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Influence of Co-Doped Bimetallic Impurities on the Metastable Zone Width and Induction Period for Nucleation of KDP from Aqueous Solutions

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Abstract: The results of the influence of co-doped bimetallic Mg(II)-Ni(II), Mg(II)-Co(II), Mg(II)-Li(I) impurities on metastable zone width and induction period for the nucleation of KDP crystals are discussed in this study. In order to grow bulk crystals with faster growth rates along all the crystallographic directions, the solubility, metastable zone width, induction period and interfacial energy etc., are necessary to know to optimize the growth conditions. Metastable zone width, induction period and interfacial energy have been determined. Interfacial energy has been estimated using the experimentally determined induction period values based on the classical nucleation theory for a spherical nucleus. The presence of co-doped bimetallic Mg(II)-Ni(II), Mg(II)-Co(II), Mg(II)-Li(I) impurities is found to enhance the metastable zone width, induction period, interfacial energy and also minimizes the formation of secondary nucleation. This phenomenon may be attributed due to the absorption of impurities on the surfaces of the growing nuclei.

Key words: NLO crystal, solubility, growth kinetics, absorption

INTRODUCTION

Potassium Dihydrogen Phosphate (KDP) crystals exhibit excellent electro optical and nonlinear optical properties and are commonly used in several applications such as frequency conversions, laser fusion and electro optical modulation (Kahr and Gurney, 2001; Sasaki and Yokotani, 1990). The easy growth of large single crystals, a broad transparency range, a high optical damage threshold and a relatively low production cost make this phosphate crystal very much attractive and well suited to a variety of optical applications. Many studies on the growth kinetics of KDP crystals in the presence of impurities have been reported (Dam and Van Enckevolt, 1981; Rashkovich, 1991; Alexandru *et al*., 1996; Kuznetsov *et al*., 1998; Kubota *et al*., 2000; Sangwal and Palczynska, 2000; Podder, 2002). In many cases, a small amount of impurities (viz $10^{-9}<x<10^{-3}$ mole concentration) may affect nucleation kinetics in aqueous solutions (Shanmugam *et al*., 1984).

The solubility study of KDP with Ni^{3+} and Mg^{2+} were performed by Fu *et al*. (2000). They observed that the solubility decreased marginally which is attributed to the addition of impurities. The effect of divalent and trivalent impurity ions on the growth kinetics and

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surface morphology of KDP crystals was studied by Eremina *et al.* (2005). They found that divalent impurity ions are incorporated at the surface crystal layer more strongly into the kink sites than trivalent ions and cations like $Co^{2+}$and Ni^{2+} may form both isolated and interstitial defect centers. The optical and structural characterization of KDP in presence of bimetallic Ni^{3+}-Mg^{2+} was studied by Claude *et al.* (2006). So far our knowledge is concerned; the study of induction period and the interfacial energy of KDP in presence of Mg(II) along with the combination of Ni(II), Co(II) and Li(I) ion has not yet been performed. It is expected that the introduction of bimetallic dopants may promote the nucleation behavior by chemical complexions. Mg(II) as a smaller cation has a stronger interaction with water molecules in the coordination sphere and Mg(II) combined with transition metal cations like Ni(II), Co(II) and Li(I) might play an important role in modifying the growth behavior. The value of the metastable zone width, induction time and effect of impurities on it could give information in designing the crystallization processes. The aim of this study is to see the influence of bimetallic impurities on the growth phenomenon and to report the results of metastable zone width and induction period for the nucleation of KDP from aqueous solution containing bimetallic cations Mg(II)-Ni(II), Mg(II)-Co(II), Mg(II)-Li(I) in molar ratios 1:0.005:0.005, respectively.

MATERIALS AND METHODS

Analar grade KDP with purity 99% (E-Merck), $MgSO_4 \cdot 7H_2O$, $CoSO_4 \cdot 7H_2O$, $NiSO_4 \cdot 7H_2O$ and $LiSO_4 \cdot H_2O$ impurities and double distilled water were used for the preparation of solutions for experimental purposes. The solubility of KDP was determined at different fixed temperatures between 30 and 50°C by adding small amounts of KDP solute till complete dissolution at a preselected temperature maintained with an accuracy of ±0.01°C. This study was conducted in the Crystal Growth Lab., Department of Physics, Buet, Dhaka in December 2008. It was found that KDP solubility determined by this method agrees well with that reported in the literature (Mullin, 1992) and addition of impurities at concentrations used in this study (i.e., about 0.12 g for 0.005 mole concentration of Mg, 0.14 g of Ni and Co and 0.07 g of Li for 0.005 mole concentration) practically does not change the KDP solubility.

