Synthesis and spectroscopic characterization of calcium oxalate

G. Viswanadha¹, V. Sahadeva Reddy¹*

¹. Dept. of Physics
S.V.D. College, Kadapa-516003, India

Corresponding authors email: G. Viswanadha — gvnphy@gmail.com

Abstract: Synthesis of calcium oxalate nano particles is carried out by thermal double decomposition of solutions of oxalic acid dihydrate (C₂H₂O₄·2H₂O) and calcium chloride dihydrate (CaCl₂·2H₂O) by employing CATA-2R microwave reactor. It is characterized by using X-ray diffraction (XRD), Optical absorption and NIR spectroscopy. Nano calcium oxalate dihydrate cell constants are calculated as a=11.91 A.U, and c=11.64 A.U by XRD. The optical absorption spectrum reveals that the Ca²⁺ is present in tetragonal environment. NIR results are indicating that the presence of water fundamentals in the compound.

Keywords: calcium oxalate, tetragonal structure, XRD, Optical absorption and NIR spectroscopy.

1. Introduction:

Nanoparticles are of great interest in chemical, electronic and optoelectronic industries because of the novel properties afforded by their small size and high surface-to-volume ratio [1]. Surface and quantum effects result in the modification of the properties like optical, magnetic and dielectrics of nano-sized particles [2]. Nature is a reservoir of natural oxalates. Some natural oxalates are weddelite, whewellite, moolooite, humboldtine, glishinskite, natroxalate and oxamate. Among them calcium oxalate crystals occur in plants in two principal forms, monohydrate (CaC₂O₄·H₂O) and dihydrate (CaC₂O₄·2H₂O). Each of this has a different crystal structure. The monohydrate form known as whewellite belongs to the monoclinic system of crystallization and dihydrates form known as weddellite belongs to tetragonal system [3-4]. Weddellite and whewellite are very often occur together with gypsum on the surface of calcareous artifacts exposed in the mediterranean urban environment, as main constituents of reddish patinas called in Italy seialbatura [5]. In this communication we report the synthesis of calcium oxalate nanocrystals and their structural properties are studied by XRD, Optical absorption and NIR spectroscopy.

2. Experimental:

2.1 Synthesis of nano calcium oxalate compound

In the synthesis all the chemicals used are analytical grade only. Double distilled water is used for the preparation of the required solutions. 6.3035g of oxalic acid dihydrate (C₂H₂O₄·2H₂O), dissolved in 100 mL water and 7.351g CaCl₂·2H₂O is dissolved in 100 mL of double distilled water separately. Both the solutions are mixed slowly with rigorous stirring. Then we added 3-5 ml of acetone to the mixture solution for particle size reduction. The mixture is taken in a reflux flask of 250 mL with magnetic stirrer and kept in cavity of CATA-2R microwave reactor, supplied by Catalyst Systems, Pune, India. The reaction is performed at boiling conditions by 5 minutes in the reactor. Then the solution is allowed to cool until to get the room temperature and then filtered by using succession pump. The white colored precipitate washed with water and dried in air about 2days. The yield is nano copper oxalate dihydrate, CaC₂O₄·2H₂O.

\[
\text{CaCl}_2\cdot2\text{H}_2\text{O} + \text{H}_2\text{C}_2\text{O}_4\cdot2\text{H}_2\text{O} \rightarrow \text{CaC}_2\text{O}_4\cdot2\text{H}_2\text{O} + 2\text{HCl} + 2\text{H}_2\text{O}
\]
2.2 Spectral techniques
X-ray powder diffraction pattern of nano calcium oxalate dihydrate is recorded in Philips X-ray diffractometer operated in reflection geometry at 30 mA, 40 kV with Cu-Kα (λ = 1.54060 A.U) source at 25 °C in the range 10°-75°. Data is collected using a continuous scan rate of 1° 2 min⁻¹, which was then refined into 2 theta steps of 0.02°. Optical absorption spectrum of oxalate sample is recorded at room temperature on Carey 5E UV-Vis-NIR spectrophotometer in null form in the range 450 - 2200 nm. Band component analysis is undertaken using the Jandel “PEAKFIT” software package which enabled the type of fitting function to be selected and specific parameters to be fixed or varied accordingly. Band fitting was carried out using a Lorentz–Gauss cross product function with a minimum number of component bands used for the fitting process. The Lorentz–Gauss ratio was maintained at values greater than 0.7 and fitting was undertaken until reproducible results were obtained with squared correlations of r² greater than 0.9970.

