

Growth and Structural Characterization of Gel Grown Pure and Mixed KDP-ADP Crystals

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ABSTRACT:

High quality single crystals of pure and mixed KDP-ADP are grown by gel method. The grown crystals are confirmed by single crystal X-ray diffraction analysis which reveals that the mixed KDP-ADP belongs to Tetragonal system with $I4_2d$ space group. FTIR studies to ascertain the metal coordination and the presence of various functional groups. Scanning Electron Microscopy (SEM) to assess the surface morphology and to study the quality of the crystal and Atomic Absorption Spectroscopy (AAS) Analysis to quantitatively analyze the incorporation of potassium ions in the crystal lattice.

Keywords: Gel growth; Characterization; X-ray diffraction; SEM; AAS

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I. INTRODUCTION

Potassium dihydrogen phosphate (KDP) and ammonium dihydrogen phosphate (ADP) are the typical hydrogen bond crystals with excellent piezoelectric and nonlinear optical properties [1–5], their growth rates and qualities have been improved rapidly to meet the requirements of practical applications [6–9]. However, the origin of their outstanding performances is still ambiguous and the corresponding promotion strategies are explored [10–13]. In recent years, the strong dependences of the structure distortion and hydrogen bond on the nonlinear optical coefficients are discussed [14–16]. As an effective method to tune the crystal structure and the hydrogen bond states, the growth of the mixed crystals of KDP and ADP, and the determination of the detailed crystal structure with respect to composition are therefore important for understanding the variation of crystal performances [17–21]. However, most of the previous works on mixed KDP-ADP were limited at the two ends of the composition range, because of the non-availability of the high-quality single crystals with intermediate compositions. Therefore, the comprehensive investigation of the variation of crystal structure and the corresponding crystal growth process may complement the cognition of these kinds of mixed crystals. So in our present study we use gel method to obtain high quality single crystals of pure and mixed KDP-ADP.

II. EXPERIMENTAL PROCEDURE

2.1 Synthesis

For the growth of $(KDP)_{0.8}(ADP)_{0.2}$ crystal, analytical grade KDP and ADP are taken in the ratio of 0.8:0.1 and then dissolved in double distilled water. The solution is filtered and heated in a water bath at a constant temperature. The gelation is achieved by mixing this solution with sodium metasilicate solution of density 1.08 g/cc. After making several trials, the optimized pH was found to be 4.8. The growth experiments are performed with straight test tubes of length 15 cm and diameter 2.5 cm. The gel is found to be perfectly set within 15 hours. In order to initiate the solubility reduction process, ethyl alcohol is added on top of the set gel without affecting the gel. The period of growth for growing good-sized quality crystals ranged between 30 to 40 days. Similar procedure is repeated for pure KDP, ADP and other mixed crystals in the ratio 1.0:0.0, 0.0:1.0, 0.6:0.4, 0.4:0.6 and 0.2:0.8 respectively.

The growth rate of a crystal mainly depends on various crystal growth parameters like temperature, concentration of nutrients, pH of the solution and other physicochemical properties [22]. For mixed KDP-ADP crystals, the concentration of the ADP solution is varied from 3.3 to 3.7 M. Similarly the concentration of KDP solution is varied from 2 to 3 M. On lowering the concentration of the nutrients, the nucleation is not affected. But the needle shaped crystals were very tiny. In the case of the inner reactant being KDP

solution, after adding the outer reactant being ADP on top of the set gel, thin needle crystals start appearing near the interface. In the middle region, a large number of flower like crystals are seen. The flower like crystal growth is large and closely packed; the needles of KDP-ADP are broader. When the mixed KDP and ADP solution was taken as the reactant with the gel, the needles were very thick and lesser glitter. In both the trials, the growth was completed within 40 days' time. The predomination of needle morphology during the growth of these crystals indicates that the growth is unidirectional. Hence in order to grow good-sized crystals, attempts have been made to control the rate of nucleation.

