Studies on $\text{Ce}_2(\text{C}_2\text{O}_4)_3 \cdot n\text{H}_2\text{O}$ crystals grown in hydro-silica gel

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Abstract. Single crystals of cerium oxalate are grown by the gel method. $\text{Ce}(\text{NO}_3)_3$ is allowed to diffuse into a gel in which oxalic acid is incorporated. Cerium oxalate crystals are formed by chemical reaction and the growth process is observed. Crystals are yellow-white in colour. Morphology and size of the crystals are highly influenced by the acidity of the feed solution. With 30% HNO_3 long needle shaped, with 50% HNO_3 thin hexagonal and with 100% HNO_3 , well developed crystals are obtained. Natural etch pits are observed on the grown crystals due to the presence of HNO_3 . Appearance of a single, large interfacial crystal is observed for 0.5 M cerium nitrate. IR spectrum confirms the presence of water molecules and carboxylic group. X-ray diffractogram gives well defined peaks. Peaks are indexed. Unit cell dimensions are determined. Thermal analysis of the samples done using TGA and DTA show the release of water molecules (endothermic) and of CO and CO_2 (exothermic) with the rare earth oxide as stable residue.

Keywords. Cerium oxalate crystals; gel growth; optical and IR spectroscopy; XRD; TGA; DTA.

1. 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. Ce^{3+} is used as a co-dopant in certain photo refractive crystals like LiNbO_3 , KNbO_3 and $\text{Sr}_x\text{Ba}_{1-x}\text{Nb}_2\text{O}_6$ (Raj Kamal *et al* 1992) and laser crystals like $\text{Y}_3\text{Al}_5\text{O}_{12} : \text{Nd}$ and $\text{YAlO}_3 : \text{Nd}$ (Mares 1991). 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 (Rao 1992). No report has been noticed on the study of cerium oxalate. Hence growth of this crystal is attempted. Cerium oxalate can be grown by gel technique since it has very low solubility in water. Growth and characterization of several oxalates and mixed rare-earth oxalates in silica gel have already been reported (Shedam and Venkateswara Rao 1993; Cyriac Joseph *et al* 1995; Varghese John *et al* 1997). Grown crystals are characterized by different methods.

2. Experimental

Solution of sodium meta silicate in double distilled water has been prepared with a density of 1.03 g/cc. This solution is poured into a clean glass test tube of 15 mm inner diameter and 150 mm in length. Over this solution

1 molar oxalic acid solution is added until the mixture attains a pH of 6. At this pH, gelling is completed within two days. Over this fully gelled mixture, 0.5 cerium nitrate acidified with conc. HNO_3 is poured carefully and kept undisturbed. Cerium nitrate solution is found to diffuse slowly through the gel reacting with the oxalic acid already incorporated in the medium. Reaction will take place according to the equation,

Insoluble cerium oxalate crystals are formed due to this reaction. The gel medium prevents turbulence and being chemically inert, it provides a three-dimensional structure which permits reagents to diffuse at a controlled rate. This experiment has been conducted at ambient temperature. Initially nucleation centres are found to occur starting from 1 cm below the gel interface. Already formed nuclei then continued to grow for three weeks and growth tapered off afterwards. Number, size and morphology of crystals varied with gel density, pH, concentration of feed solution, acidity of feed solution and strength of oxalic acid.

3. Observations and investigations

3.1 Optical microscopic studies

Crystals grown under different conditions are collected and observed under Carl-Zeiss metallurgical microscope. Yellow-white transparent crystals with well developed

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faces together with a few opaque crystals are observed. The morphology of crystals are found to vary according to the conditions of growth. With 30% HNO_3 long thin crystals—clusters as well as single ones—are obtained. As the strength of the acid increases, they become thin plates and finally have a thick cubical or hexagonal shape. Figure 1 shows a well developed crystal. Closer examination under the microscope shows that the faces are plane in the case of hexagonal crystals and striations are observed on long ones. Some of the crystals are found to be etched heavily (figure 2). Etching may be caused by HNO_3 present in the medium. Shallow and deep etch pits are formed. Deeper ones may be due to dislocation present in the crystal.

Marked difference in number and size of the crystals is observed for crystals grown under different concentrations of the feed solution. Number of crystals decreases with decrease in concentration. In the case of 2 M and 1 M feed solutions, number of crystals decreases and

size increases towards the bottom of the test tube. For 0.5 M and 0.25 M feed solutions, large sized crystals are formed in the upper region of the crystallization zone and size decreases towards the bottom. Diffusion of the reacting ions from the feed solution depends on its concentration. In higher concentrations, chances for nucleation are greater in the upper layer itself resulting in large number of crystals and less spacing between growing crystals which minimize size of the crystals. But towards bottom layers, less nucleation occur, but sufficient ions are present for the crystals to grow in large size.

In lower concentrations of the feed solution (0.5 M and 0.25 M), chances of nucleation are less in the upper layer of the crystallization zone and more space and more ions are available for the growing crystals. So they become large in size. Towards bottom, nucleation is still less and due to the lack of reacting ions, their size is also small. This observation indicates that a particular minimum concentration of the reacting ions is necessary for nucleation.

Occasionally it is observed that single as well as cluster of crystals are found to grow at the gel interface. Figure 3 shows a typical case of such a single crystal grown in 0.5 M cerium nitrate solution. This is due to the diffusion of oxalate ions upwards through the gel and reaction with cerium ions in the supernatant solution. It requires more time for the formation of a nucleus on the interface (about 10 days). The slow diffusion restricts the number of nuclei and once a nucleus is formed it became large in size because of the large availability of Ce^{3+} ions in the solution.

