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X-ray diffraction studies and its application on the examination of defect and growth mechanism of some laser host materials

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ABSTRACT Crystallization of non-linear optical (NLO) single crystals has become an important field of research in recent years in view of industrial applications in modern optical and optoelectronics devices for the efficient processing of optical signals. Potassium dihydrogen phosphate (KDP), urea, ammonium oxalate (AO) etc. are the well-known non-linear optical materials and have vast applications in the solid-state laser source devices. The laser source materials KDP and AO have been grown from low temperature aqueous solutions with the addition of different mole concentration of urea and some rare earth impurities like La, Sm, Gd to improve the quality of the crystal and their non-linear optical properties. X-ray diffraction studies were carried out on the grown single crystal using a Shimadzu X-ray Diffractometer with CuKα radiation. X-ray study reveals that the structures of the doped crystals were slightly distorted compared to the pure crystal. From the X-ray diffraction pattern, the 2θ, 'd'- spacing and relative intensity values for the corresponding hkl values were calculated. The deviation in 2θ (i.e. $\Delta 2\theta = 2\theta_{Exp} - 2\theta_{Cal}$) for the experimental and calculated values suggests that the structures are slightly distorted. This may be attributed to strain on the lattice by the adsorption of impurities. The lattice constant values are found to be varied with the addition of impurity concentrations and satisfy the Vegard's law.

(Single crystal, X-ray diffraction, Impurity adsorption, Vegard's law)

INTRODUCTION

Crystallization of single crystals has been developed as an important field over the years both for academic and industrial application in different areas. Now a day non-linear optics has emerged into vast areas of research since it attracts and demands the collective contribution of Physicists, Chemists, Technologist, Engineer's and Industrialists from many disciplines. Today crystals are the pillars of modern technology, with out crystals there would be no electronic industry, no photonics industry, no fibre optic communications. From technological point of interest an attempt has been made to grow large dislocation free single crystals of both inorganic as well as semi organic and organic crystals. Among the various techniques, low temperature solution growth technique is less expensive.

Potassium dihydrogen phosphate (KDP) crystals have many advantages like wide transparency wavelength range, high efficiency of frequency conversion, high damage threshold against high power lasers and AO is also reported to have large electro-optic effect and optical second harmonic generation property [1-3]. The structure of KDP belongs to the scalenohedral (twelve-face polyhedron) class of tetragonal crystal system. AO is optically negative and orthorhombic with space group $P2_12_12$, Z= 2 and a = 8.034Å, b = 10.309 Å and c = 3.795 Å [4]. AO crystallizes from aqueous solution in the form of monohydrate $[(NH_4)_2 C_2O_4 .H_2O]$. In many industrial crystallization processes, the size and shape of the crystals is an important factor, since the undesirable habits such as plate like or needle like causes the problems of separating, washing and drying. To improve the quality of the KDP and ammonium oxalate crystals some organic and rare earth compounds are added as impurities to see their influence on the growth kinetics, habit modification as well as to grow high quality large size single crystal.

EXPERIMENTAL

Analar grade potassium dihydrogen phosphate, urea, ammonium oxalate with purity 99.99 % (E-Merck) and Millipore water were used in the growth experiments. Saturated aqueous solutions were prepared at room temperature following the solubility curve. Seed crystals were prepared by isothermal evaporation of solvent at ambient temperature. Good quality seed crystals of reasonable size were obtained within 3 days. Saturated solutions of KDP (each 200ml) separately mixed with 1 M%, 5 M%, and 10 M% urea as dopant were prepared and taken in three petridishes and allowed to evaporate at room temperature by conventional isothermal method. Similarly AO solutions were mixed with 0.1M% La oxalate, 0.1M % of Sm sulfate, and 0.1M % Gd oxide respectively. Powder X-ray diffraction data were collected for the grown urea doped KDP and La, Sm, and Gd doped AO crystals using a Shimadzu X-ray Diffractometer model XD 01 with CuKα radiation (λ= 1.5405 Å) with an operating applied voltage 30 kV and current 20mA. Scanning rate was maintained at 1^0 per minute.

