



Growth and characterization of gel grown potassium hydrogen levo- tartrate crystals

Jayesh Govani¹ and Mihir J Joshi^{2*}

¹Materials Science and Engineering Department, University of Texas at El Paso, El Paso, TX 79968 U S A

²Crystal Growth Laboratory, Department of Physics, Saurashtra University, Rajkot 360 005, Gujarat, India

E mail mshilp24@rediffmail.com

Received 29 February 2008, accepted 11 June, 2008

Abstract Potassium hydrogen levo-tartrate (KHLT) crystals were grown by the single diffusion gel growth technique in silica hydro gel medium Potassium chloride containing supernatant solution was poured on tartaric acid impregnated set gel KHLT crystals in dendritic form were grown near the gel-liquid interface and prismatic crystals were grown at the bottom of the test tubes Sodium chloride solution was added in different amounts to potassium chloride containing supernatant solution and its effect was studied in terms of change in crystal morphology, crystal dimension and number of grown crystals The powder XRD analysis confirmed the growth of single-phase KHLT crystals The grown crystals were characterized by FT-IR and thermo-gravimetric analysis The crystals were found to be thermally stable up to 300 °C and decompose into oxide on further heating The kinetic parameters of decomposition were estimated by employing two different relations, viz, the Coats and Redfern relation as well as the Horowitz and Metzger relation The thermodynamic parameters of decomposition were also calculated

Keywords Gel growth, FTIR, powder XRD, TGA, Kinetic and thermodynamic parameters

PACS No. 81 10 Dn, 82 70 Gg, 65 40 G

1. Introduction

There are numerous applications of tartrate compounds in science and technology [1]; for example, calcium tartrate [2], sodium-potassium tartrate [3] and rubidium hydrogen tartrate [4] exhibit ferroelectric applications; sodium ammonium tartrate [5], rubidium hydrogen tartrate [4] can be used for ferroelectric and ferro-elastic applications and lithium thiallate tartrate [6] exhibits dielectric applications

Corresponding Author

Gel growth is the simplest technique under ambient condition, which is suitable for the crystal growth of compounds sparingly soluble in water and decomposes at low temperature [7]. However, attempts have been made to grow crystals, which are soluble in water, by the gel-growth technique [8-10]. Since, gel growth technique has several advantages over few disadvantages, it has attracted the attention of several researchers. Several crystals of various tartrates have been successfully grown in the author's laboratory and characterized, which includes calcium tartrate [11], iron tartrate [12], zinc tartrate [13], cadmium tartrate [14], iron-manganese mixed levo-tartrates [15], calcium-strontium mixed calcium levo-tartrates [16], Mn^{++} and Cu^{++} doped calcium levo-tartrate [17,18].

Potassium hydrogen tartrate (KHT), also known as cream of tartar or potassium bitartrate, possesses many applications and some of them are patented, for instance in chemical removal of dental plaque [19] and in treatment of infectious and viral diseases [20]. The formation of KHT crystals in wine bottles is unwanted and efforts are made to avoid it by a trap process or by influence of external electric field [21]. The nucleation study of KHT in model solutions and wines is reported [22]. In the earlier studies KHT crystals have been grown by solution growth technique and hillocks, macro-spirals and growth layers of typical features were observed [23]. A method has been developed for growing KHT crystals of cross-shaped in a gel-matrix and patented [24].

