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GROWTH AND CHARACTERIZATION OF GEL GROWN BARIUM DOPED NICKEL–TARTRATE CRYSTALS

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Abstract: In the present investigation the Barium doped Nickel tartrate (Ba-Ni-Tartrate) crystals were grown by the single diffusion gel growth technique. The optimum condition was established by varying various parameters such as pH of gel solution, gel concentrations and gel setting time. The optimum condition found for the barium dopped Nickel tartrate crystals by using the mixture of 1M $BaCl_2$ (3 mL) and 1M $NiCl_2$ (15 mL) with 1M tartaric acid at pH 4.7 in SMS gel. The light green an opaque spherulite crystal clusters were grown. The maximum size of the grown crystal was 15 mm x 8 mm and the thickness about 6 mm, the crystals were characterized by FTIR spectroscopy, powder XRD and TGA analysis.

IndexTerms **- Mixed crystals; gel growth; Barium doped nickel tartrate; FTIR; powder XRD; TGA.**

INTRODUCTION:

The crystals and compounds of different metal tartrates draw attention of scientific community due to its applications in science, technology, advanced materials, pharmaceuticals and even in medical sciences. The considerable attention has been devoted to tartrate salts due to their interesting electrical and optical properties. The advanced development in modern materials and technologies significantly depends on the crystal quality, packing and morphology. [1-5] Some crystals play an important role in the ferroelectric [6] or piezoelectric materials which are the key part in transducers and mechanical devices [7,8].

Organic tartrate compounds and metallic tartrate find various applications in the different fields and several papers and patents are reported for the materials, catalyst as well as in medicines. [9] The crystals of iron tartrate were grown and studied their thermal stability [10] also such type of iron tartrate complexes are plays as key role as contrast blocks of renal tissues prior to their dehydration.[11] The pure octahedral Nickel tartrate crystals were reported by synthetic strategy using the chiral tartaric acid and nickel sulphate to study their geometry also the synthetic chiral complexes show the magnetic properties.[12, 13] Different types of tartrate crystals grown in hydro silica gel. Growth and characterization of different crystals of pure and doped metal tartrate were reported by many researchers [8, 14].

In the present investigation, the Barium doped Ni-Tartrate (Ba-Ni-Tartrate) crystals were grown in sodium metasilicate gel. Cell parameters and crystal structure evaluated by powder X-ray diffraction and the functional groups and co-ordination of ligand to metal bonds confirmed by the FT-IR spectroscopic analysis.

MATERIALS AND METHODS:

EXPERIMENTAL:

Single diffusion gel growth technique was used to grow the mixed barium-nickel-tartrate crystals. The glass test tubes were used as crystallization assembly. Dimensions of glass test tubes were 25 mm diameter and 250 mm length. Hydro silica gel was used as a gel media to grow barium-nickel-tartrate crystals. The hydro silica gel was prepared by aqueous sodium metasilicate solution having 1.04 specific gravity. The pH of the sodium metasilicate was adjusted to pH 4.7 using 1 M tartaric acid to make the solution acidic. The viscous solution was transferred to glass test tubes or crystallization assembly and allowed to set into gel, the gel was set within two days duration. After the setting and aging of the gel, 18 ml of supernatant solution was gently poured over a set gel without break it. The supernatant solution was prepared by mixing of 15 mL - 1 M $NiCl_2 \cdot 6H_2O$ and 3 mL - 1 M $BaCl_2 \cdot 2H_2O$ solution. The flower like bunch of crystals were grown after 20-21 days. After the complete crystal growth, it was observed that the maximum amount of supernatant solution was absorbed by the gel and flower like green opaque spherulite crystal clusters were grown within the gel as shown in Figure 1(a). Some good quality crystals of Ba-NI-tartrate are shown in Figures 1(b). The largest crystal having the weight about 0.061 g and size 15 mm x 8 mm x 6 mm.

