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Crystal growth of novel bimetallic nikel, magnesium (Ni^{3+}, Mg^{2+}) potassium di hydrogen phosphate (NMKDP) 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 Nikel-Magnesium (Ni^{3+}, Mg^{2+}) to form Nikel-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.

KEYWORDS

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 characterize ation 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 x 5 x 5 mm^3 to 40 x 20 x 20 mm^3.

Crystals of pure and bimetallic Ni^{3+}, Mg^{2+} KDP were grown by solution growth technique Solubility studies of pure KDP and KDP with Nikel 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 Nikel 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. 100 ml of the saturated solution was kept in the cryostat and the temperature reduced at 5°C hr^{-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.

STRUCTURAL 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 CuKa radiation having l = 1.5405 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 (Figure 1) as well as bimetallic Nikel-Magnesium (Ni^{3+},Mg^{2+}) KDP (Figure 2) had three prominent peaks at (200), (112), (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 $Å^3$.

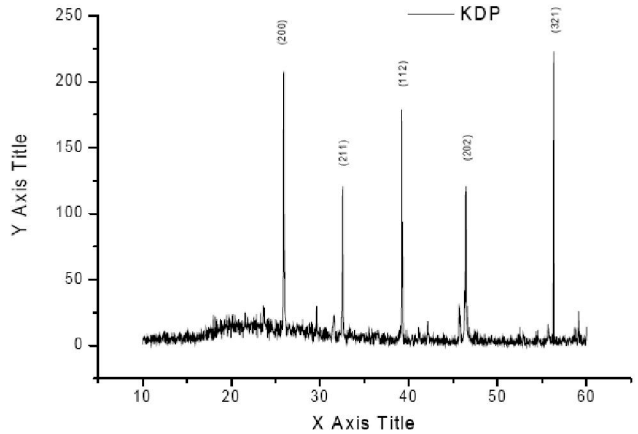

Figure 1 : Powder XRD of pure KDP crystal

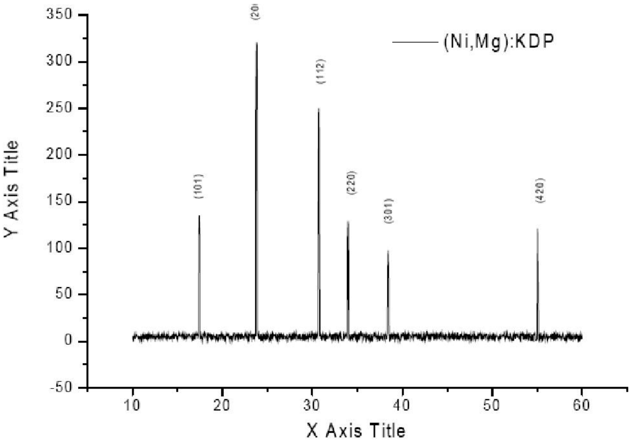

Figure 2 : Powder XRD of (Ni-Mg) KDP

FTIR INVESTIGATIONS

FTIR spectra of the KDP (Figure 3) and bimetallic (Ni, Mg) KDP (Figure 4) were done on a Perkin-Elmer 781 spectrophotometer in the regions 400 to 4000cm^{-1} using a KBr pellet. Many useful observations[6] were observed. In the region between 1300 and 650cm^{-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. N_2, O_2 and H_2) 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 to 100cm^{-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, 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. The absorption band was much more prominent in the Nikel Magnesium bimetallic crystal (Figure 4) which had an increased absorbance at 3231cm^{-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.

