

X-ray Diffractometry, EDAX and SEM Studies on Gel Grown Cerium Tartrate Crystals

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Abstract—Cerium tartrate crystals were grown from sodium metasilicate gel and water solutions of tartaric acid and cerium chloride as the reactants. Crystals grown were spherulitic in size. X-ray diffractometry, EDAX, SEM Studies were carried out on Gel Grown Cerium Tartrate Crystals. X-ray studies reveal the crystallinity of $Ce_2(C_4H_4O_6)_3 \cdot 6H_2O$. Grown crystals exhibit varied morphology such as spiky spherulites, multi-arm dendrites and rectangular platelets. Qualitative elemental analysis (EDAX) shows presence of Ce.

Keywords: - Gel Method, XRD, EDAX, SEM, Cerium Tartrate

I. INTRODUCTION

Cerium is unique among other rare earth metals with only a single electron in the 4f shell when it is in ionic state. Its optical, luminescent and magnetic properties are studied widely. Cerium (Ce^{3+}) is used as a co-dopant in certain photo refractive crystals like $LiNbO_3$, $KNbO_3$ and $Sr_xBa_{1-x}Nb_2O_6$ [1] and laser crystals like $Y_3Al_5O_{12} : Nd$ and $YAlO_3$ [2]. Several compounds containing cerium are under study for their ferromagnetic, antiferromagnetic and superconducting properties. Optical and luminescent properties of laser scintillator crystals like YAG and YAP doped with Ce^{3+} ions are studied [3]. Studies on cerium oxalate crystals grown in hydro-silica gel have been reported [4]. Growth and characterization of several oxalates and mixed rare earth oxalates in silica gel also have been reported [5-7]. No report has been noticed on the study of cerium tartrate. Hence growth of these crystals is attempted. Cerium tartrate can be grown by gel technique since it has very low solubility in water. Growth and characterization of several tartrates and mixed rare earth tartrates in silica gel have already been reported. Grown crystals were characterized by XRD, SEM and EDAX.

II. EXPERIMENTAL

Cerium tartrate crystals were grown from sodium metasilicate gel and water solutions of tartaric acid and cerium chloride. The growth of cerium tartrate crystals were accomplished by the controlled diffusion of Ce^{3+} ions through the silica gel impregnated with tartaric acid. A stock solution for the gel formation was prepared according to Henisch [8] by taking 22gm $Na_2SiO_3 \cdot 9H_2O$ and 250 ml water. All experiments were carried out by single tube diffusion method. The tubes employed were borosilicate glass tubes of 2.5cm diameter and 20cm long. The experiments were carried out at ambient temperature. Silica gel was prepared by adding a solution of sodium metasilicate of specific gravity $1.05 gm/cm^3$ to tartaric acid (0.25M-1.0M), drop by drop with continuous stirring to avoid excessive local ion concentration, which may cause premature gelling and make the final solution inhomogeneous. The pH of the gel was adjusted between a value of 3.4 and 4.8. The solution with the desired value of pH was then transferred to several glass tubes. Once gelled, an aqueous solution of cerium chloride (0.25M-1.5M) was carefully poured with the help of a pipette over the set gel, in order to avoid any gel breakage. The mouth of the test-tube is then covered with cotton plug to avoid the inclusions of impurities. The grown spherulitic crystals of cerium tartrate were further characterized by XRD, EDAX and SEM techniques.

III. SCANNING ELECTRON MICROSCOPY

Scanning electron micrographs of gel grown cerium tartrate crystals at different magnifications are shown in Figs. 1 to 5. It shows the layered type spherulitic formation of cerium tartrate. It is also observed that spherulites are grown along with single crystals. The layers are clearly circular in shape when examined

under a high magnification as shown in Fig. 2. Few such a spherulites are further observed under still higher magnification as shown in Fig.3. It reveals that the circular layered structure is actually clustering of small crystallites in spherical envelope. Each tiny crystallite has well defined habit faces and is either a platelet like or prismatic rod formation. An aggregate of crystallites spread over the surface of a spherulitic formation at still higher magnification is shown in Fig.4. That these crystallites collectively tend to orient themselves as to be in a spherical formation as revealed in Fig.2. In Fig. 3. petal like formation of the elongated aggregate crystal is shown. These spherulites were found to take a form from perfect sphere to oval shape, having crystallites emerging outward from the centre. Thus, the surface of each isolated spherulite is composed of tiny crystallites aggregated in spherical formation. Here the spherulitic formation is not due to radially diverging crystal fibers from centrally located nuclei, but it is, in fact, an agglomeration of tiny crystallites accommodating themselves in a spherical envelope. This spherulitic formation is just a collection of randomly oriented crystallites arranging themselves in spherical shape, probably due to requirement of minimum volume. Each crystallite is a platelet with well-defined faces. The observations reported here are in close resemblance with some of those reported earlier [9-11]

