Applied Innovative Research
Vol. 1, March 2019, pp. 52-57

Development of Advanced Hybrid, Nano-Sized, Brine Sludge Impregnated MWCNT Composite Material Useful for Broad Application Spectrum

Sarika Verma*, S K Sanghi & A K Srivastava

Materials for Radiation Shielding and Cement Free Concrete Division,
CSIR-Advanced Materials and Processes Research Institute, Bhopal 462 026, India

Received 18 September 2018; accepted 21 January 2019

A novel microwave irradiated process has been developed for the synthesis of advanced hybrid, nano-sized, functionalized, brine sludge impregnated MWCNT composite material useful for broad application spectrum. MWCNTs and brine sludge are mainly used as raw materials and are heated in flask using microwave synthesizer in the temperature range of 50-60 ºC for the duration of 20- 25 minutes. Brine sludge act as a novel agent wherein simultaneously and synergistically in-situ funtionization of MWCNTs takes place and therefore enabling synthesis of dark grey colored advanced hybrid, nano-sized, functionalized, brine sludge impregnated MWCNT composite material useful for broad application spectrum. The synthesized advance material has been characterized by various complementary techniques namely XRD, FTIR, FESEM and EDXA. FESEM study reveals the increase in the thickness of the MWCNT wall thereby confirms the brine sludge impregnation on MWCNT. The applications of synthesized material lie in the area such as radiation shielding materials, hybrid polymeric materials to advanced chemically designed composite (ACDC) materials useful for broad application spectrum.

Keywords*:* Hybrid, nanosized, MWCNTs, Brine Sludge, Microwave irradiation

Introduction

In the recent years carbon nano tubes (CNT) has attracted a great attention to the scientific community due to its exclusive structure and unbeatable properties like high conductivity and aspect ratio, small diameter and mechanical strength[1,2]. These carbon nano tubes are useful in various sectors like electronics, automotive and aerospace etc. Recently MWCNTs (Multiple walled carbon nano tubes) have find its application in the area of development of radiation shielding materials especially for U.V, EMI and X rays. Sarika Verma *et al.*[3] reported the synthesis and characterization of advanced red mud and MWCNTS based EMI shielding material via ceramic processing. Radiation shielding composite material including radiation absorbing material and method for preparing the same has been reported by Wei-Hung Chiang *et al.*[4] Toshihiko Fujimori *et al.*[5] reported the enhanced X-ray shielding effects of carbon nanotubes[3-6].

Further, brine sludge is an industrial by -product generated in chloral alkali industry wherein, the production of NaOH and chlorine is carried out by the electrolysis of purified brine solution, i.e., 26 % sodium chloride solution and the process of purification of impure brine solution involves removal of sulphate and chloride salts of magnesium and potassium. Removal of sulphate species is carried out by adding barium carbonate and leads to the generation of brine sludge waste containing barium sulphate[7-9]. Further removal of chloride species is carried out by adding calcium carbonate leading to the generation of brine sludge containing calcium carbonate and magnesium hydroxide. The generated brine sludge waste contains barium sulphate, calcium carbonate, magnesium hydroxide, sodium chloride, clay and other elements.

The demand for the use of microwave synthesizer for the production of new products have been increased and preferred over Convention method of heating due to its various advantages like solvent free or less solvent conditions, low cost, save energy, time and offers high yield of product[10, 11]. Microwave irradiation accelerates the particle collisions, which makes the sample, well dispersed and well crystallized there by reducing the synthesis time of product and also helps in obtaining the product with significantly higher yield[12].

Taking into consideration all the above points, the objective of the current work is development of

*Corresponding author (E-mail: drsarikaverma@hotmail.com)

advanced hybrid, nano-sized, brine sludge impregnated MWCNT composite material useful for broad application spectrum. The developed advanced material finds its application ranging from radiation shielding materials, hybrid polymeric materials and to advanced chemically designed composite (ACDC) materials. The uniqueness of our approach consists of in-situ funtionalization of MWCNTs in the reaction process by using microwave synthesizer followed by ceramic treatment to obtain advanced hybrid, nano-sized, functionalized, brine sludge impregnated MWCNT composite material useful for broad application spectrum.

