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XRD, EDAX, FE-SEM and Raman spectroscopic studies of disodium trans-diaquabis(oxalato)cobaltate(II) hexahydrate

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Abstract : The crystals of disodium trans-diaquabis(oxalato)cobaltate(II) hexahydrate $\{Na_2[Co(C_2O_4)_2\ (H_2O)_2]\cdot 6H_2O\}$ were characterized by X-ray powder diffraction (XRD), quantitative elemental analysis of EDAX, field emission scanning electron microscopy (FE-SEM) and Raman Spectroscopy. This material crystallizes in the triclinic system with space group $P\bar{1}$ and shows one-dimensional (1D) chain structure. The elements present in the grown crystal were confirmed by Energy Dispersive X-ray Analysis. The microstructural features on the surface of the single crystal were determined using a field emission scanning electron microscope. The polycrystalline nature of the material was confirmed using powder XRD. The vibrational assignments of the material were confirmed using Raman spectroscopy.
Keywords : Inorganic material; Morphology; X-ray diffraction; Raman spectroscopy.

1. Introduction

Current past, the oxalate complexes are mainly used as molecular-based magnetic materials [1-5] and precursors to nanocrystalline metallic oxides [6-8] for technological applications. The attention in using metals with oxalate ions is due to the adaptable bonding form of oxalate ions through metal ions. The negative charge, planar condition and good donor capability due to the existence of four oxygen donors, generate oxalate ligand suitable to make coordination polymers in its interface with metal ions [9-11].

The structural overall flexibility of metal oxalate complexes is potential to developing of multifunctional materials mainly in the field of photophysics and molecular based magnetism [12]. Crystal structure, luminescence, thermal and magnetic properties of disodium trans-diaquabis(oxalato)cobaltate(II) hexahydratecompound were studied within our laboratory and published earlier [13]. In this paper, the results on powder XRD, EDAX, FE-SEM and Raman spectroscopic studies are reported.

2. Experimental

Energy dispersive analysis of X-rays (EDAX) was obtained from X-ray energy analyzer OXFORD INSTRUMENTES (MODEL: Inca Penta FET x3)attached to Carl Zeiss SEM (MODEL: EVO MA 15).The FE-SEM images of the compound were recorded using Carl Zeiss Ultra 55 model. The powder X-ray diffraction studies were carried out using JEOL-JDX-8P X-ray diffractometer with CuK_α (λ = 1.54056 Å) radiation. Raman spectrum of the grown crystal was recorded at room temperature using a micro-Raman spectrometer (LABRAM-HR) with a laser excitation of 514.5 nm.

3. Results and discussions

3.1. Synthesis and crystal growth

All the chemicals were reagent grade and used without further purification. The single crystals of $Na_2[Co(C_2O_4)_2(H_2O)_2].6H_2O$ were grown by adding sodium oxalate ($Na_2C_2O_4$), potassium oxalate monohydrate ($K_2C_2O_4.H_2O$), and cobaltous sulphate heptahydrate ($CoSO_4.7H_2O$) in 250 ml of distilled water in equimolar ratio. This solution was heated for 1 hour and filtered at cold condition to eliminate any remaining residue. After filtration the pink color solution was kept for slow evaporation at room temperature for 6 days to get crystals. The crystals were dried after remove from beaker. The as grown crystal is shown in Figure 1.

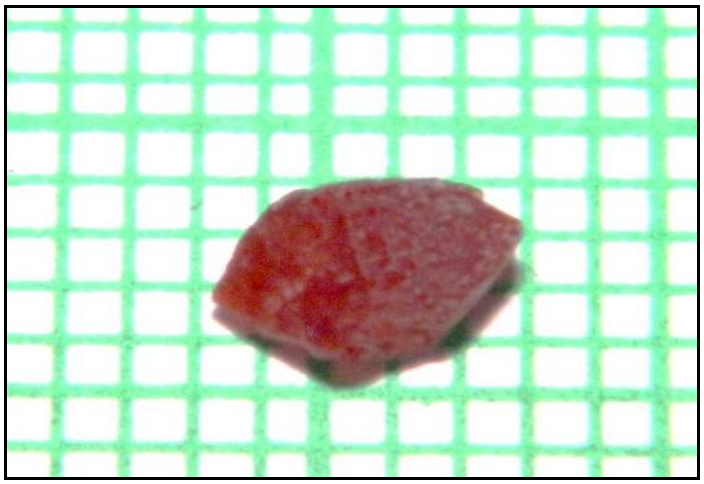

Figure 1: Photograph of $Na_2[Co(C_2O_4)_2(H_2O)_2]\cdot 6H_2O$.