Distance of crystallization zone from the gel interface is also different with difference in concentration of the

Figure 1. Crystal grown with 100% HNO_3 ($\times 50$).

Figure 2. Natural etch pits on grown crystals ($\times 100$).

Figure 3. A single large interfacial crystal for 0.5 M cerium nitrate ($\times 2$).

feed solution. For higher concentrations, it is just 1 cm below the gel interface and this distance increases up to 2 cm for lower concentration. This distance may be indicating the formation of supersaturation of the reacting ions in different cases inside the gel.

3.2 Spectral studies—IR spectra

A Shimadzu IR-470 spectrometer is employed to obtain infrared absorption spectrum using KBr pellet method (figure 4).

Figure 4. IR spectrum of cerium oxalate.

The crystal has water of crystallization which is evidenced by the intense broad peak at $3500\text{--}3200\text{ cm}^{-1}$. $1620\text{--}1600\text{ cm}^{-1}$ relate to bending mode of water and asymmetric stretch of CO_2 (Petrov and Soptrajanov 1975). 1360 cm^{-1} and 1310 cm^{-1} correspond to CO_2 symmetric stretch. The sharp IR band observed at 800 cm^{-1} has been assigned to M–O band where M = Ce (Fujita *et al* 1962). 490 cm^{-1} represent the CO_2 wagging mode (Cyriac Joseph *et al* 1997).

3.3 X-ray powder diffractometry

X-ray diffraction pattern of the sample obtained using Philips PW 1710 X-ray generator is shown in figure 5. Patterns are recorded using Ni filtered $CuK\alpha$ radiation. Well defined Bragg peaks at specific (2θ) angles indicate the crystallinity of the samples. The observed d values are found to agree with the calculated d values.

The XRD patterns are indexed using least square program LATPAR. The indexing results seem to be very accurate as the difference involved in $d(\text{obs})$ and $d(\text{cal})$ as well as error ($\pm$) in the values of cell parameters are very small. The unit cell dimensions are $9.96213\text{ \AA}$, $11.9533\text{ \AA}$, $13.15118\text{ \AA}$ for orthorhombic system and unit cell volume is $1566.056\text{ \AA}^3$.

3.4 Thermal analyses (TGA and DTA)

TGA and DTA data are obtained on 18 mg and 30 mg

Figure 5. X-ray powder diffractogram of $Ce_2(C_2O_4)_3 \cdot nH_2O$.

Table 1. Thermal analysis results of $\text{Ce}_2(\text{C}_2\text{O}_4)_3 \cdot n\text{H}_2\text{O}$.

	Decomposition temp. ($^{\circ}\text{C}$)	Loss of material	Observed mass loss (%)	Calculated mass loss (%)	Endo/exo
Stage 1	50 $^{\circ}\text{C}$ –220 $^{\circ}\text{C}$	9 H_2O	22.22	22.94	endo
Stage 2	220 $^{\circ}\text{C}$ –555 $^{\circ}\text{C}$	3CO + 3CO $_2$	30.00	30.59	exo

Beyond 555 $^{\circ}\text{C}$ the residue mainly consists of Ce_2O_3 which is fairly stable.

Results can be tabulated as given in table 1. Observed mass loss correspond to the loss of 9 H_2O .

4. Conclusions

- (i) The gel grown cerium oxalate sample reported in the present work is yellow-white in colour and is crystalline in nature as evidenced by the well defined edges and corners as well as by the natural etch pits on the surface (figures 1 and 2) and by X-ray diffractometry. The unit cell parameters from X-ray analysis are $a = 9.96213 \text{ \AA}$, $b = 11.95337 \text{ \AA}$, $c = 13.15118 \text{ \AA}$ and $\alpha = \beta = \gamma = 90^{\circ}$.
- (ii) Presence of water molecules in the sample is evidenced by the peaks at 3600 cm^{-1} and 3200 cm^{-1} .
- (iii) Presence of carboxylic group is evidenced by the peaks at 1600 cm^{-1} and 1300 cm^{-1} .
- (iv) Loss of 9 H_2O from $\text{Ce}_2(\text{C}_2\text{O}_4)_3 \cdot 9\text{H}_2\text{O}$ is proved from the thermal analysis by the dehydration around 180 $^{\circ}\text{C}$ (endothermic) and the evolution of CO and CO $_2$ around 350 $^{\circ}\text{C}$ (exothermic), yielding stable residual rare earth oxide beyond 555 $^{\circ}\text{C}$.

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Figure 6. TGA and DTA plots of cerium oxalate.

samples, respectively by scanning at 5 $^{\circ}\text{C}/\text{min}$ under the atmosphere of argon. Thermogravimetric runs were taken on Shimadzu thermobalance and runs were taken on DTA set up coupled with Rikadenki multiplier recorder and endotherm temperature programmer (figure 6).

Cerium oxalate is characterized by the loss of the bulk of water of crystallization in a single peaked endotherm in the range 100 $^{\circ}\text{C}$ –200 $^{\circ}\text{C}$. Complete dehydration is only on the onset of oxalate decomposition as observed by Fuller *et al* (1980). DTA curve in the region 325 $^{\circ}\text{C}$ –400 $^{\circ}\text{C}$ is characterized by an exothermic peak which shows the oxalate decomposition.

The loss of weight in the temperature range 50 $^{\circ}\text{C}$ –220 $^{\circ}\text{C}$ relates to the loss of water of crystallization (endothermic reaction) as follows:

Loss of weight in the temperature range 220 $^{\circ}\text{C}$ –555 $^{\circ}\text{C}$ relates to the release of CO and CO $_2$ which are exothermic in character. The chemical reaction is as follows:

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