The X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), field emission scanning electron microscopy (FESEM), energy-dispersive X-ray spectroscopy (EDXA) data of MWCNT, brine sludge and the developed advanced hybrid, nano-sized, functionalized, brine sludge impregnated MWCNT composite material is reported in this paper.

Experimental

Materials and method

Brine sludge

The sample of brine sludge procured from Nagda Grasim, M. P, was dried at 110 °C for 48 hrs, cooled to ambient temperature and analyzed for various chemical constituents by wet chemical analysis as per the test procedures prescribed in the standard[13]. The sludge was alkaline in character as indicated by its pH and was ground in a ball mill to a fineness of 85% passing through 150 micron IS sieve. The mineralogical characterization of brine sludge shows the presence of Barite, Brucite, Calcite and Halite phases. The results of mineralogical behavior and chemical analysis of brine sludge are given in Fig. 1.

Chemicals

MWCNT (>95% in purity, 20~25 μm in length, was kindly provided by nano-solution Co., Korea., Sodium hydroxide, Cetyltrimethylammonium bromide (CTAB), Acetone, procured from Rankem and Ethylene glycol was procured from Merck. All the chemicals were used as such without further purification. Millipore water (Milli-Q system) was used for the preparation of solutions.

Experiment

To obtain the advanced hybrid, nano-sized, brine sludge impregnated MWCNT composite material following procedure was performed. 5 g MWCNT, 30 g of brine sludge, 6 g of sodium hydroxide, 250 mL of ethylene glycol, 5 g of Cetyl trimethylammonium bromide and 20 mL of water is taken in a round bottom flask to obtain the homogenized mixture which was further heated in flask using microwave synthesizer in the temperature range of 50-60^{o}c for the duration of 20- 25 minutes and the material so obtained was further filtered and dried in an air oven at 110 ºC for a period of 1 h. The dried precursor powder so obtained was compacted and heated at the temperature of 450 ºC for the duration of 2 h to obtain dark grey colored advanced hybrid, nano-sized, brine sludge impregnated MWCNT composite material useful for broad application spectrum.

Characterization

Microwave irradiated synthesis of the developed material was carried out in open glass vessel on a modified microwave oven model 2001 ETB with

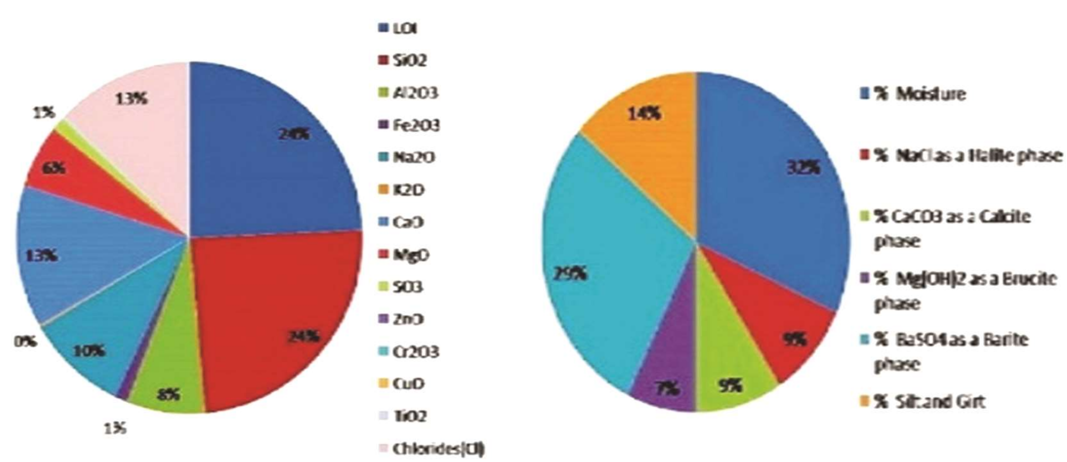

Fig. 1 – Mineralogical behaviour and chemical analysis of brine sludge.

rotating tray and a power source 230 V, microwave energy output.