The effect of gel density was studied by changing the density of the gel from 1.05 g/cc to 1.12 g/cc. Even though, crystallization occurred in the entire range of the density of the gel solution, well-defined crystals were harvested with gel solution of density 1.08 g/cc. Further, at lower density, the gel being very soft, the outer reactant seeped quickly through the top surface of the gel enhancing the rate of reaction. This condition is not favouring a slowed-down reaction, wherein only good qualities of pure and mixed KDP-ADP crystals are possible. It is observed that when the gel density is 1.09 g/cc and above, the set gel is very hard and therefore it impedes the growth of good sized pure and mixed KDP-ADP crystals. Hence, to obtain good quality pure and mixed KDP-ADP crystals, gel solution of density 1.08 g/cc is found to be suitable.

To study the effect of pH, growth experiments were performed by varying pH from 4 to 5.2. At lower pH values, very tiny, colourless needles of pure and mixed KDP-ADP were formed and their number was considerably less. When the pH was around 4.8, the needles of mixed KDP-ADP had a considerably better dimension as 2 to 3 mm width and 1.0 cm length. The needles were quite spaced apart. At a pH of 5 to 5.2, there were star like clusters below these fine dendrites.

Figure 1: Photograph of pure and mixed KDP-ADP single crystals (a) pure KDP (b) $(\text{KDP})_{0.8}(\text{ADP})_{0.2}$ (c) $(\text{KDP})_{0.6}(\text{ADP})_{0.4}$ (d) $(\text{KDP})_{0.4}(\text{ADP})_{0.6}$ (e) $(\text{KDP})_{0.2}(\text{ADP})_{0.8}$ (f) pure ADP

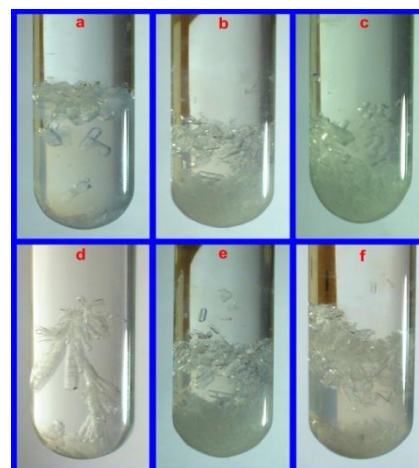


Figure 1 show the photographs of as gel grown crystals of pure and Mixed KDP-ADP. From the Figure 1 it is found that all the grown crystals are stable, colourless and transparent. The mixed crystals obtained in KDP-rich $(\text{KDP})_{0.8}(\text{ADP})_{0.2}$ or ADP-rich $(\text{KDP})_{0.2}(\text{ADP})_{0.8}$ solutions preserve their ideal morphologies as that of KDP or ADP, respectively, though slight taper appears at the end of each run due to the competition between different cations and the decrease of the growth driving force [23]. When the concentration of either of the components increases continuously, twin, multiple twin and dendritic growth occur. Consequently, the obtained $(\text{KDP})_{0.6}(\text{ADP})_{0.4}$ and $(\text{KDP})_{0.4}(\text{ADP})_{0.6}$ crystals change from bulk to thick needles (the needles frequently self-assemble into a sphere), and the crystal qualities degrade rapidly. It was found that the transparency i.e. optical quality of the $(\text{KDP})_{0.6}(\text{ADP})_{0.4}$ and $(\text{KDP})_{0.4}(\text{ADP})_{0.6}$ crystals are lesser than that of the pure KDP, $(\text{KDP})_{0.8}(\text{ADP})_{0.2}$ and $(\text{KDP})_{0.2}(\text{ADP})_{0.8}$ and ADP crystals. Crystals harvested in a short period were found to be more transparent and inclusion free. The dimensions of mixed crystals are found to be less than that of pure KDP and ADP. The optimized conditions for the growth of pure and mixed KDP-ADP single crystals are presented in Table 1.