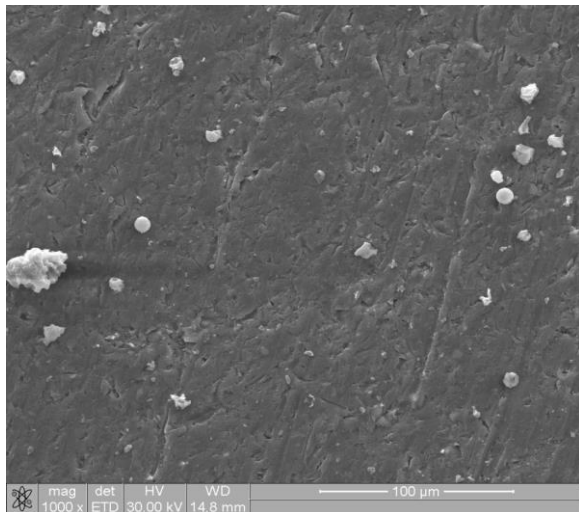


Fig. 1 Scanning electron micrograph depicting a spherulites of cerium tartarate crystals at magnification 1000x
Size of the spherulites = 9.02um

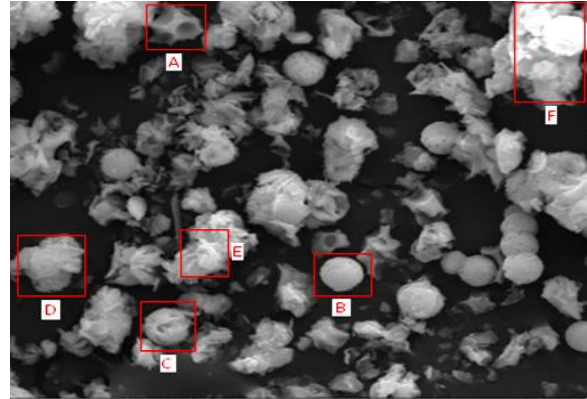


Fig. 2 Scanning electron micrograph depicting a spherulites of cerium tartarate crystals at magnification 2500x. Size of the spherulites = 9.33um

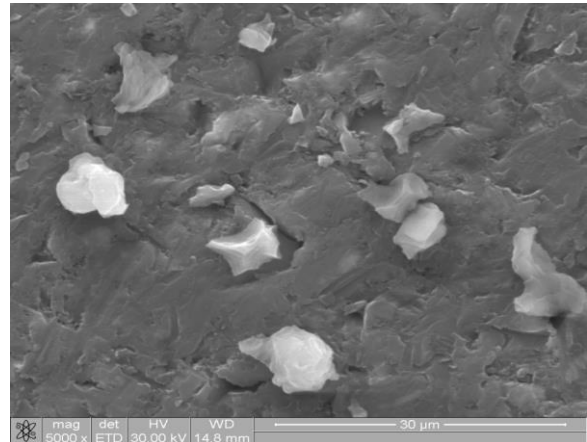


Fig. 3 Scanning electron micrograph depicting a spherulite of cerium tartarate crystals at magnification 5000x

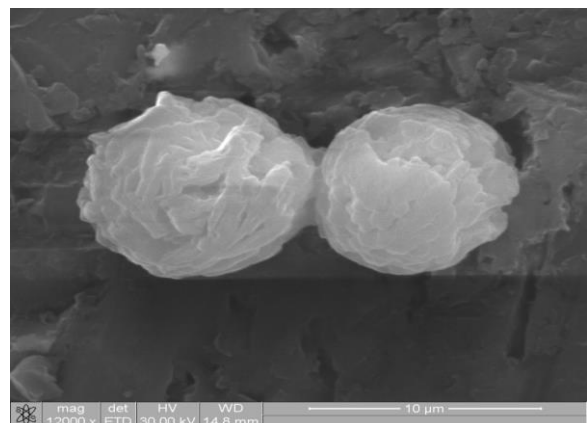


Fig.4 Scanning electron micrograph depicting a spherulite of cerium tartarate crystals at magnification 12000x.
Size of the spherulites = 10.13um
Average size of the spherulites = 9.49um