To identify the different phases present in MWCNT, brine sludge and the developed advanced material the X-ray diffraction pattern was obtained on D8 advance X-ray diffractometer using Cu Kα radiation. The X-ray diffraction intensity was recorded as a function of Bragg's 2Θ in the angular range of 5-70 deg in 2θ.

The Infra red spectra of the brine sludge and developed advanced material was taken to determine the functional group present in the sample between 500- 4000 cm^{-1}. The spectra was obtained in Infra red spectrometer of Agilent technologies.

The morphology of the MWCNT and the developed advanced material were observed in model NOVA NANOSEM-430 of COMFEI. The samples were sonicated for a period of 15 min and were placed on an aluminium sample stub before mounting for FESEM and EDXA.

The image and the elemental content of MWCNT and the developed advanced material were obtained with Model X-MAX of Oxford.

Results and Discussion

Characterization of advanced hybrid, nano-sized, brine sludge impregnated MWCNT composite material

X-ray diffraction studies

Identification of the various phases present in MWCNT, brine sludge and the developed advanced material were carried out by comparing the 2θ angle and intensities of the peaks with those of the respective likely substances listed in the JCPDS standard X-ray diffraction (XRD) data files[14]. The X-ray diffraction spectrum (XRD) of the MWCNT, brine sludge and the developed advanced material is shown in Figs. 2 (a, b & c), respectively.

In Fig. 2 (a) the characteristic peaks for MWCNTs at the positions of 2 theta at 25º and 43.2º were clearly found in MWCNTs. In the X ray diffraction pattern of brine sludge, the JCPDS data indicated the presence of peaks of $BaSO_4$, $CaCo_3$, $Mg(OH)_2$, NaCl, $CaSO_4$, SiO_2, $3Al_2O_32SiO_2$. Barium sulphate, $BaSO_4$, JCPDS 24-1035, Calcium carbonate, $CaCO_3$, JCPDS 17-763, Magnesium hydroxide, $Mg(OH)_2$, JCPDS 7-23, S-Sodium chloride, NaCl, JCPDS 5-628,Calcium sulphate,$CaSO_4$ 30-279, Q-Quartz, syn: Silicon oxide, SiO_2, JCPDS 46-1045,M- Mullite, Aluminium silicate, $3Al_2O_32SiO_2$, JCPDS 06-0258) as shown in Fig. 2 (a).

In Fig. 2 (c) of developed advanced material, the XRD patterns are composed of sharp peaks, multiple peaks indicating that the synthesized material has good crystalline structure. The characteristic diffraction peaks for the developed advanced material at 2 theta are majorly at 23.850, 24.75, 25.75, 26.75, 27.75, 28.75, 29.750, 30.0, 31, 32, 33, 34, 36, 40, 42, 43, 45 and so on as shown in figure till 70 degree theta. Further, the characteristic peaks for MWCNTs at the positions of 2 = 25.9º and 43.2º were not clearly found as the main peak of MWCNTs at around 25º