Table 1: Optimized conditions for the growth of pure and mixed KDP-ADP single crystals

Crystal	Gel density (g/cm ³)	Strength of solution		pH of gel	Growth period (days)
		KDP molar	ADP molar		
KDP	1.08	2.5	0.0	4.8	35
(KDP) _{0.8} (ADP) _{0.2}	1.08	2.0	1.5	4.8	40
(KDP) _{0.6} (ADP) _{0.4}	1.07	2.1	1.4	4.9	40
(KDP) _{0.4} (ADP) _{0.6}	1.07	1.4	2.1	4.9	40
(KDP) _{0.2} (ADP) _{0.8}	1.08	0.7	2.8	4.8	45
ADP	1.08	0.0	3.5	4.8	38

III. STRUCTURAL CHARACTERIZATION

3.1 Single Crystal XRD Analysis

The unit cell parameters of pure and mixed KDP-ADP single crystals are presented in Table 2. It is observed from the table that the cell parameters and the volume of the mixed KDP-ADP crystals slightly differ from those of the pure KDP and ADP, which may be attributed to the incorporation of ADP in KDP crystals. Both pure and mixed crystals are

found to be tetragonal in structure belonging to $\bar{I}42d$ space group. The XRD results suggest that the presence of ADP has not altered the basic structure of the KDP crystal. It is observed from the XRD data that the unit cell volume increase with the increasing concentration of ADP in the host KDP, also lattice parameter values of pure KDP and ADP are in good agreement with the reported values in literature [24, 25].

Table 2: Calculated lattice parameter values of pure and mixed KDP-ADP single crystals from single crystal XRD.

DATA	KDP	(KDP) _{0.8} (ADP) _{0.2}	(KDP) _{0.6} (ADP) _{0.4}	(KDP) _{0.4} (ADP) _{0.6}	(KDP) _{0.2} (ADP) _{0.8}	ADP
a=b (Å)	7.467	7.479	7.488	7.461	7.504	7.526
c (Å)	6.923	6.967	7.015	7.346	7.433	7.529
V(Å ³)	385.99	389.71	393.33	408.93	418.55	426.45
α (°C)	90	90	90	90	90	90
β (°C)	90	90	90	90	90	90
γ (°C)	90	90	90	90	90	90
Crystal System	Tetragonal	Tetragonal	Tetragonal	Tetragonal	Tetragonal	Tetragonal
Space Group	$\bar{I}42d$	$\bar{I}42d$	$\bar{I}42d$	$\bar{I}42d$	$\bar{I}42d$	$\bar{I}42d$

3.2 Powder XRD Patterns

The powder XRD (PXRD) patterns obtained for the pure and mixed KDP-ADP crystals grown in the present study are shown in Figures 1.2-1.7. The obtained XRD patterns of pure KDP and ADP crystals in the present study are well matched with the published ones [26]. The numerous sharp peaks found in the XRD patterns give a clear cut proof of the crystalline nature of all the grown crystals. The phases have been clearly indexed and shown in Figure 1.8. The lattice parameters are calculated from the indexed pattern by using the software powder X [27] and are summarized in Table 1.3. From Figure 1.8, it reveals that the diffraction peaks gradually shift to

lower angle side from pure KDP (JCPDS file No. 35-0807) to pure ADP (JCPDS file No. 37-1479) with increase of ADP content in host KDP lattices. The calculated lattice parameter values are well matched with the data obtained from the single crystal XRD.

The lattice parameters (a and c) and cell volume (v) of mixed KDP-ADP crystals, increase with the addition of ammonium though small deviations exist. In more detail, for the crystal frames along both a and b directions are primarily constructed by the phosphates via strong hydrogen bonds. The contribution of cations is small, the increments of the parameters 'a' and 'b' with ammonium concentration are, therefore, practically

negligible. Oppositely, the phosphate tetrahedrons are directly packed together along c-axis through intermediate cations; the parameter c is thus dependent on the radii of both the constituent anions and cations. When the bigger ammonium ions incorporate in the mixed crystals, the unit cell extends along c-axis obviously and the cell volume v expands accordingly [28].

