Investigation of the metal ions effect on the growth of KDP crystal with emphasize on Al$^{3+}$ ions effect

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Abstract
Effect of Al$^{3+}$ ions on the optical quality, growth rate, shape, and structure of potassium dihydrogen phosphate (KDP) crystal was investigated. Growth method was based on the “point seed” method in a solution with optimum concentration, following spontaneous growth at room temperature. FTIR spectrum showed neutralization of O-H group in KDP crystal by Al$^{3+}$ ions. UV-Visible spectrum of the crystal containing Al$^{3+}$ displayed an undesirable increase of the optical absorption in the 200-300 nm region with a maximum at 270 nm. It seems that the absorption in the 200-300 nm region is due to substitution of phosphorus by Al ions. In fact, (AlO$_4$)$_2^-$ ions are present in the KDP crystals and give rise to ultraviolet absorption.

Keywords: KDP crystal, harmonic generations, growth rate, growth from solutions, impurity

1. Introduction
KH$_2$PO$_4$ or KDP is a tetragonal crystal at room temperature. It is soluble in water and shows piezoelectric property [1]. This crystal is mostly applied in the conversion of frequency in laser and for the frequency conversion applications from the near-infrared and visible to the ultraviolet. KDP crystal includes 2 growth faces (figure 1) [2]: prismatic (100) and pyramidal (101).

It is well known that impurity is one of the main effective factors in the growth, the shape, and the quality of KDP crystal. Control of impurity in the crystal growth process from solution is important from several view points such as stability of growth solution, interaction of host solution and impure ions, relative amount of impure and host ions in crystal structure, and crystallographic similarities between pure and impure crystals [1, 3].

Impurity can affect the rate of crystal growth. Ions impurity act on certain faces of crystal structure. Their effect depends on the concentration, super-saturation, temperature and solution pH [2]. The apparent growth rate of crystals from aqueous solution has been the subject of many theoretical researches [3, 4] and some theoretical predictions, precisely describe the effect of impurity on the crystal growth [3, 5].

In particular, trivalent metal cations (e.g. Al$^{3+}$, Fe$^{3+}$ and Cr$^{3+}$) are adsorbed only onto the (100) face and strongly prevent the crystal growth of (100) face and the crystal shape becomes more slender. This is the reason why K$^+$ cation and H$_2$PO$_4^-$ anion exist on (101) face and (100) face, respectively.

Inhibitor effect of impurity has already been analyzed by the Gaussian software. The affinity between various metals and crystal surface has also been clarified considering the electrostatic potential distribution of different impurities. In that line of research, some characteristics of the impurity effect of metal ions have been determined by ESP analysis. Through such an analysis, firstly, the reason for metal ion attacks on the (100) face of KDP crystal became clearer. Secondly, changes of impurity effect by pH were explained by ESP data for each component. Reasons for stronger impurity effect from trivalent metal ion than that from bivalent metal ion and also the stronger impurity effect of Al$^{3+}$ compared to Cr$^{3+}$ and Fe$^{3+}$ were explained through the averaged and the relative ESP values. As a result, the relative electrostatic potential distribution as a function of pH is considered useful for good understanding of impurity effect [6].

The importance of KDP crystal application in laser engineering is well known. The proper optical properties of KDP are mandatory for this application. Thus, it is important to identify and characterize all potentially harmful absorption bands in nonlinear optical crystals [7].
The most prominent unwanted optical absorption band in KDP has a peak near 270 nm. It is always accompanied by an additional peak near 210–215 nm. These broad bands are present in many KDP crystals and are usually taken as a measure of the purity of the crystal. In fast-growth material, they are always found to be large in the prismatic sector and much smaller in the pyramidal sector [8]. It has become common place to associate the 270 nm absorption peak with the presence of transition metal ions, and Fe$^{3+}$ is often the first candidate mentioned. Dieguez et al. [9] and Pritula and Velikhov [10] observed that the 270-nm band, and its related band at shorter wavelength, were significantly enhanced when a KDP crystal was doped during growth with Fe. Although not always stated, it is usually assumed that the majority of the Fe is present in the KDP crystals as Fe$^{3+}$ ions substituting for K$^+$ ions. Support for this assumption comes from the electron paramagnetic resonance (EPR) work of Tsuchida and Abe [11], where an Fe$^{3+}$ spectrum was observed and characterized in a doped KDP crystal.