Table 1: Optimum condition for the Ba-Ni-Tartrate crystal growth

Conditions	Single diffusion
Specific gravity of sodium meta silicate gel	1.040
Gel pH	4.7
Concentration of Nickel chloride hexahydrate	1 M
Concentration of Barium chloride dihydrate	1 M
Concentration of tartaric acid	1 M
Reactant Ratio	$BaCl_2 \cdot 2H_2O$: $NiCl_2 \cdot 6H_2O$ - Ratio 1:5
Gel aging and setting period	2 days
Period of growth	20-21 days
Temperature	Room temperature (27 °C)
Colour and Quality	Flower like green opaque spherulite crystal clusters
Size (Length x Width x Height)	15 mm x 8 mm x 6 mm

Figure 1 (a): Ba-Ni-Tartrte Crystal in Gel
Figure 1 (b): Some good quality extracted opaque spherulite crystal clusters

RESULT AND DISCUSSION:

The single diffusion crystal growth optimum condition was given in the Table 1. The mass transfer, nucleation and growth process are the main aspects in the crystal growth. In the crystal growth the pH of the solution, the optimum pH at 4.7 found more suitable for the setting and aging of the gel. The parameters such as gel density, gel setting time, gel aging time, reactant concentration have a considerable effect on rate of crystal growth [15].

In the conventional single diffusion method, the test tube of 25 mm diameter and 250 mm length was used as crystallization assembly. The mixture of $BaCl_2$-$NiCl_2$ supernatant solution was absorbed in the maximum amount and flower like green opaque spherulite crystal clusters were grown with the tartrate supported with the Sodium meta silicate gel. The grown crystals were analyzed by the following analytical tools.

FTIR ANALYSIS:

The FTIR analysis technique that provides information about the chemical bonding or molecular structure of the materials. The FTIR spectrum of the grown crystals is shown in Figure 2. In the present IR study Attenuated Total Reflection (ATR) method was used. The Infra-Red analysis done on Agilent Cary 630 FTIR Spectrometer. The spectrum was recorded in the range 4000-500 cm^{-1} at room temperature. The relations of the molecular group vibrations and the characteristic absorption bands were assigned according to the theories of infrared spectra given in the Table 2 [15,16].

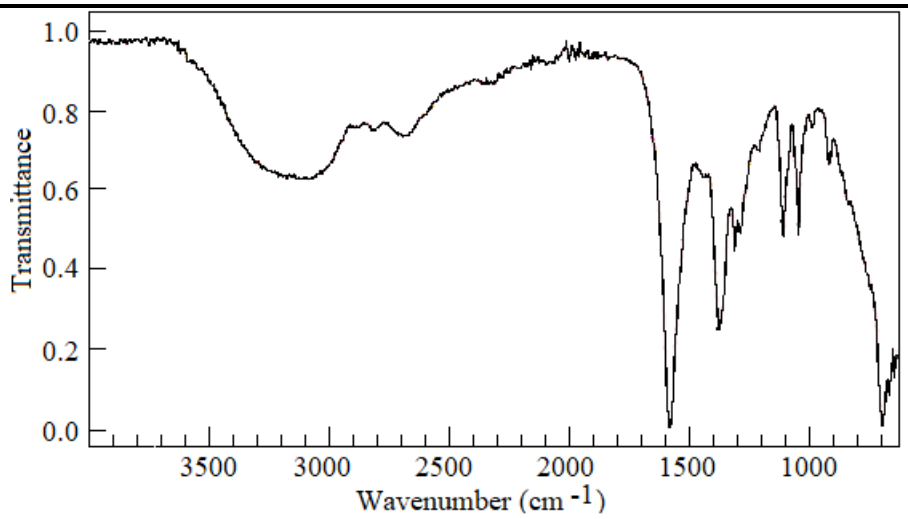

Figure 2: FTIR spectrum for BaNiTa crystal

In the FTIR spectrum, the strong broad absorption bands in the region 3121 cm^{-1} and 2696 cm^{-1} are due to the alcoholic and carboxylic acid -OH stretching mode respectively. The strong and sharp band at 1589 cm^{-1} is attributed to the >C=O stretch of carbonyl group. The strong peak at 1388 cm^{-1} is assigned to >C=O symmetric and δ(O-C=O) mode. The peaks at 1126 and 1058 cm^{-1} are assigned to >C-O stretching and >C-C< stretching modes. The peak at 706 cm^{-1} is due to the deformation vibrations of CO_2.

