

Lattice variation and thermal parameters of gel grown KDP crystals added with some ammonium compounds

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Abstract. Pure and impurity added (with NH_4Cl , NH_4NO_3 , $\text{NH}_4\text{H}_2\text{PO}_4$, and $(\text{NH}_4)_2\text{SO}_4$) KDP single crystals were grown by the gel method using silica gels. X-ray diffraction data were collected for powder samples and used for the estimation of lattice variation and thermal parameters like Debye–Waller factor, mean-square amplitude of vibration, Debye temperature and Debye frequency. The thermal parameters do not vary in a particular order with respect to impurity concentration. The results obtained are reported and discussed.

Keywords. Impurity added KDP crystals; gel method; x-ray diffraction analysis; lattice parameters; Debye–Waller factors; Debye temperatures; Debye frequencies.

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1. Introduction

Potassium dihydrogen orthophosphate (abbreviated as KDP), KH_2PO_4 , belongs to the scalenohedral (twelve-sided polyhedron) class of tetragonal crystal system and has created considerable interest among several research workers. Although more sophisticated models are now available to determine the atomic vibration in crystals, the Debye model and the concept of Debye temperature are still useful. An efficient method of determining the Debye temperature is from the Debye–Waller factor that is obtained from the x-ray powder diffraction data [1]. As this method is suitable for any crystal system, it can be used to determine the Debye temperature for the KDP crystal.

A research programme on the growth and physical properties of pure and impurity added KDP crystal is on hand in this laboratory. As a part of the programme, Debye–Waller factors, Debye temperatures and Debye frequencies have been determined from x-ray diffraction intensities for pure and four ammonium compound impurity added KDP systems. $\text{NH}_4\text{H}_2\text{PO}_4$ having the common anion $(\text{H}_2\text{PO}_4)^-$ and NH_4Cl , NH_4NO_3 and $(\text{NH}_4)_2\text{SO}_4$ having no common ion with KDP are the impurities (added in the solution used for the growth of single crystals with impurity concentration in the range of 2000 to 10000 ppm, i.e. 0.2 to 1.0 mole %) considered in the present study. We report and discuss here the results obtained in our study.

2. Experimental

KDP crystals were grown in silica gels prepared from sodium metasilicate (SMS) by the reduction of solubility method. Analytical reagent (AR) grade samples of KDP, ammonium chloride [NH₄Cl], ammonium nitrate [NH₄NO₃], ammonium dihydrogen orthophosphate [NH₄H₂PO₄] (also called ADP) and ammonium sulphate [(NH₄)₂SO₄] along with double distilled water and ethyl alcohol were used.

KDP was added with NH₄Cl, NH₄NO₃, NH₄H₂PO₄ and (NH₄)₂SO₄ separately each in six different KDP: impurity molecular ratios, viz. 1 : 0.000 (pure KDP), 1 : 0.002, 1 : 0.004, 1 : 0.006, 1 : 0.008 and 1 : 0.010. The impurity was dissolved in 2.5 M solution of KDP.

SMS solution of density 1.08 g/cc was added to 2.5 M KDP solution in the volume ratio 1 : 4 (SMS : KDP). This prepared gel solution was then transferred to test tubes (of diameter 2.5 cm) (20 ml in each tube) and was allowed to set at room temperature. Gelation occurred in about 15 hrs. Then it was kept as such for one day for gel ageing. After that an equal volume of ethyl alcohol was added slowly above the gel and the test tubes were tightly closed with rubber corks to prevent evaporation of alcohol. Alcohol reduces the solubility of KDP, which first precipitates at the gel–alcohol interface. Diffusion of alcohol into the gel was followed by formation of nuclei, which then grew larger. Completion of crystallization took about 15 to 20 days. Scalenohedral morphology was exhibited by all the crystals grown.

It would be better if there is a possibility to estimate quantitatively the concentration level of the impurity that is present in each crystal. But, it is not easy since the impurities considered in the present study are ammonium compounds without any metal atom. Hence, in order to understand qualitatively (at least) whether the added impurity has entered into the KDP lattice or not, we have carried out the density measurement by using the floatation technique. It was observed that the difference in densities of crystals grown in the same container was very small and negligible.

X-ray diffraction data were collected from powder samples of crystals using an automated x-ray diffractometer (Ritz) with monochromated CuK_α radiation ($\lambda = 1.5418 \text{ \AA}$) and scintillation counter at a temperature of $25 \pm 1^\circ \text{ C}$ (scan speed = $0.02^\circ/\text{s}$; 2θ range: 10 to 70°). The reflections were indexed following the procedures of Lipson and Steeple [2]. Processing of the raw intensity data was done following the procedures of Warren [3]. Lattice parameters were determined from the indexed data using high angle reflections. Density and lattice parameters together with volume (V) values are presented in table 1.