Garaces et al. [7] described the results obtained in their study of a KDP crystal doped with 5 ppm of Fe. The 270-nm absorption peak and the Fe$^{3+}$ EPR spectrum were monitored both before and after an X-ray irradiation at room temperature, and then during thermal annealing up to 1508°C after the irradiation. The behavior of the two spectral features did not correlate, which led them to suggest that Fe may occupy more than one site in the KDP crystal. In particular, they proposed that much of the Fe in these crystals would substitute for phosphorus, and they attributed the absorption band near 270 nm to (FeO$_4$)$^{2-}$ molecular units.

2. Method

In this research, “point seed” method in solution with a definite concentration was applied for spontaneous growth of the crystal at room temperature. The growth from solution was examined in different containers of varied sizes and shapes. Ultimately, the crystals were found to be better formed in cylindrical containers with a volume of 100 ml, cross-section diameter of 3.5 cm, and height of 13 cm. Special shapes of these containers provided us with the possibility of having a cross-section of optimal evaporation. In fact, we considered the fact that in ordinary vessels with wide cross-section for evaporation, formation of tiny-grained crystal sediments at the bottom, which is known to be a preventive factor, would be inevitable. A KDP solution of varied concentrations was prepared for the test and finally growth solution concentration of about 25 gr of KDP in 100ml of H$_2$O was selected since it would provide a maximum concentration and cause minimum undesirable seeding in our test. However, different concentrations can be used for various tests. To reach a steady solution, the mixture was stirred during 24 hours. For minimizing undesirable impurity, the solution was refined by a vacuum filter. The seeds were prepared from a super-saturated solution using spontaneous growth method. For a more precise comparison, seeds must be selected in approximately identical sizes and shapes and placed on the growth plane (application of a surface in which the middle of the solution does not lie at the bottom of the vessel while the primary seed is located over it) in the solution.

3. Results and discussion

3.1. Effect of impurity on the apparent growth

Comparative effect of Fe$^{3+}$ and Al$^{3+}$ ions to that of Cu$^{2+}$ is presented in figure 2. In order to investigate the effect of other trivalent metal ions on the Growth of KDP Crystal and compare it with that of Al$^{3+}$ ions effect, Fe(NO$_3$)$_3$, and Cu(NO$_3$)$_2$ were used as Fe and Cu ion precursors. Figure 2 illustrates a comparison of the effect of Cu$^{2+}$, Fe$^{3+}$, and Al$^{3+}$ ions on the apparent growth of KDP crystal. These crystals were grown under the above-mentioned conditions in aqueous solution of KDP (25 gr KDP/100ml H$_2$O) with 0.001 wt% of Al(NO$_3$)$_3$, Fe(NO$_3$)$_3$, and Cu(NO$_3$)$_2$ as impurity during 9 days.

Presence of positive metal ions in KDP solution increases the growth of pyramidal faces and prevents the growth of prismatic faces. For this reason, the crystal undergoes a longitudinal growth and takes a needle shape. This shape confirms theoretical evaluations of the effect of positive metal ions on each surface very well [6].

3.2. Effect of impurity amount on growth process

Control of impurity percentage in growth solution is one of the major effective factors in crystal growth. Thus, amount of impurity can increase, decrease, or completely stop crystal growth. In our experiments, metal ions present in the solution caused a considerable decrease of the growth process of prismatic face. In this part, we used a higher concentration of KDP solution to have a better comparison. Figure 3 presents a good comparison of crystals grown from aqueous solutions of KDP (34 gr KDP/100 ml H$_2$O) with different amounts of impurity of Al$^{3+}$ ions during a 5-day period.

