



## Synthesis of well dispersed, elliptical shaped Barium Sulphate nanoparticles via Water – Chloroform mixed solvent

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### ABSTRACT

Mixed solvent system has been found as an excellent method for the preparation of well dispersed barium sulphate nanoparticles. Spherical and elliptical shaped barium sulphate nanoparticles with barite structure were synthesized through precipitation in water medium and water – chloroform mixed solvent system. Six different compositions of mixed solvents, including pure water, 20 vol.%, 30 vol.%, 50 vol.%, 70 vol.% and 90 vol.% of chloroform were used. Particle characterization was accomplished by X-ray diffraction (XRD), Field Emission Scanning Electron Microscopy (FESEM) with Energy Dispersive X-ray Spectrum (EDX) and Fourier Transform Infrared Spectroscopy (FTIR) techniques. The synthesized particles are having orthorhombic structure with elliptical morphology with an average size of 46.6 nm. It is seen that the water – chloroform mixed solvents protect the nanoparticles against agglomeration.

**Keywords:** Mixed solvents, Well dispersed, Elliptical particles, Water – chloroform, Precipitation.

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### INTRODUCTION

Nanoscaled particles have many good properties. A lot of applications of nanoparticles have been developed. One of the important issues in the synthesis of nanoparticles is to curb the particle size and its distribution [1]. Recently the synthesis of inorganic nanoparticles with controlled morphology has attracted great interest due to its important applications in various fields. Barium sulphate commonly referred to as barite, is one of the most important fillers used in the plastics, rubber and paint industries and also used in pharmaceutical formulations. Barium sulphate have been incorporated into polymers to form electrically insulating barium sulphate/epoxy composites with X-ray attenuation properties. It is also applied in the studies of

biomineralization and molecular recognition [2-4]. It is a very good thermoluminescence material, which is used in the radiation dosimeter field. Such an important nanoparticle have been synthesized through precipitation method. So far so many methods have been proposed to produce the barium sulphate nanoparticles such as precipitation [5], microemulsion [6], filtration dispersion method [7], modifying different organic acids [8], membrane dispersion [9], presence of polymeric additives [10] and so on. Nowadays, it is an important challenge to obtain the nanoparticles by simple and powerful method. Among these methods, precipitation is the most attractive due to its simple operation, easy of mass production and demand less apparatus compared to other process. But there is a task to be met for controlling and preventing against agglomeration. It is necessary to explore for an efficacious method to resolve this distract to extent the application of precipitation. To exert of a mixed solvent is doubtless a new approach path in materials synthesis and processing [11]. However, there are only few studies are carried out on the formations of nanoscale materials in the mixed solvent method.

In the present work, water – chloroform mixed solvent have been worked to synthesize barium sulphate nanoparticles in the precipitation method. By varying the volume percentage of chloroform in the mixed solvent, the obtained particles are in well dispersed, elliptical shaped and also in the nanometer range.

## MATERIALS AND METHODS

The mainly used raw materials were barium chloride, sodium sulphate and chloroform. All these chemicals were used directly without any further purification. The particles were synthesized by two methods, common direct chemical precipitation and mixed solvent precipitation method.

### Synthesis of barium sulphate in direct chemical precipitation

As to the preparation of the barium sulphate nanoparticles by direct chemical precipitation method, equal molar ratio of (0.1M of 50ml) both reagents was prepared separately. Then the barium chloride solution was added into the sodium sulphate solution by drop wise under high speed magnetic stirring condition for half an hour and it kept stable for complete precipitation. The precipitation was collected and washed with various solvents for several times afterwards it was dried in the oven at 100°C for 12 hours and it was taken to the characterization process.

### Synthesis of barium sulphate in mixed solvent system

In the case of precipitation in the mixed solvent, five different compositions 20 vol.%, 30 vol.%, 50 vol.%, 70 vol.% and 90 vol.% of water – chloroform were used.