As it was difficult to determine the impurity concentration in the crystal (quantitative estimation), no experiment was carried out to determine this. However, as the quantitative estimation was necessary for calculating the structure factor values, we followed an approximate method available in the literature [4] to do the same.

If X and Y are the initial concentration (g/100 cc) of A and B the final stoichiometry will be $(X - A_x) : (Y - A_y)$ where A_x and A_y are the solubilities of components A and B respectively.

If we simply use this relation, in the present study, we would get negative value for $(Y - A_y)$. So, in order to avoid this situation, we modified the above ratio as $(10000X - A_x) : (10000Y - A_y)$. The values obtained are expected to be reasonable ones and any inaccuracy, if present, will be negligible and the percentage error will be within the tolerance limit. The molecular weight and solubility in water (at 30° C) values [5] used are presented in table 2. The estimated impurity concentrations in the crystal are presented in table 3.

Table 1. Densities and lattice parameters of pure and impurity added KDP crystals.

System (impurity in mole %)	Density (g/cc)	<i>a</i> (Å)	<i>c</i> (Å)	<i>V</i> (Å ³)
Pure KDP	2.344	7.3930	7.0484	385.25
NH ₄ Cl added KDP				
0.2	2.341	7.4765	6.9069	386.09
0.4	2.332	7.4810	6.9326	387.99
0.6	2.309	7.5134	6.8783	388.28
0.8	2.249	7.5004	6.9260	389.64
1.0	2.178	7.5996	6.7704	391.03
NH ₄ NO ₃ added KDP				
0.2	2.330	7.5091	6.8529	386.41
0.4	2.321	7.5033	6.8764	387.17
0.6	2.313	7.4789	6.9742	390.09
0.8	2.280	7.4842	6.9947	391.79
1.0	2.240	7.4921	6.9980	392.81
NH ₄ H ₂ PO ₄ added KDP				
0.2	2.334	7.4925	6.9289	388.97
0.4	2.295	7.4888	6.9673	390.74
0.6	2.250	7.5224	6.9539	393.50
0.8	2.201	7.5401	6.9698	395.93
1.0	2.141	7.5075	7.0704	398.63
(NH) ₂ SO ₄ added KDP				
0.2	2.339	7.4810	6.9326	387.99
0.4	2.331	7.5133	6.8782	388.28
0.6	2.322	7.4888	6.9466	389.58
0.8	2.299	7.4809	6.9831	390.81
1.0	2.246	7.5328	6.9079	391.98

Table 2. Molecular weight and solubility data used.

Substance	Molecular weight	Solubility (g/100 g water)
KDP	136.09	28.0
NH ₄ Cl	53.49	41.4
NH ₄ NO ₃	80.04	242.0
ADP	115.03	46.4
(NH ₄) ₂ SO ₄	132.14	78.0

The mean Debye–Waller factors (*B*) were determined by the Wilson plot method [6]. For the calculation of structure factors, the atomic-scattering factors were taken from the literature [7,8]. For pure KDP crystal, the structure factor is

$$F = 4f_K + 8f_H + 4f_P + 16f_O = F_{\text{KDP}}$$

The density and lattice parameters show qualitatively that the impurity molecules have entered into the KDP lattice. The estimated impurity concentration in the crystal (see

Table 3. Estimated concentration (mole %) of impurities in the crystal.

Impurity substance	Impurity concentration (mole %) in the crystal for the KDP: Impurity molecular ratio taken in the solution used for the growth of crystal				
	1 : 0.002	1 : 0.004	1 : 0.006	1 : 0.008	1 : 0.010
NH ₄ Cl	0.066	0.145	0.224	0.302	0.381
NH ₄ NO ₃	0.047	0.164	0.282	0.399	0.517
ADP	0.155	0.324	0.494	0.663	0.832
(NH ₄) ₂ SO ₄	0.171	0.365	0.560	0.754	0.948

table 3) shows that the impurities are mainly occupying the interstitial positions. Moreover, the impurity concentrations considered in the present study are small. So, for impurity added KDP crystals, the impurity molecules are assumed to be added in the KDP lattice in the same amount (ratio) as estimated. Hence, for impurity added KDP crystals, the structure factors are:

$$F = F_{\text{KDP}} + P(4f_{\text{N}} + 16f_{\text{H}} + 4f_{\text{Cl}})$$

for NH₄Cl added KDP crystals;

$$F = F_{\text{KDP}} + P(8f_{\text{N}} + 16f_{\text{H}} + 12f_{\text{O}})$$

for NH₄NO₃ added KDP crystals;

$$F = F_{\text{KDP}} + P(4f_{\text{N}} + 24f_{\text{H}} + 4f_{\text{P}} + 16f_{\text{O}})$$

for NH₄H₂PO₄ added KDP crystals; and

$$F = F_{\text{KDP}} + P(8f_{\text{N}} + 32f_{\text{H}} + 4f_{\text{S}} + 16f_{\text{O}})$$

for (NH₄)₂SO₄ added KDP crystals. P is having the values of impurity concentration (mole % $\times 10^{-2}$, i.e. values provided in table 3 multiplied by 10^{-2}).