3. Results and discussion:
3.1 XRD-Spectral analysis
Fig.1 presents the X-ray diffraction pattern of calcium oxalate dihydrate nano crystal recorded on Philips diffractometer. The peaks are characterized by using Scherrer formula. The X-ray peak list is presented in Table-1. With these Miller indices the unit cell constants obtained are a=11.91A.U and c=11.64A.U. This suggests that the nano calcium oxalate is in tetragonal structure. The average particle grain size of the sample is calculated using Debye-Scherrer formula, D =0.9λ/β₁/₂cosθ [6]. Here D is the average particle grain size, λ is the wavelength of the incident X-ray, θ is the corresponding Bragg angle and β₁/₂ is the full width half maximum of the corresponding peaks. For calcium oxalate the average grain size is calculated as D=8.6676A.U. The X-ray density dₓ of the sample calculated using the formula dₓ=ZM/NV [7]. Where Z(8) represents the number of atoms containing the unit cell, M (164.1g) is molecular weight, N is Avogadro’s number and V (1651X10⁻²⁴ cc) is volume of the unit cell. For calcium oxalate the X-ray density is dₓ=1.32g/cm³ is obtained. The percentage porosity of the sample calculated by using the relation [8], Percentage porocity ρ%= \[1-d/dₓ\]. 100%
Here d=bulk density of the sample [d=2.12g/cm³], dₓ=X-ray density of the sample. The percentage porocity calcium oxalate is calculated as 60.6.

3.2 Optical absorption spectroscopy
3.2.1 UV- Vis spectroscopy
Optical absorption spectrum of the compound recorded in the null form at RT from 450 - 2200 nm is shown in Fig.2. The band component analysis of the spectrum in the range 400 - 1300nm consists of bands at 8295, 13320 (average of 12670 and 1396 cm⁻¹) and 15915 cm⁻¹ are attributed to the same transitions for Ca(II) ions. Based on these indicates an axial elongation in tetragonal field and also conforms the ground state [9-10].

3.2.2 NIR Spectral analysis
The NIR spectrum of the compound is also shown in fig.2. In the NIR region several bands are observed in the sample. These bands are due to overtones and combination of tones of water fundamentals. Water has C₂ᵥ symmetry. It gives three fundamental modes. They are symmetric OH stretch (v₁), the H-O-H bending mode (v₂) and the asymmetric OH stretch (v₃). In vapour phase they are v₁, v₂ and v₃ occur at 3652, 1595 and 3756 cm⁻¹ respectively. [11] In liquid phase they are shifted to 3219, 1645 and 3445 cm⁻¹, where as in solid phase they are shifted to 3220(v₃), 1620(v₂) and 3400(v₁)
The shifts of ν₁ and ν₃ towards the lower frequency side and the shift of ν₂ towards the higher frequency side are characteristic of hydrogen bonding. Water molecules are relatively distorted when bands are broad and water molecules are located in well defined ordered sites when the bands are sharp [13].

**The 1300 to 1800 nm spectral region**

In this spectral region where the first overtones of the OH stretching of the vibrations are shown in Fig.2. The oxalate sample shows unique maximum intensity broad spectrum centered at 6775 cm⁻¹ and three component bands at 6325, 5815, and 5665 cm⁻¹. It may also be explained that the complexity of bands due to long chain and may be resolved into a series of overlapping bands. This may be attributed to the combination of OH stretching fundamental and metal-OH deformation modes. In the NIR all the spectral features are due to the vibrations of the hydroxyl and oxalate ions.

From the Fig.3 it is clear that only two groups of bands are noticed in the region 1300- 1800 nm. These are 6775, 6320 cm⁻¹ and 5815, 5665 cm⁻¹. Whenever water is present in compound, in general two characteristic bands appear around 6500 cm⁻¹ due to 2ν₃ and 5220 cm⁻¹ due to (ν₂ + ν₃). The first overtone and combinations of the stretching mode produce the numerous relatively sharp features centered at 6310 cm⁻¹ and the combination of the stretching and bending modes produce the feature near 4320 cm⁻¹. When the bands are broad it indicates that water molecules are relatively disordered and when the bands are sharp it indicates that water molecules are located in well defined ordered sites [13]. Accordingly first set of sharp bands around 6270 cm⁻¹ and another set centered at 5985 cm⁻¹ with four components is attributed to water due to the (ν₂ + ν₃) and due to 2ν₃ vibrations. The group of bands observed in range 5810 to 5665 cm⁻¹ centered at 5720 cm⁻¹ is identified as overtones and combination tones of oxalate ion.

**The 1800 to 2200 nm spectral region**

Fig.2 shows two groups of very sharp bands. The maximum intense sharp profile of band at 4760 cm⁻¹ and another sharp band 5110 cm⁻¹ with split component at 5080 cm⁻¹ which is identified as due to H-O-H bend and asymmetric OH stretch. Whereas the profile of bands with maximum intensity at 4760 cm⁻¹ is due to combinational modes of oxalate molecule

### 4. Conclusion

1. XRD spectral studies are indicating that the calcium oxalate is in tetragonal symmetry with cell constants a=11.91Å and c = 11.64 Å. The average particle grain size is calculated as D=8.67Å.

2. Optical absorption spectrum of the compound is due to Ca(II) ions with distorted tetragonal environment.

3. NIR results are due to water fundamentals and oxalates which indicate that water molecules are not free but are bounded to the metal ions as ligands.

### 5. Acknowledgments:

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Fig. 2 Optical absorption spectrum of calcium oxalate in the range 450 – 2200 nm
Table 1 Peak fit analysis of calcium oxalate

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Average particle grain size (D) = 8.6676 A.U.