Journal of Thermal Analysis and Calorimetry, Vol. 94 (2008) 1, 21–25

EFFECT OF CHELATING AGENT (1,10-PHENANTHROLINE) ON POTASSIUM HYDROGEN PHTHALATE CRYSTALS

S. P. Meenakshisundaram[1], *S. Parthiban*[1], *G. Madhurambal*[2] *and S .C. Mojumdar*[3,4*]

[1]Department of Chemistry, Annamalai University, Annamalainagar 608 002, India
[2]Department of Chemistry, ADM College for Women, Nagapattinam, India
[3]Department of Chemical Engineering and Applied Chemistry, University of Toronto, 200 College St., Toronto, ON, M5S 3E5, Canada
[4]University of New Brunswick, Saint John, NB E2L 4L5, Canada

The influence of a new organic additive, chelating agent 1,10-phenanthroline (Phen) (~$5.0\cdot10^{-3}$ M L^{-1}) on potassium hydrogen phthalate (KHP) single crystals at 30°C is investigated. The crystals were grown from the aqueous solutions of pH ~4.5 at constant temperature by solvent evaporation technique. The chelating agent leads to an increase in metastable zone width and assists the bulk growth process. The growth rate of crystals in the presence of Phen decreases considerably with an increase in impurity concentration. Not much variation is observed in FTIR and cell parameter values, determined by XRD analysis. It appears that the growth promoting effect (GPE) of Phen is caused by the adsorption of the organic additive on the prism of KHP crystals. Differential scanning calorimetry (DSC) and TG-DTA studies reveal the purity of the sample and no decomposition is observed up to the melting point. Scanning electron microscope (SEM) photographs exhibit the effectiveness of the impurity in changing the surface morphology of KHP crystals. Contrary to expectations, Phen depresses the NLO efficiency of KHP, suggesting that the molecular alignments in the presence of Phen results in cancellation effects disturbing the non-linearity.

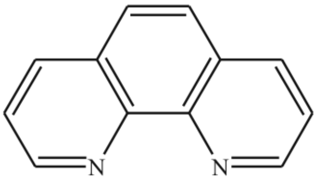
Keywords: *KHP, non-linear optical materials, organic dopants, TG-DTA, XRD*

Introduction

It was observed that organic compounds like ethylenediaminetetraacetic acid (EDTA), urea and thiourea lead to an increase in the growth rate and improvement in the quality of different crystals [1]. The GPE is due to the complexation of trace metal ion impurities in solution. The resulting complex is not entering into the crystal. Since the complexing agent prevents the entry of impurities into the crystal by complex formation, the growth process is rapid and the crystalline perfection of the crystal improves. Also, in the presence of these additives, secondary nucleation is effectively controlled.

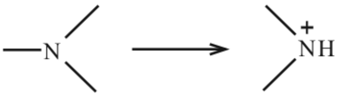
Potassium hydrogen phthalate (KHP) ($C_8H_5KO_4$), crystals are used as the second, third and fourth harmonic generators for Nd:YAG and Nd:YLF lasers. The crystals are widely used for electro-optical applications as Q-switches for Nd:YAG, Nd:YLF, Ti:Sapphire and Alexandrite lasers, as well as for acoustic-optical applications.

The homogeneous phase must be metastable i.e. supersaturated in general for the crystallisation to occur. A small quantity of an impurity leads to an increase in the metastable zone width of the solution if the complex adsorption on the growing surface is not very stable [1]. This helps a lots the bulk growth process. A surfactant like EDTA is a good additive and the main reason for the rapid growth process in the presence of EDTA is its ability to form complex with impurities, mainly the trace metal ions in solution. These positive aspects of the chelating agents lead us to investigate the crystal growth of KHP crystals in the presence of a new additive 1,10-phenanthroline.



1,10-Phenanthroline

It can easily undergo protonation.



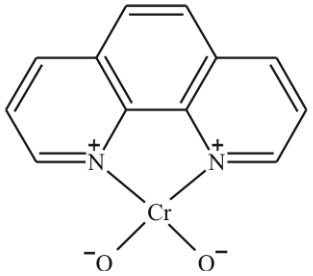
It can easily form complexes with metal ions in solution. For instance, it can form a complex with chromium [2].

