4) which had an increased absorbance at 3231 cm⁻¹. The prominence of the absorption was also seen due to expansion of the absorption band. This was due to the influx of bimetallic dopants in the crystal lattice.

MICROHARDNESS MEASUREMENTS

The strength of the grown crystals were verified by microhardness test samples of pure KDP and bimetallic

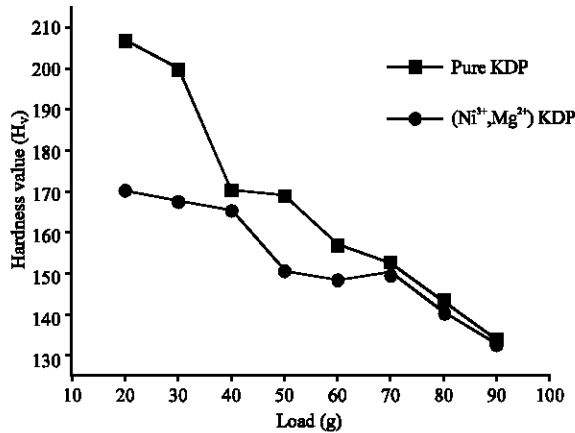


Fig. 5: Microhardness curve of pure and bimetallic KDP

Nikel-Magnesium KDP were indented using a Lietz-Wetzler P1191 microhardness tester fitted with a Vickers pyramidal indenter having an optical angle of 136° between the opposite pyramids of the indenter. Observations of the various indentation tests were done using the Metallux-II Metallurgical Microscope.

An indentation time of 10 sec were applied uniformly for loads 20 to 90 g. The hardness value of the cut and polished Lithium Niobate crystal samples (Fig. 5) were found to decrease slowly with the applied loads until 40 g. Further application of higher loads showed that the hardness values sharply decreased and developed mild cracks on the pyramidal indentation edges. Beyond 90 g the samples developed large prominent cracks due to the attainment of the threshold mechanical stress. The hardness values were calculated using the formula:

$$H_v = \frac{1.8544 \times P}{D^2} \text{ kg mm}^{-2}$$

Where, H_v is the hardness number, P is the indenter load in g and D is the diagonal length of the pyramidal impression in mm. The micro hardness value was taken as the average of the several impressions made diagonally.

In the present study, the hardness of the pure KDP was found to be higher than that of bimetallic Nickel Magnesium KDP crystal. This can be attributed to the incorporation of the Nickel and Magnesium (Ni^{3+} , Mg^{2+}) ions into the crystal lattice forming defects that generate stresses on the crystal surface.

UV-VIS-NIR SPECTRAL ANALYSIS

The UV-Vis-NIR spectral transmittance was studied using a Shimadzu UV-1061 UV-Vis spectrophotometer

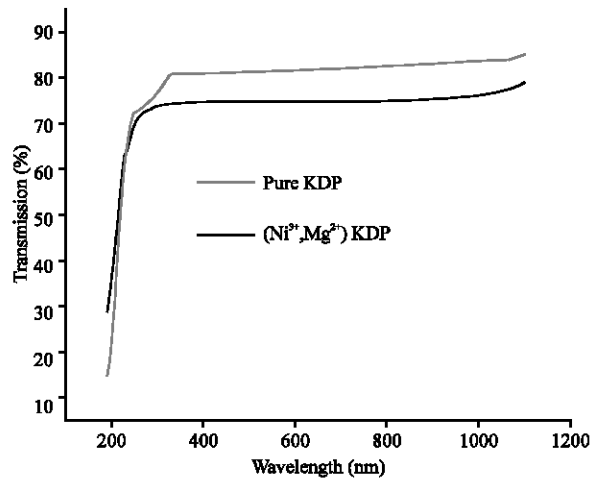


Fig. 6: UV-Vis-NIR spectra of KDP and bimetallic KDP

with a single crystal of 4 mm thickness in the range of 200 to 1200 nm. The crystal has sufficient transmission in the entire visible and IR region. The lower cut off wavelength is around 300 nm; the transmission percentage of Nickel and Magnesium (Ni^{3+} , Mg^{2+}) added KDP crystal is around 83%, as compared to pure KDP, which was 75% (Fig. 6). It was found that the bimetallic (Ni^{3+} , Mg^{2+}) KDP crystals had higher transparency ranges than the pure undoped KDP crystals.