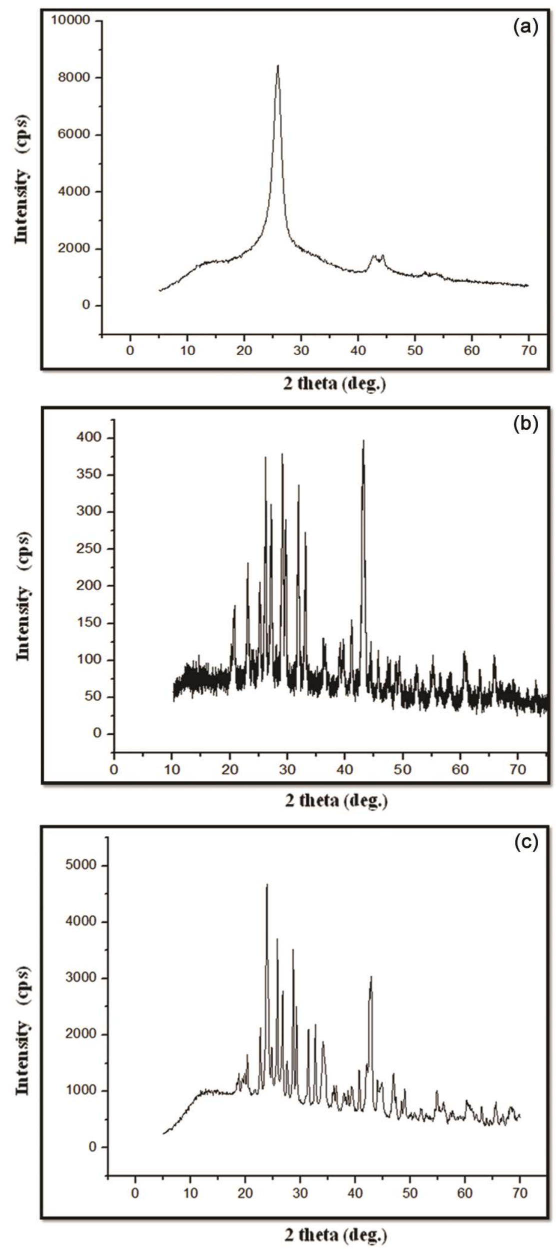

Fig. 2 – (a) XRD pattern of MWCNT, (b) XRD pattern of brine sludge and (c) XRD pattern of developed advanced material.

was overlapped with that of brine sludge peak at around 25º. Since the crystalline extent of brine sludge is stronger than that of MWCNTs the peaks of brine sludge material tends to shield those of MWCNTs in the developed advanced hybrid, nano-sized, brine sludge impregnated MWCNT composite material.

FTIR studies

The relevant vibration bands of the brine sludge and the developed advanced material in FTIR spectra were determined in the range of 500–4000 cm^{-1} and are shown in Fig. 3 (a) and 3 (b), respectively[15,16].

The FTIR spectrum of brine sludge is shown in Fig. 3 (a). The broad band observed at 3696 cm^{-1} and 3448 cm^{-1}, are ascribed to stretching and deformation of adsorbed water molecule, $Mg(OH)_2$, SiO_2, $CaSO_4$. Band at 563 cm^{-1} is assign to hematite. The band at 712 cm^{-1} is assign to $CaCO_3$. Small peak observed at 1796 cm^{-1} and 1635 cm^{-1} are due to H-O-H, SiO_2 and $CaSO_4$ stretching vibrations. The sharp peaks obtained at 621 cm^{-1} are due to the out of plane bending vibration of sulphates. Sulphates of calcium, magnesium, barium are assigned to the broad peak centred at about 1169 cm^{-1} and 1092 cm^{-1} .

The IR spectra of the developed material shown in Fig. 3 (b) has nearly the peaks at different places, thereby confirming the formation of new peaks in the developed advanced hybrid, nano-sized, brine sludge impregnated MWCNT composite material.

Morphological analysis

FESEM and EDXA analysis

Several particles were investigated to determine the size, shape and chemical composition of MWCNTS and developed advanced material using FESEM and EDXA respectively. FESEM Images are shown in Figs. 4a and 4b respectively. Fig. 4 (a) confirms that the MWCNTS have long convoluted CNTs.

Figure 4 (b) at higher magnification exhibits that various brine sludge nanoparticles are firmly attached to the MWCNTs surface as indicated by solid red line. The nanoparticles were spread densely and harmoniously on the surface of MWCNTs.