---

[*] Author for correspondence: scmojumdar@hotmail.com

1388–6150/$20.00

Akadémiai Kiadó, Budapest, Hungary
Springer, Dordrecht, The Netherlands



The organics and inorganics are very important from the various points of view. Therefore, many authors have investigated the interactions and influences of organics and inorganics and also examined their chemical, thermal, spectral, physical, biological and many other properties [3–23]. The KHP crystals are grown in the presence of a small quantity of Phen. In the present paper, we are reporting a systematic investigation of the effect of chelating agent, 1,10-phenanthroline on KHP.

Experimental

Crystal growth

KHP and Phen doped ($5\cdot10^{-3}$ M L^{-1}) single crystals were grown by solvent evaporation technique. The crystal growth and the quality of the crystals are much better, when the solution is acidic and the pH of the growth medium is ~4.5. A considerable GPE of Phen on KHP crystals is observed.

Studies follow the general trend that the growth rate of crystals in the presence of impurities always decreases with an increase in the impurity concentration. At high concentrations of Phen, the solution becomes reddish and the red colour shades are visible inside the crystal too. High concentrations of the dopant, results in the adsorption of film blocking the growth surface and thereby inhibiting the growth process [24]. Bulk crystals are grown using the optimized growth parameters (Fig. 1).

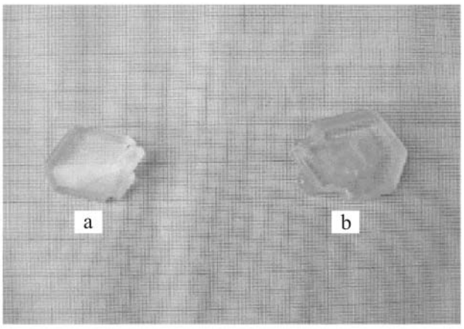


Fig. 1 Photographs of as grown crystals of a – Pure KHP and b – Phen added KHP

Metastable zone width

Solubility was analysed gravimetrically. Since a very small quantity of additive is added and the additive Phen is nonionic, there is not much of variation in the solubility of KHP. Metastable zone width was measured by conventional polythermal method [25, 26]. Metastable zone width is an essential parameter for the growth of large size crystals from solution, since it is a direct measure of the stability of the solution in its supersaturated region [27]. Metastable zone width is determined for Phen added KHP solutions and the comparison shows that it is wider than the case of pure KHP solutions. Widening of metastable zone width results in GPE. Also, in the presence of Phen, secondary nucleation is controlled to a considerable extent. It effectively depresses the shearing action of the solution tearing off the small particles from crystal surface and thus preventing the secondary nuclei formation.

Morphology

Morphology of Phen added sample is given in Fig. 2.

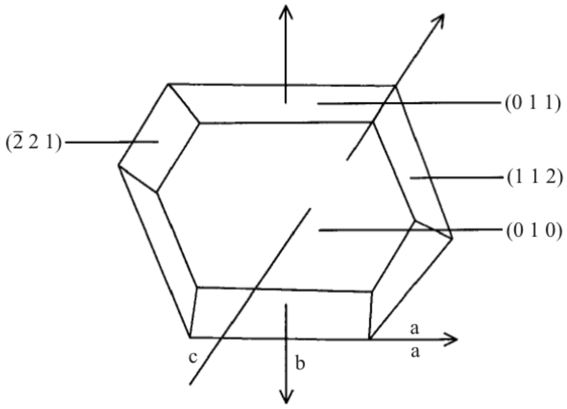


Fig. 2 Morphology of Phen added KHP

Results and discussion

Single crystal X-ray diffraction study

Single crystal X-ray diffractometry (XRD) analysis was performed using ENRAF(BRUKER)NONIUS CAD4 single crystal X-ray diffractometer. The lattice parameters are a=9.6329 Å, b=13.3035 Å, c=6.4786 Å and V=830.1192 Å^3. It belongs to orthorhombic system and the lattice parameters are in good agreement with the reported values (JCPDS data card No. 00-031-1855). XRD analysis shows that additive has not entered into the crystal and it has not changed the crystallinity of the material.

FTIR spectra

The FTIR spectra was recorded for both the samples including pure KHP using AVATAR 330 FTIR by KBr pellet technique in the range 500–4000 cm^{-1}. The characteristic vibrational frequencies of pure KHP and organic additive Phen added KHP are very similar (Figs 3a and b).

XRD and FTIR studies clearly reveal that the GPE of organic dopant is not connected with the additive entering into the crystal. When the impurity distribution coefficient is very low, the impurities are practically not incorporated into the crystal [28]. The rapid growth process is caused by the adsorption of the impurity at the flat surface or at the step edge [29]. It has been reported that at low dopant concentrations, adsorption can take place at kink sites (Bliznakov mechanism) or at the surface terrace (Cabrera Vemilyea mechanism) [30].

