GROWTH, STRUCTURAL AND OPTICAL STUDIES OF PURE AND KBR DOPED ADP CRYSTALS

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Abstract

Pure and KBr doped crystals of ADP were grown by slow evaporation technique from the supersaturated solution of ADP at room temperature. The tetragonal structure of the grown crystals was observed by powder X-ray diffraction analysis. FTIR spectra revealed the presence of functional groups present in the grown crystals. The UV-Vis spectral analysis shows high transparency in the entire visible region. The band gap value of the pure ADP crystal was found assuming indirect transition.

Key Words**:** *ADP, Powder XRD, FTIR, Band gap*

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1. INTRODUCTION

Ammonium dihydrogen phosphate, $NH_4H_2PO_4$ (abbreviated as ADP) is a well-known antiferroelectric crystal. A study on ADP crystals is very interesting in view of their dielectric, anti ferroelectric and optical properties. Most important applications of ADP crystals are that they are used as electro-optical modulator, harmonic generators, and parametric generator and as monochromators for X-ray fluorescence analysis [1]. ADP was belongs to scalenohedral (twelve faced) class of tetragonal crystal system [2, 3]. It is well known that, the crystal habit of ammonium dihydrogen phosphate can be modified by certain ions when they are incorporated into crystal lattice. In this study pure ADP and KBr doped ADP crystals were grown by solution growth using slow evaporation technique at room temperature. The grown crystals were subjected to Powder X-ray diffraction, FTIR and UV-Visible spectral studies. The characterization results are reported here.

2. EXPERIMENTAL

2.1 Crystal Growth

Single crystals of pure ADP and KBr doped ADP were grown from supersaturated solution of AR grade salt of ADP and Potassium bromide, respectively. The pure and doped crystals were grown separately by the supersaturated solution. For doped ADP crystal, 0.01 mol% of KBr was added to the super saturated solution of ADP. Both the solutions were stirred well up to get homogeneous solution using magnetic stirrer. The homogeneous solutions were filtered using filter paper. The filtered solutions were allowed to slow evaporation, placing in a dust free zone. Colourless crystals were grown within 15-30 days. Transparent good quality crystals were used for characterizations.