The EDXA spectra of MWCNT and developed hybrid, nano-sized, brine sludge impregnated MWCNT composite material at a particular point are shown in Figs. 5a and 5b respectively. Fig. 5a revealed that the predominance of carbon along with oxygen having composition (weight %) 94.36% and 5.64% in MWCNT, respectively. Figure 5 (b) revealed the predominance of main elements like carbon, oxygen; sulphur and barium with their composition (weight %) 32.99%, 28.06%, 6.68 %, 32.27% and 4.35% respectively in the developed advanced material.

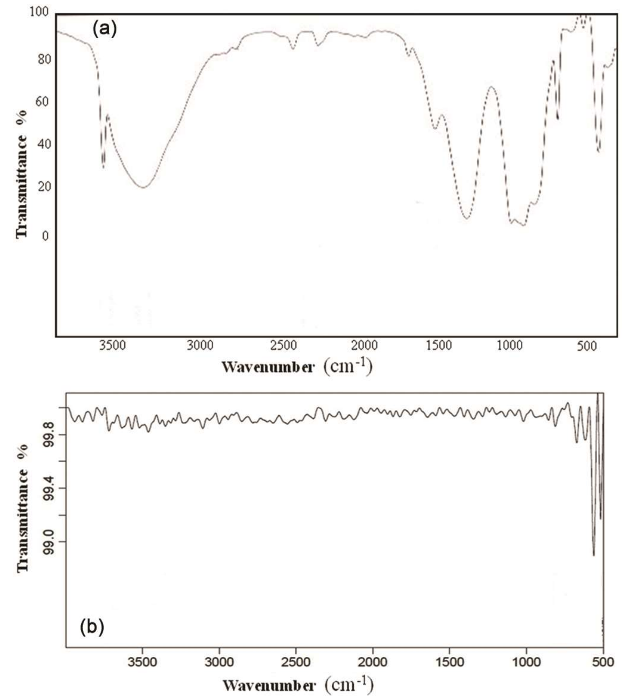

Fig. 3 – (a) FTIR spectrum of spectrum of brine sludge and (b) FTIR spectrum of spectrum of the developed advanced material.

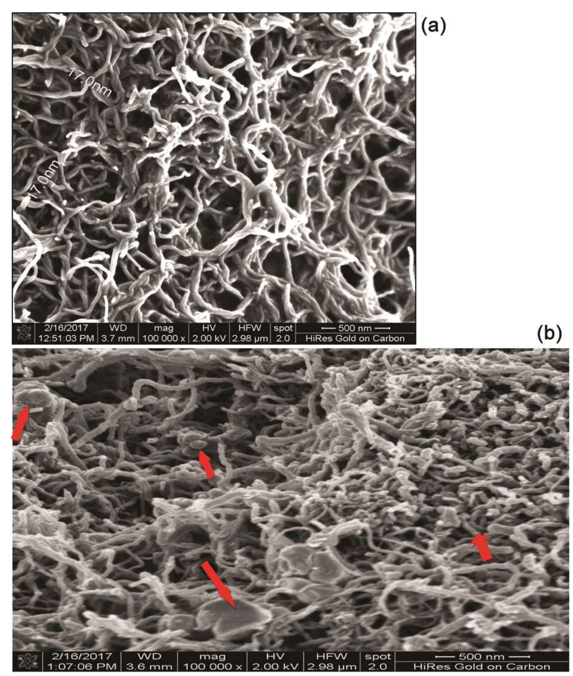

Fig. 4 – (a) FESEM image of MWCNTs and (b) FESEM image of developed advanced material.