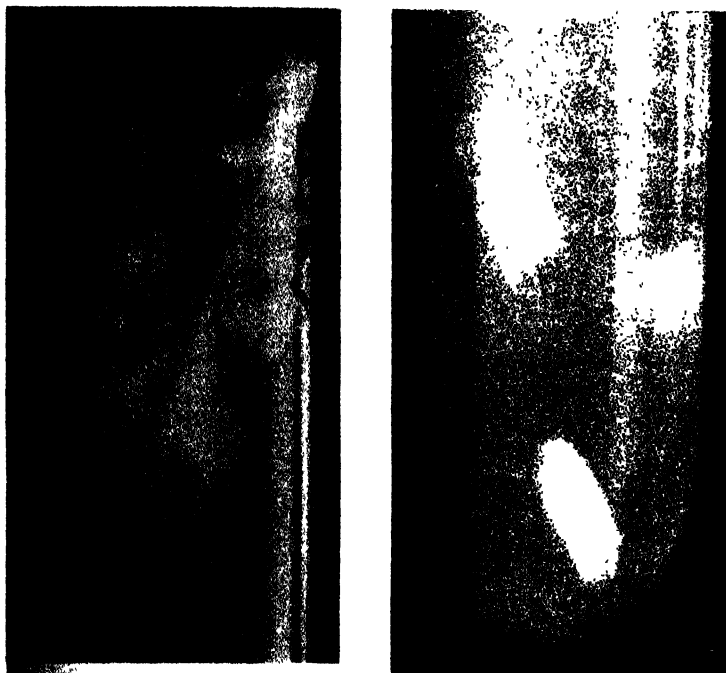
The aim of the present study is to grow KHLT (potassium hydrogen levo-tartrate) crystals by the single diffusion gel growth technique and characterize them by different techniques as well as to study the effect of addition of sodium chloride solution in supernatant solution on the growth of crystals.

2. Experimental

For crystallization, glass test tubes of 25 mm diameter and 140 mm length were used. Sodium metasilicate solution of density 1.06 gm/cm^3 was used for preparation of the gel. One molar levo tartaric acid mixed with sodium metasilicate solution and the pH of the mixture was kept at 3.6 to 3.8. The mixture was poured in different test tubes to set in to the gel. The supernatant solutions containing different proportions of 1 M sodium chloride and 1 M potassium chloride solutions were gently poured without disturbing the gel surfaces and the volume of the mixture was maintained at 10 ml.

The growth of crystals was completed within a month. For pure potassium chloride containing supernatant solution, the dendritic crystals were grown at the liquid-gel interface and their branches extended nearly 1 cm in to the gel. Prismatic single crystals were grown at the bottom. Whereas for higher volumes of sodium chloride, no single crystal growth was observed at the bottom of test tubes and a few bi-crystals were grown at the gel-liquid interface. Crystal growth was not observed in the case of pure sodium chloride even after four months. Which indicated clearly that sodium tartrate crystals were not grown but sodium chloride in the supernatant solution influenced the growth and morphology of crystals.

Figure 1(a, b) is the photograph for supernatant solution containing pure potassium chloride exhibiting top and bottom view of the test tube, respectively. It can be observed that dendritic crystals are grown at the gel-liquid interface and at the bottom of the gel prismatic single crystals are grown.



(a)

Figure 1. Crystal growth of KHLT crystals, (a) dendritic crystals at gel-liquid interface and (b) single crystals at the bottom of test tube.

3. Characterization techniques

The FT-IR spectra of powdered samples in KBr medium were recorded on Specord IR 75, Carl Zeiss (Germany) in the range of $400\text{--}4000\text{ cm}^{-1}$. Powder XRD analysis was carried out using a PW 1710 diffractometer with Cu-K_α radiations. Thermo-gravimetric analysis (TGA) on powdered samples was carried out from room temperature to 900°C in the atmosphere of air at a heating rate of $20^\circ\text{C}/\text{min}$.

4. Results and discussion

In the present investigation, the KHLT crystals were grown by gel growth method. The dendritic growth of crystals at the gel-liquid interface and prismatic growth of crystals at the bottom of gel column was observed. This may be due to high value of concentration gradient in the diffusion column at the gel-liquid interface leading to dendritic growth and comparatively lesser concentration gradient allows prismatic and good quality crystals to grow.

