Xrd Studies On Pure and Zinc Sulphate Doped L -Tartaric Acid Crystals

[*]S. Johnson Navamani[1], G. Narayanasamy[2], P. Sumithraj Premkumar[1]
[1](1Department of Physics, Pope's College, Sawyerpuram, Thoothukudi – 628251)
[2](Department of Physics, Kamaraj College, Thoothukudi – 628003)
Corresponding Author: S. Johnson Navamani

Abstract: *Pure and zinc sulphate doped L(+)- tartaric acid crystals were grown by slow evaporation technique from aqueous solution. The concentration of zinc sulphate used in the present study is 0.005M, 0.01M and 0.05M. X-ray diffraction data were collected for powder samples and used for the estimation of lattice variation and thermal parameters like Debye–Waller factor, mean-square amplitude of vibration and Debye temperature. The variation of lattice volume of the grown crystals was found which shows that the dopant has entered into the crystal lattice. The thermal parameters of pure and zinc sulphate doped L(+)- tartaric acid single crystals do not follow any particular order.*
Keywords: *L (+)-tartaric acid crystals, PXRD, lattice parameters, Debye–Waller factors, Debye temperatures.*

I. Introduction

Organic materials attract a great deal of attention due to their applications in optical devices, such as optical switches, optical modulators, optical communications, optical data storage etc. [1 – 2]. The effect of dopants on pure materials are of great interest from both solid state science as well as technological points of view. L(+) - tartaric acid ($C_4H_6O_6$) is a organic crystals and it belongs to the monoclinic system with space group $P2_1$. The unit cell parameters are a = 7.5421 Å, b = 6.0065 Å, c = 6.0650 Å, β= 100.16° with bimolecular unit cell. Growth and characterization of L(+) - tartaric acid have been reported in the Literature [3 – 7]

The Debye temperature is derivable from experimental data like specific heat, elastic constants, X-ray and neutron diffraction intensities, etc. It is possible to estimate the Debye temperature from the data like melting points, compressibility and micro hardness by the use of semi empirical relations [8], but the values obtained from them are not as accurate as those obtained from specific heat or elastic constants. Various methods of determination of Debye temperatures have been discussed in reviews by Blackman [9] and Alers [10]. An efficient method of determining the Debye temperature is from the Debye-Waller factor, which is obtained from the X-ray powder diffraction data [11 – 12]. By using this method, the Debye temperature has been estimated for hexagonal dysprosium, gadolinium, lutetium and yttrium, mixed crystals of Mg_xZn_{1-x} $SO_4.7H_2O$[13]$AgCl_xBr_{1-x}$ [14], Ni_xMg_{1-x} $SO_4.7H_2O$[15], tartrate crystals [16] and alkali halides [17 – 19] etc. As this method is suitable for any crystal system, it can be used to determine the Debye temperature for the L(+) - tartaric acid single crystals. X-ray diffraction data were collected from powder samples of the grown crystals and used for the estimation of lattice variation and thermal parameters like mean Debye-Waller factor, mean square amplitude of vibration, Debye temperature and Debye frequency. The results are reported here.

II. Experimental

Recrystallized analytical reagent (AR) grade samples of L(+) - tartaric acid and $ZnSO_4.7H_2O$ were used in the present work for the growth of single crystals from aqueous solution by slow evaporation method. Deionized water were used as the solvent in the present study. The saturated concentration of the L(+) - tartaric acid growth solution at room temperature was determined and it is found that 3.2 M. The dopant concentrations used in this study were 0.005, 0.01 and 0.05M. The dopant (zinc sulphate) was mixed with the pure solution directly. The growth solution was kept in a constant temperature bath in the predetermined temperature. Small crystals appeared in the beginning due to slow evaporation and grew larger in considerable finite time. Best crystals were selected from this and used for the measurements.

X-ray diffraction data were collected from powder samples of crystals using an automated diffractometer with monochromated CuK_α (λ = 1.5418 Å) radiation and scintillation counter at a temperature of 25±1 ∘C. The reflections were indexed using powder x [21] software. Lattice parameters were determined from the indexed data using high angle reflections.

The mean Debye–Waller factors (Bobs) were determined by the Wilson plot method. For the calculation of structure factors, the atomic scattering factors were taken from the literature [22 – 23]. For pure L(+) - tartaric acid crystal, the structure factor is:

$$F = 8f_C + 12f_H + 12f_O \qquad (1)$$

It has been reported on the doped crystals that some of the doping atoms are located in the host lattice and others are distributed at random positions, especially on the surface of the crystals [24]. So, in the present study the structure factors for impurity (zinc sulphate) added L(+) – tartaric acid crystals are:

$$F = 8f_C + 12f_H + 12f_O + p(f_{Cu} + f_S + 4f_O) \qquad (2)$$

where 'p' is the impurity concentration.

The mean Debye-Waller factor for the systems considered in the present study was found by using the Wilson plot method [25]. Mean square amplitudes of vibration and mean Debye temperatures were then calculated using the following relations: We have [26],

$$B = 8\pi^2 \langle u^2 \rangle \qquad (3)$$

where $\langle u^2 \rangle$ is the mean square amplitude of vibration.