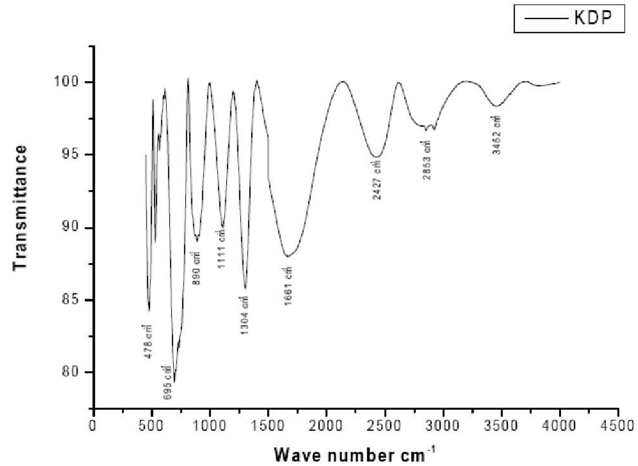

Figure 3 : FTIR spectrum of pure KDP crystal

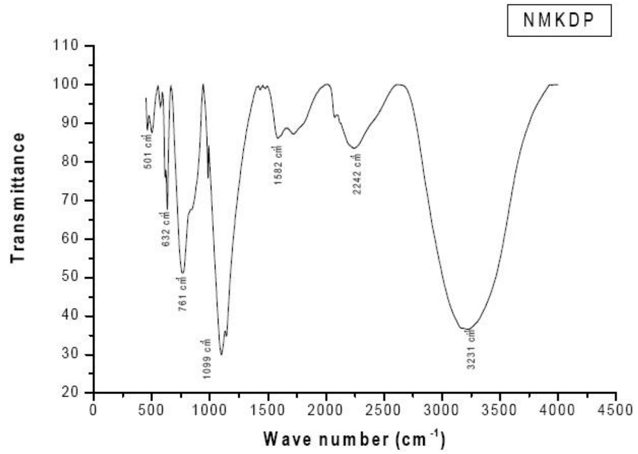

Figure 4 : FTIR spectrum of (Ni-Mg)KDP crystal

MICROHARDNESS MEASUREMENTS

The strength of the grown crystals were verified by Microhardness tests Samples of pure KDP and bimetallic Nikel-Magnesium KDP were indented using a Lietz-Wetzler P1191 Microhardness tester fitted with a Vikers pyramidal indenter having an optical angle of 136° between the opposite pyramids of the indentor. Observations of the various indentation tests were done using the Metallux-II Metallurgical Microscope.

An indentation time of 10 seconds were applied uniformly for loads 20 to 90g. The hardness value of the cut and polished Lithium Niobate crystal samples (Figure 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

$$H_v = \frac{1.8544 \times P\,kgmm^{-2}}{D^2}$$

Where H_v is the hardness number, P is the indenter load in gm 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 Nikel Magnesium KDP crystal. This can be attributed to the incorporation of the Nikel and Magnesium (Ni^{3+}, Mg^{2+}) ions into the crystal lattice forming defects that generate stresses on the crystal surface.

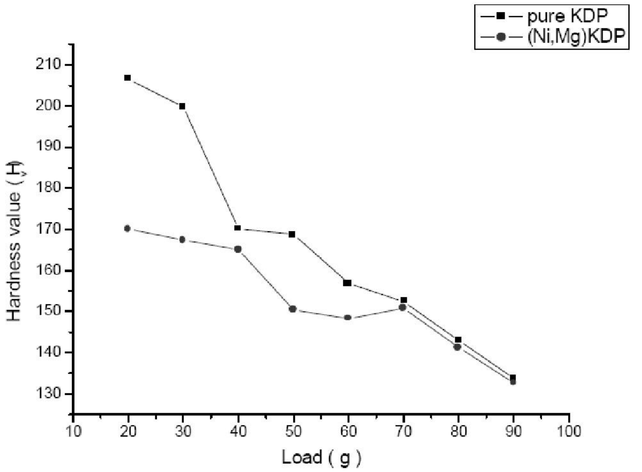

Figure 5 : Microhardness curve of pure and bimetallic KDP

UV-VIS-NIR SPECTRAL ANALYSIS

The UV-Vis-NIR spectral transmittance was studied using a Shimadzu UV-1061 UV-Vis spectrophotometer with a single crystal of 4 mm thickness in the range of 200 to1200 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 Nikel and Magnesium (Ni^{3+}, Mg^{2+}) added KDP crystal is around 83%, as compared to pure KDP, which was 75% (Figure 6). It was found that the bimetallic (Ni-Mg) KDP crystals had higher transparency ranges than the pure undoped KDP crystals.

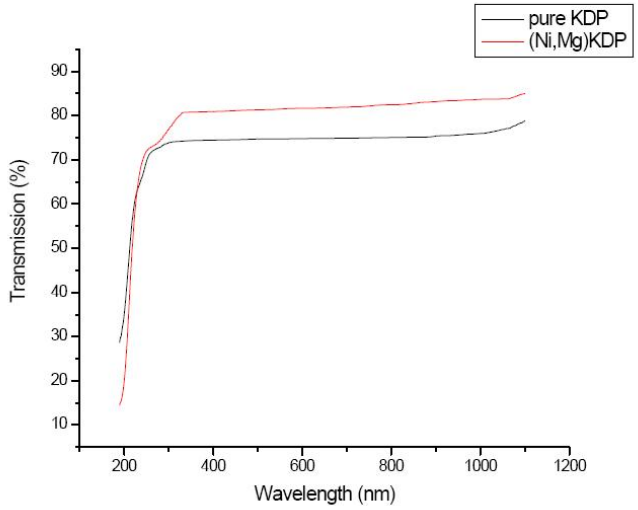

Figure 6 : UV-Vis-NIR spectra of KDP and bimetallic KDP

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 diffractometer[7] in symmetrical Bragg geometry. A well-collimated and monochromated MoKá$_1$ 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.