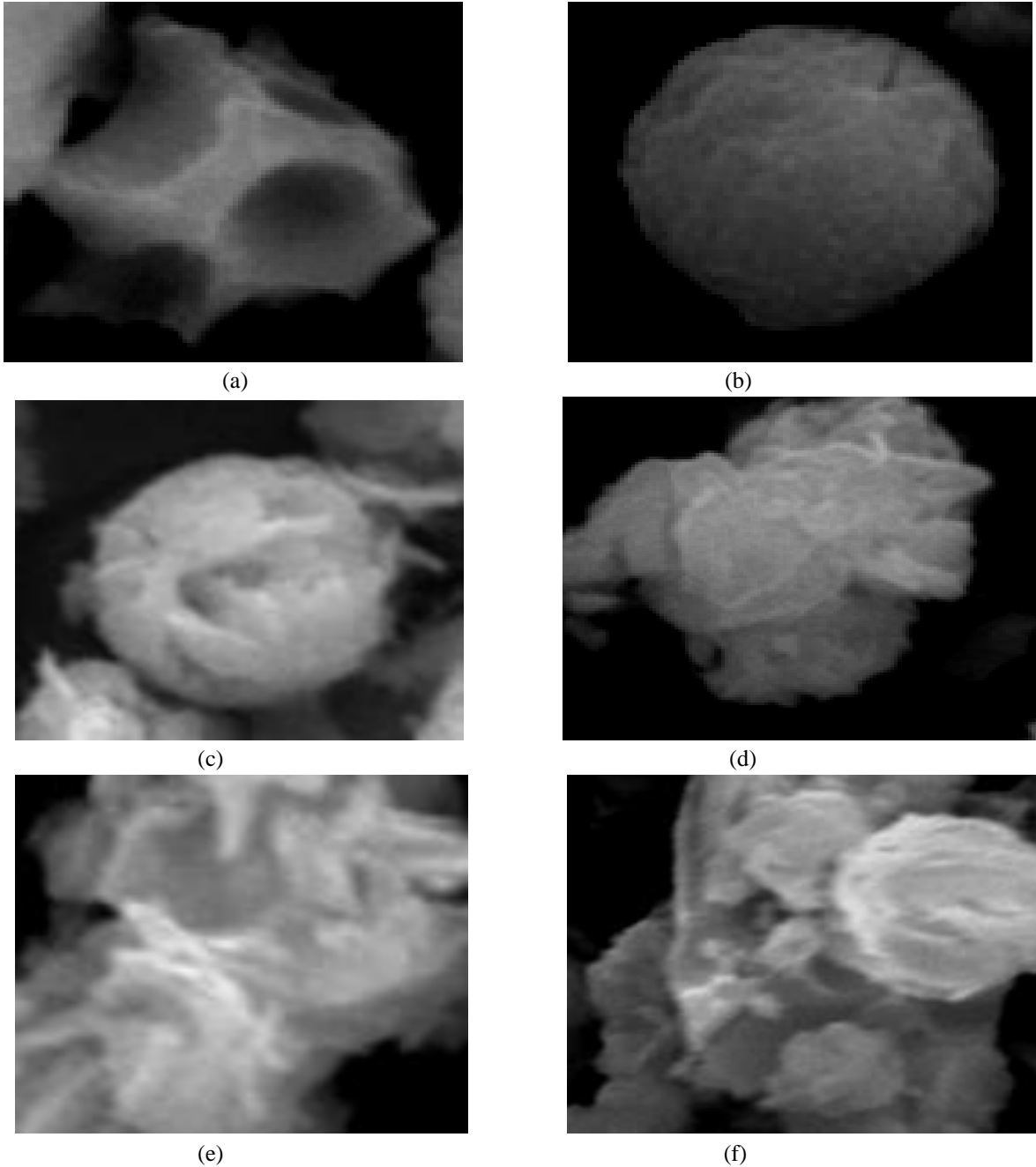


Fig. 5 Enlarged view of regions A, B, C, D, E, F, of the inset of Fig. 3

IV.XRD ANALYSIS OF CERIUM TARTRATE

X-ray powder diffractogram of the cerium tartrate sample was recorded using Reguka Miniflex, Japan, diffractometer with $\text{CuK}\alpha$ radiations of wavelength 1.54051 \AA at 30kV and 15mA with a step of 0.01° and a step time of 0.2s. The powder XRD pattern of cerium tartrate is shown in Fig .6. The diffractogram was indexed using POWD (an Interactive Powder Diffraction Data Interpretation and Indexing

Program, Version 2.2) software. The revelation of well-defined peaks at specific 2θ angle suggests that the grown crystals are polycrystalline. The diffraction peaks are indexed and the crystal system is found to be monoclinic. The unit cell parameters are $a= 7.1095 \text{ \AA}$, $b= 5.1838 \text{ \AA}$, $c = 3.4016 \text{ \AA}$ and $\alpha=90^\circ$, $\beta = 92.474^\circ$, $\gamma =90^\circ$, and unit cell volume is 125.25 \AA^3 . The powder X-ray diffraction data such as values of 2θ , 'd' values, intensity ratio and their

corresponding (hkl) plane for cerium tartrate are listed in Table 1. To the best of author’s knowledge, x-ray diffraction data on these crystals is limited only to the 2θ values and intensity [12]. Cell parameters, (hkl) values and d-spacings are reported for the first time.

Determination of Grain size from XRD spectra

From the XRD pattern, it is observed that, each peak has got a finite width. The grain size is determined by measuring the width of the line with highest intensity peak. The grain size can be calculated by using the Debye–Scherrer formula [13].

Grain size $D = 0.9\lambda / \beta \cos(\theta)$, where, β is full width of half maxima in radian and D is grain size of the crystal.

$$\begin{aligned}
 D &= 0.9 \times 1.54051 \text{ \AA} / 0.235 \times \cos(22.2^\circ) \\
 &= 1.3865 \times 10^{-10} / 0.003797 \\
 &= 365.15 \text{ \AA} \\
 &= 36.51 \text{ nm}