Figure 1.2: Powder XRD pattern of KDP single crystal

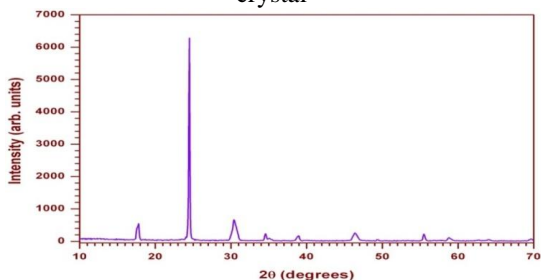


Figure 1.3: Powder XRD pattern of (KDP)_{0.8}(ADP)_{0.2} single crystal

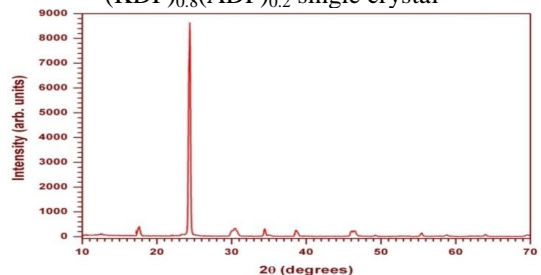


Figure 1.4: Powder XRD pattern of (KDP)_{0.6}(ADP)_{0.4} single crystal

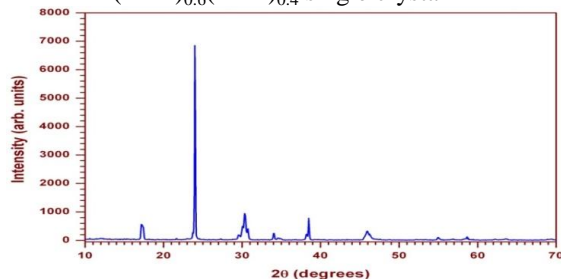


Figure 1.5: Powder XRD pattern of (KDP)_{0.4}(ADP)_{0.6} single crystal

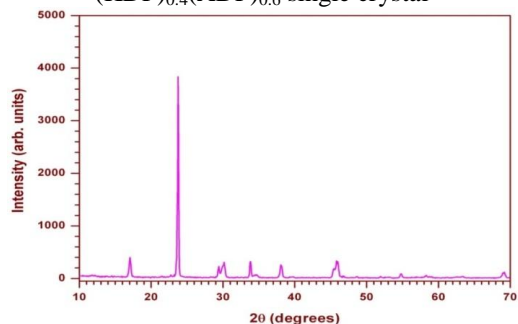


Figure 1.6: Powder XRD pattern of (KDP)_{0.2}(ADP)_{0.8} single crystal

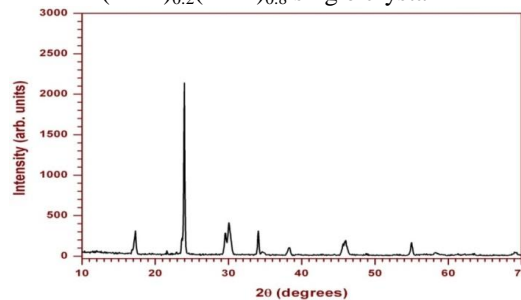


Figure 1.7: Powder XRD pattern of ADP single crystal

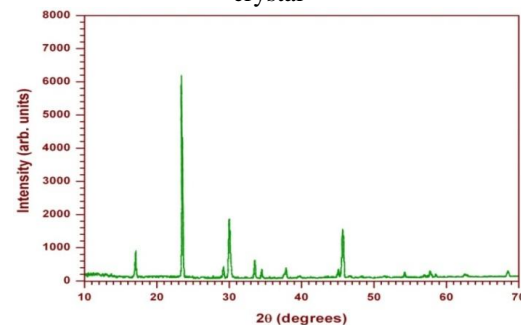


Figure 1.8: Indexed Powder XRD patterns of pure and mixed KDP-ADP single crystal (a) JCPDS pattern of KDP (b) pure KDP (c) (KDP)_{0.8}(ADP)_{0.2} (d) (KDP)_{0.6}(ADP)_{0.4} (e) (KDP)_{0.4}(ADP)_{0.6} (f) (KDP)_{0.2}(ADP)_{0.8} (g) pure ADP (h) JCPDS pattern of ADP single crystals

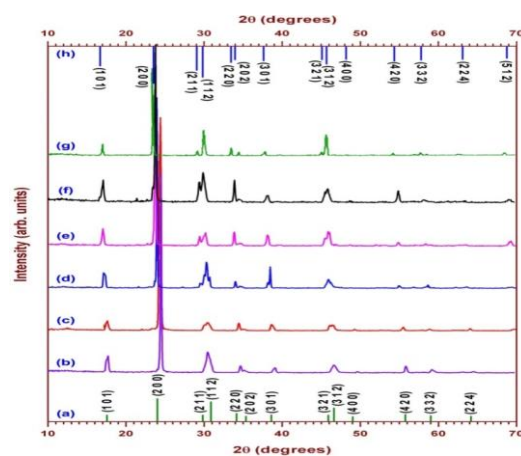
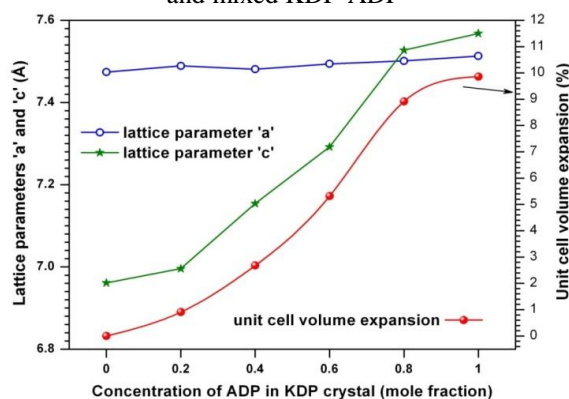


Table 1.3: Calculated lattice parameter values of pure and mixed KDP-ADP single crystals from powder XRD. (* and # indicates lattice parameter values of pure KDP and ADP from JCPDS file No. 35-0807 and 37-1479 respectively)