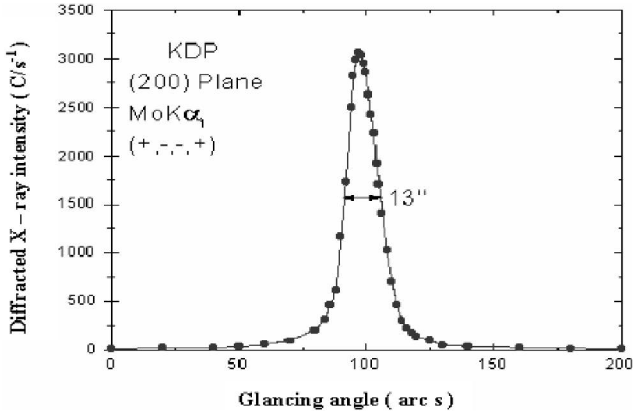

Figure 7 : HRXRD of pure KDP crystal

Both the curves were observed to have single peaks. This diffraction curve (Figure 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 Nikel-Magnesium (Ni^{3+}, Mg^{2+})KDP crystal (Figure 8) was 11". This implies that the pure crystal of KDP had a lower order of crystallinity than the Nikel and Magnesium bimetallic (Ni^{3+}, Mg^{2+})KDP crystal where dopants increased the quality of the crystal grown.

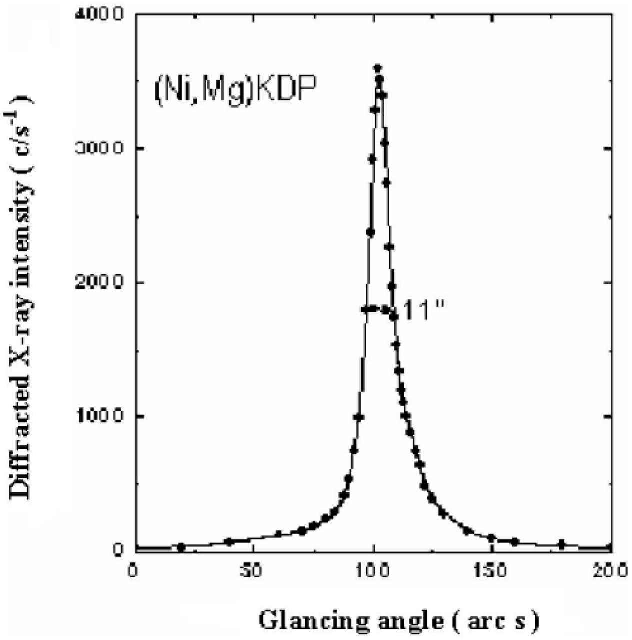

Figure 8 : HRXRD of (Ni, Mg) KDP crystal

SHG 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 Nikel Magnesium KDP crystals.

CONCLUSIONS

Bimetallic (Ni^{3+}, 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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REFERENCES

[1] You-Jun Fu, Zhang-Shou Gao, Jia-Min Liu, Yi-Ping Li, Hong Zeng, Min-Hua Jiang; The effect of anionic impurities on the growth habit and optical properties of KDP, J.Crystal Growth, **198/199**, 682-686 **(1999)**.

[2] V.A.Kuznetsov, T.M.Okhrimenko, Miroslawa Rak; Growth promoting effect of organic impurities on growth kinetics of KAP and KDP crystals, J.Crystal Growth, **193**, 164-173 **(1998)**.

[3] H.V.Alexandru, C.Berbecaru, Al.Grancea, V.Iov; KDP prismatic faces, Kinetics and mechanism of their growth from solutions, Journal of Crystal Growth, **166**, 162-166 **(1996)**.

[4] Chernov A.A; Modern crystallography-III - Crystal growth, Springer Verlag, Solid State Series, New York, **36**, 100-251 **(1984)**.

[5] You-Jun Fu, Zhang-Shou Gao, Xun Sun, Shen-Lai Wang, Yi-Ping Li, Hong Zeng, Jian-Ping Luo, Ai-Dong Duan, Ji-Yang Wang; Effects of anions in the rapid growth and growth habit of KDP crystals, Progress in crystal growth and characterization of materials, 211-220 **(2000)**.

[6] C.Petinari (Ed); Vibrational rotational and raman spectroscopies, Academic Press, 1021-1032 **(1999)**.

[7] K.Lal, G.Bhagavannarayana; A high-resolution diffuse x-rayscattering study of defects in dislocation-free silicon crystals grown by the float-zone method and comparison with Czochralski-grown crystals, **22**, 209-215 **(1989)**.

[8] S.K.Kurtz, T.T.Perry; Characterisation of NLO crystals by novel SHG technique, J.Applied Phys., **39**, 3798 **(1968)**.