Table-2: FTIR interpretation for the Ba-Ni-Tartrate

IR Frequencies in Wavenumbers (cm^{-1})	Functional Group Assignments
3121 cm^{-1} and 2696 cm^{-1}	-O-H group stretch
1589 cm^{-1}	>C=O stretch of carbonyl group
1388 cm^{-1}	>C=O symmetric and δ (O-C=O) mode
1126 and 1058 cm^{-1}	>C-O stretching
706 cm^{-1}	M-O Stretching

THERMAL GRAVIMETRIC ANALYSIS:

A real-time record of thermal gravimetric analysis of Ba-Ni tartrate crystals are shown in Figure - 3 for the temperatures in the range of 30-600 °C. In these records, it is seen that the crystals undergo decomposition in different stages, suffering weight loss in each of the stage. The study mainly reveals the decomposition of the crystal as well as the percentage weight loss at different stages of decomposition. The initial mass of the material taken in the form of powder was 5.717 mg and the final mass left after the experiment was 1.652 mg at 592.4 °C and found the total weight loss 71.11%. From the graph (Figure-3) it was seen that Ba-Ni-Tartrate crystals are stable upto 65 °C. The well define sharp peak at 65-307 °C attribute to major weight loss. The crystal exhibited the thermal stability in the oxide state at 307 °C.

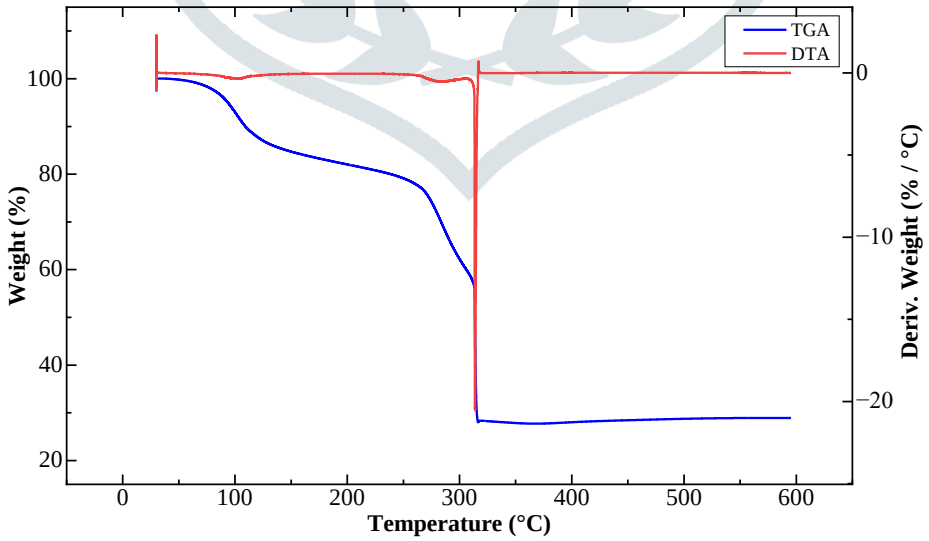

Figure - 3: TGA and DTA for Ba-Ni-Ta crystals

In DTA analysis the Sharpe single endothermic curve observed at 307 °C, due to the decomposition of hydrated Ba-Ni-Tartrate into anhydrous Ba-Ni-Tartrate. This endothermic peak observed in the DTA curve corresponds to the total weight loss of water molecule in the corresponding TG curve. In the differential thermal analysis, temperature changes in the sample were due to the reactions caused by phase changes, decomposition, oxidation, reduction, or other chemical reactions [10, 17].

POWDER XRD ANALYSIS:

The lattice parameters for Ba-Na-Tartrate obtained by the PXRD analysis and listed in the Table-3. It is evident that Ba-Ni-Tartrate crystals belong to trigonal system with space group P-3. The experimental PXRD patterns of Ba-Ni tartrate crystals are shown together in Figure-3. The indices (h k l) for the prominent peaks in these patterns are shown in Table-3. Sharp peaks observed in Figure-3 confirm the crystalline nature of the grown materials. The powder XRD has confirmed the trigonal structure of the crystal.