FTIR spectrum of KHLT is shown in Figure 2. It can be observed from the figure that the absorptions at 3317 cm^{-1} and 3271 cm^{-1} are due to O-H stretching vibrations representing water of crystallization or moisture on the surface. The absorption at 2975 cm^{-1} is due to C-H stretching vibration. The absorptions at 1869 cm^{-1} , 1718 cm^{-1} and 1560 cm^{-1} are due to C=O stretching vibration. The absorptions at 1409 cm^{-1} and 1338 cm^{-1} are due to O-H stretching in plane of deformation. Whereas, the absorptions at 1306 cm^{-1} , 1264 cm^{-1} , 1213 cm^{-1} , 1134 cm^{-1} , 1067 cm^{-1} all are due to C-O stretching and C-OH moiety. Similarly, the absorptions at 904 cm^{-1} , 878 cm^{-1} , 842 cm^{-1} , 789 cm^{-1} and 680 cm^{-1} are due to O-H deformation out of plane and C-H stretching vibrations. The absorptions at 619 cm^{-1} , 573 cm^{-1} , 522 cm^{-1} and 486 cm^{-1} are due to metal-oxygen stretching vibration. However, this spectrum is slightly different from the spectra obtained for calcium and strontium levo tartrate and for pure and mixed manganese and iron levo tartrate, which may be due to hydrogen is chelating the tartrate radical with metallic ion in form of potassium hydrogen tartrate.

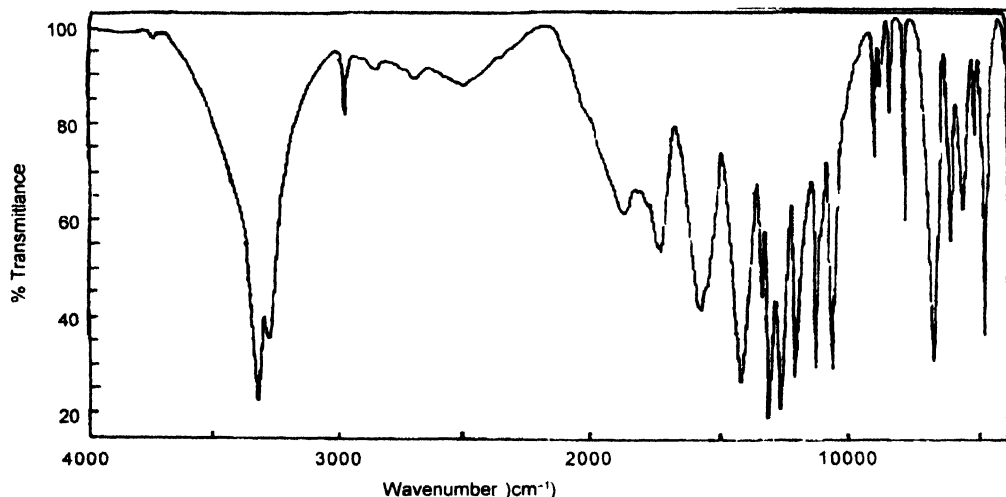


Figure 2. FTIR spectrum of KHLT crystals.

Also, FT-IR and Raman spectra of ammonium hydrogen tartrate (AHT) and KHT have been reported earlier [25]. From the FTIR spectrum the presence of water of crystallization or moisture attached to the crystal, C-H bond, the C=O bond and the metal-oxygen bond were identified.

Figure 3 shows the powder XRD pattern of the sample. The cell parameters are calculated by using the computer programs DEBYE and REFEDT.BAS, which are as follows:

$a = 7.789(1)\text{ \AA}$, $b = 10.648(3)\text{ \AA}$, $c = 7.611(4)\text{ \AA}$, Cell volume = 631.23 (\AA)^3 and orthorhombicity = 15.50.

These unit cell parameters are identical for all the samples grown with different amount of sodium chloride in the supernatant solutions. These cell parameters exactly match

with the cell parameters of the potassium hydrogen tartrate ($\text{KH}_5\text{C}_4\text{O}_6$ or $\text{KHC}_4\text{H}_4\text{O}_6$) reported in the ASTM data card for the powder XRD. This indicates that all crystals grown are potassium hydrogen tartrate crystals and no mixed crystals of potassium and sodium tartrate are formed. In earlier attempts, the structure of KHT at 100 K has been reported [26].