Fig -1: Photograph of pure ADP crystal

Fig -2: Photograph of KBr doped ADP crystal

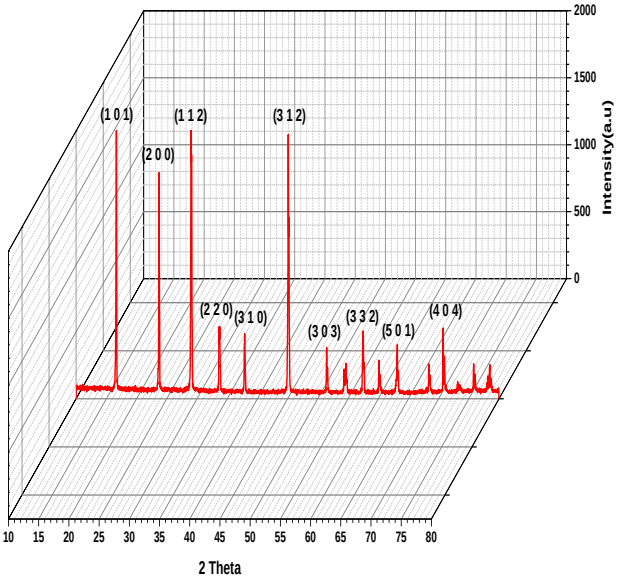

Fig -3: Powder X-ray diffraction pattern for pure ADP crystal

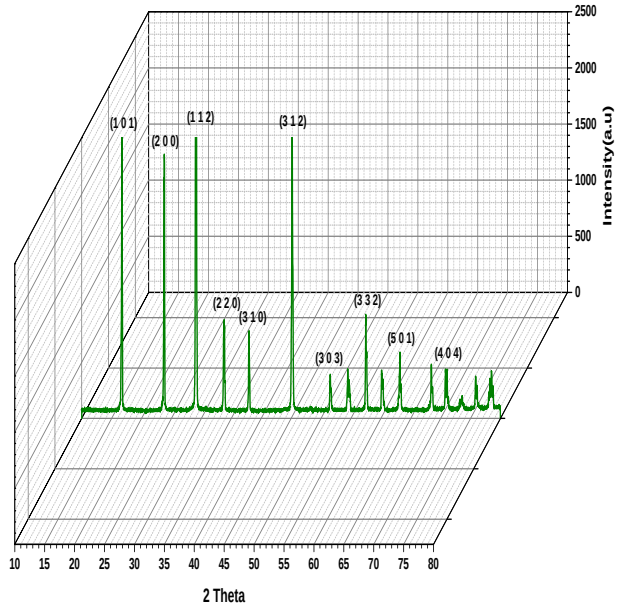

Fig -4: Powder X-ray diffraction pattern for KBr doped ADP crystal

2.2 Material Characterization

The pure and KBr doped ADP single crystals were characterized by Powder X-ray diffraction using XPERTPRO diffractometer. FTIR spectra of the grown crystals were characterized by Jasco 4100 Spectrophotometer equipped with ATR. UV-Vis absorption spectra of the grown crystals were recorded using Systronics UV-Vis double beam spectrophotometer.

3. RESULTS AND DISCUSSION

3.1 Powder X-ray diffraction analysis

The structure of the pure and KBr doped ADP crystals were identified from powder X-ray diffraction using CuKα radiation of wavelength 1.54060Å. The data were recorded in the 2θ range from 10-80˚.

Figure (3) and (4) show the powder XRD patterns of pure and KBr doped ADP crystals. The obtained data were in good agreement with standard JCPDS (JCPDS: 37-1479) of ADP crystal with tetragonal crystal system. The reflection planes were indexed in accordance with the JCPDS. The lattice parameter values of 'a' and 'c' for pure and KBr doped ADP crystals were found to be a=7.50424 Å, c=7.54530Å and a=7.49005Å, c=7.54646Å, respectively. The calculated volume for pure ADP is 424.904 $(Å)^3$ and 423.363 $(Å)^3$ for KBr doped ADP crystal. The intensity of the KBr doped ADP crystal increased when compared to pure ADP. The change in intensity, volume, lattice parameters 'a' and 'b' suggest that the structure of KBr doped crystal was slightly distorted when compared to pure ADP crystal. It is seen from the PXRD spectrum of pure and KBr doped ADP crystals that there is no additional peak, but only change in the intensity of the peaks. This confirms there is no additional phase produces due to influence of doping [4].

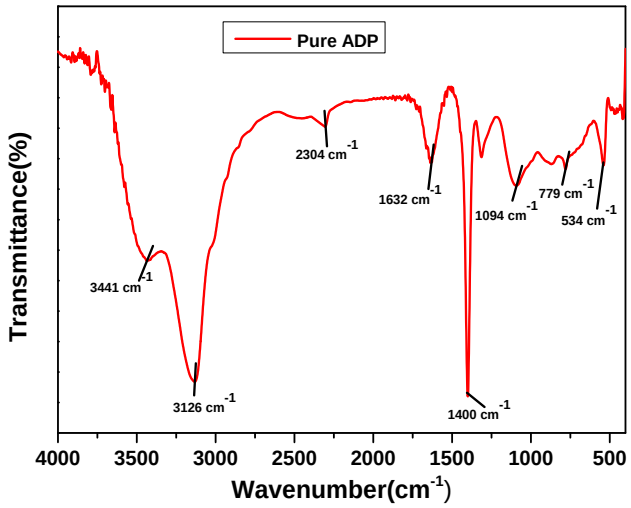

Fig -5: FTIR spectrum of pure ADP crystal

FTIR Analysis

The functional groups present in the pure and KBr doped ADP crystals were analyzed by FTIR spectroscopy. Figure (5) shows the FTIR spectrum of pure ADP crystal. For pure ADP crystal, the band at 3441 and 3126 cm^{-1} was assigned to stretching vibrational mode of O-H group [5]. Additionally the N-H vibrations were also assigned to 3441 cm^{-1}[4]. The band at 1632 cm^{-1} was assigned to bending vibrational mode of O-H group. The vibrational mode of P-O-H group was observed at 1094 cm^{-1}. The stretching vibrational mode of PO_4 group was observed at 534 cm^{-1}[6]. The vibration at 1400 cm^{-1} was assigned to stretching vibrational mode of NH_4.

