
CHARACTERISTICS AND MICROHARDNESS OF PURE AND PRASEODYMIUM DOPED CALCIUM OXALATE CRYSTALS GROWN IN SILICA GEL

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Abstract: The pure and praseodymium doped calcium oxalate crystals prepared by single diffusion growth process in silica gel medium are discussed. The influence of growth parameters like gel pH, gel aging, concentration of reactants etc have been studied. It was found that the morphology of crystals can be influenced by changing gel pH in the presence of dopants. By deploying powder X-ray diffraction analysis, the diffraction planes and cell parameters of both the crystals (pure and doped) were identified. The Fourier transform infrared (FT-IR) spectroscopy confirms the presence of major functional groups expected to be present in the crystal. The thermal behavior of the crystals was investigated by thermo gravimetric (TGA) and differential thermal analyses (DTA). The substitutional occupation of praseodymium ion in the parent lattice can be attributed from the decomposition temperatures. The grown crystals were subjected for the study of surface morphology and microhardness. All results obtained are discussed in details.

Keywords: Silica gel, Crystal growth, X- ray diffraction, FTIR, Thermal analysis, SEM

Introduction: Crystallization is the process of formation of solid crystals precipitating from solution, melts or deposited directly from gas. Crystal growth by gel technique has become more popular and used by many researchers [1, 2]. It can be used successfully at room temperature to suppress nucleation centres, and is suitable for the materials that have low solubility [3]. Various metal tartrate compounds have attracted the attention of various researchers due to their different properties and applications, which is summarized in different crystallographic studies [4, 5]

The oxalate crystals such as barium oxalate, lead oxalate, strontium oxalate etc. have been paid sufficient attention due to their applications in different fields such as bio ceramics, ionic conductivity, ferroelectrics and luminescence. Calcium oxalate consists of tetrahedral oxalate groups, linked by Ca^{2+} ions. Recently, rare earth doped crystals and glasses have been extensively investigated owing to their potential application as fibre amplifier, visible laser, optical data storage, sensors and optical communication and displays. The investigation on rare earth doped calcium oxalate [6] has become a hot research topic. Considering the significance of rare earth in modifying and altering various physical and chemical properties of host materials, further an attempt is made in this investigation to grow praseodymium doped calcium tartrate crystals and characterize them by powder X-ray diffraction (XRD), Fourier Transform Infrared Spectroscopy (FTIR), Thermo Gravimetric Analysis (TGA). Then grown crystals subjected for the study of microhardness and surface morphology.

Experimental: The dissociation of oxalic acid system can be represented by three-dissociation equilibrium and the presence of various ions at various pH values

are reported [7]. On account of these results, the gel pH in the range from 4 to 8 has been used in which the oxalate ions dominates or alone exist. The crystallization apparatus employed were glass test tube of 25 mm diameter and 150 mm long for single diffusion method. The chemicals used are pure sodium meta silicate AR grade $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$, oxalic acid $\text{C}_2\text{H}_2\text{O}_4$, calcium Chloride $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ and Praseodymium Nitrate- $\text{Pr}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$. Sodium meta silicate solution of specific gravity $1.04\text{g}/\text{cm}^3$ is mixed with 1M oxalic acid. At 4 pH, 20 ml of the solution is poured in to straight tube and kept undisturbed for getting required silica gel. 5 to 8 days taken for setting gel. 10 ml of 1M calcium chloride solution is gently poured over gel for pure crystal. 5 ml of 1M calcium chloride solution is mixed with 5 ml of 0.001M praseodymium nitrate solution. This mixture is poured over gel for praseodymium doped crystal. The solution poured over gel is called supernatant solution. Oxalic acid acts as the acidifying agent and also as the source of anions needed for crystallization of the compound [8]. Oxalic acid is lower reactant and supernatant solution is upper reactant. The diffusion of Pr^{3+} and Ca^{2+} ions through the narrow pores of the silica gel lead to reaction between these ions and the $\text{C}_2\text{O}_4^{2-}$ ions present in the gel as lower reactant. The reaction leads to the formation of pure and praseodymium doped calcium oxalate crystals in separate test tubes. 50 to 60 days taken for growth saturation of the crystals. Grown crystals (pure and doped) are colorless and transparent.