3.2. Single crystal XRD data

Single crystals of disodium trans-diaquabis(oxalato)cobaltate(II) hexahydrate were prepared according to published procedure [13].Single crystal X-ray diffraction data shown that the crystals are $Na_2[Co(C_2O_4)_2(H_2O)_2]\cdot 6H_2O$ and crystallized in the triclinic system with $P\bar{1}$ space group. The unit cell parameters are a = 6.7969(6) Å, b = 6.9292(6) Å, c = 8.8126(8) Å, α = 86.786(3)°,β = 67.652(3)°, γ = 89.192(3)° and Z = 1.

3.3. EDAX analysis

In order to confirm the presence of cobalt, sodium, carbon and oxygen, quantitative elemental analysis were performed on the application of EDAX. The EDAX spectrum showed in Figure 2 reveals the presence of chemical elements Co, Na, C and O in the crystal.

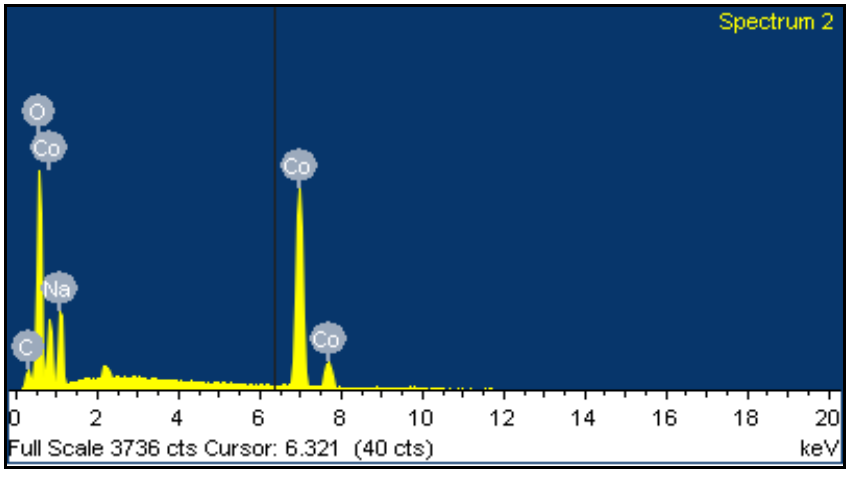

Figure 2:EDAX spectrum of $Na_2[Co(C_2O_4)_2(H_2O)_2]\cdot 6H_2O$.

3.4. FE-SEM analysis

With a view to understand the surface topography of the $Na_2[Co(C_2O_4)_2(H_2O)_2]\cdot 6H_2O$, the FE-SEM micrographs were obtained and are shown in Figure 3.It can be obtained from the figures that this material exhibited agglomerated morphology with non-homogeneous size and shape.

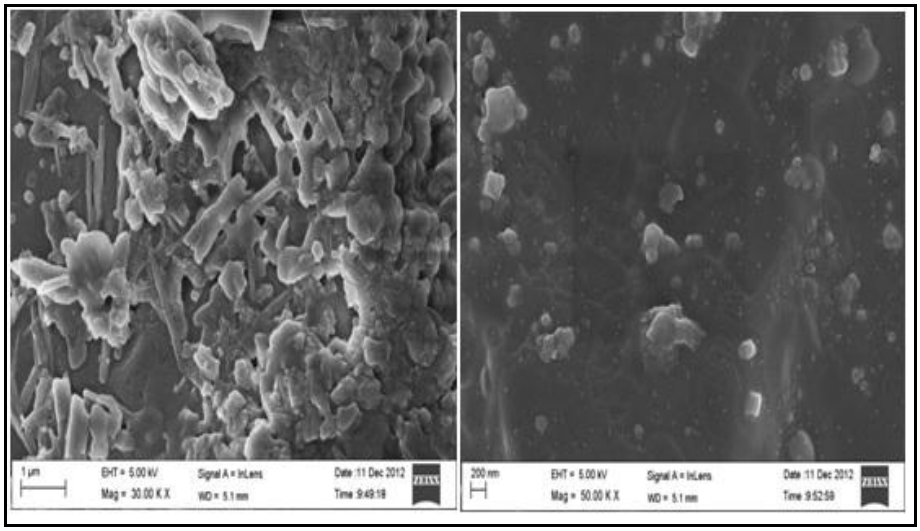

Figure 3: FE-SEM images of $Na_2[Co(C_2O_4)_2(H_2O)_2]\cdot 6H_2O$.

