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Structural Analysis of Pure and Potash Alum Doped KDP Crystals Grown by Gel Medium

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Abstract

Optically good quality pure and metal doped KDP crystals have been grown by gel method at room temperature and their characterization have been studied. Gel method is a much uncomplicated method and can be utilized to synthesize crystals which are having low solubility. Potassium dihydrogen orthophosphate KH_2PO_4 (KDP) continues to be an interesting material both academically and industrially. KDP is a representative of hydrogen bonded materials which possess very good electro–optic and nonlinear optical properties in addition to interesting electrical properties. Due to this interesting properties, we made an attempt to grow pure and Potash Alum doped KDP crystals in various concentrations (0.002, 0.004, 0.006, 0.008 and 0.010) using gel method. The grown crystals were collected after 20 days. We get crystals with good quality and shaped. The electrical conductivity increases with increase of temperature crystals. The Structural properties were found out by using FTIR and XRD studies. Results were discussed in detail.

Keywords: Gel growth, KDP, FTIR, XRD

1. Introduction

Gel growth in aqueous solution is now a wide spread technique for production of high quality crystals in a large range of solubilities and temperatures [1-3]. In gel growth, crystals are mostly formed at ambient temperature and hence are free from strain often present in crystals prepared from the melt or from the vapour [4]. In this method, two soluble reactants are diffused into a gel where they react to form an insoluble product. This is achieved by incorporating one of the reactants with the gel before setting in a test tube and adding the reactant in solution above the gel as supernatant. In this method, large scale movements like convection currents are almost completely suppressed, which otherwise could be harmful to the quality of crystal. The presence of gel does not considerably affect the rate of diffusion of crystallizing species [5] and the related crystal growth kinetics. The principle role of gel appears to be the suppression of turbulence and nucleation, [6] due to which crystallization occurs by diffusion of reactants to a small number of nucleation centre.

Potassium dihydrogen orthophosphate (KDP) KH_2PO_4 continues to be an interesting material both academically and industrially. KDP is a representative of hydrogen bonded materials which possess very good electro-optic and nonlinear optical properties in addition to interesting electrical properties. The demand for high quality large single crystals of KDP increase due to the application as frequency conversion crystal in inertial confinement fusion [7-8]. The piezo electric property of KDP crystal makes it useful for the construction of crystal filters and frequency stabilizers in electronic circuit's.

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The excellent properties of KDP include transparency in a wide region of optical spectrum, resistance to damage by laser radiation and relatively high non-linear efficiency, in combination with reproducible growth to large size. Therefore, it is commonly used in several applications such as laser fusion, electro-optical modulation and frequency conversion. Many studies on the growth and properties of KDP crystals in the presence of impurities have been reported [9-10]. Potassium dihydrogen phosphate (KDP) crystal draws persistent attention of scientists due to its excellent quality and possibility of growing large-size crystals [11-12]. Microscopically, crystal growth includes crystal morphology, crystal defects, and growth rate, which are all related to the constituent growth units and their chemical bonding process [13-14]. KDP, ADP and DKDP are the only nonlinear crystal currently used for these applications due to their exclusive properties. The grown crystals were characterized using dielectric constant, electrical properties, optical transmittance, for pure and Potash alum doped KDP crystals.

2. Materials and Methods

Pure and Potash alum doped KDP single crystals are grown in sodium meta silicate gel medium using analar grade KDP and Potash alum with in concentrations of 0.002, 0.004, 0.006, 0.008 and 0.010 of dopant and sodium meta silicate (1.08g/cm^3). During the process pH was maintained at 5-6 at room temperature. Ethyl alcohol of equal volume is added over the set gel without damaging the cell surface. When the alcohol diffuses into the set gel, it reduces the solubility. This induces nucleation and the nuclei are grown into the single crystals. The crystal growth was carried out at room temperature. The growth period was about 20 days for pure and Potash alum doped KDP crystals.

Results and Discussions

FT-IR studies on pure and Potash alum doped KDP crystals

The observed FT-IR spectra of pure and **Potash alum** doped KDP crystals are shown in figure.

From FT-IR spectra, the broad band which appears in the range 3261 to 2922 cm^{-1} is due to free O-H stretching of KDP [15]. It is seen that these are very weak bonds. The peak at 2922 cm^{-1} is due to P-O-H asymmetric stretching. The strong intensity band at 2433 cm^{-1} is due to one of the P-O-H bending of KDP. A sharp band in the spectral wavelengths of 1384 cm^{-1} is due to asymmetric bending modes. The sharp and strong intense bands appearing at 1147 cm^{-1} is due to P=O symmetric stretching. The spectrum shows an additional peak at 906 cm^{-1}. This is attributed to P-O-H stretching of KDP. Another sharp band at 537 cm^{-1} was due to bending mode of Al(H_2O)$_6$. A detailed assignment of the frequencies observed in FTIR spectrum is given table.