HIGH RESOLUTION XRD ANALYSIS

The high-resolution diffraction curves recorded for specific diffracting planes which are mentioned in the curved brackets with the multicrystal X-ray diffractometer⁸ in symmetrical Bragg geometry. A well-collimated and monochromated $\text{MoK } \alpha_1$ 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 nonsignificant.

Both the curves were observed to have single peaks. This diffraction curve (Fig. 7) shows that the quality of this crystal is very good, since the specimen contains one very low angle boundary. The FWHM of the KDP peaks were 13" and the Nickel-Magnesium (Ni^{3+} , Mg^{2+}) KDP crystal (Fig. 8) was 11". This implies that the pure crystal of KDP had a lower order of crystallinity than the Nickel and Magnesium bimetallic (Ni^{3+} , Mg^{2+}) KDP crystal where dopants increased the quality of the crystal grown.

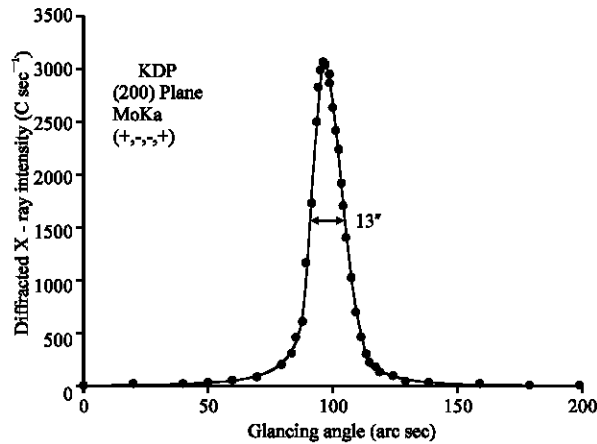


Fig. 7: HRXRD of pure KDP crystal

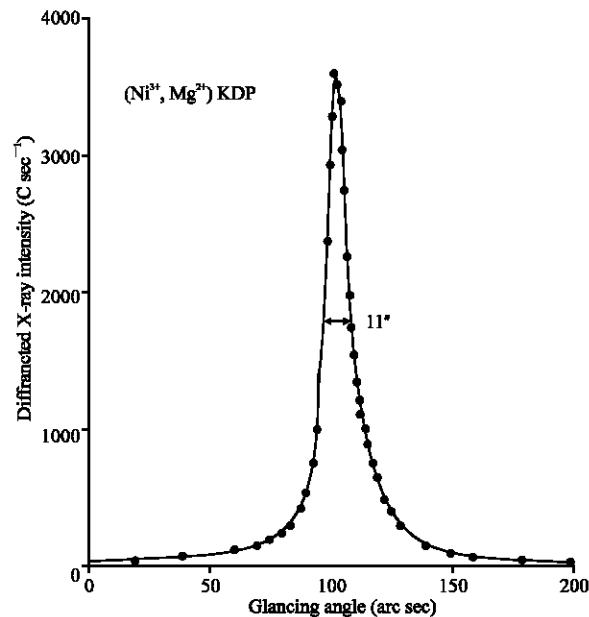


Fig. 8: HRXRD of $(\text{Ni}^{3+}, \text{Mg}^{2+})$ KDP crystal

CONVERSION EFFICIENCY

The conversion efficiency of the crystal was checked using the powder SHG technique developed by Kurtz and Perry^[8]. The crystal was ground into powder and densely packed in between two glass slides. An Nd:YAG laser beam of wavelength 1064 nm was made to fall normally on the sample cell. The emission of green light confirms the second harmonic generation on KDP as well as Nickel Magnesium KDP crystals.

CONCLUSIONS

Bimetallic $(\text{Ni}^{3+}, \text{Mg}^{2+})$ KDP crystals were grown by solution growth technique at room temperature. The

change in properties were analysed in comparison with pure KDP crystal. It was found that SHG quality bimetallic crystals of KDP showed higher crystalline behaviour than the undoped KDP crystals.

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