Metastable zone width of KDP in aqueous solutions was determined by conventional polythermal method (Nyvlt *et al.*, 1985). Solutions of pure KDP, Mg(II) doped KDP, Mg(II)-Ni(II) doped KDP, Mg(II)-Co(II) doped KDP and Mg(II)-Li(I) doped KDP saturated at different temperatures T_0 (viz., 30, 35, 40, 45 and 50°C) were prepared in accordance with the solubility data. The experiments were carried out using 100 mL solutions contained in 200 mL Pyrex glass beakers covered with polyethylene papers in a constant temperature bath maintained with an accuracy of ±0.01°C. The saturated solution was first preheated to 5°C above the saturated temperature for homogenization and the solution was maintained at the superheated temperature for 1 h before cooling at the rate of 5°C h^{-1} from the overheated temperature. The solution was continuously stirred using a Teflon-coated magnetic stirrer to ensure homogeneous concentration. The temperature T_{lim} at which the first visible nuclei were observed by the naked eye in the beakers was taken as the limit of the metastable zone. The temperature difference $\Delta T_{max} = (T_0 - T_{lim})$ was taken as the metastable zone width of the system. The ΔT_{max} data corresponding to every saturation temperature T_0 represent an average of 3 values.

Induction period is defined as the time of observation in between the creation of supersaturation and the formation of critical nuclei, of pure KDP, KDP: Mg(II), KDP: Mg(II)-Ni(II), KDP: Mg(II)-Co(II), KDP: Mg(II)-Li(I) solutions was determined at 30°C by

means of isothermal method (Nyvlt *et al.*, 1985). One hundred milliliter aqueous solutions with supersaturation ratios of 1.03, 1.05, 1.07, 1.09 and 1.11 were taken in 200 mL Pyrex glass beakers at a higher temperature. After the temperature of a solution reached the experimental temperature of the bath, the time period for the appearance of first bright nuclei seen by the naked eye at the bottom of the beakers was recorded.

RESULTS

Metastable zone width, the solubility curve and the metastability limits of pure and bimetallic doped solutions for different saturation temperatures are shown in Fig. 1. The maximum supercooling ΔT_{max} for all the solutions decrease with an increase in saturation temperature T_0 and addition of different bimetallic dopants enhances the metastable zone width of KDP solutions for all temperatures are shown in Fig. 2.

The data of induction period as a function of separation lnS are shown in Fig. 3. It may be seen that the induction period τ rapidly decreases with an increase in lnS. The above data were analyzed according to the classical theory of 3-dimensional nucleation. According to

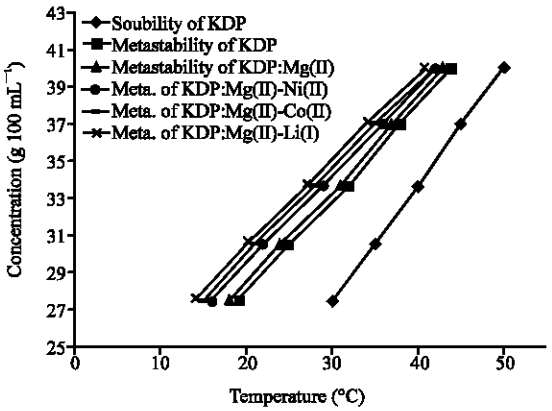

Fig. 1: Solubility and metastability limit curves for pure and different bimetallic doped KDP as a function of temperature

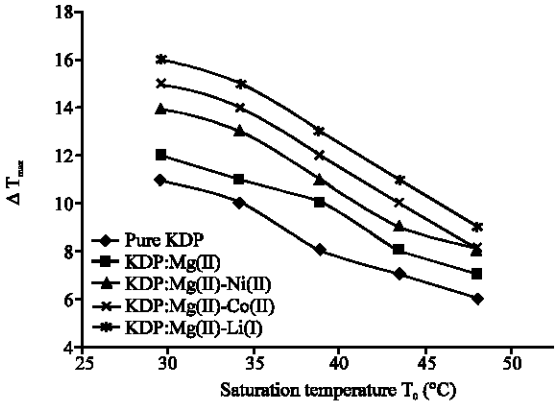

Fig. 2: Dependence of maximum supercooling ΔT_{max} on saturation temperature T_0 for KDP solutions in the presence of different bimetallic impurities

