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## Investigations on the Nucleation Thermodynamics of RbTiOXO<sub>4</sub> (X= P or As) Crystals Grown from High Temperature Solution

The nucleation thermodynamics of RbTiOXO<sub>4</sub> (where X= P or As) family crystals crystallizing from high temperature solution using the phosphate and tungstate solvents have been studied. Using the regular solution model and classical nucleation theory the nucleation thermodynamical parameters like interfacial energy, chemical potential, free energy change, critical energy barrier and radius of critical nucleus have been calculated which leads to better understanding of the nucleation process. Comparative study has also been made to investigate the metastable zone width of the above family crystals grown from different fluxes.

Keywords: RTP, RTA, flux, high temperature, nucleation

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### 1. Introduction

Potassium titanyl phosphate (KTP), Rubidium titanyl phosphate (RTP), Potassium titanyl arsenate (KTA) and Rubidium titanyl arsenate (RTA) crystals have been identified as the most attractive nonlinear optical materials (CHENG and BIERLEIN). Their large value of NLO coefficient and high optical damage resistance make them useful for second harmonic generation and optical parametric oscillation (BIERLEIN and VANHERZEELE). The lower value of ionic conductivity and dielectric loss of Rubidium titanyl phosphate and Rubidium titanyl arsenate crystals compared to Potassium titanyl phosphate and potassium titanyl arsenate crystals play a key role to make them as alternative candidates for Quasi Phase Matching (QPM) based devices (KARLSSON et al.) and electro-optical applications. Due to these excellent characteristics, many researches are being concentrated in the growth and device fabrication of these family crystals. Though these crystals are grown by both hydrothermal and high temperature solution growth technique using self-flux (OSELEDCHIK et al.; CHENG et al. (1994); HAN et al.; BOLT et al.) and/or tungstate solvents (CHENG et al.(1991)), the latter method has been followed by many workers due to its added advantages like faster growth rate and the absence of OH ions into the grown crystal lattices. It is well known that in tungstate and molybdate fluxes, which are less viscous, faster dissolution kinetics and low temperature solvents make crystal growth easy. However, incorporation of metal ions (W and Mo) into the crystal lattices which cause optical loss (YOKATANI et al.) and reduction of optical damage resistance (LOIACONO et al.) of the crystal are inevitable problems. In spite of

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phosphate and arsenate fluxes (self fluxes) having higher viscosity and lower dissolution kinetics, these solvents are found to be suitable for the growth of RTP and RTA crystals (CHENG et al. (1994)) because of the absence of metal ions into the crystal lattices. Besides, the growth of large size crystals is difficult due to the inherent properties namely high viscosity, lower solubility and supercooling value (less than KTP) may lead to the formation of spurious nucleation and solution incorporation into the growing crystals. In order to grow good quality crystals in larger size for device applications, detailed study of some other important parameters is necessary.

Solubility data play a vital role in finding these parameters. There are few reports available on the solubility studies of RTP and RTA crystals grown from self-fluxes (phosphate and arsenate) (OSELEDCHIK et al.; CHENG et al.(1994).; HAN et al.) and tungstate flux (CHENG et al.(1991)). Nevertheless, to the knowledge of the authors, no report on metastable zone width for crystal-solvent system is available which is one of the important key parameters for fixing the growth conditions. As the experimental observation of metastable zone width in high temperature solution seemed to be very difficult and time consuming process, theoretical approach is the best choice. Bearing this in mind, present study has been focussed to calculate the nucleation thermodynamical parameters such as interfacial energy and chemical potential of crystal-solvent systems with the help of available solubility data (CHENG et al. (1994), CHENG et al.(1991)) According to the assumption of regular solution model the nucleation process is considered to be homogeneous in nature and in the nucleation process solid and liquid phases coexist together. Also the nucleation process and growth mechanism involved in the growth of RTP/RTA crystals from high temperature solution growth are similar to the low temperature solution growth process. Metastable zone width value of RTP and RTA crystals grown from different solvents has been calculated using the regular solution model and a comparative study has also been made.