RESULTS AND DISCUSSION

Figures 1 and 2 show the X-ray diffraction pattern of urea doped KDP and La, Sm, Gd doped ammonium oxalate single crystals. Urea doped KDP crystals were found to have more inclusions as the urea concentration was increased. The increase in the quality of the KDP crystal in presence of urea and AO in presence of rare earth impurities is due to the suppression of trace metal ion impurities present in the solution. The Bragg's reflections were indexed for pure KDP and AO, and doped KDP and AO crystals following the procedures of Lipson and Steeple using cell parameters a = 7.448 Å and c= 6.977 Å [5-6]. The respective experimental data viz. 2θ value, d-spacing and relative intensity for the corresponding hkl values is presented in Tables 1 and 2. The deviation in 2θ (i.e. $\Delta 2\theta = 2\theta_{Exp} - 2\theta_{Cal}$) for the experimental and calculated values is given in the Tables 4 and 5. The change in 2θ values suggests that the structures were slightly distorted compared to the structure reported earlier. Hence the urea impurities having the higher solubility than that of the crystallizing substance (KDP) might have changed the thermodynamic parameters i.e. the surface concentration of the growth species and the surface energy. Urea acts as an immobile impurity particle mainly adsorbed at the terrace, which in turn produce inclusions.

An increase in solubility by the addition of urea may lead to decrease in the surface energy, which consequently decreases the rates of layers displacement that cause an increase in the growth rate. The growth mechanism is followed by the direct kink interaction in the steps. Due to the attachment of the impurities into the crystal lattice, the overall growth movement in the steps may become irregular, some may be blocked, while others may move fast over the same surface area in the same direction [7].

Table 1: X-ray Powder diffraction data for pure and urea doped KDP crystals

hkl	Pure KDP			Urea doped KDP (1M%)			Urea doped KDP (5M %)			Urea doped KDP (10 M %)		
	$2\theta_{exp}$	I/I_0 %	$d_{exp}(^\circ)$	$2\theta_{exp}$	I/I_0 %	$d_{exp}(^\circ)$	$2\theta_{exp}$	I/I_0 %	$d_{exp}(^\circ)$	$2\theta_{exp}$	I/I_0 %	$d_{exp}(^\circ)$
101	17.501	64	5.063	-----	-----	-----	17.598	14.55	5.035	17.699	13.20	5.007
200	24.199	100	3.765	24.253	52.85	3.667	24.105	100	3.690	24.102	100	3.690
112	31.102	84	2.873	31.098	100	2.873	31.007	59.58	2.882	31.003	49.40	2.882
301	38.804	28	2.319	38.405	28.99	2.342	38.698	9.92	2.325	38.807	11.10	2.319
321	46.011	28	1.971	46.002	13.39	1.971	46.007	28.85	1.971	46.105	65.18	1.967
312	46.612	80	1.947	46.811	81.84	1.939	46.805	11.66	1.939	46.806	84.25	1.939
332	59.105	76	1.562	59.112	16.72	1.562	59.011	36.08	1.564	59.212	24.90	1.559