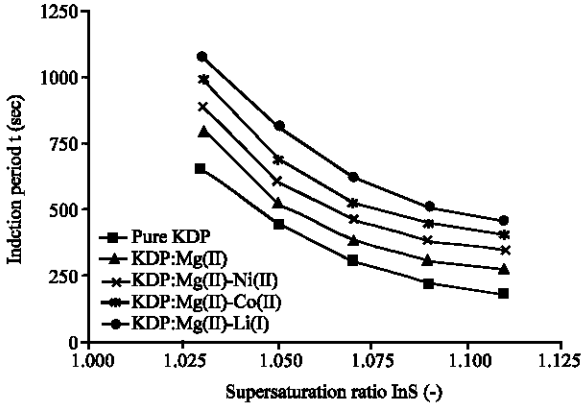

Fig. 3: Dependence of induction period τ on supersaturation ln$S$ for different impurities

the classical nucleation theory, the rate of formation of spherical nuclei (the number of nuclei formed per unit time per unit volume) is given by Eremina *et al.* (2005) and Nyvlt *et al.* (1985):

$$J = A \exp\left[-\left(\frac{16\pi}{3}\frac{\sigma^3 v^2}{(kT)^3(\ln S)^2}\right)\right] \tag{1}$$

where, the pre-exponential factor A is connected with the integration of growth units for the formation of spherical nuclei and σ is the free energy of crystal-solution interface, v is the molecular volume, k is the Boltzmann constant, T is the temperature in Kelvin and $16\pi/3$ is the shape factor for spherical nuclei.

According to Eq. 1, at a given supersaturation for a system, nucleation rate J decreases with a decrease in the pre-exponential factor A and increase in the interfacial energy σ.

Assuming that the induction period is inversely proportional to the nucleation rate J, one obtains transition has been calculated using the induction period (Eremina *et al.*, 2005; Nyvlt *et al.*, 1985):

$$\ln \tau = C + \left[\frac{16\pi}{3}\left(\frac{\sigma v^{2/3}}{kT}\right)^3\right]\frac{1}{(\ln S)^2} \tag{2}$$

where, the constant C includes the constant A of Eq. 1 and the proportionality constant relating between τ and J.

Equation 2 predicts that a linear plot of lnτ against $1/(\ln S)^2$ with intercept C and slope m given by the term included in the square bracket of Eq. 2. From the slope m one gets the interfacial energy.

$$\sigma = \frac{0.39kT}{v^{2/3}} m^{1/3} \tag{3}$$

Figure 4 shows the plots of lnτ against $1/(\ln S)^2$ for different solutions containing the impurities. It may be noted that the slope m of these plots steadily decreases with an increase in $1/(\ln S)^2$. These values are shown in Table 1.

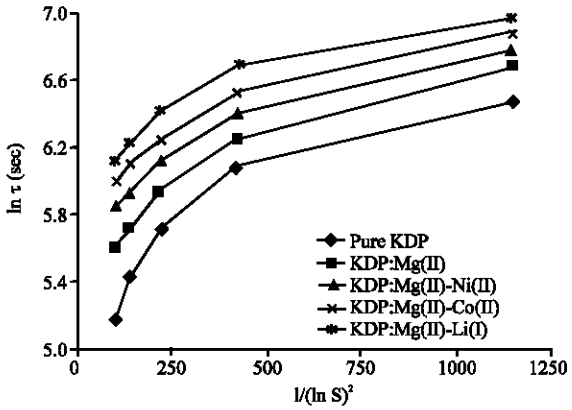

Fig. 4: Plots of lnτ against $1/(\ln S)^2$ for KDP solutions without and with different bimetallic impurities

Table 1: Values of interfacial energy σ for different systems

	Interfacial energy σ (mJ m^{-2})	
System	Homogeneous nucleation	Heterogeneous nucleation
Pure KDP	1.0840	0.6275
KDP:Mg(II)	1.0950	0.6516
KDP:Mg(II)-Ni(II)	1.0174	0.6261
KDP:Mg(II)-Co(II)	0.9316	0.6149
KDP:Mg(II)-Li(I)	1.0331	0.5659

DISCUSSION

The solubility of KDP determined by our method agrees well with that reported in the literature (Mullin, 1992) and addition of impurities at concentrations used in this study (i.e., about 0.12 g for 0.005 mole concentration of Mg, 0.14 g of Ni and Co and 0.07 g of Li for 0.005 mole concentration) practically does not change the KDP solubility. It is observed from the results that the zone widths for all the solutions decrease as the temperature increases. At the same time, addition of different bimetallic dopents enhances the metastable zone width of KDP solutions for all the temperatures and makes KDP solution more stable. It was also observed during the experiment that the number of tiny crystals formed in solutions by spontaneous nucleation was appreciably reduced in the presence of different bimetallic impurities. This is because the metal ion suppresses the activities of heterogeneous nucleation.