Results and discussion: X-ray diffraction analysis (XRD): The powder X-ray diffractogram for both calcium oxalate and praseodymium doped calcium oxalate crystals are shown in Fig(a) and (b) respectively.

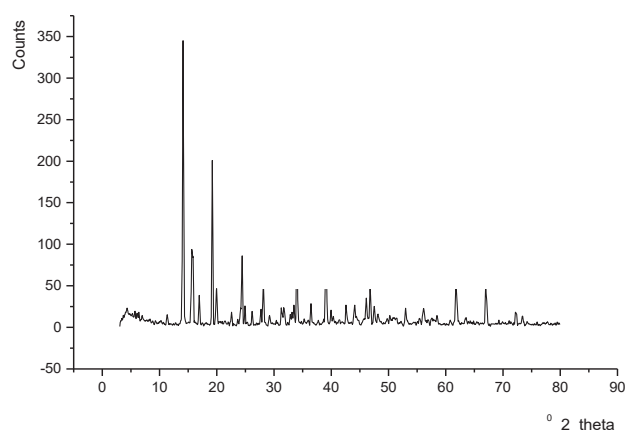


Fig (a)

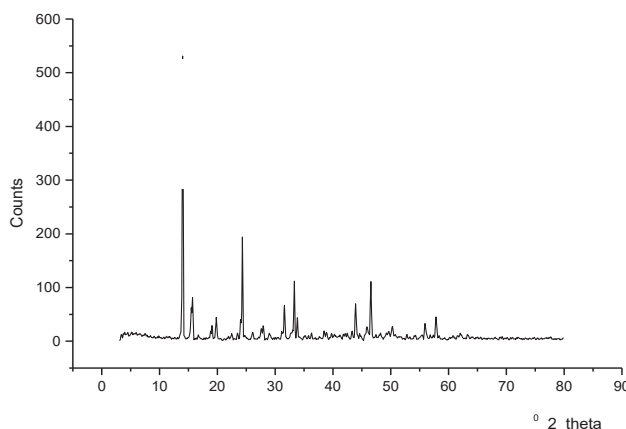


Fig (b)

The occurrence of highly resolved peak at specific 2θ Bragg angles in both the crystals indicates the crystalline nature of the grown crystals.

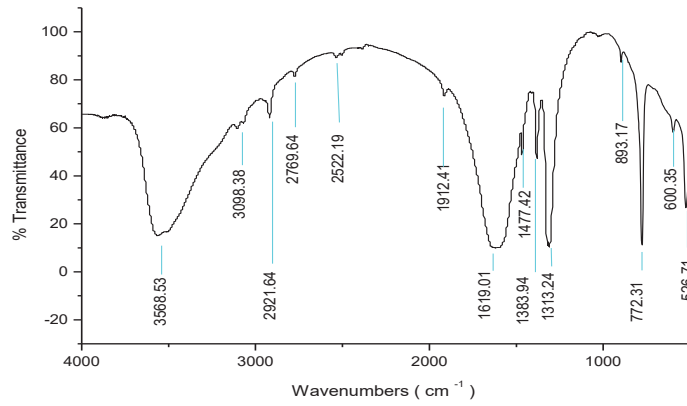
The lattice parameters obtained in case of pure calcium oxalate are: $a=14.088\text{\AA}$, $b=17.00\text{\AA}$, $c=4.586\text{\AA}$ and $\alpha=\beta=\gamma=90$ and volume of unit cell being 1098.32\AA^3 . Similarly, the lattice parameters obtained in case of doped calcium oxalate crystals are: $a=14.058\text{\AA}$, $b=16.399\text{\AA}$, $c=4.572\text{\AA}$ and volume of unit cell being 1054.015\AA^3 . Since the ionic radii of praseodymium and calcium are comparable, one can expect identical crystal system for both pure and doped crystals. Hence it can be confirmed that both belongs to orthorhombic crystal system. It is evident that because of praseodymium doping peak value shifts towards higher angle, indicating a decrease in the value of lattice constants and cell volume.