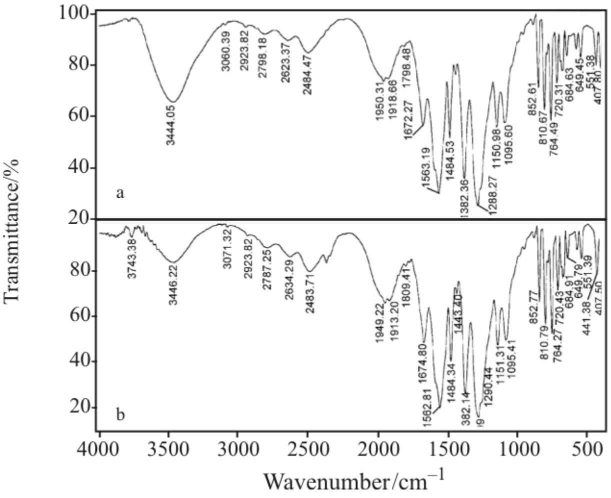


Fig. 3 FTIR spectrum of a – pure KHP and b – Phen added KHP

Thermal studies

TG-DTA

The simultaneous obtained TG-DTA curves in nitrogen (Figs 4a and b) at a heating rate of 20°C min^{-1} reveal that there is no physically adsorbed water in the molecular structure of crystals grown from Phen added KHP solution. TG curve also shows a gradual mass loss and residual mass obtained at 600°C is only 37.89% (Fig. 4b).

Differential scanning calorimetry

The DSC analysis of crystals grown from pure and Phen added KHP solutions was carried out between 50 and 600°C in the nitrogen atmosphere (Figs 5a and b). DSC shows that there is no physically adsorbed water in the molecular structure of crystals

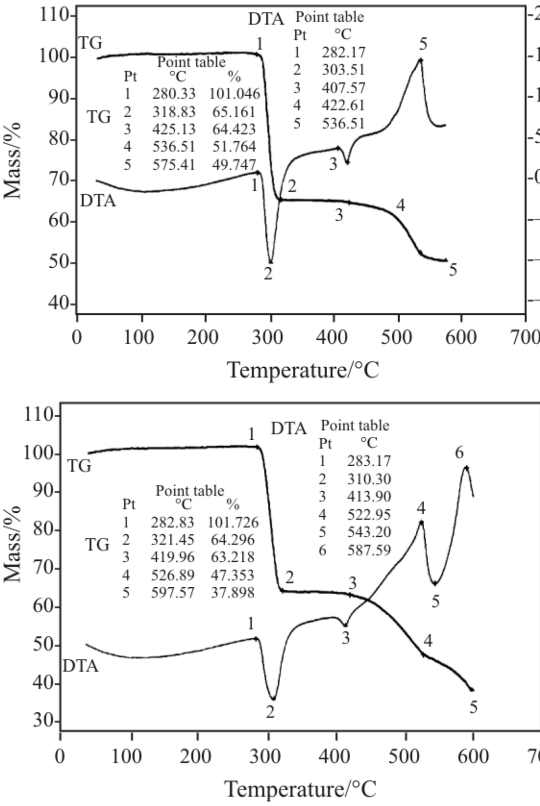


Fig. 4 TG-DTA curve of a – pure KHP (top) and b – Phen added KHP (bottom)

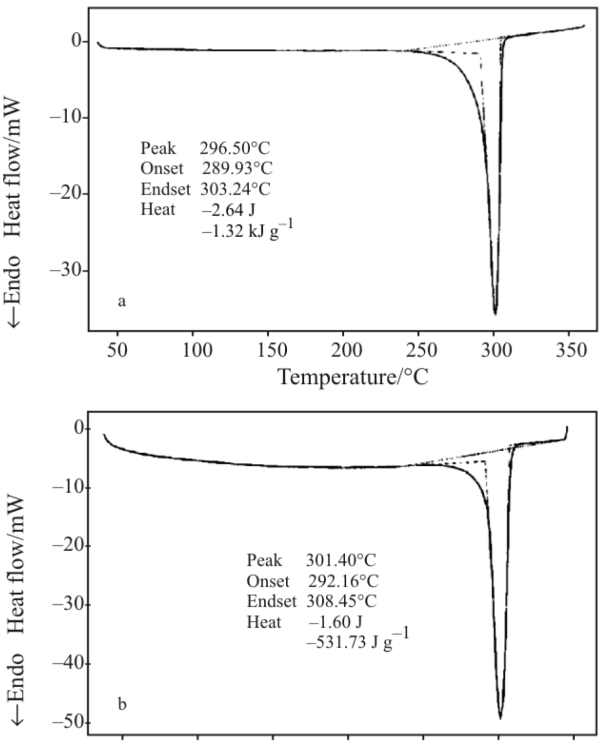


Fig. 5 DSC curve of a – pure KHP and b – Phen added KHP

grown both the solutions. Studies reveal the purity of the material. No decomposition up to melting point ensures the suitability of the material for application in lasers where the crystals are required to withstand high temperatures.

