Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 150 (2015) 712–720

Contents lists available at ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

journal homepage: www.elsevier.com/locate/saa

Synthesis, crystal structure and characterization of a new optical di-lithium di-phthalate single crystals

D. Saravanan [a], G. Ramesh Kumar [b], S. Gokul Raj [c], S. Mohan [c,*], B. Sivakumar [d]

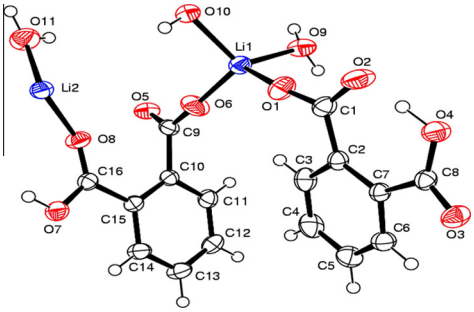
[a] Department of Physics, Sri Venkateshawaraa College of Engineering & Technology, Ariyur 605102, India
[b] Department of Physics, University College of Engineering Arni, Anna University Chennai, Arni 632317, India
[c] Department of Physics, Vel Tech University, Avadi, Chennai 600 062, India
[d] Department of Physics, University College of Engineering Kanchipuram, Anna University Chennai, Kanchipuram 631552, India

HIGHLIGHTS

- New optical di-lithium di-phthalate single crystals is synthesized.
- The crystal is a potential candidate for the third order NLO applications.
- The grown crystals were subjected to several analytical techniques to characterize the crystal.
- On improving mechanical strength, the crystal can be used in devices.

GRAPHICAL ABSTRACT

A view of the molecular complex of Df DLDP is shown above. The vibrational structure of the compound confirms the presence of various functional groups in the molecule. Mass spectrometric analysis provides the molecular weight of the compound and possible ways of fragmentations occurring in the compound. Thermal stability of the crystal was also studied by simultaneous TGA/DTA analyses. The UV–Vis–NIR spectrum was recorded to study the transmittance properties of the grown crystals.



ARTICLE INFO

Article history:
Received 22 July 2014
Received in revised form 3 June 2015
Accepted 6 June 2015
Available online 12 June 2015

Keywords:
Di-lithium diphthalate
Single crystal
Hydrogen bonds
FT-IR
UV–Vis–NIR
Mass spectrometry

ABSTRACT

Single crystals of a new alkali phthalic complex salt of di-lithium di-phthalate ($C_{32}H_{30}Li_4O_{21}$) (DLDP) were grown by slow evaporation of an aqueous solution at room temperature. The compound crystallizes in a monoclinic system with a centrosymmetric space group having the unit cell parameters; $a = 17.037(5)$ Å, $b = 5.134(5)$ Å, and $c = 21.398(5)$ Å and $\alpha = 90.000(5)°$, $\beta = 113.195(5)°$, and $\gamma = 90.000(5)°$ with $Z = 2$. The structure has been refined up to a R-value of 0.0828 from 26,248 observed reflections using a three-dimensional X-ray diffraction intensity data. The vibrational structure of the compound confirms the presence of various functional groups in the molecule. Mass spectrometric analysis provides the molecular weight of the compound and possible ways of fragmentations occurring in the compound. Thermal stability of the crystal was also studied by simultaneous TGA/DTA analyses. The UV–VIS–NIR spectrum was recorded to study the transmittance properties of the grown crystals. The obtained results are discussed in detail.

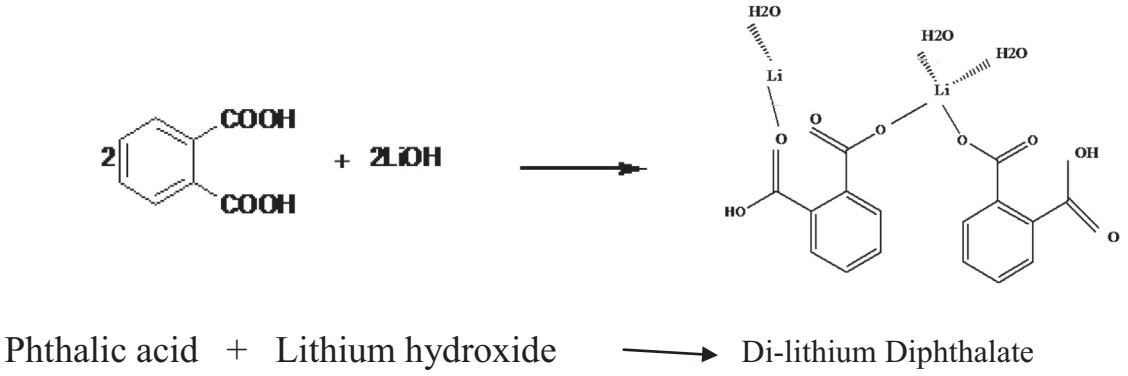
* Corresponding author.
E-mail address: smoh14@rediffmail.com (S. Mohan).