3.5. Powder XRD analysis

The purity of the $Na_2[Co(C_2O_4)_2(H_2O)_2]\cdot 6H_2O$has been determined by the powder X-ray diffraction pattern and is shown in Figure 4. The diffraction peaks were indexed using powderX program [14]. The experimental and calculated interplanar spacings (d) and corresponding miller indicess (h k l) are shown in Table 1. The crystallite size diameter (D) of the $Na_2[Co(C_2O_4)_2\ (H_2O)_2]\cdot 6H_2O$ has been calculated by Debye-Scherrer equation:

$D = 0.9\lambda/\beta\cos\theta$

Where β is the integrated breadth of reflections located at 2θ (in radians), θ is the diffraction angle in radians and λ is the wave length of X-rays (1.5406Å for Cu Kα). Crystallite size of powder has been estimated as 32 nm.

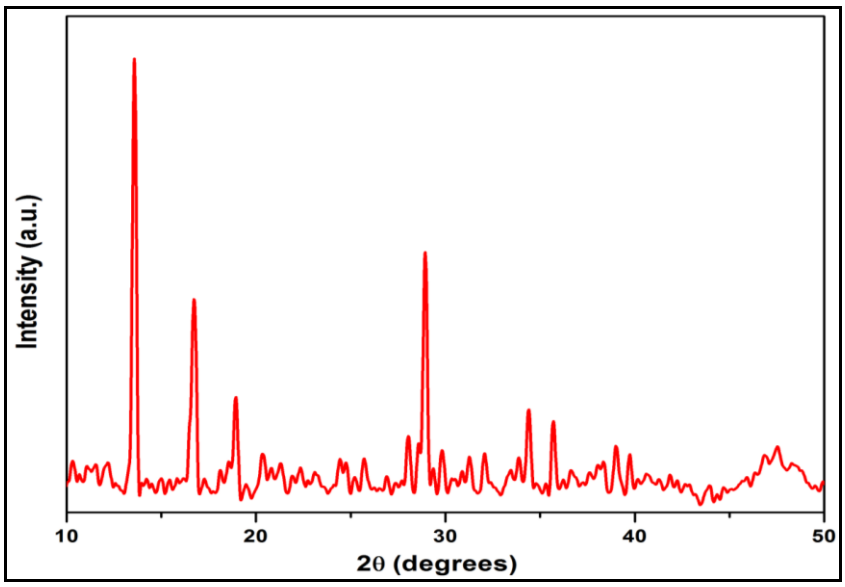

Figure4: Powder XRD pattern of $Na_2[Co(C_2O_4)_2(H_2O)_2]\cdot 6H_2O$.

Table 1:Calculated and experimental d-spacing's and 2θ values for $Na_2[Co(C_2O_4)_2(H_2O)_2]\cdot 6H_2O$.

h k l	$2\theta_{exp}$	$2\theta_{cal}$	d_{exp}	d_{cal}
0 0 1	10.911	10.873	8.102	8.130
0 1 0	12.810	12.816	6.873	6.889
1 0 1	14.167	14.173	6.246	6.249
0 1 1	16.367	16.380	5.411	5.419
1 1 1	18.808	18.812	4.714	4.719
-1 0 1	20.877	20.890	4.251	4.258
-1 -1 1	24.991	24.943	3.560	3.563
0 -1 2	26.020	26.018	3.422	3.422
2 -1 1	29.502	29.474	3.025	3.028
1 0 3	30.589	30.548	2.920	2.924
-2 1 0	31.153	31.173	2.869	2.867
-1 -1 2	33.594	33.599	2.667	2.667
2 0 3	34.541	34.531	2.594	2.595
0 -2 2	34.942	34.980	2.566	2.563
2 -2 1	37.387	37.400	2.403	2.403
0 3 0	39.084	39.106	2.303	2.302
0 3 1	40.128	40.094	2.246	2.247
-1 -2 2	41.110	41.131	2.194	2.193
3 -1 1	42.380	42.420	2.131	2.130
3 0 3	43.450	43.424	2.081	2.082
1 3 2	43.823	43.779	2.064	2.066
-1 3 1	44.076	44.068	2.052	2.053
3 1 0	45.320	45.319	2.000	2.000
0 -3 2	46.348	46.349	1.960	1.960
3 2 1	48.210	48.180	1.887	1.887
2 -3 2	49.991	49.993	1.823	1.823

