Journal of Advanced Scientific Research

Available online through http://www.sciensage.info

ISSN
0976-9595
Research Article

GROWTH AND STUDIES OF PURE AND AMMONIUM OXALATE MONOHYDRATE DOPED POTASSIUM DIHYDROGEN PHOSPHATE SINGLE CRYSTALS

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ABSTRACT

Optically good quality single crystals of pure and ammonium oxalate monohydrate doped Potassium dihydrogen phosphate (KDP) were grown from aqueous solution employing slow evaporation technique. The crystallinity and cell parameters of the grown pure and ammonium oxalate monohydrate doped KDP crystals were studied by powder X-ray diffraction analysis. The mechanical strength of the grown crystals was analyzed by Vickers microhardness test. The functional groups present in the grown crystals were identified by Fourier transform infrared studies. The various investigations indicate changes in structural, mechanical and spectroscopic properties of the KDP crystal due to the incorporation of ammonium oxalate monohydrate into the KDP crystal lattice.

Keywords: Crystal Growth, NLO Materials, Doping, Characterization

1. INTRODUCTION

Potassium dihydrogen phosphate (KDP) crystal is widely used and well studied nonlinear optical (NLO) material. The unique combination of properties like wide range of transparency, relatively high magnitude of the quadratic nonlinear susceptibility, electro-optical and piezo-optical effect, as well as the possibility of growing wide aperture crystals make KDP single crystals to have a special attention of the researchers. Currently KDP single crystals are used in industrial laser facilities as a frequency multiplier, parametric amplifier and electro-optical shutters [1-7]. The rapid growth of good quality KDP crystals, the newly developed techniques, and the effect of organic and inorganic impurities and metal ions on the properties of KDP crystals have been reported by several researchers [8-16]. In the present work, single crystals of pure and ammonium oxalate monohydrate doped KDP have been grown and characterized by powder XRD, microhardness, and FTIR studies to study the effect of ammonium oxalate monohydrate on KDP crystal.

2. EXPERIMENTAL

2.1. Crystal growth

Single crystals of pure and 1 mol% ammonium oxalate monohydrate doped KDP were grown by solution growth employing slow evaporation technique at room temperature. Using AR grade KDP salt and deionised water, the saturated solution of KDP was prepared in accordance with the solubility data. The solution was thoroughly stirred for homogenization and then filtered into a borosil beaker using Whatmann filter paper. The pH of the solution was noted as 3.8. The beaker containing the saturated solution (200 ml) was closed with perforated cover and kept in a dust free atmosphere to allow slow evaporation of the solvent. Transparent, good quality KDP crystals were harvested within 20-30 days. For the growth of ammonium oxalate doped KDP crystals, KDP salt was added to ammonium oxalate monohydrate in the molar ratio 1:0.01 to form a saturated solution. The solution was thoroughly stirred for homogenization and then filtered into a borosil beaker using Whatmann filter paper. The pH of the solution was noted as 3.8. The beaker containing the saturated solution (200ml) was closed with perforated cover and kept in a dust free atmosphere to allow slow evaporation of the solvent. Single colorless, transparent crystals of ammonium oxalate monohydrate doped KDP were harvested within 20-30 days. The photograph of pure and 1 mol% ammonium oxalate monohydrate doped KDP crystals are shown in figure1 (a) and figure 1(b) respectively.

Fig. 1(a) **Fig. 1(b)**

Photograph of pure and 1 mol% ammonium oxalate monohydrate doped KDP crystal

3. RESULTS AND DISCUSSION

3.1. Powder X-Ray Diffraction Studies

The powder X-ray diffraction studies have been carried out to confirm the crystallinity and to determine the lattice parameters of the grown crystals. Powder X-ray diffraction (PXRD) analysis was carried out using XPERT-PRO diffractometer with CuKα radiation of wavelength 1.5406Å .The 2θ range was analyzed from 10^0 to 80^0 and the prominent peaks have been indexed. PXRD studies for pure and 1 mol% ammonium oxalate monohydrate doped KDP grown crystal reveal the appearance of sharp and strong peaks which confirms the good crystallinity of the grown crystals, there are no other phases emerging besides the tetragonal system. It is found that the reflection lines of the doped KDP crystal correlate well with those observed in the individual parent compound with a slight shift in Bragg angle. PXRD pattern for pure and with ammonium oxalate monohydrate doped KDP crystals are shown in fig. 2(a) & 2(b) respectively.