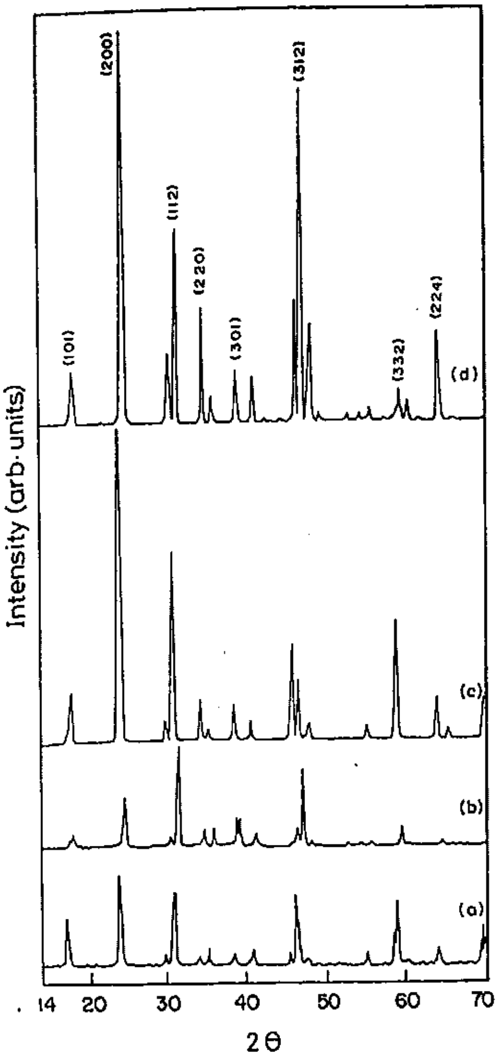

Figure 1. X-ray diffraction patterns (a) Pure KDP

(b) KDP + 1 M% urea (c) KDP + 5 M% urea
(d) KDP + 10 M% urea

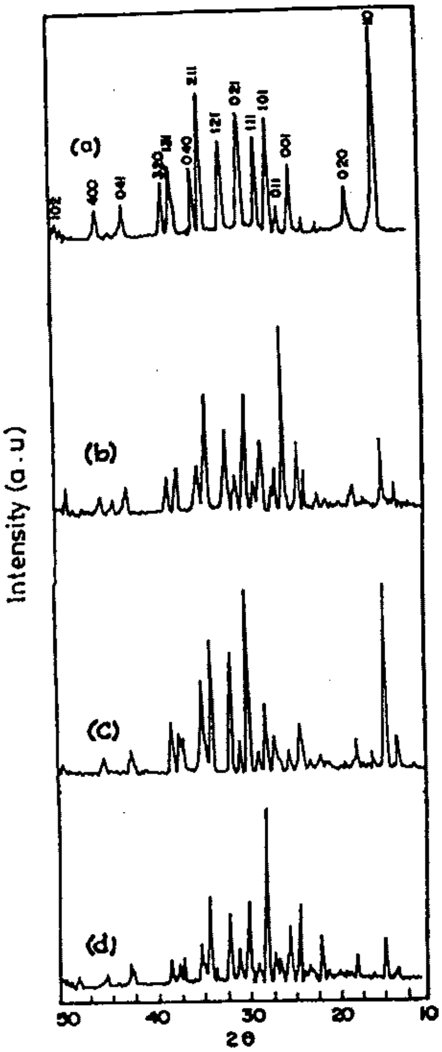

Figure 2. X-ray diffraction patterns (a) Pure AO

(b) AO + 0.1 M% La (c) AO + 0.1 % Sm
(d) AO + 0.1 M % Ga

Table 2: X-ray Powder diffraction data for pure and doped AO crystals

hkl	Pure AO			La doped AO (0.1 M %)			Sm doped AO (0.1 M %)			Gd doped AO (0.1 M %)		
	$2\theta_{exp}$	I/I_0 %	d_{exp}(°)	$2\theta_{exp}$	I/I_0 %	d_{exp} (°)	$2\theta_{exp}$	I/I_0 %	d_{exp}(°)	$2\theta_{exp}$	I/I_0 %	d_{exp}(°)
110	14.251	100	6.212	14.451	37.5	6.123	14.341	100	6.172	14.252	26.00	6.207
001	24.752	38.33	3.592	24.552	36.0	3.623	24.453	22.22	3.637	24.653	42.00	3.608
101	26.105	52.23	3.611	26.254	100	3.392	26.401	22.22	3.372	26.154	30.31	3.404
111	27.553	44.44	3.235	27.502	36.0	3.240	27.356	33.23	3.257	27.701	100	3.217
021	29.461	55.55	3.029	29.313	62.5	3.044	29.361	96.0	3.039	29.582	41.85	3.017
121	31.322	44.00	2.854	31.221	41.25	2.862	31.183	55.55	2.865	31.501	44.00	2.838
211	33.755	67.00	2.653	33.654	62.0	2.661	33.652	66.66	2.661	33.852	54.45	2.646

The addition of samarium sulfate (0.1M %) increased the quality of the crystals by decreasing the dislocation, which is apparent in the transparency of the crystal. The typical surfaces like [001] along with [011] and [021] were also clear in this specimen. However all the crystals grown by slow cooling from 30 ^{0}C to 25 ^{0}C had well faced surface in the [001] direction. The d-values and the cell parameters calculated for pure samples were found to be in good agreement with the literature values. In cases of the peak position corresponding to different planes shifted to higher angles resulting in lowering d-values as well as decrease in cell parameters shown in Table 3. The contraction of the cell parameters may be due to the loss of water molecules linking to the oxalate molecules with ammonium ions or due to stronger hydrogen bond between the rare earth impurities and oxalate ions replacing the ammonium ions. The change in the relative intensities of different peaks in the diffractogram of the grown crystals is due to the incorporation of rare earth ions in the crystals. However, there are appearances of some other peaks, which has no corresponding standard data or corresponding face. These are due to the incorporated impurities localized in any portion of the crystal. In case of urea doped KDP crystals large deviations of 2θ values are observed indicating a large distortion. The lattice parameters were calculated by the conventional method. The lattice constant values are found to be varied with the addition of impurity concentrations and satisfy the Vegard's law for both impurities added KDP and AO crystals.