## 2. Thermodynamics of nucleation

### 2.1. Driving force for nucleation

In solution growth, the change in Gibbs free energy between the crystalline phase and surrounding mother phase due to supersaturation results in crystallization. Based on the thermodynamical approach, the change in Gibbs energy can be written as

$$\Delta G = \Delta H - T\Delta S \quad (1)$$

where H is the enthalpy and S is the entropy and T is the temperature.

At the melting point  $T = T_m$ ,  $\Delta G = 0$

The change in bulk energy per unit volume is

$$\Delta G_v = \frac{\Delta H \Delta T}{v T_m} \quad (2)$$

where  $\Delta T = (T_m - T)$  is supercooling and  $v$  is the specific volume of the solute particle.

The above equation can be modified as

$$\Delta G_v = \frac{RT}{v} \ln \left( 1 + \frac{\Delta H_s \Delta T}{RT^2} \right) \text{ Since } \frac{\Delta H_s \Delta T}{RT^2} \leq 1 \tag{3}$$

$$\Delta G_v = \frac{RT}{v} \ln s \tag{4}$$

where  $s = 1 + \frac{\Delta H_s \Delta T}{RT^2}$

A supersaturated solution is usually in non-equilibrium state, though it is at constant temperature and pressure. The formation of new crystalline phase with small clusters of molecules called embryos attains the thermodynamically equilibrium condition by losing certain amount of its energy. As this embryo has the volume and surface energies, the total Gibbs free energy change associated with the process of homogeneous nucleation can be written as

$$\Delta G = \Delta G_s + \Delta G_v \tag{5}$$

Where  $\Delta G_s$  is the excess surface free energy and  $\Delta G_v$  is the excess volume free energy which is related to the change in chemical potential ( $\Delta m = \Delta G_v \cdot v$ , where  $v$  is the specific volume) between the crystalline phase and the surrounding mother phase. Since the embryo is assumed to be of spherical shape and containing  $i$  no of growth units,

$$\Delta G = A i^{2/3} + B i \tag{6}$$

Where  $A = (4p)^{1/3} (3v)^{2/3} s$ ,  $B = v \cdot \Delta G_v$  where  $v$  is the specific volume of the solute molecule and  $s$  is the interfacial energy.

### 2.2. Enthalpy of the solution

Following the Arrhenius equation, the solubility data of RTP/R<sub>6</sub>, RTP/W and RTA/R<sub>5</sub> and RTA/W (CHENG et al. (1994),: CHENG et al.(1991)) can be written as

$$\ln x_m = -\frac{\Delta H_s}{RT} + \frac{1}{R} \left( \Delta H_f + S^E \right) \tag{7}$$

where  $x_m$  is the mole fraction,  $\Delta H_f$  is the enthalpy of fusion and  $S^E$  is the excess entropy of mixing. From the equation (7) the relation between mole fraction ( $\ln x_m$ ) and  $1/T$  gives

a straight line whose slope is equal to -  $\frac{\Delta H_s}{R}$ . The Enthalpy of solution ( $\Delta H_s$ ) for different

solvents is calculated using the literature data of solubility (CHENG et al.(1994); CHENG et al.(1991)).

### 2.3. Metastable zone width

A barrier against the formation of a new phase (critical energy barrier) is not only a function of driving force but also sensitive to interfacial energy and many other factors. By assuming that the interfacial energy is independent of the size of the nucleus, critical energy barrier ( $\Delta G^*$ ) and radius of the critical nucleus ( $r = r^*$ ) are given by

$$\Delta G^* = \frac{16\pi s^3}{3 \Delta G_v^2} \quad r^* = \frac{-2s}{\Delta G_v} \quad (8)$$

where  $\sigma$  is the interfacial energy which plays an important role in determining the rate of nucleation in high temperature solution growth technique. Theoretical and experimental finding of interfacial energy ( $\sigma$ ) was reported by different authors (SANGWAL ; BENNEMA et al.; SOHNEL; MERSMANN; CHRISTOFFERSON et al.). They have predicted the linear relationship between  $\sigma$  and molar concentrations. Based on the regular solution theory, BENNEMA and SOHNEL derived an expression for the relationship between the interfacial energy and solubility as

$$s = \left( \frac{kT}{d^2} \right) [0.173 - 0.248 \ln(x_m)], \quad (9)$$

where  $x_m$  is the mole fraction of the solute,  $k$  is Boltzmann constant,  $T$  is the temperature and  $d$  is the interionic distance. The above equation shows better agreement with the experimental observations in high temperature solution grown crystal (JOSEPH KUMAR et al).