**Table 1 Experimental conditions for each examined system**

Mixed solvent System	(0.1M of BaCl <sub>2</sub> in 50ml) Solution A	(0.1M of Na <sub>2</sub> SO <sub>4</sub> in 50ml) Solution B
C1 (20 vol. %)	10ml of chloroform + 40ml of water	10ml of chloroform + 40ml of water
C2 (30 vol. %)	15ml of chloroform + 35ml of water	15ml of chloroform + 35ml of water
C3 (50 vol. %)	25ml of chloroform + 25ml of water	25ml of chloroform + 25ml of water
C4 (70 vol. %)	35ml of chloroform + 15ml of water	35ml of chloroform + 15ml of water
C5 (90 vol. %)	45ml of chloroform + 5ml of water	45ml of chloroform + 5ml of water

Various compositions of mixed solvent system were given in table 1. In general, barium chloride and sodium sulphate were soluble in water but insoluble in chloroform. This makes chloroform as a suitable anti-solvent, as further addition of chloroform the solution lowers the solubility of reagents and thus generates the super saturation. The solubility circumstance of reagents was an important viability of this method.

For example system, C2 (30 vol. %) of water – chloroform mixed solvent system, solution A was mixed drop wise with the solution B with high speed magnetic stirring. Drop wise means less amount of reactant flowed per unit of time, this extending to lower super saturation. Precipitation mechanisms are supposed to be homogeneous nucleation and controlled growth. The fact that particles are big at the fast feeding rate and also homogeneous nucleation is low. Particles were collected as for the procedure followed in the former case (direct precipitation) and it was taken for characterization.

The synthesized samples were characterized by different techniques, such as XRD, FESEM-EDX, and FTIR.

The structure and average crystalline size was determined by X-ray diffractometer. The X-ray diffractogram of the powdered sample were recorded at room temperature using XPERT-PRO PANalytical with a curved graphite crystal diffracted monochromator, with a source of Cu  $k_{\alpha}$  ( $\lambda=1.5406\text{\AA}$ ) at 40kV and 30mA, Ni filter and NaI(Tl) scintillation detector cooled by liquid nitrogen. During the recording of the diffractogram, a narrow slit of 0.1mm was used with a scanning speed of  $1/2^{\circ}$  per min and a time constant of 2s. The sample was firmly pressed into an aluminum holder, with an area of 30mm $\times$ 30mm. The diffraction patterns were obtained over 2 $\theta$  values in the region  $20^{\circ}$  -  $50^{\circ}$ .

The morphology and size of the barium sulphate particles were examined by means of FESEM (Hitachi SU6600) by an accelerating voltage of 15 kV. The spot size in FESEM is smaller than in conventional SEM and it can produce very high resolution images (better than three to six times with conventional SEM). To identify the elemental composition, the EDX spectrum also recorded which is available with the FESEM instrument.

FTIR analysis was carried out to identify the functional group present in the samples. The powdered sample was mixed with KBr at various ratios 1:10, 1:20, 1:30, 1:40, and 1:50. The pellets were prepared and FTIR spectra were recorded. The maximum absorption and large number of peaks are observed for the samples in the ratio of 1:30 (sample: KBr) and chosen for further analysis. The Perkin Elmer RX1 series FTIR spectrometer was used for recording the IR spectra of the sample. The instrument wavenumber ranges from 4000 to  $400\text{cm}^{-1}$  with an accuracy of  $\pm 0.01\text{cm}^{-1}$  and resolution of  $\pm 4\text{cm}^{-1}$ . The instrument was calibrated with the spectra of a standard polystyrene film at room temperature. Every time, before the spectrum of the sample was recorded, the spectrum of the polystyrene film was obtained and checked for its accuracy and transmittance.

## RESULTS AND DISCUSSION

### X- Ray diffraction (XRD)

Fig. (1) Shows the X-ray diffraction pattern of barium sulphate particles for six different compositions of water - chloroform mixed solvents and pure water. All the reflection planes are readily matched with orthorhombic phase of pure barium sulphate, which are in good agreement with the reported values (JCPDS card no. 76-0214) with crystalline cell constants  $a = 8.898$ ,  $b = 5.980$  and  $c = 7.155$ , space group  $P_{nma}$ . It is also observed that there is no interaction takes place on nature of barium sulphate for the various concentrations of chloroform. Only barium sulphate peaks are observed in the XRD spectra. This strongly indicates that the chloroform can not regulate the reaction paths and crystal structure. No characteristics peaks of other impurities are observed, which indicated that the product had a high purity. The synthesized particles show the broad diffraction lines which suggests that the crystallites are in nanometer range. The crystalline sizes are calculated using Scherrer's formula " $d = 0.94\lambda / \beta \cos\theta$ " [12] for the five high intensity peaks observed at  $25.95^\circ$ ,  $26.95^\circ$ ,  $28.82^\circ$ ,  $42.54^\circ$ , and

$42.88^\circ$  ( $2\theta$ ) with hkl values (210), (102), (211), (113), and (312) respectively. Where,  $D$  – diameter of the crystal,  $\lambda$  - X-ray wavelength,  $\beta$  - half width of the peak (full width at half maximum) and  $\theta$  - Bragg's diffraction angle. Calculated crystalline sizes of various compositions are presented in table 2.