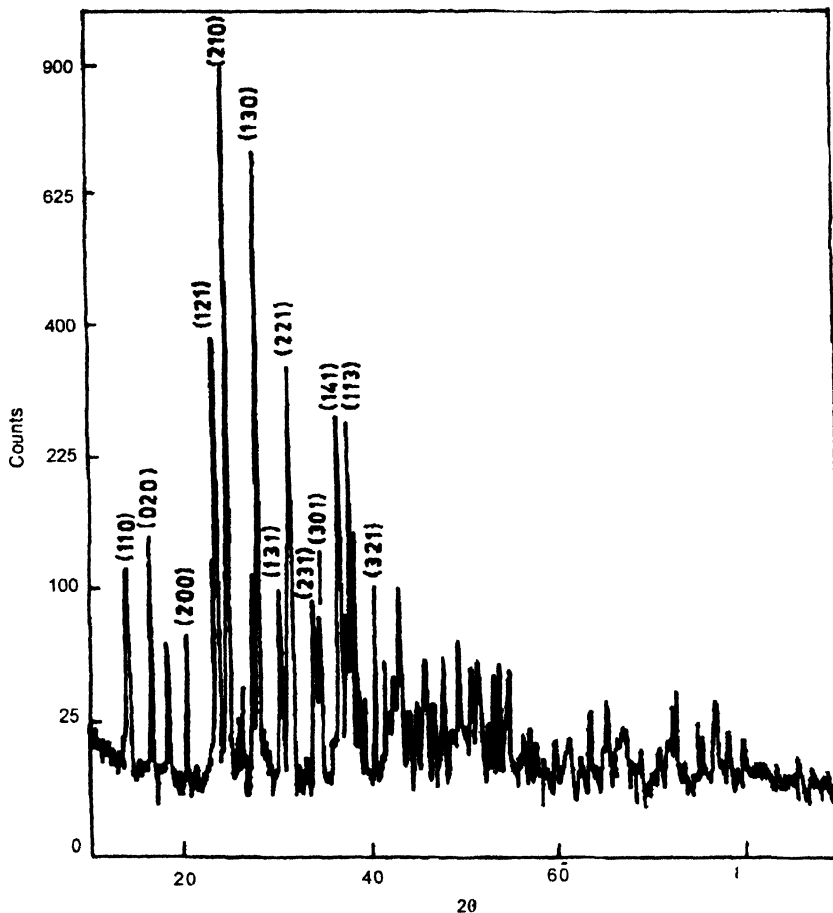


Figure 3. Powder XRD patterns of KHLT crystals

The thermal stability of crystals and kinetics of dehydration have been studied by employing thermogravimetry for several tartrate compounds [12-16, 27]. Figure 4 shows the thermogram of sample. The sample starts decomposing at 280°C and it suddenly decomposes into meta stable KOHCO_3 , which is occurring at 290°C , thereafter, the sample further decomposes into K_2O at 320°C , and finally decomposes into $\text{KO} + (3/2)\text{O}$ at 460°C and remains stable up to the end of the analysis. No water of hydration is found to be associated with the crystals. Table 1 is of theoretical and practical values of weight-losses at different temperatures. The thermo-grams for all other samples are found to be nearly the same.

This indicates that the NaCl solution in the supernatant solution does not grow mixed potassium sodium tartrate crystals but only grow potassium hydrogen tartrate crystals. The NaCl solution modifies the morphology of crystals. The failure of growing sodium tartrate crystals may be due to high solubility product of sodium tartrate and the presence of large amount of sodium hydroxide and sodium chloride in the solution and gel. Sodium hydroxide is present in the gel due to polymerization of monosilicic acid.