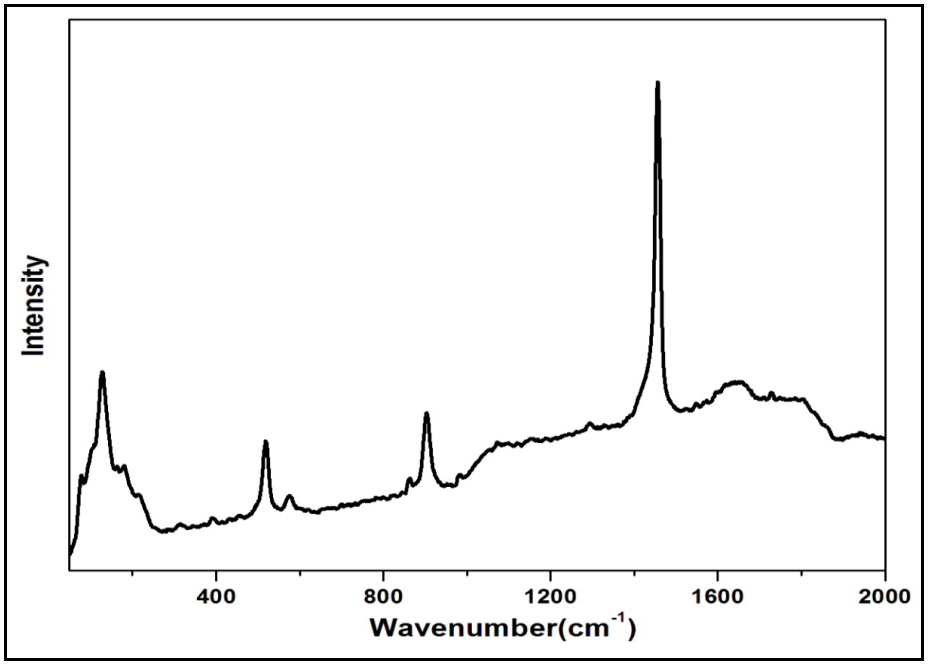

Figure5: Raman spectrum of $Na_2[Co(C_2O_4)_2(H_2O)_2]\cdot 6H_2O$.

3.6. Raman spectral studies

The Raman spectrum of $Na_2[Co(C_2O_4)_2(H_2O)_2]\cdot 6H_2O$ is shown in Figure5. The corresponding band wave numbers and proposed assignments are given in Table 2. The results are compared with those of the earlier Raman studies on similar compounds [15, 16]. The bands at 132, 220, 315, and 516 cm^{-1} are assigned to metal-ligand stretching bands of *v*(Co-O). The (C-C) symmetric stretching mode of oxalate ion and (O-C-O) deformational mode are observed at 906 cm^{-1} and 578 cm^{-1} respectively. The bands at 1304, 1495, 1620, 1675, and 1725 cm^{-1} were attributed to bidentate modes of oxalate ion.

Table 2: Raman vibrational bands and corresponding assignments of $Na_2[Co(C_2O_4)_2(H_2O)_2]\cdot 6H_2O$.

wave number	band assignment
132	*v*(Co-O)
220	*v*(Co-O)
315	*v*(Co-O)
516	*v*(Co-O)
578	*δ*(O-C-O)
906	*v*(C-C)
1304	*v*(C-O)
1495	*v*(C-O)
1620	*v*(C-O)
1725	*v*(C-O)

4. Conclusions

The single crystals of disodium trans-diaquabis(oxalato)cobaltate(II) hexahydrate were grown from slow evaporation of solutions method. The single crystal XRD studies revealed the compound crystallized in the triclinic system with $P\bar{1}$ space group. The average particle size of powder crystallite of this compound was obtained as 32 nm from powder XRD studies. The FE-SEM studies revealed that the crytslas contained agglomerated morphology with irregular shapes. Raman spectrum confirmed the functional groups associated with the oxalate ion.

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