**Table 2 The crystalline sizes of various compositions of pure and mixed solvents**

Composition of water – chloroform Vol. (%)	Particle sizes for various reflection planes					Average crystalline size (nm)
	(210)	(102)	(211)	(113)	(312)	
0 (pure water)	28.87	25.83	36.31	25.17	36.13	30.46
20	60.03	55.14	55.36	48.94	62.85	56.46
30	34.75	50.89	55.36	57.53	34.56	46.62
50	60.03	66.16	44.29	53.11	53.17	55.35
70	60.03	66.17	55.37	57.54	40.66	55.95
90	55.02	60.15	55.36	62.76	34.56	66.12

From the table 2 and figure 2, 30 vol. % of water – chloroform mixed solvent system are having minimum crystalline size (46.6 nm) compared to the other mixed solvent system. The particle sizes are increased from pure water system to 20 vol. % and then decreased for 30 vol. %. At 50 and 70 vol. % of water – chloroform mixed solvent system the crystalline sizes are saturated (both cases the

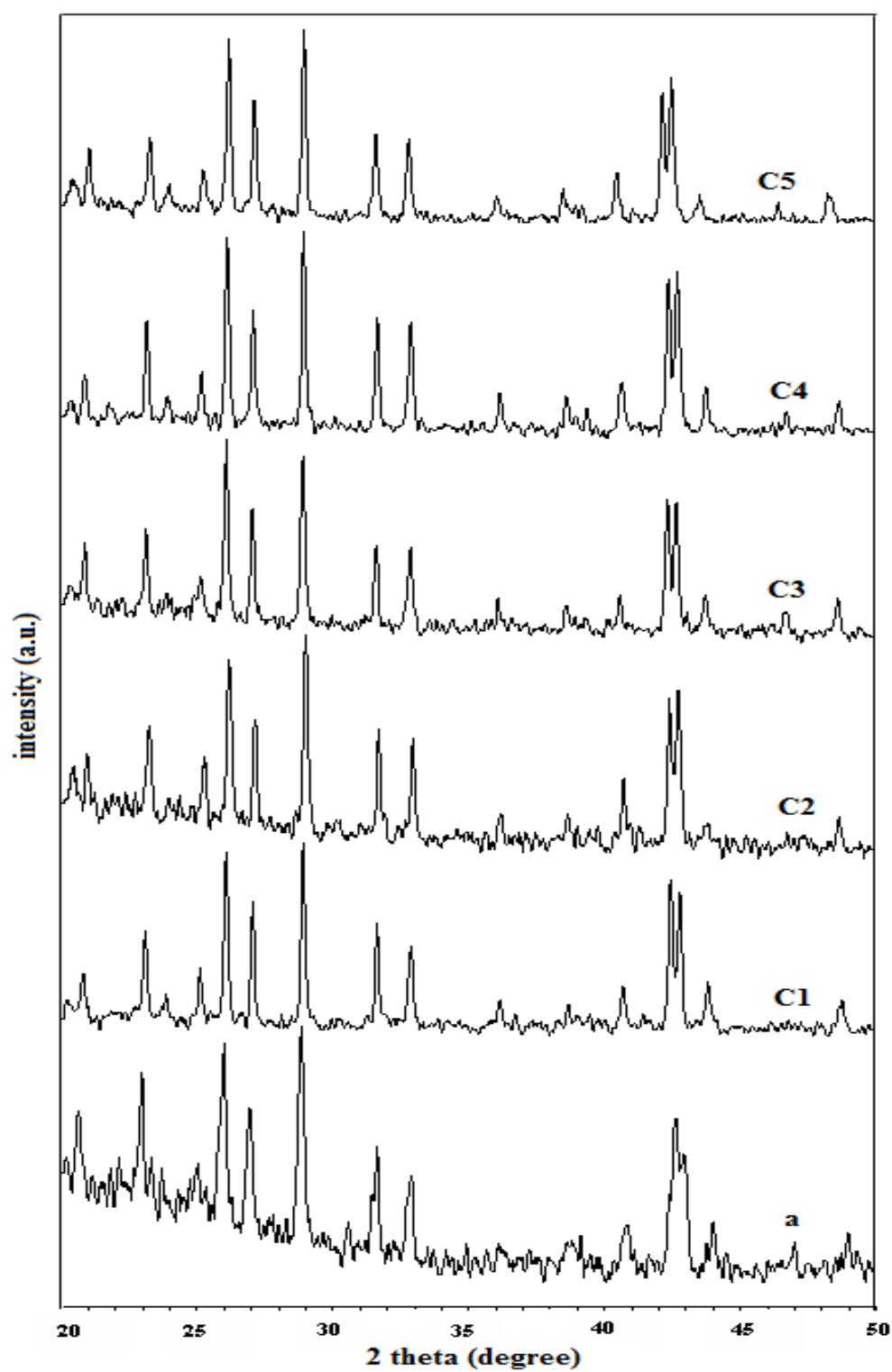
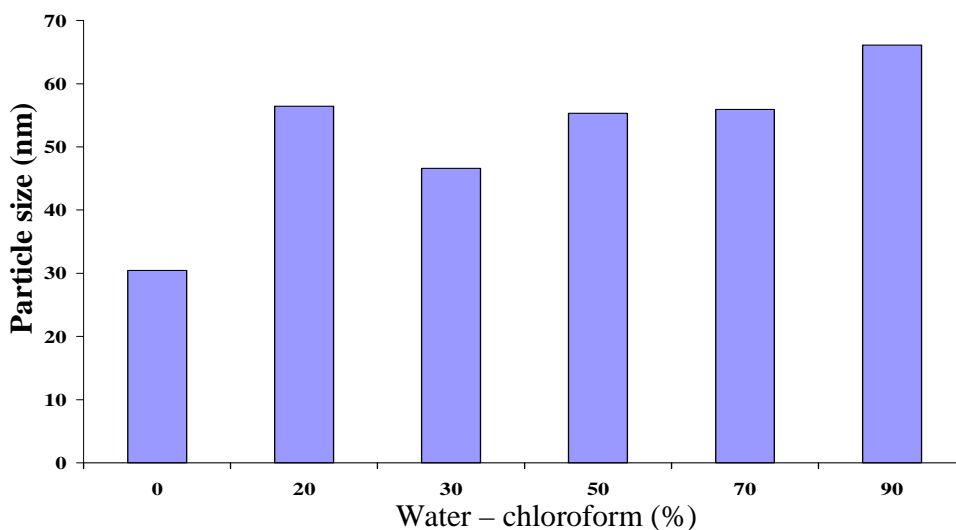


Figure 1. The X-ray diffraction pattern of barium sulphate nanoparticles for (a) pure water and five different compositions