SEM

Scanning electron microscope (SEM) study gives information about the surface nature and its suitability for device fabrication. Also, it is used to check the presence of imperfections. It has been reported that the effectiveness of different impurities in changing the surface morphology is different [30]. At low concentrations of dopants, the effects are reflected by changes in configuration of grown structures [30]. The SEM photographs are given in Figs 6a and b.

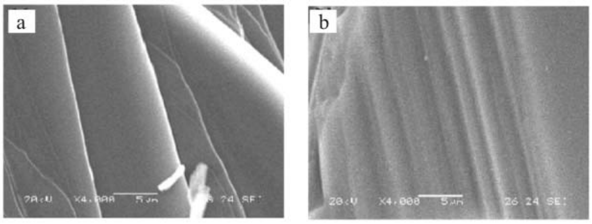


Fig. 6 SEM photographs of crystals grown from a – pure KHP and b – Phen added KHP

SEM photograph of pure KHP (Fig. 6a) shows sharp edge developments on the surface of the crystal. A markedly fine layered structure for the crystal grown from Phen doped solution is shown in SEM (Fig. 6b). It appears that the crystalline perfection improves much better in the presence of the dopant.

SHG efficiency

Second harmonic generation test on the crystals were performed by Kurtz powder SHG method [31]. A Nd: YAG laser with a modulated radiation of wavelength 1064 nm was used as the optical source and directed on the powdered sample through a filter. The doubling of frequency was confirmed by the green radiation of wavelength 532 nm.

Although many materials have been identified that have higher molecular non-linearities, the attainment of second-order effects requires favorable alignment of the molecule within the crystal structure [32]. The efficient SHG demands specific molecular alignment of the crystal to be achieved facilitating non-linearity in the presence of dopant. It has been reported that the SHG can be greatly enhanced by altering the molecular alignment through inclusion complexation [33].

Table 1 SHG output

System	$I_{2\omega}$/mV
KHP	163–165
KHP/Phen	136–138

Input radiation used is 5 millipoise/pulse. Intensity of second harmonic generation gives an indication of NLO efficiency of the material. Depressed SHG output in the case of Phen dopant is quite likely due to the disturbance of charge transfer. It appears that because of the orientational cancellation, the second-order susceptibility for SHG vanishes (Table 1).

We believe that by changing the growth conditions and the method, Phen can be an effective dopant in enhancing the NLO properties. Our belief is based on the fact that the presence of delocalized aromatic organic molecule resulting in a proper molecular alignment can result in much higher second-order NLO efficiencies. Influence of higher concentrations of Phen on SHG efficiency can reveal a lot of information and the work is in progress.

Conclusions

The incorporation of small quantities of 1,10-phenanthroline, a new additive has enhanced the metastable zone width of KHP solutions in their supersaturated region. Phen promotes the crystal growth process of KHP in slightly acidic solutions (pH ~4.5) very well. FTIR and XRD investigations reveal that the GPE of organic dopant is caused by the adsorption of dopant on the flat surface or the step edges of the crystal. High concentrations of Phen inhibit the growth process by blocking the active sites. DSC and TG-DTA studies reveal the suitability of the material for laser applications. SEM images reveal that the surface imperfections are minimized in the presence of the dopant. Depressed SHG efficiency with Phen dopant is rationalized by envisaging an unfavourable molecular alignment which affects the non-linearity.

References

1 K. Sangwal and E. Meilniczek-Brzoska, J. Cryst. Growth, 267 (2004) 662.
2 S. Meenakshisundaram and R. Markkandan, Trans. Met. Chem., 29 (2004) 308.
3 S. Y. Sawant, V. M. S. Verenkar and S. C. Mojumdar, J. Therm. Anal. Cal., 90 (2007) 669.
4 J. S. Skoršepa, K. Györyová and M. Melník, J. Thermal Anal., 44 (1995) 169.
5 E. Jóna, E. Rudinská, M. Sapietová, G. Rudinská and S. C. Mojumdar, J. Therm. Anal. Cal., 90 (2007) 687.
6 G. Madhurambal, P. Ramasamy, P. A. Srinivasan and S. C. Mojumdar, J. Therm. Anal. Cal., 90 (2007) 673.

