Lattice variation and thermal parameters of pure and impurity-added calcium tartrate tetrahydrate crystals

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Calcium tartrate tetrahydrate $CaC_4H_4O_6 \cdot 4H_2O$, is orthorhombic with a tetra molecular unit cell of dimensions $a = 9.21$, $b = 10.63$ and $c = 9.66$ Å with space group $P2_12_12_1$ [1]. The molecular weight is 260.1 and density is 1.818 g/cc [2].

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 microhardness by the use of semiempirical relations [3], 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 [4] and Alers [5]. An efficient method of determining the Debye temperature is from the Debye-Waller factor, which is obtained from the X-ray powder diffraction data [6, 7]. By using this method, the Debye temperature has been estimated for hexgonal dysprosium, gadolinium, lutetium and yttrium [8], $AgCl_xBr_{1-x}$ mixed crystals [9], alkali halides [6, 10–12], etc. As this method is suitable for any crystal system, it can be used to determine the Debye temperature for the calcium tartrate tetrahydrate 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.

The test tube diffusion method was employed to grow calcium tartrate single crystals in a gel medium. 0.5 M sodium meta silicate $(Na_2SiO_3 \cdot 9H_2O)$ was titrated with 0.5 M tartaric acid till the mixture attained the pH 4.2. This gelling mixture was allowed to set in glass tubes of length 200 mm and diameter 25 mm. The gel was set in about 48 h. After a gel aging of one day, the supernatant solution was added over the set gel. The supernatant solution was a mixture of 0.5 M calcium formate and 85% formic acid so that the pH of the solution was between 1 and 2. The details of crystal growth are discussed elsewhere [13].

Strontium added calcium tartrate tetrahydrate crystals were grown in six different impurity concentrations, viz. 0.4, 0.8, 1.2, 1.6, 2.0 and 10 mol%. Strontium chloride was mixed with the supernatant solution and allowed to diffuse into the gel medium containing tartaric acid.

Densities of the grown crystals were measured by the flotation method. The entry of the impurity into the host lattice was confirmed by atomic absorption spectroscopy (AAS). The atomic concentrations (Sr^{2+}/Ca^{2+}) were determined.

X-ray diffraction data were collected from powder samples of crystals using an automated diffractometer with monochromated Cu K_α ($\lambda = 1.5418$ Å) radiation and scintillation counter at a temperature of 25 ± 1 °C. The reflections were indexed following the procedures of Lipson and Steeple [14]. Processing of the raw intensity data was done following the procedures of Warren [15]. Lattice parameters were determined from the indexed data using high angle reflections. For the calculation of structure factors, the atomic scattering factors were taken from the literature [16, 17].

For pure calcium tartrate tetrahydrate crystal, the structure factor is:

$$F = 4f_{Ca} + 16f_C + 48f_H + 40f_O$$

Recently [18] on doing the structural characterization of doped calcium tartrate tetrahydrate crystals, it has been reported 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. In the host lattice the doping atom replaces calcium when an earth alkaline atom is used, but occupies an interstitial site when a transition metal ion is used.

So, in the present study the structure factors for impurity (strontium) added calcium tartrate tetrahydrate crystals are:

$$F = 4(1 - p)f_{Ca} + 4pf_{Sr} + 16f_C + 48f_H + 40f_O$$

where 'p' is the impurity concentration determined from AAS (mol% $\times 10^{-2}$, i.e., values provided in Table I multiplied by 10^{-2}).

The mean Debye-Waller factor for the systems considered in the present study was found by using the Wilson plot method [19]. Mean square amplitudes of

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TABLE I Lattice parameters[a], volumes, densities and impurity concentrations for pure and impurity added calcium tartrate tetrahydrate crystals

System	a (Å)	b (Å)	c (Å)	V (Å^3)	d (g/cc)	p (mol%)
Pure	9.227(13)	10.622(28)	9.652(8)	945.99	1.817	–
Impurity added (concentration in mol%)						
0.4	9.352(27)	10.556(10)	9.578(21)	945.50	1.839	1.740
0.8	9.282(8)	10.658(75)	9.558(103)	945.50	1.845	1.600
1.2	9.390(144)	10.683(72)	9.421(19)	945.06	1.863	1.636
1.6	9.476(205)	10.578(31)	9.492(54)	951.09	1.883	2.770
2.0	9.315(66)	10.694(154)	9.644(67)	960.69	1.904	2.740
10.0	9.534(64)	10.754(139)	9.521(113)	976.20	1.933	4.660

[a]esd's are given in parentheses.

vibration and mean Debye temperatures were then calculated using the following relations:

We have [20],

$$B = 8\pi^2 \langle u^2 \rangle$$

where $\langle u^2 \rangle$ is the mean square amplitude of vibration. From the Debye-Waller theory,

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

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,

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

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

$$\varphi(x) = \int^x \{e^y/(1 - e^y)\}\, dy.$$

The values of $W(x)$ for a wide range of x are tabulated by Benson and Gill [21]. 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 [22], $\theta_D = f_D(h/k)$ where h is Planck's constant and k is Boltzmann's constant.

Lattice parameters a, b, c and volumes of the grown crystals estimated in the present study are given in Table I. The estimated standard deviations were also calculated and presented in Table I. The lattice parameters obtained for the pure crystal in the present study compares very well with the values found in the literature [1]. The density observed for pure calcium tartrate tetrahydrate compares well with the values reported in the literature [2]. The value of density was found to increase with increasing impurity concentration and also the densities of the impurity-added calcium tartrate tetrahydrate crystals were higher than the pure ones. This shows that the impurity had entered into the lattice of the calcium tartrate tetrahydrate crystal. The lattice volumes were increasing with impurity concentration. However, the variation is not linear. The impurity concentrations determined from AAS also show that the uptake of impurity into the host lattice is not linear.

TABLE II Thermal parameters for pure and impurity added calcium tartrate tetrahydrate crystals

System	B (Å^2)	$\langle u^2 \rangle$ (Å^2)	θ_D (K)	$f_D(\times 10^{12}$ Hz)
Pure	11.2295	0.1422	181.2	3.7716
Impurity added (concentration in mol%)				
0.4	11.8590	0.1502	177.3	3.6960
0.8	9.6050	0.1216	197.1	4.1087
1.2	14.476	0.1833	160.5	3.3458
1.6	13.9735	0.1770	162.9	3.3958
2.0	10.6345	0.1347	187.2	3.9024
10.0	9.0565	0.1147	202.8	4.2276

The impurity concentration found in the crystals is more than that taken for crystallization for all the concentrations except for the highest one (10 mol%) (see Table I). Torres *et al.* [23] have also observed a similar result (5 mol% doping leads to 8.4 mol% in the crystal).

Values of Debye-Waller factor (B), mean square amplitude of vibration ($\langle u^2 \rangle$), Debye temperature (θ_D) and Debye frequency (f_D) are provided in Table II. 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 [24–26].

No comparison is made with other studies on the same material since there is no data available in the literature for the systems considered in the present study.

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