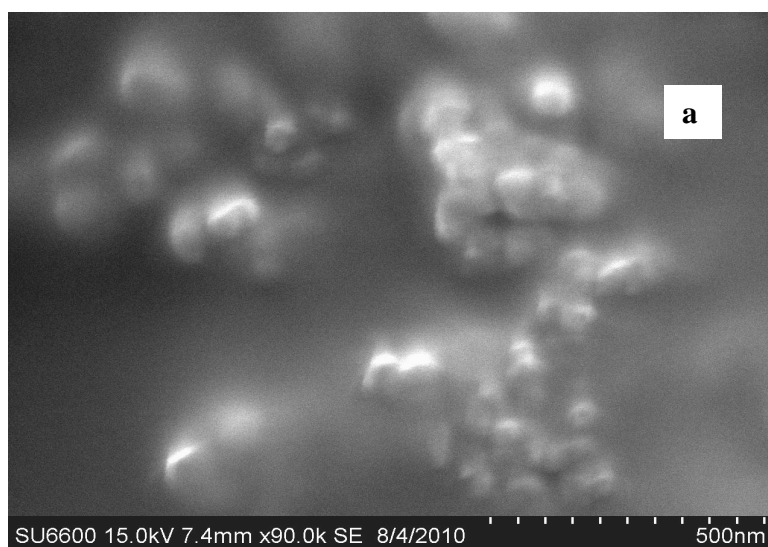


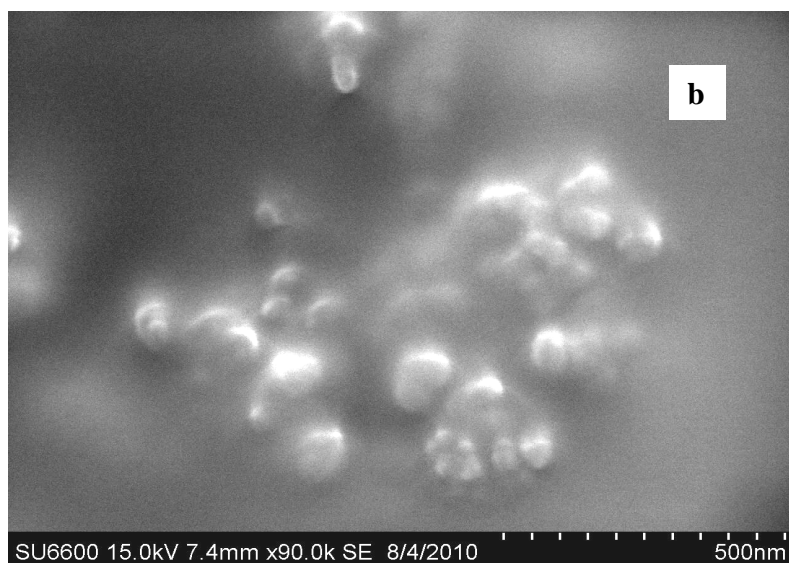
**Figure 2** The particle size distribution of different compositions of water – chloroform mixed solvent system

crystalline sizes are 55 nm). Then, for 90 vol. % of water – chloroform mixed solvent system, the average crystalline size is again increased (66.1 nm). Thus, 30 vol. % of water – chloroform mixed solvent system has selected as the best concentration in the process of barium sulphate nanoparticle formation from water – chloroform system.

#### **Field Emission Scanning Electron Microscopy (FESEM)**

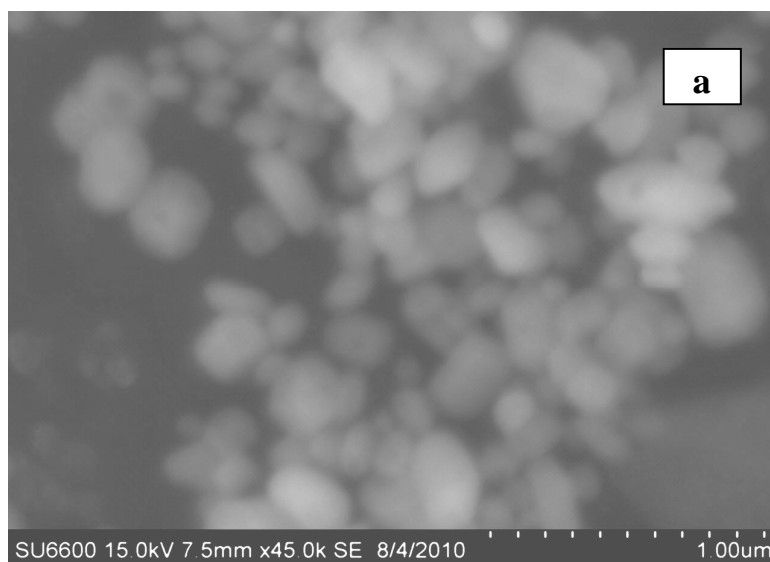
Figure 3 (a and b) show the FESEM images of particles synthesized through pure water. From the images, the morphology of the particles are in spherical shape with agglomeration. The average sizes of the particles are ranged from 20-35 nm. To overcome the particle agglomeration, an effective method of mixed solvent process was chosen.





**Figure 3. (a and b) FESEM images of BaSO<sub>4</sub> nanoparticle using pure water precipitation**

Figure 4 (a and b) show the FESEM images of particles synthesized through the mixed solvent system (30 vol. %) at various magnifications. From these images, it is clear that the particles are having the morphology of elliptical in shape and the size in the range of 40-50 nm. The particle size is slightly increased compared to the former case (pure water), however it is having different morphology without agglomeration.