Sl. No.	Sample name	Calculated lattice parameters		
		a=b Å	c Å	Volume Å ³
1.	KDP	7.474 7.453*	6.961 6.974*	388.84 387.42*
2.	(KDP) _{0.8} (ADP) _{0.2}	7.489	6.996	392.37
3.	(KDP) _{0.6} (ADP) _{0.4}	7.481	7.154	399.26
4.	(KDP) _{0.4} (ADP) _{0.6}	7.494	7.292	409.52
5.	(KDP) _{0.2} (ADP) _{0.8}	7.501	7.527	423.51
6.	ADP	7.513 7.502 [#]	7.568 7.554 [#]	427.18 425.16 [#]

The variation in lattice parameter (a and c) due to the variation of concentration of ADP in KDP crystal is plotted in Figure 1.9. As can be noticed, addition of ADP in KDP leads to lattice expansion in 'a' and 'c' direction. Due to the lattice expansion the overall unit cell volume expansion takes place. In pure KDP and KDP rich mixed crystals, the lattice constant 'a' is higher than 'c'. But in the case of pure ADP and ADP rich mixed crystals the values get reversed i.e. the lattice constant 'c' is higher than 'a'. This clearly proves that the addition of ADP in host KDP crystal is well alloyed with each other. The uniform unit cell volume expansion reveals that concentration of ADP may play a role in lattice construction but does not modify the lattice structure of KDP.