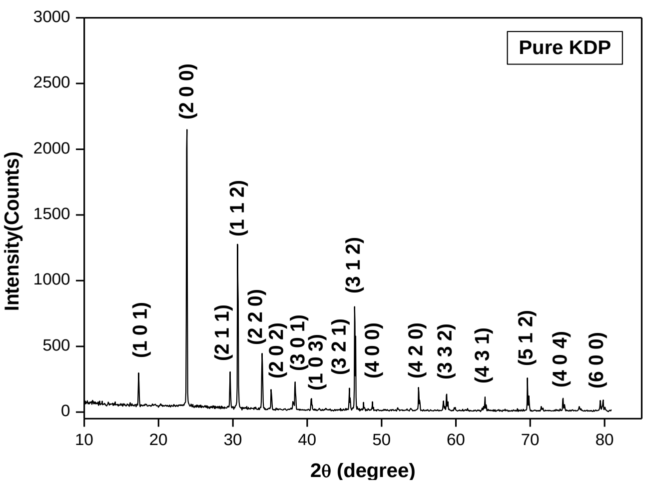

Fig 2(a): Powder XRD pattern of pure KDP crystal

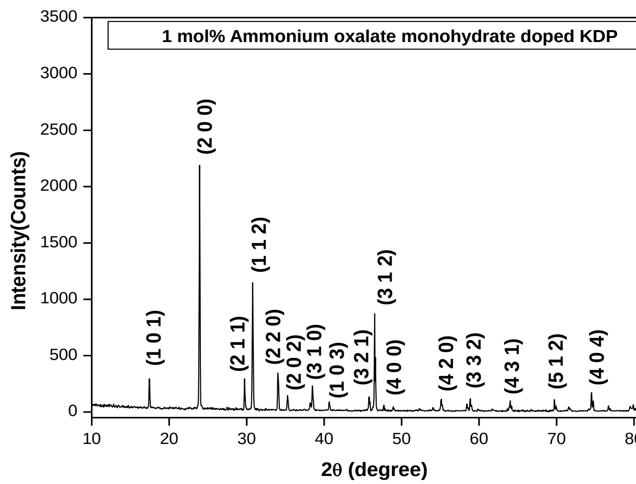

Fig 2(b): Powder XRD pattern of 1mol% ammonium oxalate monohydrate doped KDP crystal

The lattice parameters and cell volume are calculated using 'UNIT CELL' software package. The unit cell parameters of pure KDP are a=b= 7.4556 Å, c= 7.0015 Å, $\alpha=\beta=\gamma=90^0$ and it belongs to tetragonal system. The unit cell parameters of 1 mol% ammonium oxalate monohydrate doped KDP are a=b= 7.448 Å, c= 6.971 Å, $\alpha=\beta=\gamma=90^0$. There is a slightly variation found in the lattice parameter values, compared to pure KDP crystal. This change in the lattice parameters confirms the incorporation of ammonium oxalate monohydrate into the KDP crystal lattice. The comparison of unit cell parameters of the doped crystals with pure KDP suggests that both pure and doped KDP crystals crystallize in the body centered tetragonal structure with the space group $I\bar{4}2d$ and have tetramolecular unit cell. The compound retains almost single phase structure and exhibits very slight variations on doping. The results of the present work are in good agreement with the reported values [17, 18].

3.2. MICROHARDNESS MEASUREMENTS

Microhardness characterization is a measure of the resistance a material offers to local deformation. The micro-indentation test is a useful method for studying the nature of plastic flow and its influence on the deformation of the materials, higher hardness value of a crystal indicates that greater stress is required to create dislocation. To find surface hardness of the grown pure KDP crystal and KDP crystal doped with 1 mol% of ammonium oxalate monohydrate. Microhardness was measured for 25g, 50g and 100g load using Shimadzu HMV-2 microhardness tester. The transparent crystal free from cracks was selected for hardness measurement. The Vickers hardness number (H_v) calculated from the relation $Hv = 1.8544\ P/d^2\ kg/mm^2$ where P is the applied load in kg and d is the diagonal length of the indentation mark in mm.