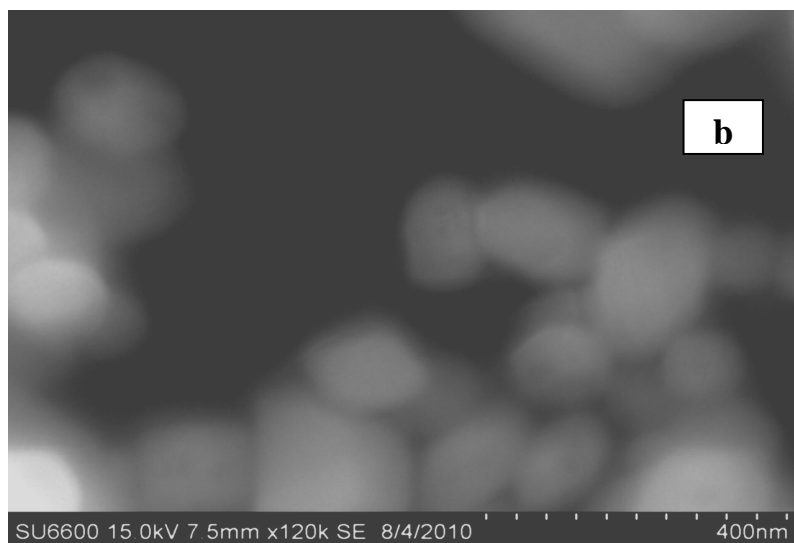


Figure 4. (a and b) FESEM images of BaSO<sub>4</sub> nanoparticles using water – chloroform (30 vol. %) with various magnifications

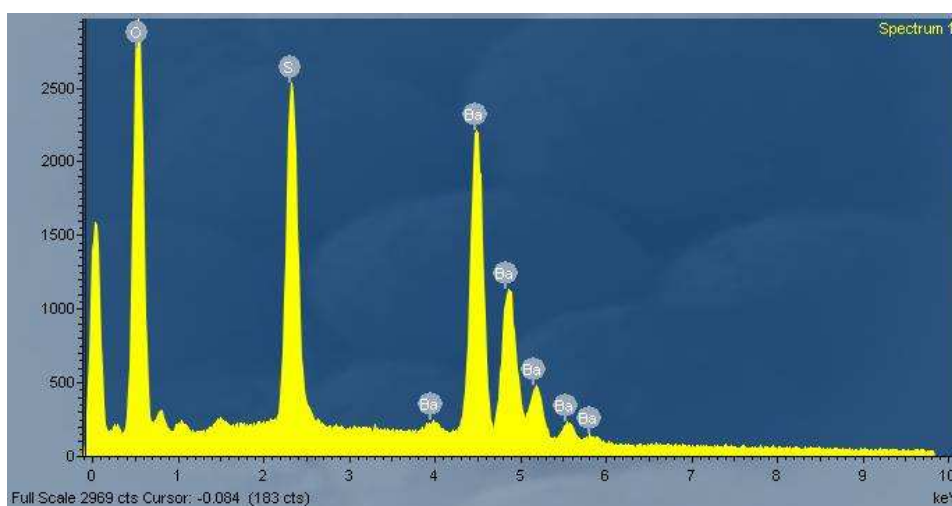


Figure 5. The EDX spectrum of BaSO<sub>4</sub> nanoparticles synthesized by 30 vol. % of water – chloroform system.