In general, a region of supersaturation is divided into metastable and labile region and the boundary between them indicates the maximum supersaturation at which the excess solute does not crystallize under any conditions. Metastable zone width provides information about the level of supersaturation, which is available to grow the crystal. This metastable zone width is based on the rate of nucleation, which is unknown in the growth experiment.

Since the nucleation is a thermally activated process, the number of critical nuclei formed per unit time per unit volume is known as the rate of nucleation 'J'.

$$J = A \exp\left(\frac{-\Delta G^*}{kT}\right) \quad (10)$$

Substituting the values of  $\Delta G^*$

$$J = A \cdot \exp\left[\frac{-16\pi s^3 v^2}{3 k^3 T^2 (\ln s)^2}\right] \quad (11)$$

where  $A$  is the pre-exponential factor and it varies very slowly with supersaturation compared to exponential factor. Its value is assumed to be  $10^{30}$  for the nucleation from melt

and solution (ZETTLEMOYAR). The above equation reveals that the rate of nucleation depends on the interfacial energy  $\sigma$ , temperature T and supersaturation s. The critical supercooling  $\Delta T_c$ , required for one nucleus to be formed per unit volume in one second, is called metastable zone width or Ostwald - Miers region. Since the Metastable zone width measures the stability of the solution, it plays a vital role in high temperature solution growth. The values of  $\Delta T_c$  and other nucleation parameters for RTP and RTA systems grown from self fluxes and tungstate fluxes were calculated by setting the value of  $J = 1$  in equation (10) and using equations (4), (8) and (9).

**3. Results and discussion**

Figure 1 represents the variation of interfacial energy with temperature for RTP and RTA crystals crystallizing from self and tungstate fluxes. It is seen from the figure that the interfacial energy values are increasing with decrease in temperature and this trend is very similar to the experimental observations during the high temperature solution (JOSEPH KUMAR et.al.). It is also observed that the interfacial energy changes drastically with temperature for RTP and RTA crystals grown from tungstate fluxes compared to phosphate fluxes, which may be due to the lower viscosity of the tungstate fluxes. The interfacial energy value of RTA crystal grown in self ( $Rb_5As_3O_{10}$ ) and tungstate ( $K_2WO_4 \cdot 3KPO_3 \cdot Li_2WO_4$ ) fluxes has been found to be higher than that of RTP crystal grown in self ( $Rb_6P_4O_{13}$ ) and tungstate fluxes which results in lowering the solubility of RTA crystal. The above behavior is consistent with the experimental observation of solubility measurements (CHENG et.al. (1994)).

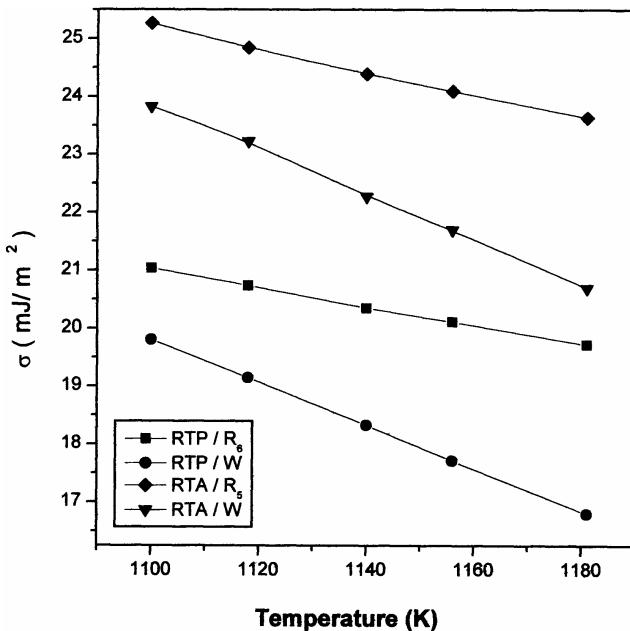


Fig. 1: Variation of Interfacial energy with temperature for RTP, RTA crystals grown from self and Tungstate fluxes