 \end{aligned}$$

The calculated average grain size is 36.51nm. The analysis of different diffraction peaks indicates the formation of monoclinic system. The diffraction peaks at 2θ very carefully and converted into ‘d’ value using the Bragg’s equation putting n=1. By measuring the peak heights above the background in nm and scaling the value up so that the tallest peak has a value of 100.

Table 1 Powder X-ray diffraction data for cerium tartrate crystals

Line No	2 theta (deg.)		FWHM	Intensity (CPS)	I/I ₀	d-Value (Å)		Diff	Indices (hkl)
	Obs.	Cal.				Obs.	Cal.		
1	21.20	21.20	0.235	34	70	4.1873	4.1873	0.000	110
2	26.20	26.20	0.235	31	65	3.3984	3.3984	0.000	001
3	28.60	28.60	0.235	32	66	3.1185	3.1185	0.000	-101
4	29.60	29.60	0.235	31	66	3.0153	3.0153	0.000	101
5	30.40	30.48	0.235	38	80	2.9378	2.9298	-0.085	210*
6	31.80	31.45	0.235	32	67	2.8116	2.8421	0.351	011?
7	36.40	36.88	0.235	32	67	2.4661	2.4349	-0.484	120?
8	39.40	--	0.471	35	72	2.2850	--	--	--
9	40.00	39.87	0.235	32	66	2.2521	2.2592	0.131	-211*
10	41.00	41.36	0.235	35	73	2.1994	2.1809	-0.363	211
11	44.40	43.89	0.235	48	100	2.0386	2.0609	0.507	021?
12	45.60	45.71	0.471	32	66	1.9877	1.9832	-0.108	-301*
13	47.80	47.71	0.235	39	80	1.9012	1.9045	0.088	301*
14	52.40	52.29	0.235	32	67	1.7446	1.7481	0.112	320
15	53.40	52.94	0.235	48	100	1.7143	1.7279	0.456	030
16	56.20	56.15	0.235	42	88	1.6353	1.6367	0.050	102*
17	57.00	56.98	0.235	31	64	1.6143	1.6147	0.016	012
18	57.40	57.46	0.235	38	80	1.6040	1.6025	-0.058	-401
19	59.40	59.44	0.471	45	95	1.5546	1.5538	-0.035	230
20	61.80	61.83	0.471	40	83	1.4999	1.4992	-0.030	131
21	65.60	65.64	0.235	36	75	1.4219	1.4211	-0.044	022
22	66.00	66.25	0.235	38	80	1.4142	1.4096	-0.245	-302*
23	67.80	67.64	0.471	36	76	1.3810	1.3839	0.158	122?
24	68.80	68.82	0.471	33	69	1.3634	1.3630	-0.020	-421
25	75.80	75.72	0.235	30	63	1.2539	1.2550	0.081	-402*
26	77.20	76.93	0.706	48	99	1.2346	1.2383	0.273	-322
27	78.00	78.32	0.471	31	64	1.2239	1.2198	-0.316	-412?