Table 3: Variation of lattice parameters with doping concentration

Sample	Lattice parameters, a (Å)	Lattice parameters, b (Å)	Lattice parameters, C (Å)
Pure KDP	7.4545	7.4545	6.8192
KDP + 1 M% urea	7.4546	7.4546	6.8197
KDP + 5 M% urea	7.4597	7.4597	6.8046
KDP + 10 M% urea	7.4311	7.4311	6.8354
Pure AO	8.0038	10.4090	3.7950
AO + (0.1M%) La	7.9810	10.3440	3.7740
AO + (0.1M%) Sm	7.9690	10.3310	3.7391
AO + (0.1M%) Gd	7.4520	10.4231	3.7220

Table 4: Indexed powder diffraction data for pure and urea doped KDP crystals

Samples	hkl	$2\theta_{cal}$(°)	I/I %	$2\theta_{exp}$(°)	Δ2θ
Pure KDP	200	23.874	100	24.199	+ 0.325
	112	30.719	84	31.102	+ 0.383
	301	38.436	28	38.804	+ 0.368
	312	46.456	80	46.612	+ 0.156
	332	58.843	76	59.105	+ 0.262
Urea doped KDP (1M%)	200	23.874	52.85	24.253	+ 0.379
	112	30.719	100	31.098	+ 0.379
	301	38.436	28.99	38.405	- 0.031
	312	46.456	81.84	46.811	+ 0.355
	332	58.843	16.72	59.112	+0.269
Urea doped KDP (5M%)	200	23.874	100	24.115	+ 0.231
	112	30.719	59.58	31.007	+ 0.288
	301	38.436	9.92	38.608	+ 0.262
	312	46.456	11.66	46.805	+ 0.349
	332	58.843	36.08	59.111	+ 0.168
Urea doped KDP (10 M%)	200	23.874	100	24.102	+ 0.228
	112	30.719	49.40	31.003	+ 0.284
	301	38.436	11.10	38.807	+ 0.371
	312	46.456	84.25	46.806	+ 0.350
	332	58.843	24.90	59.212	+ 0.369

Table 5: Indexed powder diffraction data for pure and doped AO crystals

Samples	hkl	$2\theta_{cal}$(°)	I/I %	$2\theta_{exp}$(°)	$\Delta 2\theta$
Pure AO	110	14.045	100	14.251	+ 0.206
	101	25.954	52.23	26.105	+ 0.151
	111	27.333	44.44	27.553	+ 0.220
	021	29.158	55.55	29.461	+ 0.303
	121	31.247	44.00	31.322	+ 0.075
	211	38.534	67.00	33.755	+ 0.221
La doped AO (0.1M%)	110	14.045	37.50	14.451	+ 0.406
	101	25.954	100	26.254	+ 0.300
	111	27.333	36.00	27.502	+ 0.169
	021	29.158	62.50	29.313	+ 0.155
	121	31.247	41.25	31.221	- 0.026
	211	38.534	62.00	33.654	+ 0.120
Sm doped AO (0.1M%)	110	14.045	100	16.341	+ 0.296
	101	25.954	22.22	26.401	+ 0.447
	111	27.333	33.23	27.356	+ 0.023
	021	29.158	96.00	29.361	+ 0.203
	121	31.247	56.55	31.183	- 0.064
	211	38.534	66.66	33.652	+ 0.188
Gd doped AO (0.1 M%)	110	14.045	26.00	14.252	+ 0.207
	101	25.954	30.31	26.154	+ 0.200
	111	27.333	100	27.701	+ 0.368
	021	29.158	41.85	29.582	+ 0.424
	121	31.247	44.00	31.501	+ 0.254
	211	38.534	54.45	33.852	+ 0.318

CONCLUSION

KDP doped with urea and ammonium oxalate doped with some rare earth impurities with different mole concentrations have been crystallized by the low temperature solution growth technique. X-ray powder diffraction study revealed that the impurities were adsorbed and distorted the crystal lattice. Variation of the lattice constant with doping concentration was found to satisfy the Vegard's law. For industrial application in the areas of laser technology, optical communication and data storage technology good quality single crystals free from any dislocations and defects are required. But the growth of perfect single crystal is extremely difficult. In reality, most crystals have a considerable amount of defects. In this connection, the present study presenting the 2θ, d-spacing and relative intensity values that will be helpful for any scientist interested in finding the lattice distortion in a laboratory grown crystals.