Fourier Transform Infrared Spectroscopy (FTIR): FTIR was widely used for the identification of chemical bonds, functional units and internal structure of molecules present in grown composition. The peaks were identified in comparison with standard data. Fig. (c) deals the FTIR spectrum of pure and doped crystals. Fundamental IR frequencies

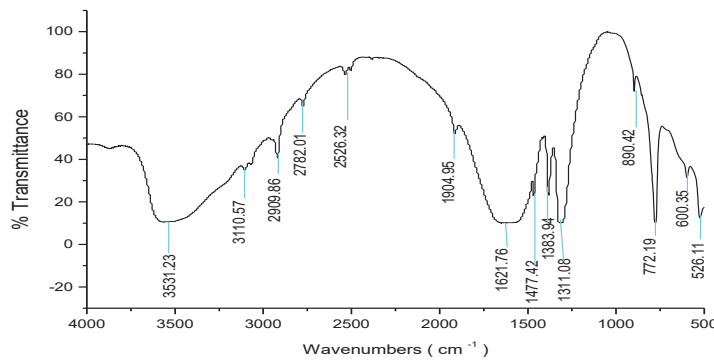
observed in other oxalate compounds were also found in the present case, which confirms the presence of oxalate group in the grown crystal. The peaks at 3487 and 3518cm^{-1} in pure calcium oxalate and praseodymium doped calcium oxalate crystals respectively are due to weakly H bonded O-H vibrations. The bands at 2660 and 2446cm^{-1} in pure crystal related to the intermolecular Ca-O phonon bands and O-H stretching of the hydrogen oxalate anions, respectively. These bands are shifted towards 2698 and 2484cm^{-1} in the case of PrBHP crystals. The band centred at 2361.41 in BHP and 2415.50cm^{-1} in doped crystals are attributed to the presence of Si-H bond. The bands located at 1735 and 1257cm^{-1} are referred to vibration of hydrogen ions in $\text{H}^+ - \text{C}_2\text{O}_4^-$ and in plane C-O-H bending. The CO stretches in the C_2O_4 fragment of calcium oxalate are characterized by two bands at 1071 and 984cm^{-1} . The C-O(H) stretching and liberation of H_2O molecules are attributed by 892cm^{-1} band. The peaks occurring at 532.92 and 563.21 , are due to the presence of metal oxygen bond in pure and doped calcium oxalate crystals respectively. There is no additional peak or band present in praseodymium modified crystal except

shifting or broadening of peaks and bands. A slight shift in some of the characteristic vibration frequency of the doped crystal's spectrum was observed with respect to pure crystal because of doping with praseodymium. The difference in mass of calcium and praseodymium ions leads to a change in molecular geometry and mechanical vibrations that

results into a shift in bands. The shift in the wave number was due to difference in mass number of Pr and calcium ions. This is due to the lattice strain developed as a result of doping. The peaks corresponding to other functional groups were also present and comparative assignments of prominent peaks of FTIR spectra are mentioned.



Pure

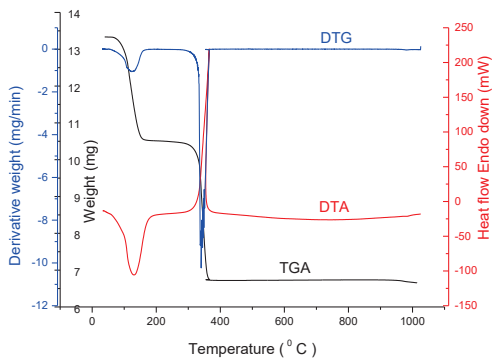


Doped

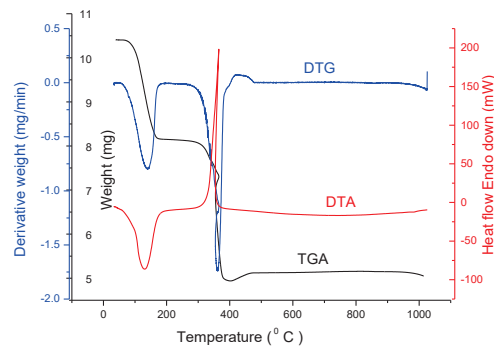
Fig (c) FTIR spectrum of pure and doped calcium oxalate crystals

Thermal studies: Thermal decomposition stages of pure and doped crystals were investigated by thermogravimetric analysis and the thermograms are shown in fig d. The thermo gravimetric analysis

(TGA) was carried out in the temperature range 25–800°C at a heating rate of 25°C/min. DTG curve has also been recorded at the same temperature range.