http://dx.doi.org/10.1016/j.saa.2015.06.010
1386-1425/

Introduction

Synthesizing metallo-organic crystals have been reported as a new approach for materials with interesting nonlinear optical properties [1–4]. In metallo-organics, polarizable organic molecules are stoichiometrically bound with in an inorganic host [5]. The advantage of metallo-organic materials is that the crystal can be grown from aqueous solution and they form three-dimensional crystals which can be easily cut and polished [6]. The other favourable properties are high optical damage threshold, large thermal conductivity, adequate birefringence for phase matching and good mechanical characteristics. The low-temperature solution growth is an important technique for growing large-size nonlinear optical crystals. The crystals grown by this technique find wide spread applications in key areas like inertial confinement fusion [6], X-ray spectroscopy and laser energy measurement [7] etc., In order to grow large crystal, one has to ensure that the available nutrient is deposited on the chosen seed only during the growth period. Otherwise, any spontaneous nucleation occurring during the growth will take away a portion of the solute, thus making it difficult or impossible to grow a single large crystal. Although crystals of different orientations with different morphology are grown by conventional solution growth technique, the specific orientation with good quality is needed for applications.

Several metallo-organic large-size good-quality single crystals such as Potassium acid phthalate (KAP), Sodium acid phthalate (NaAP) and Lithium acid Phthalate (LiAP) were successfully grown by this method [8–11]. Crystals of phthalic acid derivatives are potential candidates for NLO and electro-optic processes [12]. Rubidium acid phthalate (RbAP), Cesium acid phthalate (CsAP), Thallium acid phthalate (TiAP) and Ammonium acid phthalate (NH_4AP) are well-known reported metallo-organic phthalic acid crystals. The inorganic hydrogen phthalate crystals are widely known for their applications in the long-wave X-ray spectrometers. Their optical, piezo-electric, NLO and elastic properties were already reported by Belyeav et al., [13]. In the present investigation, a new mixed Lithium Phthalate single crystal has been grown by the conventional slow cooling technique. The preliminary X-ray structure investigation revealed that the colourless crystals of



Scheme 1. Reaction of DLDP.

Table 1
Crystal data and structure refinement for di-lithium diphthalate.

Identification code	DLDP	
Empirical formula	$C_{32}H_{30}Li_4O_{21}$	
Formula weight	778.32	
Temperature	293(2) K	
Wavelength	0.71073 A°	
Crystal system, space group	Monoclinic, *P*2/*n*	
Unit cell dimensions	*a* = 17.037(5) Å	*α* = 90.000(5)°
	b = 5.134(5) Å	*β* = 113.195(5)°
	c = 21.398(5) Å	*γ* = 90.000(5)°
Volume	1720.4(18) $Å^3$	
Z, calculated density	2, 1.503 Mg/m^3	
Absorption coefficient	0.125 mm^{-1}	
F(000)	804	
Crystal size	0.30 × 0.20 × 0.20 mm	
Theta range for data collection	1.30–36.24°	
Limiting indices	$-23 \leqslant h \leqslant 28$, $-7 \leqslant k \leqslant 8$, $-35 \leqslant l \leqslant 34$	
Reflections collected/	Unique 26,248/7861 [*R*(int) = 0.0223]	
Completeness to theta	=25.00 100.0%	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.952 and 0.901	
Refinement method	Full-matrix least-squares on F^2	
Data/restraints/parameters	7861/6/287	
Goodness-of-fit on F^2	1.054	
Final *R* indices [*I* > 2sigma(*I*)]	R1 = 0.0480, wR2 = 0.1306	
R indices (all data)	R1 = 0.0828, wR2 = 0.1559	
Extinction coefficient	0.0014(5)	
Largest diff. peak and hole	0.445 and −0.214 e A^{-3}	