Texture Coefficient:

The texture coefficient proposed by Charles S. Barret and T.B. Massalski [14] is based on Harris’s work [15]

$$\text{Texture coefficient} = \frac{I(hkl)}{I_0(hkl)} \cdot \frac{1}{\sum \frac{I(hkl)}{I_0(hkl)}}$$

Where $I_{(hkl)}$: Measured relative intensity

$I_{o(hkl)}$: Relative intensity of the corresponding plane given in JCPDS data.

n: Number of reflections.

The point is if a few reflections are available (i.e. number of n is small), the above equation becomes

inaccurate. The average texture coefficient calculated from above equations for cerium tartrate is 0.999902

Intensity (cps)

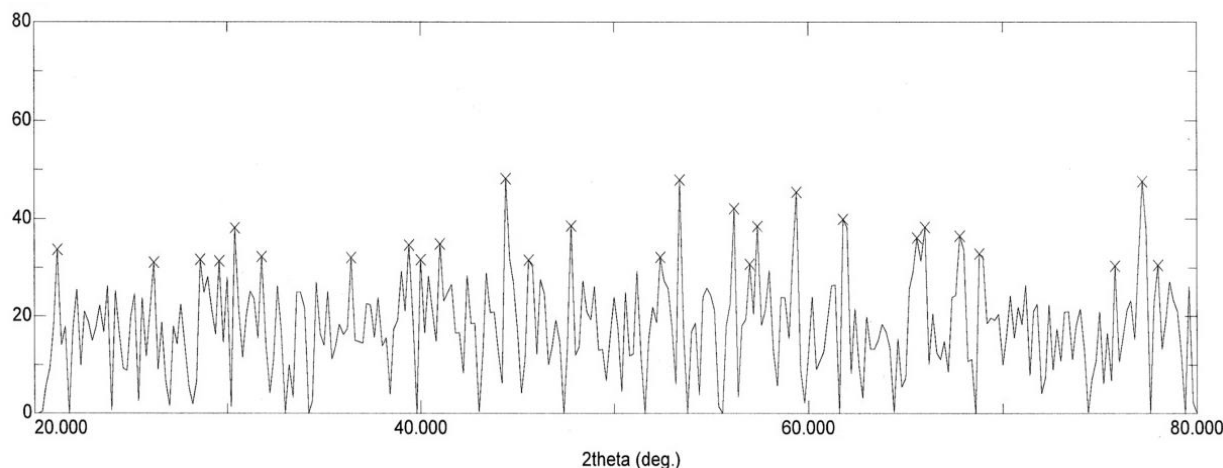


Fig. 6 X-ray diffractogram of cerium tartrate crystals

V. ENERGY DISPERSIVE X-RAY ANALYSIS OF CERIUM TARTRATE CRYSTALS

The output of EDAX analysis is an EDAX spectrum as shown in Fig. 7. The EDAX spectrum is just a plot of how frequently an X-ray is received for each energy level. The energy of an X-ray line (energetic position of the line in the spectrum) is the indicator for it, which element it concerns (Mosely's law). The 'Strength' of the line depends on the concentration of the element within the sample. The position of lines (peaks with appropriate energies) gives information about the qualitative composition of the sample. The number of the X-ray quanta is the measure for the concentration of the elements (peak-height or peak area). There is not linear connection between concentration portions of the elements. Analyzing with EDAX it was possible to obtain the percentage of different elements present in a single sample. Using EDAX the amount of C, O, and Ce present in the sample could be well understood.