Pure



Doped

Fig. d. Thermograms of pure and doped calcium oxalate crystals.

The thermal stability of the grown material can be explained in two steps. The curve shows that the material is almost thermally stable upto 330°C with a weight loss of only 1% and thereafter it starts decomposing. In the case of pure calcium oxalate crystal, the first stage of decomposition begins from 330°C and continues upto 540°C resulting in a weight loss of 4.5%, whereas in doped crystal, the first stage of decomposition starts from 290°C and ends in 487°C with a weight loss of 5.1%. This weight loss is attributed to the loss of water molecule from grown crystal. In the case of doped crystal the decomposition process starts and ends at a temperature lower than that of pure crystal. It may be due to the incorporation of the Pr dopant in the

lattice of the doped crystal. Beyond decomposition temperatures, the samples tend to be stable.

Surface morphology: The surface morphology or grain morphology had been analyzed by means of scanning electron micrographs. The Geol JSM – 6390LA Analytical Scanning Microscope is used for the surface morphology analysis of grown crystals. The images were taken at different magnifications and at different spot sizes and are shown in fig. e. The SEM images are almost identical for both pure and doped crystals.

All sets of images taken at the same accelerating voltage 25 kV and spot sizes and magnifications are selected as different.

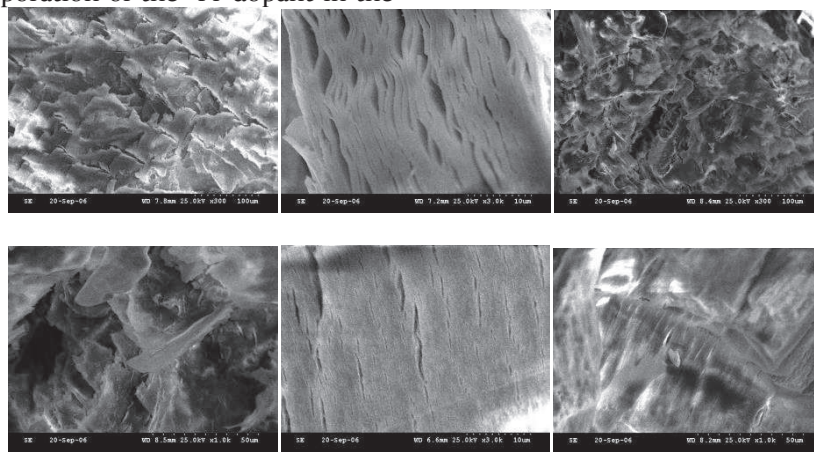
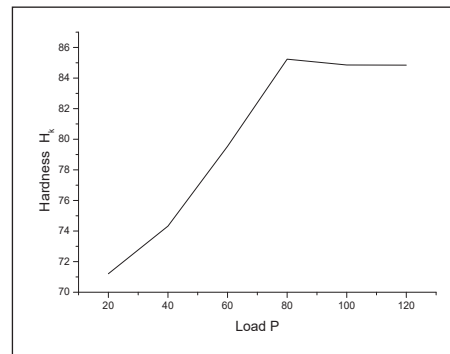
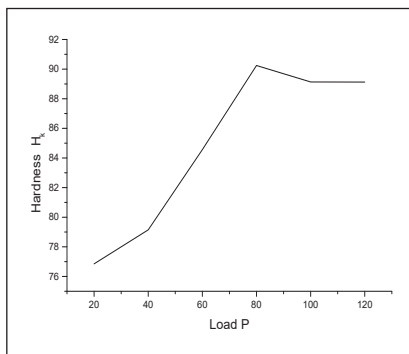
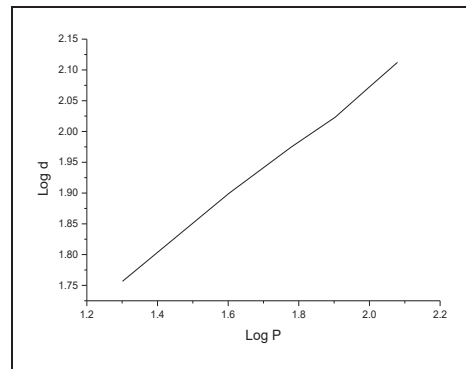
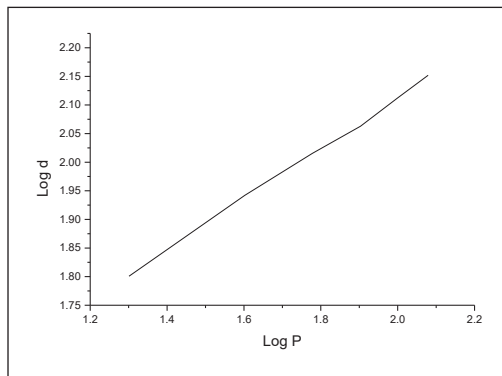