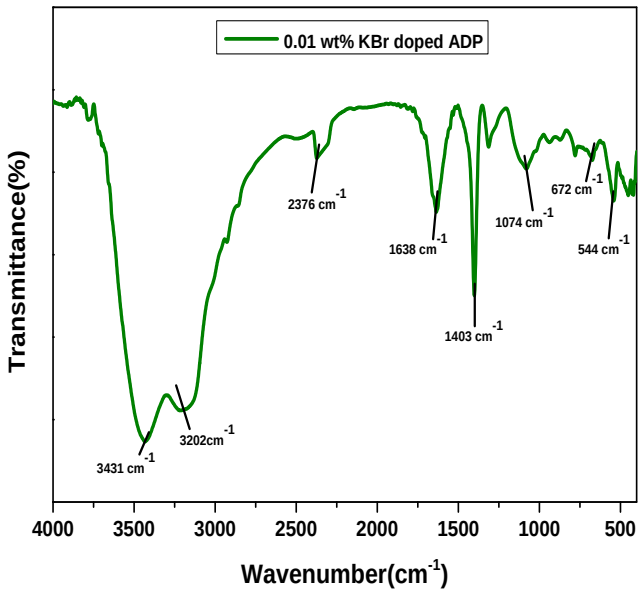

Fig -6: FTIR spectrum of KBr doped ADP crystal

Figure (6) shows the FTIR spectrum of KBr doped ADP crystal. Very slight shifts in vibrational bands were observed for KBr doped ADP crystal due to inclusion of doping. The vibrational band at 3431cm^{-1} was also assigned to vibration of N-H band. The band at 1638 cm^{-1} was assigned to bending vibrational mode of O-H group. The vibrational mode of P-O-H group was observed at 1074 cm^{-1}. The stretching vibrational mode of PO_4 group was observed at 544 cm^{-1}. The shifting band of NH_4 was observed at 1400 cm^{-1}. All these vibrational bands were well matched with the previous report [7]. The vibrations of KBr were not clearly resolved from the FTIR spectrum of the pure ADP, it might happen in a trace amount below the deductibility limit.