The dependence of ΔT_{max} on T_0 has been reported for different systems. The KDP aqueous solutions containing different organic and inorganic impurities (Dhanaraj *et al*., 2008; Shimamura and Suzuki, 1989) indole-3-aldehyde in different organic solvents (Haja *et al*., 2003) and potassium tetraborate tetrahydrate in water (Sahin *et al*., 2007). It is found that, with a decrease in T_0, ΔT_{max} increases in some cases; it decreases in others while it remains practically constant still in others. Although, these trends are known, no satisfactory explanation has been reported so far. However, the increase in ΔT_{max} caused by additives in a system may be attributed to the inhibition of growth of nuclei to visible dimensions i.e., impurities lead to an increase in the induction period τ for nucleation. The latter observation of decrease in the number of nuclei in the presence of impurities, on the other hand, implies that impurities lead to a decrease in the nucleation rate J as a result of

increase in the interfacial energy or a decrease in the rate of integration of growth units in the presence of impurities due to their adsorption on the surfaces of the growing nuclei.

This type of behavior of plots of $\ln\tau$ against $1/(\ln S)^2$ is frequently observed for pure solutions as well as solutions containing deliberately added impurities to supersaturated solutions of various compounds (Eremina *et al*., 2005; Shanmugam *et al*., 1984; Sohnel and Mullin, 1982). The main cause of this behavior is that heterogeneous nucleation occurs practically in every system at low supersaturation (i.e., high $1/(\ln S)^2$) due to the presence of trace amounts of different impurities inherently present in the solute used for the preparation of starting solutions for induction period measurements (Hao *et al*., 2005; Shanmugam *et al*., 1984; Sohnel and Mullin, 1982). However, homogeneous nucleation occurs only at high supersaturation (i.e., low $1/(\ln S)^2$). Consequently, the slopes m of the plots of $\ln\tau$ against $1/(\ln S)^2$ were obtained for $100<1/(\ln S)^2<240$, i.e., $0.1>\ln S>0.07$ and for $450<1/(\ln S)^2<1150$, i.e., $0.05>\ln S>0.03$ Taking the values of $k = 1.38\times10^{-23}$ J·K^{-1}, T = 303 K, $\nu = 0.96445\times10^{-30}$ m^3 and m from Fig. 4 in the intervals of lnS values corresponding homogeneous and heterogeneous nucleation, values of the interfacial energy σ were calculated.

As seen from Table 1, the values of interfacial energy σ remain practically almost constant in the presence of different impurities in the high and low supersaturation regions and do not depend on the type of impurities. This means that for the impurities investigated in this study the decrease in the nucleation rate J by the impurities is caused by decrease in A which is associated with the hindered integration of growth units to the aggregating stable nuclei. Physically, this process of inhibition may be attributed to the competition of growth units and impurity ions for the sites (i.e., kinks) available on the surfaces of the growing nuclei.

CONCLUSION

The effect of co-doped bimetallic Mg(II)-Ni(II), Mg(II)-Co(II), Mg(II)-Li(I) impurities on the growth of KDP from supersaturated solutions has been investigated experimentally by measuring the metastable zone width, the induction period and interfacial energy. The presence of co-doped bimetallic impurities in KDP solution was found to increase significantly the metastable zone width and the induction period. All the bimetallic cations selected in this article appreciably reduced the formation of tiny crystals by spontaneously nucleation and also leads to decrease the nucleation rate. This phenomenon may be attributed due to incorporation of cations like Mg(II), Ni(II), Co(II) and Li(I) into the kinks sites. This study would be useful in growing good quality bulk KDP crystals from aqueous solutions with faster cooling rate due to larger metastable zone width obtained in the presence of transition metals (like nickel, cobalt) and lithium ions along with magnesium. Further studies viz., structural, optical and thermal are in progress and to be reported soon.

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