Fig.e. SEM images of pure and doped calcium oxalate crystals

Microhardness: The resistance offered by a material to indentation by a much harder body is known as hardness. It is a measure of the ability of the substance to resist scratching and permanent deformation. As defined by [9] hardness is a term having different meaning to different people. It is resistance to penetration to a metallurgist, a measure of flow stress to a design engineer, resistance to scratching to a mineralogist and resistance to cutting to a machinist. Microhardness studies find wide applications in the study of material properties of solids [10]. The hardness study undertaken so far for studying the strength of solids and effects of various treatments on the hardness of a solid, have proved some what useful.

Crystals of pure calcium oxalate and praseodymium doped calcium oxalate grown in silica gel were used for microhardness study. The study was carried out on as grown faces of all crystals. Crystals having thickness 2mm were fixed on a glass plate with an

adhesive. The leveling of the specimen was tested by using table microscope. Knoop pyramidal indenter was used to produce indentation mark. The micrometer eyepiece was used to measure the surface dimensions of the indentation marks. In order to avoid the influence of one indentation mark on the other, the distance between two consecutive indentations were maintained at least four times the diagonal length of the indentation mark, the indentation time for all specimens was kept as 10 seconds. The load was varied from 20 g to 120 g. All measurements were carried out at room temperature. Crystals of approximately same size were selected for the measurements. The longer diagonals of the Knoop indentation marks produced by various loads were measured. A typical set of observations recorded by plotting a graph with log 'P' versus log 'd' and log 'p' versus microhardness, are shown in fig. f, where 'p' is the load in grams and 'd' is the indentation.



Pure

Doped

Fig.f. Log p vs log d and log p vs microhardness of pure and doped crystals

References:

1. Cullen G W and Wang C C *Hetroepitaxial semiconductor devices, Springer Verlag Series* (1978)
2. Zulehner w J. *Crystal Growth* **65** (1983), 189
3. Brice J C *Crystal Growth Process, Blcke, Glogow and London Halsted Press, a division of John Wiley and Sons, New York* (1986)
4. Bridgman P W *Proc. of Nat. Acad. Sci.* **10** (1925) 411
5. Stockbarger D C *Rev. Sci.Instr* **7** (1936) 133
6. Chernov A A *Modern Crystallography III-Crystal Growth, Springer Verlag, Berlin* (1984)
7. Henisch H K *Cryst. Grow. in Gels, Pennsylvania: The Pennsylvania State Uni. Press,* (1970)
8. Pella G, Baggie R T, Marghi E and Deperezze P K J. *Cryst. Grow.* **67** (1984) 4
9. Shah M C 'The Science of Hardness Testing and its Research Applications', edited by J H Westbrook and H Conrad, ASM, Ohio (1973)
10. Haribabu V and Subrarao U V 'Growth and Characterization of alkali halide mixed crystals' *Prog. Crystal Growth Charact.* **Vol. 8** (1984)

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