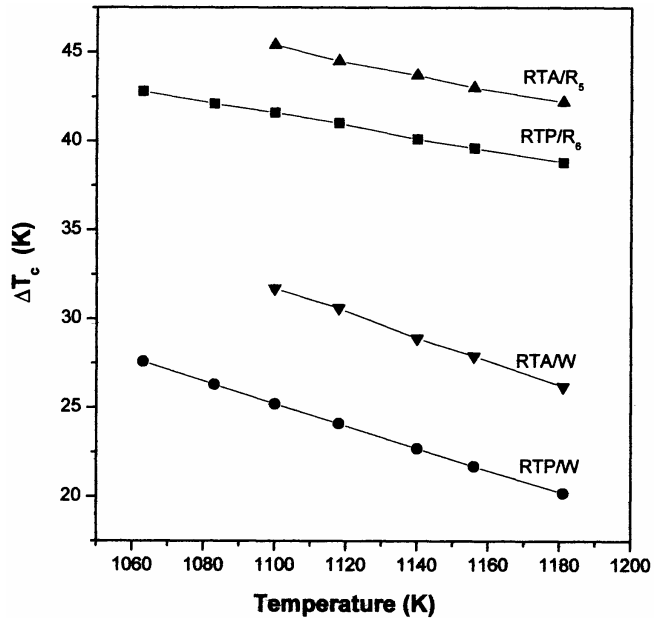


Fig. 2: Variation of metastable zone width with temperature for RTP and RTA crystals grown from self and Tungstate fluxes

Figure 2 shows the variation of metastable zone width ( $\Delta T_c$ ) with temperature for RTP and RTA crystals grown from self and tungstate fluxes. From the figure, it is observed that the metastable zone width value decreases with increase in temperature for both the crystals. But in the case of RTA crystal grown from self-flux, metastable zone width was found to be wider than RTP crystal grown from self-flux. The above result indicates that the higher value of solubility lowers the metastable zone width value. It is also observed that for both the systems, the metastable zone width is wider for self-fluxes than tungstate fluxes. Hence it is concluded that the metastable zone width decreases from arsenate to phosphate and self-fluxes to tungstate fluxes ( $RTA_{self} > RTP_{self} > RTA_{Tung} > RTP_{Tung}$ ). Since the metastable zone width measures the stability of the solution, self-fluxes such as  $Rb_6P_4O_{13}$  and  $Rb_5As_3O_{10}$  are suitable solvents than tungstate fluxes for the growth of RTP and RTA crystals respectively.

Other nucleation parameters such as Gibbs free energy, critical energy barrier, chemical potential and radius of critical nucleus for RTP and RTA crystals have been calculated and presented in table I and II respectively. From the tables, it has been inferred that the self fluxes are highly preferable for the growth of RTP and RTA crystals than tungstate fluxes due to their higher chemical potential and lower critical energy barrier values which supports the formation of controlled nucleation. Moreover, the number of growth units in the critical nucleus is higher for crystals grown from tungstate fluxes than self fluxes which may lead to the incorporation of metal ions (W or Mo ions) into the crystal lattices which reduces the device performances. Since we considered only the homogeneous nucleation, the calculated metastable zone width for RTP and RTA crystal systems are the maximum possible values. The above nucleation thermodynamical parameters give a better understanding of the crystallization process and a comparative picture of the metastable zone width values of  $RbTiOPO_4$  and  $RbTiOAsO_4$  crystals grown from different solvents.