From the Debye-Waller theory,

$$B = 6h^2 W(x)/(mkT) \qquad (4)$$

where h is the Planck's constant, m is the mean atomic mass of the crystal, k is the Boltzmann's constant and T is the absolute temperature. We have,

$$W(x) = \{\varphi(x)/x^2\} + (x/4) \qquad (5)$$

where $x = \theta_D/T$ (θ_D is the Debye temperature) and

$$\varphi(x) = \int_0^x \{e^y/(1 - e^y)\}\, dy \qquad (6)$$

The values of $W(x)$ for a wide range of x are tabulated by Benson and Gill [27]. From $W(x)$, x was found from the tables mentioned above. From x, Debye temperatures (θ_D) for systems considered in the present study were calculated. Knowing the Debye temperatures, the Debye frequencies were calculated using the relation [28], $\theta_D = f_D(h/k)$ where h is Planck's constant and k is Boltzmann's constant.

III. Result And Discussion

The maximum size of the grown crystals were harvested and all the crystals grown were found to be stable. The photograph of the pure and zinc sulphate doped L(+) - tartaric acid crystals is shown in fig 1. It is observed that the morphology of the doped L(+) - tartaric acid crystals is similar that the morphology of pure L(+) - tartaric acid crystal. The indexed XRD pattern of pure and ZnSO₄ doped L(+) - tartaric acid crystals are presented in fig. 2 and fig.3 respectively.
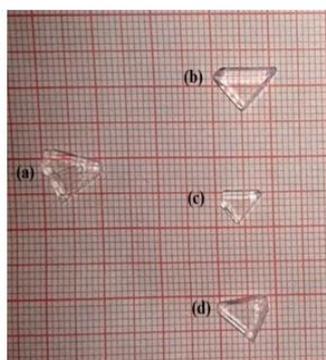

Fig.1: Photograph of the (a) pure (b) 0.005M (c) 0.01M (d) 0.05M ZnSO₄ doped L (+) - tartaric acid crystals
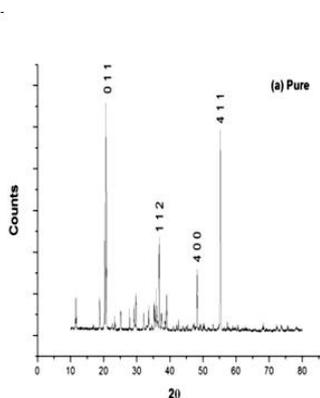
Fig. 2: Indexed x-ray diffraction pattern of pure L (+) - tartaric acid crystals
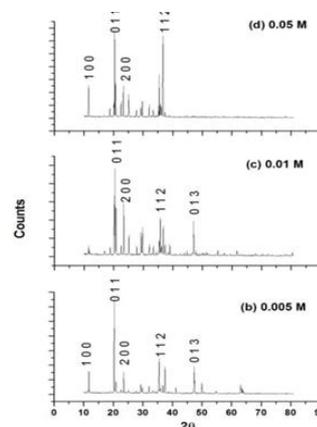
Fig. 3: Indexed x-ray pattern of zinc sulphate doped L (+) - tartaric acid crystals

The indexed data of pure L(+) - tartaric acid was compared with JCPDS data [File No. 33 1883]. The x-ray diffraction pattern of ZnSO₄ doped L(+) - tartaric acid single crystals are slightly differed in their relative intensities of pure L(+) - tartaric acid single crystals. Lattice parameters a, b, c and volumes of the pure and ZnSO₄ doped L(+) - tartaric acid single crystals estimated in the present study are given in table 1. Lattice variation was observed in the doped crystals in comparison with the pure crystals. The Debye-Waller factor (B), mean square amplitude of vibration ($\langle u^2 \rangle$), Debye temperature (θ_D) and Debye frequency (f_D) values of pure and zinc sulphate doped L(+) - tartaric acid crystals are provided in Table 2. No particular order was observed in the case of thermal parameters obtained with respect to impurity concentration. Debye frequencies observed in the present study lie in the infrared range. Similar results have been observed for the impurity added KDP (potassium dihydrogen orthophosphate) crystals [29–30].

Table 1: Lattice parameter of pure and doped L(+) - tartaric acid crystals

System	a (Å)	b (Å)	c (Å)	V (Å³)
Pure L(+) - tartaric acid	7.4868	6.0091	5.9547	263.70
0.005M ZnSO₄ doped L(+) - tartaric acid	7.5783	5.9817	6.0719	270.93
0.01M ZnSO₄ doped L(+) - tartaric acid	7.6036	5.9991	6.1179	274.69
0.05M ZnSO₄ doped L(+) - tartaric acid	7.6191	6.0073	6.1169	275.58

Table 2: Thermal parameters for pure and doped L(+) - tartaric acid crystals

Crystals	B (Å²)	$\langle u^2 \rangle$ (Å²)	θ_D(K)	$f_D(10^{12}$Hz)
Pure L(+) - tartaric acid	9.15	0.1160	208.6	4.345
0.005M ZnSO₄ doped L(+) - tartaric acid	12.42	0.1575	178.8	3.724
0.01M ZnSO₄ doped L(+) - tartaric acid	3.67	0.0465	1192.0	24.83
0.05M ZnSO₄ doped L(+) - tartaric acid	2.01	0.0255	1788.0	37.24

IV. Conclusion

Pure and ZnSO₄ doped L(+) – tartaric acid crystals were grown from aqueous solution in a predetermined temperature. The concentration of dopant used in the present is 0.005M, 0.01M and 0.05M. X-ray diffraction studies of all the grown crystals were carried out and the lattice parameter were determined. The variation of lattice parameter of doped L(+) – tartaric acid crystals compared to pure L(+) – tartaric acid crystals were observed and which confirms the entry of dopant in to the pure crystal lattice. The thermal parameters of pure and ZnSO₄ doped L(+) – tartaric acid crystals were determined and these parameters does not follow any particular order.

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