Figure 1.9: Variation of lattice parameters of pure and mixed KDP-ADP



From Figure 1.8, the expansion of cell volumes of the mixed crystals are larger than that of KDP and smaller than that of ADP, the space around the positive sites provided by the surrounding anions is mismatched for both

potassium and ammonium. When potassium enters the larger positive sites, the bond length between potassium and the adjacent anion is longer than the ideal length in KDP. The bond valence sum of the center potassium is, therefore, smaller than the ideal value. The residual bond valence of potassium attracts the adjacent anions to shorten the bond length, that is, some segments of the stable anionic network shrink to satisfy the bond valence sum around potassium. On the other hand, ammonium is filled in a relatively small room and the local areas of the crystal frame expand to accept the larger cations. With the increase in the doped content, the distortion of the crystal frame is accelerated, and the accumulated internal stress ultimately produces numerous crack lines and defects in (KDP)_{0.6}(ADP)_{0.4} and (KDP)_{0.4}(ADP)_{0.6} crystals.

3.3 FTIR Spectrum Analysis

Fourier transforms infrared observed vibrational frequencies of pure and mixed KDP-ADP single crystals are shown in Table 1.4. Assignments were made on the basis of relative intensities, magnitudes of the frequencies and from the literature data [29-33]. There is a broad strong absorption between 1500 and 1700 cm⁻¹ resulting from hydrogen [32] bonded N-H stretching bands. Absorption in this region is characterized by fine structure on the lower wave number side of the band. The bands which appeared at 3600 cm⁻¹ in pure KDP and mixed KDP-ADP were assigned to free O-H stretching [33]. The broad absorption band appeared at 3420, 3423, 3424, 3437, 3408 and 3437 were assigned to hydrogen bonded O-H stretching frequencies in pure KDP, (KDP)_{0.8}(ADP)_{0.2}, (KDP)_{0.6}(ADP)_{0.4}, (KDP)_{0.4}(ADP)_{0.6}, (KDP)_{0.2}(ADP)_{0.8} and pure ADP, respectively. The

absorption around 3400 cm^{-1} for O–H stretching was in close agreement with the experimentally obtained one for pure KDP at 3420 cm^{-1} . Its deviation from pure KDP to lower side in mixed KDP-ADP indicated clearly the interaction of ADP with P–O–H group of KDP and in weakening the strength of the bond between oxygen and hydrogen. This leads to the decrease in the frequency of O–H stretching and confirmed the non-linear optical property of pure and mixed KDP-ADP crystals at these sites in

the crystal lattice. This property is also reflected in the P O, P–O, P–OH stretching and HO–P–OH bending vibrations at around 900, 1100 and 1300 cm^{-1} (see Table 3.4). The present IR study on pure and mixed KDP-ADP clearly indicates the effect of concentration of ADP on the crystal structure of pure KDP, which leads to the change in the absorption of IR frequencies and the non-linear optical property of both the pure and mixed KDP-ADP crystals.