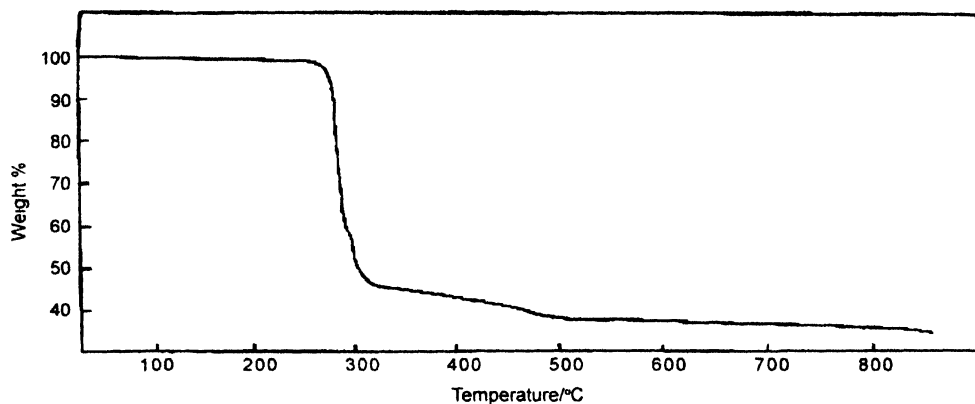


Figure 4. Thermo-gram of KHLT crystals

Many researchers have used thermo gravimetric data to calculate the kinetic parameters of solid-state reaction including weight loss [12, 14, 28-30]. By using the kinetic parameters of pyrolysis such as order of reaction, frequency factor and energy of activation, the shape of curve is determined. With the help of Coats and Redfern [28] relation, the kinetic parameters were calculated. Coats and Redfern relation is given by

$$\log_{10} \left[\frac{1 - (1 - \alpha)^{1-n}}{T^2(1-n)} \right] = \left\{ \log_{10} \left[\frac{AR}{\alpha E} \right] \left[1 - \frac{2RT}{E} \right] - \frac{E}{23RT} \right\} \quad (1)$$

Where $\alpha = (W_0 - W)/(W_0 - W_f)$, W_0 the initial weight, W the weight at time t , W_f the final weight, n the order of reaction, A the frequency factor, E the activation energy of the reaction, R a gas constant, and α the heating rate in $^{\circ}\text{C}/\text{min}$.

Table 1. Thermal decomposition of KHLT crystals

Sample	Temperature in $^{\circ}\text{C}$	Theoretical weight %	Observed weight %
$\text{KH}_5\text{C}_4\text{O}_6$	260	100	100
KOHCO_3	290	61.71	60
K_2O	320	50.08	46
$\text{KO} + 3/2\text{O}$	460	42.04	42

To determine the value of activation energy and order of reaction, a plot of $\log_{10}\left[\frac{1-(1-\alpha)^{1-n}}{T^2(1-n)}\right]$ versus $1/T$ is drawn for different values of n and the best linear plot gives the correct values of n . This equation is valid for all values of n except $n = 1$.

Figure 5 is a plot of Coats and Redfern equation for the crystals grown by using pure potassium chloride. The values of activation energy, frequency factor and the order of reaction are found to be 191.47 kJ mol⁻¹, 61.93 × 10²⁷ and 2/3, respectively.

Horowitz and Metzger [29] obtained equation for pyrolysis, where only a fraction of total weight is lost as in the loss of water of hydration from a hydrated salt. Horowitz and Metzger relation is given by

$$\log_{10}\left[\frac{1-C^{1-n}}{1-n}\right] = \frac{E\theta}{2303} RT_s^2 \tag{2}$$

where $C = (W - W_f)/(W_0 - W_f)$, W_0 initial weight, W_f the final weight, E the activation energy, and n the order of reaction.

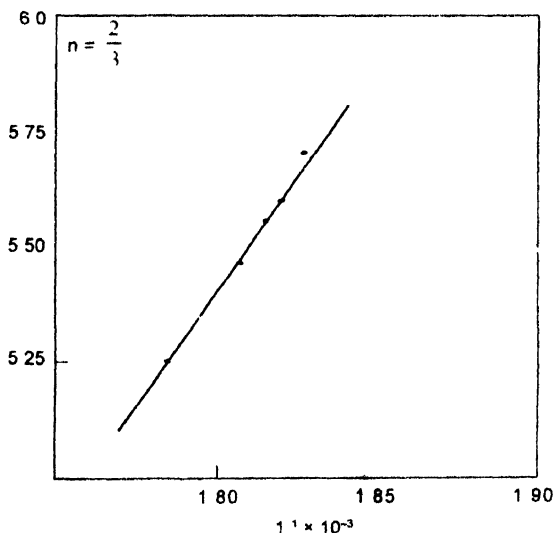


Figure 5 A plot of Coats and Redfern relation for KHLT crystals, Where $Y = \log_{10}\left[\frac{1-(1-\alpha)^{1-n}}{T^2(1-n)}\right]$ and $X = 1/T$