7 K. G. Varshney, V. Jain, A. Agrawal and S. C. Mojumdar, J. Therm. Anal. Cal., 86 (2006) 609.
8 M. T. Saleh, S. C. Mojumdar and M. Lamoureux, Res. J. Chem. Environ., 10 (2006) 14.
9 R. A. Porob, S. Z. Khan, S. C. Mojumdar and V. M. S. Verenkar, J. Therm. Anal. Cal., 86 (2006) 605.
10 S. C. Mojumdar, K. G. Varshney and A. Agrawal, Res. J. Chem. Environ., 10 (2006) 89.
11 G. Madhurambal, P. Ramasamy, P. A. Srinivasan and S. C. Mojumdar, J. Therm. Anal. Cal., 86 (2006) 601.
12 S. C. Mojumdar, L. Raki, N. Mathis, K. Schmidt and S. Lang, J. Therm. Anal. Cal., 85 (2006) 119.
13 S. C. Mojumdar, G. Madhurambal and M. T. Saleh, J. Therm. Anal. Cal., 81 (2005) 205.
14 E. Jóna, M. Pajtasova, D. Ondrusova and P. Šimon, J. Anal. Appl. Pyrolysis, 63 (2002) 17.
15 S. C. Mojumdar, L. Martiška, D. Valigura and M. Melník, J. Therm. Anal. Cal., 81 (2005) 243.
16 D. Czakis-Sulikowska, A. Czylkowska and A. Malinowska, J. Therm. Anal. Cal., 65 (2001) 505.
17 S. C. Mojumdar, J. Miklovic, A. Krutošíková, D. Valigura and J. M. Stewart, J. Therm. Anal. Cal., 81 (2005) 211.
18 S. C. Mojumdar, Res. J. Chem. Environ., 9 (2005) 23.
19 G. Madhurambal, S. C. Mojumdar, S. Hariharan and P. Ramasamy, J. Therm. Anal. Cal., 78 (2004) 125.
20 S. C. Mojumdar, J. Therm. Anal. Cal., 64 (2001) 1133.
21 E. A. Ukraintseva, V. A. Logvinenko, D. V. Soldatov and T. A. Chingina, J. Therm. Anal. Cal., 75 (2004) 337.
22 S. C. Mojumdar, J. Therm. Anal. Cal., 64 (2001) 629.
23 K. G. Varshney, A. Agrawal and S. C. Mojumdar, J. Therm. Anal. Cal., 90 (2007) 721.
24 V. A. Kuznetsov, J. M. Okhrimenko and Miroslawa Rak, J. Cryst. Growth, 193 (1998) 164.
25 J. Nyvlt, R. Rychly, J. Gottfried and J. Wurzelova, J. Cryst. Growth, 6 (1970) 151.
26 N. P. Zaitseva, L. N. Rashkovich and S. V. Bagatyareva, J. Cryst. Growth, 148 (1995) 276.
27 H. E. Buckley (Ed.), Crystal Growth, Wiley, Network, 1951.
28 Miroslawa Rak, N. N. Eremin, J. A. Eremina, V. A. Kuznetsov, T. M. Okhrimenko, N. G. Furmanova and E. P. Efremova, J. Cryst. Growth, 273 (2005) 577.
29 Miroslawa Rak, N. N. Eremin, J. A. Eremina, V. A. Kuznetsov, T. M. Okhrimenko, N. G. Furmanova and E. P. Efremova, J. Cryst. Growth, 273 (2005) 586.
30 K. Sangwal, Prog. Cryst. Growth Charact., 32 (1996) 3 and references therein.
31 S. K. Kurtz and J. J. Perry, J. Appl. Phys., 39 (1968) 3798.
32 S. R. Hall, P. V. Kolinsky, R. Jones, S. Allen, P. Gordon, B. Boshwell, D. Bloor, P. A. Norman, M. Hursthouse, A. Karaulov and J. Baldwin, J. Cryst. Growth, 79 (1986) 745.
33 Y. Wang and D. F. Eaton, Chem. Phys. Lett., 120 (1985) 441.

DOI: 10.1007/s10973-008-9182-0