The two dominant peaks at 280eV and 487eV correspond quite well with the K_{α} energies of

carbon and oxygen in the crystal. These energy values are in good agreement with standard values 277 and 525eV respectively [16-17]. The intense peak at 4.8484keV corresponds to $L_{\alpha 1}$ energy of cerium giving a clue that the amount of cerium is in the detectable range of the instrument. This energy value is in good agreement with standard value 4.840keV. The lesser intense peaks at 5.2613 and 5.6226keV well corresponds to $L_{\beta 1}$ and $L_{\beta 2}$ energies of cerium which are in good agreement with the standard energy values 5.262 and 5.6134keV respectively. The two peaks present at 1.756 and 2.60keV may correspond to impurities present. The intense peak at 4.8484keV suggests the strong transition of $L_{\alpha 1}$ while lesser intense peaks at 5.2613 and 5.6226keV suggest that $L_{\beta 1}$ and $L_{\beta 2}$ transition are weak. Thus the presence of C, O and Ce in the cerium tartrate crystals is evident from the characteristics K_{α} , L_{α} , and L_{β} peaks of these elements. The quantitative results are given in Table. 2. In the quantitative analysis, Ce could be detected, since the quantity of the element is in the detectable limit of the instrument.

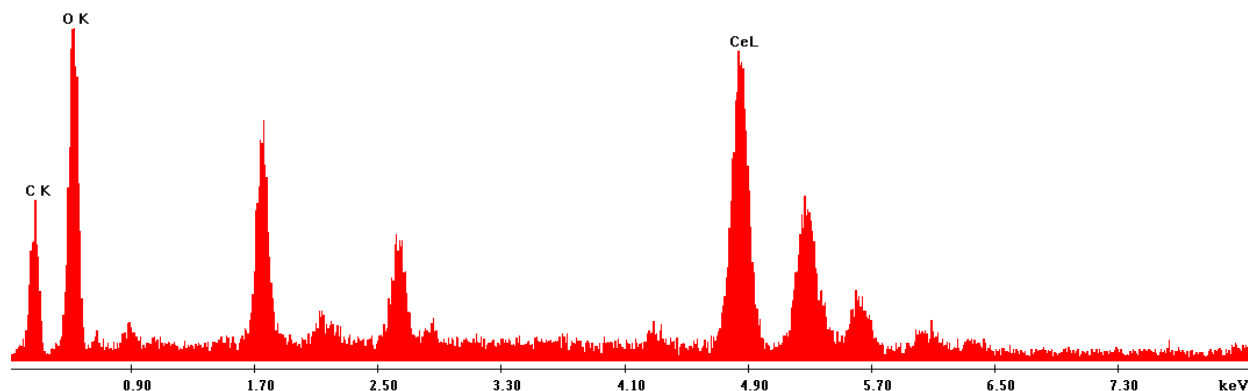


Fig. 7 EDAX spectrum of cerium tartrate crystals

Table 2 Quantitative EDAX Results of Ce Tartrate

Element	Wt %	At %	K-Ratio	Z	A	F
C	30.30	51.08	0.1141	1.0782	0.3492	1.0004
O	34.64	43.85	0.0856	1.0629	0.2326	1.0000
Ce	35.06	5.07	0.3288	0.8069	1.1623	1.0000
Total	100.00	100.00				

VI.CONCLUSIONS

1. X-ray studies reveal the crystallinity of $Ce_2(C_4H_4O_6)_3 \cdot 6H_2O$. Calculations of cell parameters reveals that the pure crystal belongs to monoclinic crystal system with unit cell parameters $a = 7.1095 \text{ \AA}$, $b = 5.1838 \text{ \AA}$, $c = 3.4016 \text{ \AA}$ and $\alpha = 90^\circ$, $\beta = 92.474^\circ$, $\gamma = 90^\circ$, and unit cell volume is 125.25 \AA^3 .
2. Qualitative elemental analysis (EDAX) shows presence of Ce.
3. Layered type spherulitic formation of cerium tartrate is revealed from SEM studies. Each crystallite is a platelet with well-defined faces.

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