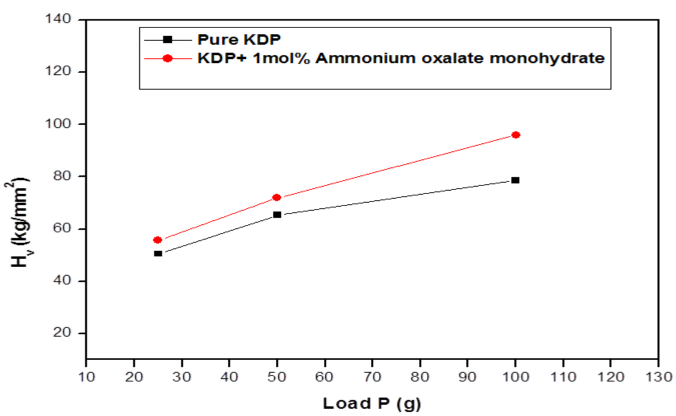

Fig 3: Variation of Vickers hardness number with load for pure and 1mol% ammonium oxalate monohydrate doped KDP crystals

Fig.3 shows the variation of Vickers hardness number with load for pure and ammonium oxalate monohydrate doped KDP crystals. From the results of microhardness studies, it is observed that hardness number Hv increases with load for all the grown pure and ammonium oxalate monohydrate doped KDP crystals. When the load increases, a few surface layers are penetrated initially and then inner surface layers are penetrated by the indenter with increase in the load. The 1 mol% of ammonium oxalate monohydrate doped KDP crystal has hardness number greater than pure KDP crystal [19].Thus the mechanical strength of the 1 mol% ammonium oxalate monohydrate doped KDP crystal is good compared to pure KDP crystal.

3.3. FTIR SPECTRAL ANALYSIS

The functional groups present in the grown crystals were ascertained using FTIR spectral analysis. The FTIR spectra for pure KDP, ammonium oxalate monohydrate doped KDP crystals were recorded in the frequency region of 400-4000 cm^{-1} using the Perkin Elmer Spectrometer. The FTIR spectrum is shown in figure 4(a) for pure KDP crystal. Figure 4(b), for ammonium oxalate monohydrate doped KDP crystals. Assignments were made on the frequencies and from the literature data [20-22].

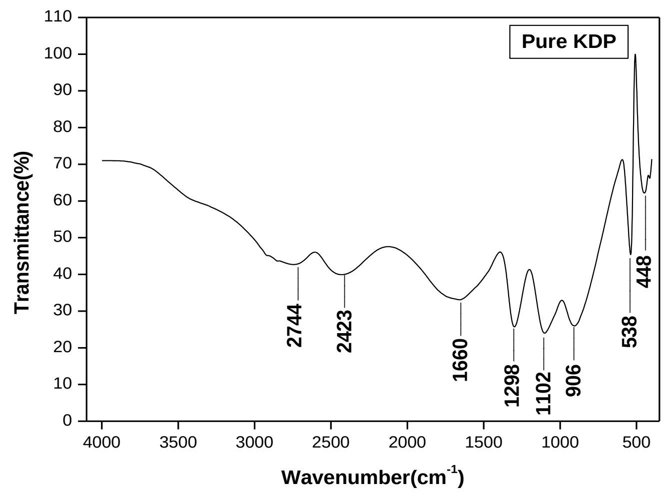

Fig 4(a): FTIR spectrum for pure KDP crystal

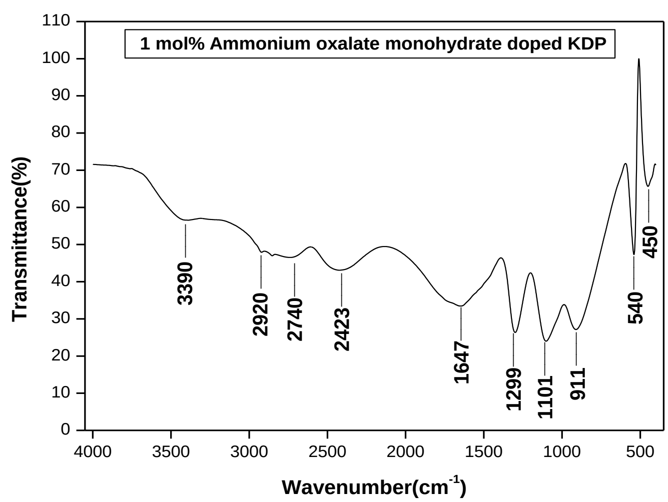

Fig 4(b): FTIR spectrum for 1 mol % ammonium oxalate monohydrate doped KDP crystal

Observed vibrational spectra of ammonium oxalate monohydrate doped KDP crystals are similar to the vibrational spectra of pure KDP crystal with very slight shifts in frequency. In the doped crystals, the same peaks have been observed with shift in the frequencies, some new absorption peaks are found to be present compared to that of pure KDP crystals. This shows the interaction and inclusion of the dopants into the KDP crystal lattice.