In figure 3(a), the crystal nearly shows a spontaneous growth. With the increase of the amount of impurity, the effect would be more evident. In figure 3(b) and 3(c), growth of prismatic faces are completely stopped and even a negative process is observed with crystals narrowing with sharp points. With further increase of the amount of impurity, the single crystals are developed to poly crystals in such a way that in figure 3(d), they are seen to grow as a series of adjacent needle-shaped crystals attached together. Finally, in figure 3(e) growth is nearly stopped by the great amount of impurity.
3.3 Dependence of growth rate on Al$^{3+}$ solution impurity

Single crystals of pure and doped KDP under the above-mentioned conditions in 0.001 wt% of Al(NO$_3$)$_3$ doped KDP solution were grown from aqueous solutions of KDP (25 gr of KDP/100 ml of H$_2$O) during 10 days (figure 4).

The experimental data of KDP crystals grown in the presence of Al$^{3+}$ ions illustrate the effect of impurity on the growth rate of different faces of KDP crystals (table 1).

Positive metal ions are attracted by prismatic faces and prevent its growth to a great degree. By addition of Al$^{3+}$ ion to the solution, the mean growth rate increases along the [001] direction while it remains almost constant or decreases along the [100] direction. A similar effect of Fe$^{3+}$ and Cr$^{3+}$ on the growth rate of KDP crystals has been reported previously [2, 12]. Different types of models describing the adsorption process and growth reduction have been reported, too [1, 3-5].

As shown in table 1 and figure 4(b), the decrease in growth rate of the (100) face of KDP crystal should be a kinetic effect involving a reduction in the value of the kinetic coefficient for the motion of steps [3, 4]. An increase in the growth rate along the [001] direction of KDP crystals may be attributed to a decrease in the free energy of the face (thermodynamic effect), which decreases with an increase in impurity concentration [13].

The above discussion suggests that, besides other factors, the kinetic or thermodynamic effect depends on the structure of crystal face, i.e. atomic arrangement. To explain the growth of impurities in detail, one needs to collect more experimental data, including the data on the micromorphology of crystal surfaces as well as growth kinetics.

3.4 FT-IR spectral studies

In FTIR spectrum of a pure KDP, a wide optical absorption band in the 2500-3700 cm$^{-1}$ region is observed, which is attributed to O-H bond vibration. Therefore, the peak broadening in this range suggests the presence of a hydrogen bond in the crystal [14]. Since changes in O-H bond provide a wide absorption band, general reduction of absorption intensity in
Figure 5. FTIR spectrum of pure KDP and KDP doped with 0.003 wt% of Al(NO₃)₃ and 0.015 wt% of Al(NO₃)₃ as impurity.

Table 2. IR absorption frequencies of KDP reported previously and obtained in this work from pure solution of KDP and from the solution of KDP with 0.003 wt% of Al(NO₃)₃ and 0.015 wt% of Al(NO₃)₃ as impurity.

<table>
<thead>
<tr>
<th>IR frequencies observed (cm⁻¹)</th>
<th>Assignments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Free O–H stretching hydrogen bonded of KDP</td>
<td>3401</td>
</tr>
<tr>
<td>P–O–H symmetric stretching</td>
<td>2775</td>
</tr>
<tr>
<td>P–O–H bending of KDP</td>
<td>1630</td>
</tr>
<tr>
<td>H₂O bending</td>
<td>1630</td>
</tr>
<tr>
<td>P=O stretching of KDP</td>
<td>1298</td>
</tr>
<tr>
<td>P–O stretching of KDP</td>
<td>1100</td>
</tr>
<tr>
<td>P–O–H stretching of KDP</td>
<td>908</td>
</tr>
<tr>
<td>HO–P–OH bending</td>
<td>534</td>
</tr>
</tbody>
</table>

The FTIR spectra of all the samples were recorded by KBr pellet technique on a Spectrum-100 model spectrophotometer using 1064 nm output of a cw diode pumped Nd:YAG laser as a source of excitation in the region 450–4000 cm⁻¹.