From the Debye–Waller theory

$$B = (6h^2/mkT)W(x),$$

where m is the mean atomic mass, T the absolute temperature at which the intensities are measured and h and k the Planck's and Boltzmann's constants respectively. The function $W(x)$ is given by

$$W(x) = [\phi(x)/x^2] + (1/4)x,$$

where $x = (\theta_{\text{D}}/T)$ and $\phi(x)$ is an integral. The values of $W(x)$ for a wide range of x are tabulated by Benson and Gill [9]. From the above equations Debye temperatures (θ_{D}) can be evaluated. The mean square amplitude of vibration (\bar{u}^2) can be obtained from [10]

$$B = 8\pi^2\bar{u}^2.$$

The Debye frequency (f_{D}) can be obtained from [11]

$$\theta_{\text{D}} = f_{\text{D}}(h/k).$$

3. Results and discussion

The density measured for pure KDP in the present study (2.344 g/cc) compares well with that reported (2.338 g/cc) in the literature [5]. For all the four impurities considered in the present study, the observed decrease of density of KDP crystal caused by the impurities indicates that the impurities have entered into the lattice of KDP crystals. Moreover, it can be seen that the density decreases further with the increase in impurity concentration of the aqueous solution of KDP used for the growth of crystals. Similarly, the observed increase of volume of KDP crystal caused by the impurities also indicates that the impurities have entered into the lattice of KDP crystals. The volume increases further with the increase of impurity concentration of the aqueous solution of KDP used for the growth of crystals.

In real crystals, the concentration of interstitials is expected to be of the order of $10^{15} - 10^{20} \text{ cm}^{-3}$, i.e., up to a maximum of 1% (here concentration of molecules is assumed as 10^{22} cm^{-3}). All the impurity substances considered in the present study are expected to occupy the interstitials. SO_4 is having a similar tetrahedral structure with PO_4 . So, in the case of $(\text{NH}_4)_2\text{SO}_4$ impurity, replacement of $(\text{H}_2\text{PO}_4)^-$ is also possible. ADP is isomorphous to KDP and forms solid solution (mixed crystal) with KDP.

In the present study, the estimated impurity concentrations (see table 3) show that the impurity concentration in the crystal is less for NH_4Cl and NH_4NO_3 impurities while it is highly significant for ADP and $(\text{NH}_4)_2\text{SO}_4$ impurities. This shows that, in the case of NH_4Cl and NH_4NO_3 impurities, the impurities are mainly occupying the interstitial positions whereas, in the case of ADP and $(\text{NH}_4)_2\text{SO}_4$ impurities, the impurities are occupying both interstitial and substitutional positions.

The values of B , \bar{u}^2 , θ_D and f_D are presented in table 4. No particular order was observed in the case of thermal parameters obtained, viz. B , \bar{u}^2 , θ_D and f_D with respect to impurity concentration. No comparison is made with other studies since there is no data available in the literature for the systems considered in the present study.

The Debye frequencies observed in the present study lie in the infrared range and that for the pure KDP ($3.512 \times 10^{12} \text{ s}^{-1}$ at 25°C) compares well with the frequency of the ν' mode ($2.5 \times 10^{12} \text{ s}^{-1}$ at 27°C) [12] assigned to oscillation modes of protons. This is one order of magnitude lower than that obtained by O'Keeffe and Perrino ($3 \times 10^{13} \text{ s}^{-1}$) [12,13] for the proton jump frequency and that found ($4 \times 10^{13} \text{ s}^{-1}$) [12] for oscillation frequencies of the P–O–H group in orthophosphates.

The dc electrical conductivity is easily calculated [14] to be

$$\sigma = Ne^2a^2/(kT\tau),$$

where τ is a mean jump time, perhaps different from that for dipolar orientation but still given by an equation like

$$\frac{1}{\tau} = \frac{1}{\tau_0} \exp\left(\frac{-E}{kT}\right),$$

where a is the distance of a jump. The factor $1/\tau_0 = \omega_0$ (nearly equal to $2\pi f_D$) is the ionic vibrational frequency around its equilibrium position and $\exp(-E/kT)$ is the statistical Boltzmann factor. A jump is attempted with each vibration, but only a fraction succeeds, depending on the (activation) energy E required in order to squeeze through the barrier to neighbouring equilibrium position. N stands for the number of perfect bond or the

Table 4. Thermal parameters of pure and impurity added KDP crystals.