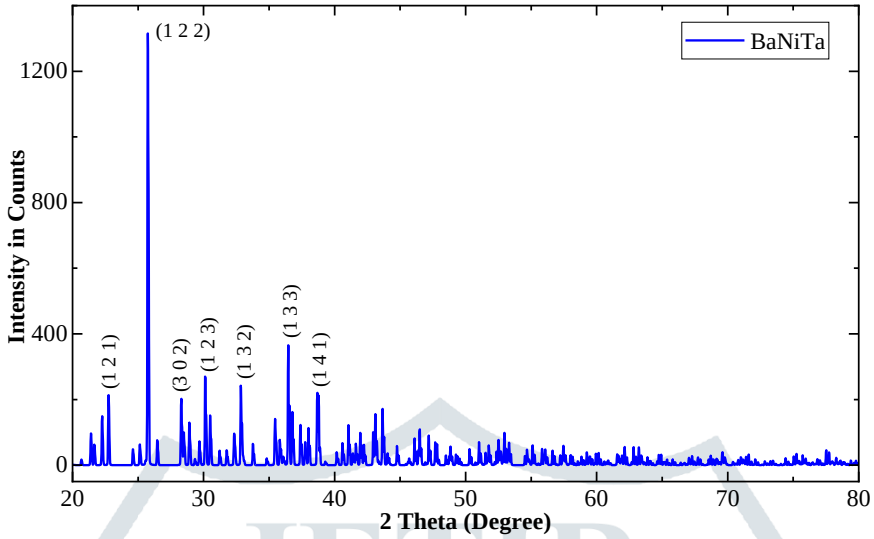

Figure-4: Powder XRD pattern for Ba-Ni-Tartrate crystal

Table 3: Ba-Ni-Tartrate XRD data

2θ	d Å	Relative Intensity (cts)	Indices
22.74	3.9074	213.01	(1 2 1)
25.74	3.4572	1314.97	(1 2 2)
28.30	3.1512	201.80	(3 0 2)
30.12	2.9649	269.70	(1 2 3)
32.84	2.7252	241.88	(1 3 2)
36.46	2.4624	365.36	(1 3 3)
38.68	2.3257	220.38	(1 4 1)

Table-4: Crystal parameters of Ba-Ni-Tartrate crystals

Crystal Parameters	a Å	b Å	c Å	α°	β°	γ°	Volume Å^3	Crystal system
BaNiTa	12.50	12.20	12.86	90	90	120	1741.82	Trigonal

The powder XRD studies were carried out using Small Angle X-ray Scattering, ANTON PAAR, (SAXSPACE) with CuKα radiation (λ=1.54056 Å). The samples were scanned over the range of 2θ values (200 to 800). The powder XRD pattern of Ba-Ni-Tartrate in Figure-3. It was indexed using Rietveld refinement method to identify the reflecting planes. The XRD data was analyzed using FullProf Suite software and Crystallography Open Database (COD) CIF file. The sharp and well-defined peaks at specific 2θ values testify the excellent crystalline nature and purity of the grown crystal. The indices of the major peaks for Ba-Ni-Tartrate in decreasing order of intensity are (121), (122), (302), (123), (132), (133) and (141). The 2θ values, d values and the indices of major peaks observed in the spectra of the Ba-Ni-Tartrate are given in Table 3.

Calculation of cell parameters reveals that Ba-Ni-Tartrate belong to trigonal crystal system having space group P-3. The cell parameters of crystal are worked out using FullProf software and are a=12.50 Å, b=12.20 Å, c=12.86 Å, α=90.0º, β=90.0º, γ=120.0° and unit cell volume 1741.82 Å3. The experimental d-values are in conformity with the calculated ones using the above cell parameters for pure doped crystals. Mixing has brought a change in cell dimensions due to the change in bond length [10,18].

CONCLUSION:

A well-defined Barium doped Nickel-Tartrate crystal like flower as green opaque spherulite crystal clusters was obtained by using Sodium meta silicate gel. The growth parameters are tuned to obtain a reasonably good size, quality and morphology of the crystals.

Various functional groups specially Meal-Oxygen bonding of the grown crystals have been identified by FTIR spectral analysis. The crystalline nature of the Ba-Ni-Tartrate crystals was confirmed by the powder X-ray diffraction analysis.

The decomposition of the Tartrate crystals in the form of dehydration, decarbonization and carbonation were studied by thermogravimetric analysis.

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