FTIR spectrum was obtained from pure KDP and KDP + 0.003 wt% of Al(NO₃)₃ and KDP + 0.015 wt% of Al(NO₃)₃ samples from a solution of 34 gr of KDP in 100 ml of H₂O (figure 5). Comparison of IR absorption frequencies from literature with those of present investigation are outlined in table 2.

As in KDP crystals grown by K₂CO₃ and KSCN impurities [14, 15], the FTIR spectrum of KDP crystal grown by Al(NO₃)₃ impurity shows a slight decrease in intensity for all the peaks. This is attributed to the neutralization of acidic O-H group of KDP by Al(NO₃)₃.

Drastic changes occurred for the peaks in the spectrum of 0.015 wt%Al(NO₃)₃ doped KDP. Hence the O-H groups might be much more neutralized than in 0.003 wt%Al(NO₃)₃ doped KDP.

3. 5. UV-Visible spectral studies

For application in fusion lasers, the third and fourth harmonics would also gain a special importance. For example, the 1064 nm fundamental of an Nd: YAG laser can be converted to its 355 nm third harmonic or its 266 nm fourth harmonic by using KDP crystals. The performance of these frequency conversion devices can be seriously degraded if there are defect-associated absorption bands in the crystals which overlap the fundamental pump wavelength or one of the output wavelengths. Thus, it is important to identify and characterize all potentially harmful absorption bands in nonlinear optical crystals [7].

Therefore, quality and optical absorption of UV region and its vicinity would find a special significance. The UV-Visible spectra of all the samples were recorded from solid phase samples on a Lambda45 model spectrophotometer in the region 200–800 nm.

In figure 6, absorption spectrum in the UV-Visible region is observed for surface (100) of pure KDP crystal.
Figure 6. absorption spectrum of UV-Visible region for surface (100) of (a) pure KDP crystal and (b) KDP + 0.001 wt% Al(NO$_3$)$_3$.

and KDP crystal grown in a KDP solution (25 gr of KDP in 100 ml of H$_2$O) with 0.001 wt% of Al(NO$_3$)$_3$ salt. The crystal consisting of Al$^{3+}$ impurity has an additional absorption in the 200-350 nm regions with a peak at 270 nm. The crystal with Al$^{3+}$ impurity displayed an additional absorption in the 200-350 nm regions. Maximum unwanted optical absorption appears at 270 nm due to the replacement of K$^+$ by Al$^{3+}$ in the crystal lattice. Optical absorption of Fe ions in KDP crystal also presents absorption peak exactly at 270 nm and it has been suggested that (FeO$_4$)$^{2-}$ molecular units are present in the KDP crystals and give rise to ultraviolet absorption [7]. For the same reason, we also suggest a considerable part of Al$^{3+}$ ions in KDP crystal can be inserted in (PO$_4$)$^{2-}$ units to offer (AlO$_4$)$^{2-}$.

4. Conclusions

Additive Al(NO$_3$)$_3$ was added to KDP solution, and KDP crystals, pure and doped with Al additive of different concentrations were grown by “point seed” method at room temperature. By addition of Al$^{3+}$ ion to the solution, the mean growth rate increases along the [001] direction and decreases along the [100] direction. The FTIR spectrum of KDP crystal grown by Al(NO$_3$)$_3$ impurity shows a slight decreases in intensity for all the peaks. This is attributed to the neutralization of acidic O-H group of KDP by Al(NO$_3$)$_3$. Neutralization of O-H groups by Al(NO$_3$)$_3$ might be the cause for enhanced NLO(nonlinear optical) property, as electron delocalization is much more enhanced than pure KDP. The absence of additional absorption in the UV-Visible spectrum of Al(NO$_3$)$_3$ doped KDP in the 200-350 nm regions by a peak exactly at 270 nm can be due to the fact that a considerable part of Al$^{3+}$ ions in KDP crystal can be inserted in (PO$_4$)$^{2-}$ units to offer (AlO$_4$)$^{2-}$.

References