Table 1: Solubility, Enthalpy and nucleation parameters for RTP crystals from self and tungstate fluxes

System	Temp. (K)	Mole fraction ( $x_m$ ) <sup>(a,b)</sup>	Gibbs Free Energy ( $\Delta G_v$ ) x $10^6$ J/ m <sup>3</sup>	Critical Energy Barrier ( $\Delta G^*$ ) x $10^{-19}$ J	Interfacial Energy ( $\sigma$ ) mJ/m <sup>2</sup>	Radius of critical nucleus ( $r^*$ ) x $10^{-9}$ m	Chemical Potential ( $\Delta\mu$ ) x $10^{-21}$ J
RTP/R <sub>6</sub>	1181	0.6481	10.6850	11.2570	19.7216	3.6914	1.1885
(self-flux)	1156	0.6181	11.1154	11.0336	20.1129	3.6189	1.2364
$\Delta H_s = 22.6$ kJ/mol. K <sup>(a)</sup>	1140	0.5994	11.3960	10.8750	20.3515	3.5717	1.2676
	1118	0.5498	11.8510	10.6409	20.7396	3.4998	1.3183
	1100	0.4837	12.1976	10.4883	21.0399	3.4498	1.3568
RTP/W	1181	0.7663	8.4099	11.2350	16.8011	3.9955	0.9354
(Tungstate-flux)	1156	0.7107	9.2059	10.9919	17.7154	3.8486	1.0240
	1140	0.6760	9.7343	10.8857	18.3277	3.7655	1.0828
$\Delta H_s = 33.9$ kJ/mol. K <sup>(b)</sup>	1118	0.5938	10.5014	10.6656	19.1475	3.6466	1.1681
	1100	0.4879	11.1182	10.5337	19.8078	3.5631	1.2367

( $x_m = \text{g solute} / \text{g solvent}$ )

<sup>(a)</sup> Data of CHENG, et al (1994)

<sup>(b)</sup> Data of CHENG, et al (1991)

Table 2: Solubility, Enthalpy and nucleation parameters for RTA crystals from self and tungstate fluxes

System	Temp. (K)	Mole fraction ( $x_m$ ) <sup>(c,d)</sup>	Gibbs Free Energy ( $\Delta G_v$ ) x $10^6$ J/ m <sup>3</sup>	Critical Energy Barrier ( $\Delta G^*$ ) x $10^{-19}$ J	Interfacial Energy ( $\sigma$ ) mJ/m <sup>2</sup>	Radius of critical nucleus ( $r^*$ ) x $10^{-9}$ m	Chemical Potential ( $\Delta\mu$ ) x $10^{-21}$ J
RTA/R <sub>5</sub>	1181	0.4877	14.0486	11.2127	23.6379	3.3651	1.6734
(self-flux)	1156	0.4600	14.5786	11.0265	24.0939	3.3053	1.7365
$\Delta H_s = 29.7$ kJ/ mol.K <sup>(c)</sup>	1140	0.4424	14.9885	10.8199	24.3892	3.2543	1.7853
	1118	0.4173	15.5135	10.6748	24.8433	3.2028	1.8478
	1100	0.3958	16.0365	10.5694	25.2668	3.1511	1.9101
RTA/W	1181 <sup>(d)</sup>	0.5816	11.5026	11.2324	20.7002	3.5991	1.3701
(Tungstate-flux)	1156	0.5327	12.4573	11.0276	21.6966	3.4833	1.4838
	1140	0.5045	13.0466	10.8752	22.2721	3.4142	1.5540
$\Delta H_s = 38.8$ kJ/ mol.K <sup>(d)</sup>	1118	0.4622	14.0184	10.6870	23.2292	3.3141	1.6698
	1100	0.4341	14.7062	10.4845	23.8305	3.2408	1.7517

( $x_m = \text{g solute} / \text{g solvent}$ )

<sup>(c)</sup> Data of CHENG, et al (1994)

<sup>(d)</sup> Data of CHENG, et al (1991)

#### 4. Conclusion

The nucleation parameters of RbTiOXO<sub>4</sub> (X = P or As) crystals grown from different solvents have been calculated. As there are no sufficient data available in the literature the present theoretically estimated values will be useful for the growth of these crystals.

Moreover, the results indicate that the crystal grown from self-fluxes give more stability to the solution and favors for the growth of large size inclusion free crystals for device applications.

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