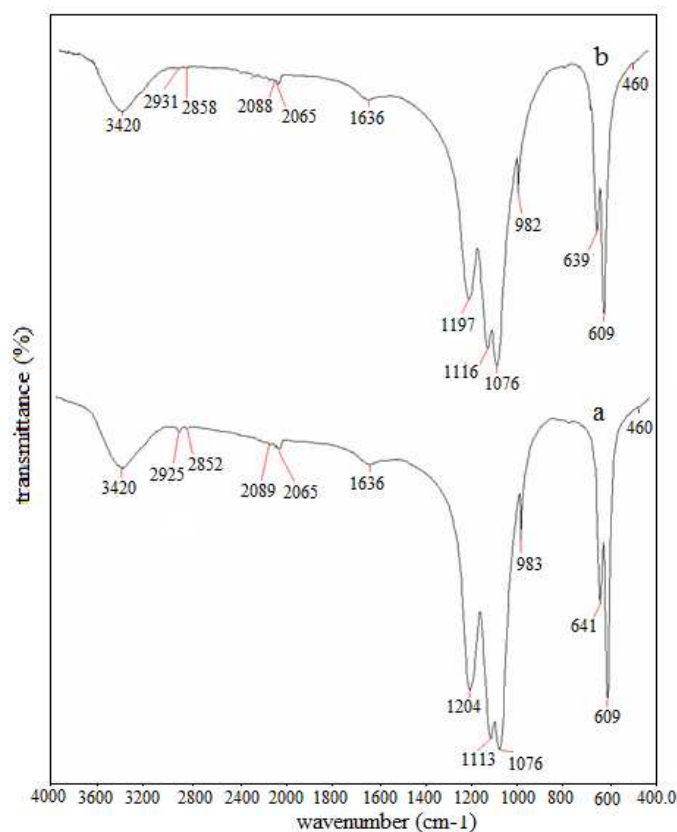
Figure 5 shows the EDX spectrum of barium sulphate nanoparticles synthesized by 30 vol. % mixed solvent composition. It reveals that the particles are having of Ba (60.58 %), S (12.31 %) and O (27.10 %) elements only.

#### Fourier Transform Infrared (FTIR)

Fig. 6 (a) and (b) show the FTIR spectrum of barium sulphate nanoparticles using pure water and mixed solvent (30 vol. %). The sulphate group has 4 fundamental vibrational modes. One non degenerate ( $\nu_1$ ), one doubly degenerate ( $\nu_2$ ) and two triply degenerate ( $\nu_3$  and  $\nu_4$ ). Generally frequency characteristic vibrations of  $\nu_3$  appear between 1200 – 1080 cm<sup>-1</sup> [13]. In the case of pure water (a), the broad band centered at 1204 – 1076 cm<sup>-1</sup> and in the case of mixed solvent



system (b), it is obtained in the region  $1197 - 1076 \text{ cm}^{-1}$  which are due to the asymmetric stretching vibration of  $\nu_3$  vibrational mode in sulphate group. The slight shift in the peak positions may be due to (a) the particle size and (b) the interaction of chloroform. The peaks obtained in both cases at  $639 \text{ cm}^{-1}$  and  $604 \text{ cm}^{-1}$  are due to the out of plane bending  $\nu_4$  vibrational mode in sulphate group [8]. In both cases the shoulder at  $982 \text{ cm}^{-1}$  is attributed to  $\nu_1$  vibrational mode. The peaks at  $460 \text{ cm}^{-1}$  corresponds to symmetrically bending  $\nu_2$



**Figure 6. The FTIR spectra of BaSO<sub>4</sub> nanoparticles (a) pure water and (b) mixed solvent water - chloroform (30 vol. %).**

vibrational mode. The absorption peaks appeared at about  $3433 \text{ cm}^{-1}$  and  $1634 \text{ cm}^{-1}$  are due to stretching and deformation of adsorbed water molecule. The weak absorption band at  $2925 \text{ cm}^{-1}$  and  $2852 \text{ cm}^{-1}$  could be assigned to symmetric and asymmetric vibrations of  $-\text{CH}_2$  and  $-\text{CH}_3$  groups. The peaks appeared at around  $2000 \text{ cm}^{-1}$  are overtones and combination bands of the sulphur-oxygen stretching and bending vibrations. These peaks do not affect the identification of the substance involved in the experiment [14].

## CONCLUSION

Well dispersed, unagglomerated barium sulphate nanoparticles were successfully synthesized using precipitation in water – chloroform mixed solvent system. The XRD study manifest that the synthesized samples are pure barium sulphate particles and having orthorhombic structure. 30 vol. % of mixed solvent system is fixed as the optimum concentration. The average size of the

particles obtained in pure water as 30.4 nm and in the case of mixed solvent system it is 46.6 nm. From the FESEM images, the particles morphology is altered from spherical to elliptical shape when using water – chloroform mixed solvent and also agglomeration is inhibited. The EDX analysis, confirm the presence of Ba, S and O elements. FTIR study reveals the presence of sulphate group. Thus, from the above different characterization we conclude water – chloroform mixed solvent is one of the best and easy way of approach to synthesize unagglomerated and elliptical shaped barium sulphate nanoparticles. This type of unagglomerated and morphology altered mixed solvent systems (without using polymers or additives) are most applicable in industrial oriented purpose for synthesis of nanomaterials.

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