Figure 1

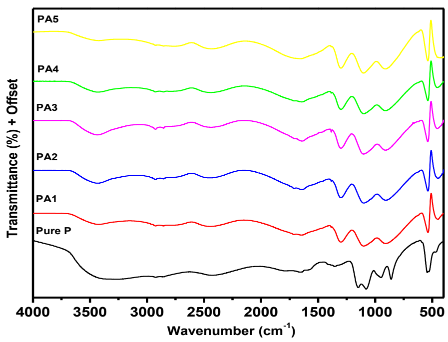

Figure 1. shows the FTIR pattern of (a) Pure KDP and (b) PA1 (c) PA2 (d) PA3 (e) PA4 (f) PA5 are doped Potash alum in different concentration

Pure KDP	PA1	PA2	PA3	PA4	PA5	Assignments
3261vw	3422vw	3432vw	3433vw	3431vw	3422vw	Free–O-H stretching
2922s	2925s	2926s	2925s	2925s	2923s	P-O-H Symmetric

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						stretching
------	1384	1384	1384	1384	1384	Asymmetric Bendingmode
1147vs	1100vs	1100vs	1101vs	1100vs	1102vs	P=O stretching of KDP
948vs	906vs	906vs	906vs	909s	912s	P-O stretching
543sh	536sh	537sh	538sh	537sh	537sh	Bending mode of $Al(H_2O)_6$

vs – very strong; s – strong; vw – very weak; sh – sharp

Powder XRD Studies

The powder X-ray Diffractometer analysis (XPERT-PRO) has been carried out for the rapid identification and quantification of grown crystal at 2 theta position of 10° to 80°. At maximum intensity the various structure parameters like the crystalline size, micro strain and dislocation density has been calculated by Debye-Scherer's formula and tabulated below [16-17].

$$D = 0.9\,\lambda / \beta \cos\theta$$

where λ is wavelength of the X-ray radiation, β is full width at half maximum (FWHM) of diffraction peak (in rad), and θ is scattering angle.

Further, the dislocation density (δ) and micro strain (ε) was estimated by the relation

$$\delta = 1/D^2 \quad \text{and} \quad \varepsilon = \beta \cos\theta/4$$

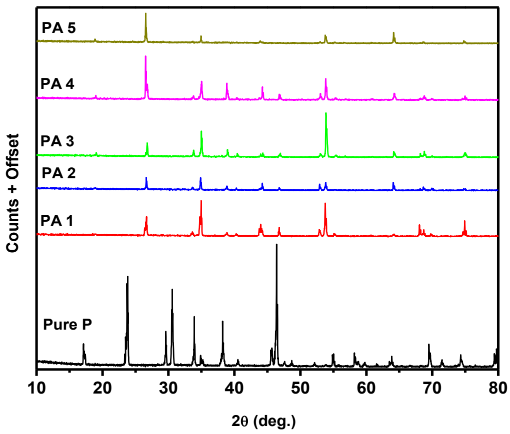

Figure 2. shows the Powder XRD pattern of (a) Pure KDP and (b) PA1 (c) PA2 (d) PA3 (e) PA4 (f) PA5 are doped Potash alum in different concentration.

X-Ray Diffraction data (crystalline size, micro strain and dislocation) for KDP doped with PA1-0.002, PA2-0.004, PA3-0.006, PA4-0.008, PA5-0.01 concentration of Potash alum

Sample	d spacing	2θ	FWHM - β	Crystalline Size nm	Dislocation 10^{14} $1/m^2$	Microstrain 10^{-4}
Pure KDP	3.738	23.784	0.0047	31.487	10.085	11.497
KDP+ PA1	3.728	23.866	0.0011	126.830	0.6217	2.690
KDP+ PA2	3.733	23.833	0.0014	97.720	1.0472	3.424
KDP+ PA3	3.711	23.974	0.0018	87.086	1.4143	4.401
KDP+ PA4	3.746	23.749	0.0012	123.321	0.6575	2.935
KDP+ PA5	3.742	23.774	0.0008	184.997	0.2921	1.957

Conclusion

Pure KDP crystals and metal doped KDP crystals were grown by gel method. In gel growth, due to the three dimensional structures, the crystals were free from microbes. KDP crystal is a queen of all crystals because of its high transparency and best NLO property. Addition of Potash alum with KDP gives some changes in its basic character. Here the characteristic properties of pure KDP and Potash alum with KDP crystal has been investigated through FTIR, XRD analysis The lower the value of dielectric constant more is the enhancement of SHG signals. The electrical conductivity of the pure KDP and Potash alum doped KDP crystals were found to be increase with increase of temperature and frequencies. The FT-IR spectral studies confirm the presence of all the functional groups and also the presence of Potash alum in the grown crystals. The presence of additional peaks in the XRD spectrum of doped KDP crystals shows the presence of additional phases due to doping.

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