3.3. UV-Vis Spectral analysis

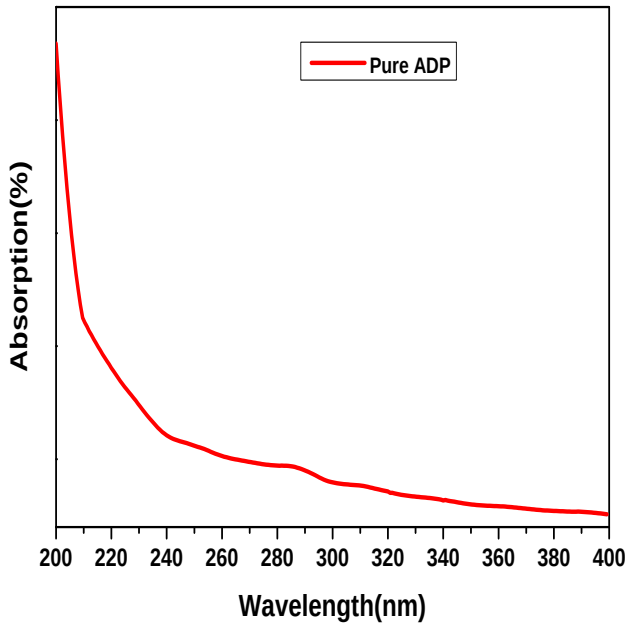

Fig -7: UV-Vis absorption spectrum of pure ADP crystal

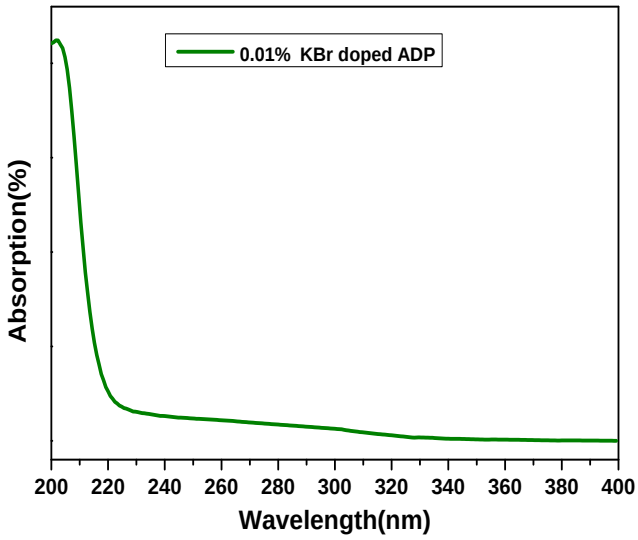

Fig -8: UV-Vis absorption spectrum of KBr doped ADP crystal

UV-Vis absorption spectrum of pure and KBr doped ADP crystals were recorded in the range of 200-600 cm^{-1}. Figure (7) and (8) show the UV-Visible absorption spectrum of pure and KBr doped ADP crystal. The spectrum of pure and KBr doped ADP crystals shows the full transmission in the entire visible region. So the pure and KBr doped ADP crystal is a very good material for electro – optic and NLO applications [8].

The optical band gap value of pure and KBr doped ADP crystals were calculated using the Tauc's relation,

$(\alpha h\nu)^n = A\,(h\nu - E_g)$

Where 'α' is the absorption coefficient, 'A' is a constant, 'Eg' is the band gap energy, 'ν' is the frequency of incident beam, 'h' is the Planck's constant, 'n' is the index value depends on nature of the transition. For direct allowed transitions n = 2 and for indirect allowed transition n = 1/2. Assuming the indirect band gap, the plot is drawn $(\alpha h\nu)^{1/2}$ against hν. The intercept of the straight line on the hν axis gives the indirect band gap value [9].