A plot of $\log_{10}[1 - C^{1-n}]/(1 - n)$ versus θ gives best straight line with its slope equal to E/RT_s^2 . Figure 6 is a plot of Horowitz-Metzger relation for the crystals grown by using pure potassium chloride. From the plot the values of activation energy and order of reaction are found to be 210.70 kJ mol⁻¹ and 2/3, respectively. The difference in the values of kinetic parameters obtained by Coats and Redfern as well as Horowitz and Metzger relations are due to different mathematical models used in these equations. Notwithstanding, these

two equations employ the Arrhenius law in analysis, but subsequent mathematical treatments and assumptions differ, which gives two different equations. This has been discussed by Dabhi and Joshi [13].

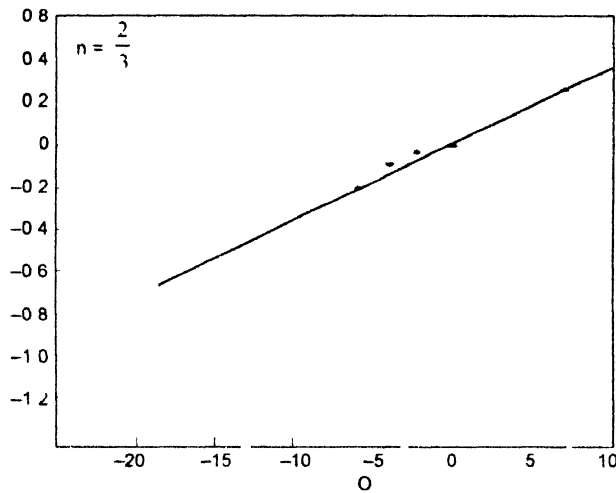


Figure 6 A plot of Horowitz and Metzger relation for KHLT crystals Where $Y = \log_{10}[1-C^{1-n}]/(1-n)$ and $\lambda = 0$

The thermodynamic parameters have been evaluated from the decomposition stage of thermogram of potassium tartrate crystals using the standard relations [31]. The standard enthalpy of activation $\Delta^{\#}H^0$ was calculated by using the following relation

$$\Delta^{\#}H^0 = E - 2RT \quad (3)$$

The standard entropy of activation $\Delta^{\#}S^0$ was calculated by using the relation

$$\Delta^{\#}S^0 = 2.303 \times R \times \log_{10} \frac{Ah}{kT_m} \quad (4)$$

Where, k is the Boltzmann constant, h the Planck constant, T_m the temperature and A the frequency factor

The standard Gibbs energy of activation, $\Delta^{\#}G^0$ is estimated by using the following equation,

$$\Delta^{\#}G^0 = \Delta^{\#}H^0 - T \Delta^{\#}S^0 \quad (5)$$

Estimated values of standard enthalpy, standard entropy and standard Gibbs free energy are $182.16 \text{ kJmol}^{-1}$, $130.73 \text{ kJmol}^{-1}$ and $108.95 \text{ kJmol}^{-1}$, respectively

The values of different thermodynamic parameters obtained for different samples. Positive values of the standard enthalpy and the standard entropy of activation suggest that the

process is spontaneous at high temperatures and the positive value of standard Gibbs free energy suggests the process is thermodynamically unstable

5. Conclusion

Pure Potassium hydrogen levo tartate (KHLT) crystals were grown using gel growth technique and crystals were characterized by different techniques. The powder X-ray diffraction analysis confirmed single-phase compound. Comparing with standard ASTM data for powder X-ray diffraction it has been found that all grown crystals are KHLT crystals. From thermo-gravimetric analysis crystals are found to be thermally stable up to 280⁰ C and they decompose into oxide through the short meta -stable state of KOHCO₃. Different volumes of sodium chloride solutions in supernatant solution affect the morphology but do not grow doped or mixed crystals. The same nature of Powder XRD patterns, FT-IR spectra and thermograms for various samples indicate the formation of only one compound that is KHLT.