4. SUMMARY AND CONCLUSION

High quality stable and transparent pure and ammonium oxalate monohydrate doped KDP crystals can been grown from aqueous solution by slow evaporation technique at room temperature. The structural, mechanical, spectroscopic properties of pure KDP single crystals and KDP doped with 1mol % ammonium oxalate monohydrate have been studied. PXRD studies shows that the grown crystals are crystalline in nature and tetragonal in structure with slight changes in lattice parameters when KDP is doped with ammonium oxalate monohydrate. Micro hardness number increases with the applied load and the ammonium oxalate monohydrate doped KDP crystal have the hardness number greater than the pure KDP crystal. Thus the mechanical strength of ammonium oxalate monohydrate doped KDP crystal is better compared to pure KDP crystal. The presence of dopant ammonium oxalate monohydrate in the crystal was qualitatively investigated by the FTIR studies. The important functional groups associated with the grown crystals and the absorption bands have been identified and assigned. The shift in absorption bands and the presence of new bands in the FTIR spectrum confirms that the dopant ammonium oxalate monohydrate is incorporated into the KDP crystal lattice.

5. REFERENCES

1. Hussaini SS, Dhumane NR, Dongre VG, Ghughare P, Shirsat MD, et al. *J. Optoele. Adv. Mat.*, 2007; **1**:707.
2. Suresh Kumar B, Rajendra Babu K, et al. *Indian J. Pure Appl. Phys.*, 2008; **46**:123.
3. Parikh KD, Parekh BB, Dave DJ, Joshi MJ, et al. *Cryst. Res. Technol.*, 2010; **45(6)**:603.
4. Ferdousi Akhtar, Jiban Podder, et al. *Journal of Crystallization Process and Technology*, 2011; **3**:55.
5. Jagadish P, Rajesh NP, et al. *J. Optoele. Adv. Mat.*, 2011; **13**:962.
6. Muley GG. *Journal of Science and Technology*, 2012; **2(5)**:109.
7. Kanagatharal N, Anbalagan G, et al. *International Journal of Optics*, 2012; **2012**:6.
8. Hussaii SS, Dhumane NR, Rabbani G, Karmuse P, Dongre VG, Shirsat MD, et al. *Cryst. Res. Technol.*, 2007; **42** :1110.
9. Ananda Kumari R, Chandramani R, et al. *Bull. Mater. Sci.*, 2003; **26**:255.
10. Dhanaraj PV, Mahadevan CK, Bhagavannarayanan G, Ramasamy P, Rajesh NP, et al. *J. Cryst. Growth*, 2008; **310**:5341.
11. Dhanaraj PV, Rajesh NP, Mahadevan CK, Bhagavannarayana G, et al. *Physica B*, 2009; **404**:2503.
12. Kumeresan P, Moorthy Babu S, Anbarasan PM, et al. *J. Cryst. Growth*, 2008; **310**:1999.
13. Parikh KD, Dave DJ, Parekh BB, Joshi MM, et al. *Bull. Mater. Sci.*, 2007; **30**:105.
14. Shirsat MD, Hussaini SS, Dhumane NR, Dongre VG, et al. *Cryst. Res. Technol.*, 2008; **43**:756.
15. Balamurugan S, Ramasamy P, Yutthapong Inkong, Prapun Manyum, et al. *Mater. Chem. Phys.*, 2009; **113**:622.
16. Sureshkumar B, Rajendra Babu K, et al. *Indian J. Pure &Appl. Phys.*, 2008; **46**:123.
17. Prasanyaa T, Haris M, et al. *Arch. Phy. Res.*, 2011; **2(4)**:60.
18. Ambhore PS, Gambhire AB, Devade SK, Muley GG, et al. *Physical Science International Journal*, 2014; **4(10)**:1340.
19. Balamurugan S, Ramasamy P, et al. *Mater. Chem. Phys.*, 2008; **112**:1.
20. Muleya GG, Rodeb MN, Pawar BH, et al. *Acta Physica Polonica A.*, 2009; **116**:1033.
21. Mary Sheeja OV, Mahadevan CK, et al. *Int. Journal of Engineering Research and Applications*, 2014; **4**:55.
22. Delci Z, Shyamala D, Karuna S, Senthil A, Thayumanavan A, et al. *International Journal of Chem. Tech. Research.*, 2012; **4**:816.