Table 1.4: FTIR frequency assignments of pure and mixed KDP-ADP single crystals

Sl. No	Wave number (cm^{-1})						Assignment
	Pure KDP	(KDP) _{0.8} (ADP) _{0.2}	(KDP) _{0.6} (ADP) _{0.4}	(KDP) _{0.4} (ADP) _{0.6}	(KDP) _{0.2} (ADP) _{0.8}	Pure ADP	
1.	3778	3779	3778	3778	3767	3769	O-H stretch
2.		3703	3703	3703	3697	3699	O-H stretch
3.	3419	3423	3423	3437	3408	3437	O-H,N-H stretch
4.	-	-	-	-	3269	-	N-H stretch
5.	2920	2920	2922	2922	2922	2920	O-H,N-H stretch
6.	2856	2860	2860	2860	2858	2856	P-O-H symmetric stretching
7.	2478	2480	2486	2497	-	2480	NH ₃ ⁺ bending superimposed with P–O–H stretching
8.	-	-	-	2386	2380	-	P–O–H bending of KDP
9.	1730	1728	1724	1724	1724	-	N-H stretch
10.	1647	1647	1637	1637	1637	1647	O=P-OH asymmetric
11.	-	-	1458	1460	1446	-	N-H stretch
12.	1300	1298	1296	1298	1286	1298	P=O stretch
13.	1099	1099	1099	1099	1100	1099	P=O stretch
14.	904	910	908	906	912	906	P=O stretch
15.	543	545	546	545	553	545	HO-P-OH bending
16.	-	449	449	459	461	447	N-H Torsional oscillation

3.4 SEM Analysis

The external morphology of the sample is derived from signals received from electron sample interactions. A two dimensional image is generated over a selected area of the surface of the sample for analysis. The recorded scanning electron microscopy (SEM) images of pure and mixed KDP-ADP single crystals are shown in Figure 3.18-3.2. From these figures it is clear that the crystal possesses almost

smooth surface and free from cracks. However, very few inclusions/micro crystals are seen on the surface. These inclusions were formed during the crystal growth and they were influenced by the growth conditions. In the case of KDP and ADP rich mixed crystals {(KDP)_{0.8}(ADP)_{0.2} and (KDP)_{0.2}(ADP)_{0.8}} the smoothness of the surface is lesser than the pure KDP and ADP crystal.

Figure 1.10: SEM image of pure KDP single crystal

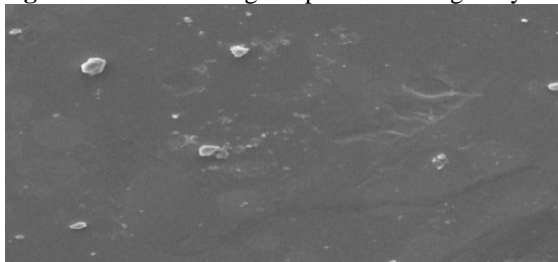


Figure 1.11: SEM image of pure KDP single crystal

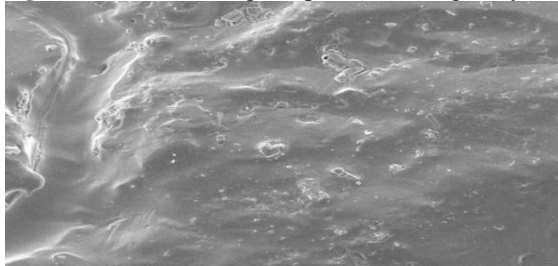


Figure 1.12: SEM image of pure $(\text{KDP})_{0.8}(\text{ADP})_{0.2}$ single crystal

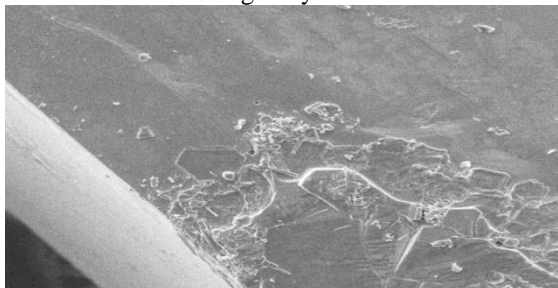


Figure 1.13: SEM image of mixed $(\text{KDP})_{0.6}(\text{ADP})_{0.4}$ single crystal