Acknowledgment

The authors are thankful to Prof. K. N. Iyer (Saurashtra University, India) and Dr. Felicia Manciu (University of Texas at El Paso, U.S.A) for their keen interest. The author (Dr. M. J. Joshi) is thankful to UGC, New Delhi, India, for SAP grants.

References

- [1] G. A. Kiosse *Crystal Structure of Inorganic Compounds*, (Kishinev Shtinstsa Press) (1974)
- [2] H. B. Gon *J. Crystal Growth* **102** 521 (1990)
- [3] J. Valasek *Phys. Rev.* **17** 475 (1921)
- [4] C. C. Desai and A. H. Patel *J. Mater. Sci. Lett.* **8** 361 (1989)
- [5] K. Aizu *J. Phys. Soc. Jap.* **31** 1521 (1971)
- [6] E. Sawaguchi and L. E. Cross *Ferroelectrics* **2** 37 (1971)
- [7] H. K. Henish *"Crystal Growth in Gels"* (Pennsylvania Univ. Press, University Park) (1970)
- [8] D. A. Glocker and I. F. Soest *J. Chem. Phys.* **51** 3143 (1969)
- [9] B. Brezina and J. Havrankova *Mater. Res. Bull.* **87** 537 (1971)
- [10] K. Ambujam *Study on the growth and characterization of NLO active single crystals of KDP, γ -glycine, BGHC, CMTc and ZMTC*, Ph.D. Thesis, University of Madras (2005)
- [11] V. S. Joshi and M. J. Joshi *Indian J. Phys.* **75A** 159 (2001)
- [12] S. Joseph and M. J. Joshi *Indian J. Phys.* **71A** 183 (1997)
- [13] R. M. Dabhi and M. J. Joshi *Indian J. Phys.* **76 A** 211 (2002)
- [14] R. M. Dabhi and M. J. Joshi *Indian J. Phys.* **76 A** 481 (2003)
- [15] S. J. Joshi, B. B. Parekh, K. D. Vohra and M. J. Joshi *Bull. Mater. Sci.* **29** 307 (2006)
- [16] K. D. Parikh, B. B. Parekh, D. J. Dave and M. J. Joshi *Indian J. Phys.* **80** 719 (2006)
- [17] S. R. Suthar and M. J. Joshi *Cryst. Res. and Technol.* **41** 664 (2006)
- [18] S. R. Suthar, S. J. Joshi, B. B. Parekh and M. J. Joshi *Indian J. Pure Appl. Phys.* **45** 48 (2007)
- [19] US Patent no. 64819675, "Chemical removal of dental plaque"

- [20] US Patent no 4708952, "Method of treatment of infectious and viral diseases by one time interference "
- [21] V Guillet, N Gabas, M Comtat and J L Favarel *J Appl Electrochem* **32** 1313 (2002)
- [22] M A Lafortune, E M Henning, M J Lake, V Gerbaud, N Gabas, C L Lagurie and J Blouin *J Cryst Growth* **166** 172 (1996)
- [23] K Sangwal and S Veintemillas-Verdaguer *Cryst Res And Technol* **29** 634 (1994)
- [24] US Patent no 6793732, *Method and Kit for growing Cross shaped crystals.*
- [25] P Kolandaivel and S Selvasekarapandian *Cryst. Res and Technol.* **28** 665 (1993)
- [26] J Bushmann and P Luger, *Acta Cryst* **C41** 206 (1985)
- [27] M M Abdul-Kader, Z H El-Tanahy, A Abdul Razik, M Abdutaleb and A El-Shawarby *J. Mater Sci Materials in Electronics* **6** 178 (1995)
- [28] A W Coats and J P Redfern *Nature* **201** 183 (1964)
- [29] H H Horowitz and G Metzger *Anal Chem* **35** 1464 (1963)
- [30] P N Kotru, K K Raina and M L Koul, *J Mater Sci* **21** 3933 (1986)
- [31] K J Laidler *Chemical Kinetics* (New York Harper and Row) (1987)