REFERENCES

1. Sasaki, T., Yokotani, A. (1990) *J. Crystal Growth* **99**, 820.
2. Vasilewskaya, A. S, Kuzentsova, I. S. Rez, I.S. Sonin, A. S., (1968) *Sov. Phys. Solid State* **10**, 733.
3. Izrailenko, R, Orlov, R. Yu and Kopson, V. A. (1968), *Sov Phys. Crystallogr.* **13**, 136.
4. Robertson, J. H. (1965), *Acta Cryst.* **18**, 410.
5. Lipson, H., Steeple, H.: Interpretation of X-ray powder diffraction patterns, Macmillan, New York, (1970)
6. Hendricks, S., B. (1927), *Amer. J. Sci.* **14**, 269.
7. Podder, J, Ramalingom, S, Kalkuara, S.N. (2001), *Cryst. Res. Technol.* **36**, 6, 551.

Table 5: Indexed powder diffraction data for pure and doped AO crystals

Samples	hkl	$2\theta_{cal}$(°)	I/I %	$2\theta_{exp}$(°)	Δ2θ
Pure AO	110	14.045	100	14.251	+ 0.206
	101	25.954	52.23	26.105	+ 0.151
	111	27.333	44.44	27.553	+ 0.220
	021	29.158	55.55	29.461	+ 0.303
	121	31.247	44.00	31.322	+ 0.075
	211	38.534	67.00	33.755	+ 0.221
La doped AO (0.1M%)	110	14.045	37.50	14.451	+ 0.406
	101	25.954	100	26.254	+ 0.300
	111	27.333	36.00	27.502	+ 0.169
	021	29.158	62.50	29.313	+ 0.155
	121	31.247	41.25	31.221	- 0.026
	211	38.534	62.00	33.654	+ 0.120
Sm doped AO (0.1M%)	110	14.045	100	16.341	+ 0.296
	101	25.954	22.22	26.401	+ 0.447
	111	27.333	33.23	27.356	+ 0.023
	021	29.158	96.00	29.361	+ 0.203
	121	31.247	56.55	31.183	- 0.064
	211	38.534	66.66	33.652	+ 0.188
Gd doped AO (0.1 M%)	110	14.045	26.00	14.252	+ 0.207
	101	25.954	30.31	26.154	+ 0.200
	111	27.333	100	27.701	+ 0.368
	021	29.158	41.85	29.582	+ 0.424
	121	31.247	44.00	31.501	+ 0.254
	211	38.534	54.45	33.852	+ 0.318

CONCLUSION

DP doped with urea and ammonium oxalate loped with some rare earth impurities with lifferent mole concentrations have been rystallized by the low temperature solution rowth technique. X-ray powder diffraction tudy revealed that the impurities were adsorbed nd distorted the crystal lattice. Variation of the attice constant with doping concentration was ound to satisfy the Vegard's law. For industrial pplication in the areas of laser technology, ptical communication and data storage echnology good quality single crystals free from ny dislocations and defects are required. But the rowth of perfect single crystal is extremely lifficult. In reality, most crystals have a onsiderable amount of defects. In this onnection, the present study presenting the 2θ, l-spacing and relative intensity values that will e helpful for any scientist interested in finding he lattice distortion in a laboratory grown rystals.

REFERENCES

1. Sasaki, T., Yokotani, A. (1990) *J. Crystal Growth* **99**, 820.
2. Vasilewskaya, A. S, Kuzentsova, I. S. Rez, I.S. Sonin, A. S., (1968) *Sov. Phys. Solid State* **10**, 733.
3. Izrailenko, R, Orlov, R. Yu and Kopson, V. A. (1968), *Sov Phys. Crystallogr.* **13**, 136.
4. Robertson, J. H. (1965), *Acta Cryst.* **18**, 410.
5. Lipson, H., Steeple, H.: Interpretation of X-ray powder diffraction patterns, Macmillan, New York, (1970)
6. Hendricks, S., B. (1927), *Amer. J. Sci.* **14**, 269.
7. Podder, J, Ramalingom, S, Kalkuara, S.N. (2001), *Cryst. Res. Technol.* **36,** 6, 551.