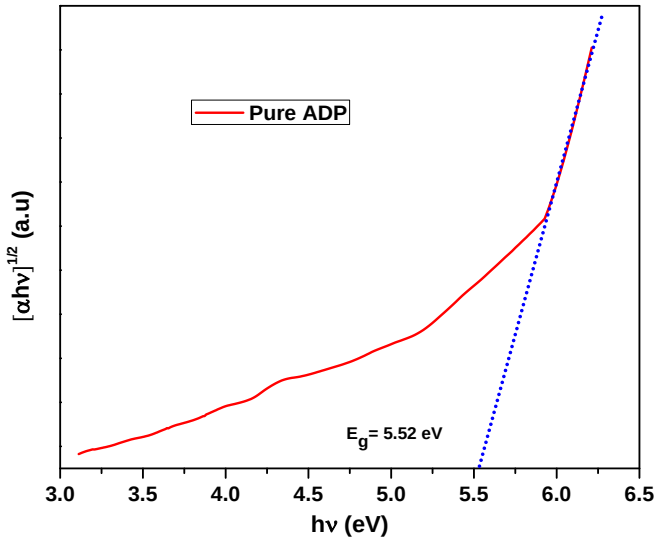

Fig -9: Tauc plot of ADP crystal

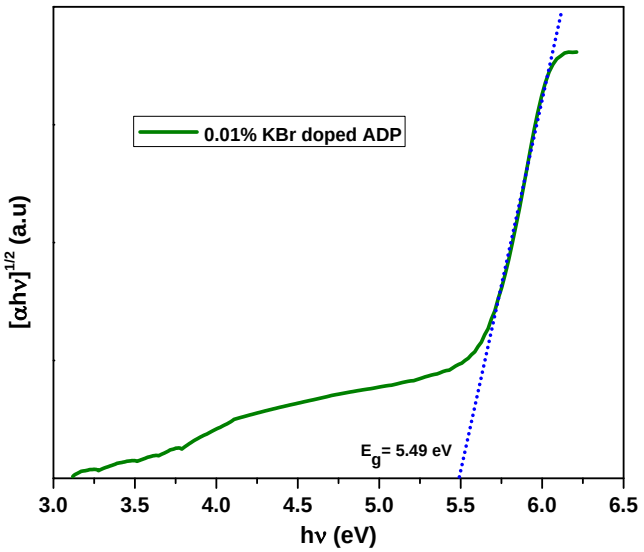

Fig -10: Tauc plot of KBr doped ADP crystal

Figure (9) and (10) show the Tauc's plot for pure and KBr doped ADP crystals respectively. The indirect band gap value of pure and KBr doped crystals found from the Tauc plot is 5.52 and 5.49 eV, respectively. This band gap value is close to the reported value of 4.7 eV [10].

4. CONCLUSIONS

Pure and KBr doped ADP crystals were grown using low temperature solution growth technique by slow evaporation method. X-Ray powder diffraction revealed the distortion in the crystal lattice due to the inclusion of doping material KBr. FTIR spectra confirms the vibrational modes of ADP crystal. UV-Vis spectral analysis shows the band gap value of 5.52 eV for pure ADP crystals.

5. ACKNOWLEDGEMENT

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7. REFERENCES

[1]. P. Shenoy, K. V. Bangera, G. K. Shivakumar, Growth and thermal studies on pure ADP, KDP and mixed K1-x(NH4)xH_2PO_4 crystals, Cryst. Res. Technol. 45 (2010) 825 – 829.

[2]. M. Meena and C. K. Mahadevan, Growth and electrical characterization of L-arginine added KDP and ADP single crystals, Cryst. Res. Technol. 43 (2008) 166 – 172.

[3]. K. Sethuraman, R. Ramesh Babu, R. Gopalakrishnan, P. Ramasamy, Unidirectional growth of <110> ammonium dihydrogen orthophosphate single crystal by Sankaranarayanan–Ramasamy method, Journal of Crystal Growth, 294 (2006) 349–352.

[4]. P.V. Dhanaraj , G. Bhagavannarayana, N.P. Rajesh, Effect of amino acid additives on crystal growth parameters and properties of ammonium dihydrogen orthophosphate crystals, Materials Chemistry and Physics, 112 (2008) 490–495.

[5]. Briyan C. Smith, Infrared Spectral Interpretation-A systematic Approach, CRC Press (1999), New York.

[6]. J. Anitha Hudson, C.K. Mahadevan, C.M. Padma, Growth and Characterization of ADP Single Crystals Added With CdS, International Journal of Engineering Research and Applications, 4 (2014) 257-266.

[7]. P.V.Dhanaraj, N.P.Rajesh, Crystallisation and material Science of Modern artificial and natural crystals (Edited by Dr.Elena Borisenko, (2012) 79.

[8]. P. Rajesh, P. Ramasamy, Binay Kumar, G. Bhagavannarayana, Effect of cobalt and DL-malic acid on the growth rate, crystalline perfection, optical, mechanical, dielectric, piezoelectric properties and SHG efficiency of ADP single crystals, Physica B, 405 (2010) 2401–2406.

[9]. Sunil Chaki, M. P. Deshpande, Jiten P. Tailor, Mahesh D. Chaudhary, Kanchan Mahato, Growth and Characterization of ADP Single Crystal, American Journal of Condensed Matter Physics, 2 (2012) 22-26.

[10]. R.N. Shaikh, M. Anis, M.D. Shirsat, S.S. Hussaini, Investigation on the Linear and Nonlinear Optical Properties of L-Lysine Doped Ammonium Dihydrogen Phosphate Crystal for NLO Applications, IOSR-Journal of Applied Physics, 6 (2014) 42-46.

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