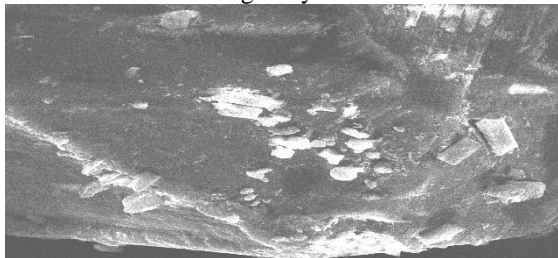


Figure 1.14: SEM image of mixed $(\text{KDP})_{0.4}(\text{ADP})_{0.6}$ single crystal

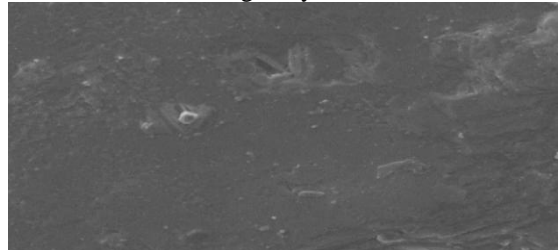


Figure 1.16: SEM image of mixed $(\text{KDP})_{0.2}(\text{ADP})_{0.8}$ single crystal

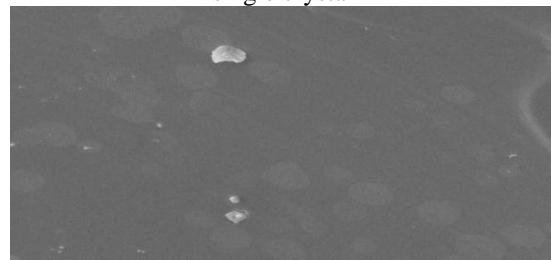
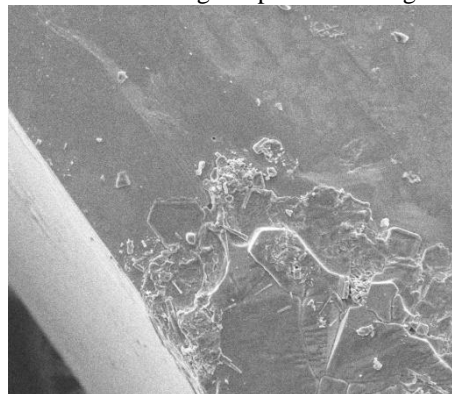


Figure 1.17: SEM image of pure ADP single crystal



3.5 Atomic Absorption Spectroscopy (AAS) Analysis

Atomic absorption spectroscopy (AAS) is one of the common instrumental methods for analyzing the metals and some metalloids. Atomic absorption spectroscopy (AAS) determines the presence of metals in liquid samples. The presence of potassium in mixed

KDP-ADP single crystal was quantified by AAS. In order to determine the mole percentage of potassium incorporated in the grown mixed crystals, finely powdered pure KDP and mixed KDP-ADP crystals weighing about 100 mg are dissolved in 10 ml of dilute acid and then subjected to AAS. The results of AAS are presented in Table 1.5. It is observed that the amount of potassium present in the crystal lattice is higher than its original concentration in the solution.

Table 1.5: AAS estimate for potassium in mixed KDP-ADP single crystals

Crystal	Molar concentration of potassium taken for growth experiment	Molar concentration of potassium present in crystal
	mole	mole
(KDP) _{0.8} (ADP) _{0.2}	0.8	0.89
(KDP) _{0.6} (ADP) _{0.4}	0.6	0.72
(KDP) _{0.4} (ADP) _{0.6}	0.4	0.53
(KDP) _{0.2} (ADP) _{0.8}	0.2	0.31

IV. CONCLUSION

The pure and mixed KDP-ADP synthesized by gel method. The cell parameters were determined using single crystal X-ray diffraction method. Functional groups were obtained using FTIR analysis, which revealed the characteristic vibration modes of the pure and mixed KDP-ADP crystal. The scanning electron microscopy (SEM) images of pure and mixed KDP-ADP single crystals were recorded. Atomic Absorption Spectroscopy (AAS) analysis observed that the amount of potassium present in the crystal lattice is higher than its original concentration in the solution.

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