System (impurity in mole %)	B (\AA^2)	\bar{u}^2 (\AA^2)	θ_D (K)	$f_D \times 10^{12}$ (s^{-1})
Pure KDP	7.151	0.091	188.5	3.512
NH ₄ Cl added KDP				
0.2	11.103	0.141	135.1	2.814
0.4	16.619	0.210	110.3	2.298
0.6	13.338	0.169	123.2	2.567
0.8	6.235	0.078	180.7	3.765
1.0	6.310	0.079	170.6	3.743
NH ₄ NO ₃ added KDP				
0.2	7.209	0.091	167.9	3.499
0.4	7.339	0.093	166.4	3.467
0.6	10.127	0.128	141.8	2.955
0.8	10.115	0.128	141.7	2.952
1.0	9.064	0.115	149.8	3.120
NH ₄ H ₂ PO ₄ added KDP				
0.2	3.243	0.041	251.7	5.244
0.4	7.189	0.091	168.3	3.506
0.6	17.723	0.224	106.9	2.228
0.8	8.647	0.109	153.5	3.198
1.0	9.783	0.123	144.3	3.007
(NH) ₂ SO ₄ added KDP				
0.2	9.745	0.123	144.3	3.007
0.4	7.314	0.093	166.9	3.477
0.6	6.289	0.079	180.3	3.757
0.8	9.162	0.116	149.2	3.110
1.0	7.671	0.097	163.4	3.404

number of charges per unit volume. The frequency $1/\tau_0 \approx 10^{13} \text{ s}^{-1}$. Also $1/\tau \leq 10^{-11} \text{ s}^{-1}$ and $1/\tau$ will be very much smaller than this at temperatures much below the melting temperature [14].

We have estimated the values of $1/\tau$ using the E values estimated from dc electrical conductivity measurements on the systems considered in the present study [15].

The values of E , $1/\tau_0$ and $1/\tau$ are presented in table 5. Since the present experimental temperature (25°C) is much below the melting temperatures ($>350^\circ\text{C}$), the values of $1/\tau_0$ and $1/\tau$ obtained in the present study compare well with those expected by the model. This shows that the values of thermal parameters determined in the present study for pure and ammonium compound impurity added KDP crystals are reasonable and valid.

4. Summary

Pure and ammonium compound impurity added KDP single crystals were grown by the gel method using silica gels. Lattice and thermal parameters like Debye–Waller factor,

Table 5. Values of E , $1/\tau_0$ and $1/\tau$ for pure and impurity added KDP crystals.

System (impurity in mole %)	E (eV) along		$1/\tau_0 \times 10^{13}$ (s^{-1})	$1/\tau \times 10^9$ (s^{-1}) along	
	a -direction	c -direction		a -direction	c -direction
Pure KDP	0.220	0.216	2.205	3.846	4.501
NH ₄ Cl added KDP					
0.2	0.222	0.211	1.768	3.106	4.767
0.4	0.291	0.269	1.444	0.173	0.407
0.6	0.309	0.277	1.613	0.096	0.333
0.8	0.300	0.279	2.365	0.199	0.451
1.0	0.325	0.311	2.352	0.075	0.129
NH ₄ NO ₃ added KDP					
0.2	0.217	0.233	2.198	4.692	2.516
0.4	0.213	0.242	2.179	5.434	1.756
0.6	0.213	0.242	1.856	4.631	1.497
0.8	0.211	0.267	1.855	5.001	0.565
1.0	0.210	0.266	1.961	5.496	0.621
NH ₄ H ₂ PO ₄ added KDP					
0.2	0.222	0.235	3.295	5.789	3.489
0.4	0.220	0.234	2.203	4.183	2.425
0.6	0.223	0.233	1.400	2.365	1.602
0.8	0.222	0.239	2.009	3.529	1.820
1.0	0.222	0.236	1.889	3.319	1.924
(NH) ₂ SO ₄ added KDP					
0.2	0.219	0.237	1.887	3.730	1.850
0.4	0.218	0.240	2.185	4.485	1.904
0.6	0.217	0.232	2.360	4.052	2.809
0.8	0.215	0.247	1.954	4.508	1.296
1.0	0.213	0.244	2.139	4.279	1.595

Debye temperature and Debye frequency were determined from X-ray powder diffraction data. Variation of density and lattice volume with impurity concentration indicates qualitatively that the impurity molecules have entered into the KDP lattice. No particular order was observed with the variation of thermal parameters with impurity concentration for all the four impurities considered in the present study. Estimation of mean jump frequency of free carriers using the Debye frequency and activation energy shows that the thermal parameters obtained in the present study are reasonable and valid.

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