In the conventionally reported process, the initial step is generally the functionalization of MWCNTs

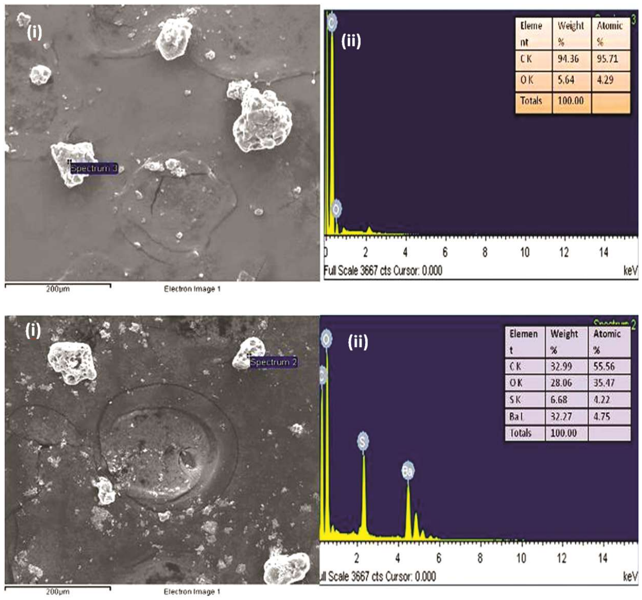

Fig. 5 – (a) EDXA image of (i) MWCNT (ii) EDXA outcomes and elemental compositions (weight% and atomic%) and (b) EDXA image of (i) synthesized advanced material (ii) EDXA outcomes and Elemental compositions (weight% and atomic%).

using various reagents like sulphuric acid, nitric acid etc to create the active functional group on the walls of MWCNTs, wherein in the reported process, it is expected that the in-situ functionalization of the MWCNTs have taken place due to the presence of formation of sulphuric acid during reaction mechanism as the brine sludge inherently consist of good amount of barium sulphate along with other constituents in it. Thus, the reported work involves the reduction in the process steps thereby saving the time; energy as well as cost of pure chemicals which are otherwise required in the conventional process. The process involves the bulk utilization of an industrial – by products and therefore making the environment cleaner and greener. As reported in the literature by various researchers that MWCNT and brine sludge individually[3-5] have capability of shielding the radiations and thus to confirm the same ,the developed advanced hybrid, nano-sized, brine sludge impregnated MWCNT composite material using both the MWCNT and brine sludge as raw material has been tested for its x-ray attenuation property at 40 kVp.The developed advanced material was compacted in a disk of dimension 15 mm diameter and 10 mm thickness and studied for its qualitative x – attenuation properties. In its initial qualitative testing, we got very encouraging and positive results. Further, the detailed studies regarding the radiation shielding property of the developed advanced hybrid, nano-sized, brine sludge impregnated MWCNT composite material is in progress and will be discussed in detail in near future. The reported present novel research work will open up the new avenues and will receive increasing attention in the near future for the development of advanced material useful for radiation shielding property.

Conclusions

Based on the results of the present study carried out for the development of advanced hybrid, nano-sized, brine sludge impregnated MWCNT composite material useful for broad application spectrum the following conclusions can be drawn:

(i) Introduction of a new era of making simultaneous in-situ synthesis of advanced hybrid, nano-sized, brine sludge impregnated MWCNT composite material useful for broad application spectrum.

(ii) The brine sludge have been utilized in totality for making highly value added material using microwave synthesizer successfully.

(iii) The FESEM studies revealed that the brine sludge nanoparticles are firmly, densely and harmoniously impregnated to the MWCNTS surface.

(iv) The XRD pattern in developed advanced material confirms the formation of new hybrid, nano-sized, brine sludge impregnated MWCNT composite material by a novel process.

(v) The process successfully involves utilization and saving the cost of costly chemicals inherently present in brine sludge otherwise required for making hybrid, nano-sized, material for broad application spectrum.

(vi) The reported process enables synergistic and simultaneous effect of various raw materials in achieving materials in advanced hybrid, homogenized, nanosphere rather than in microspheres. This will lead to the transformation era of making advanced materials from conventional microsphere to advanced and multi-functional nanosphere.

Acknowledgement

Authors are thankful to Department of Science & Technology (DST), Govt. of India for giving financial assistance to this novel work, Project sanction no

SR/WOS-A/CS-20/2016, under the Women scientist Scheme. Authors are also grateful to Director CSIR-AMPRI Bhopal for providing necessary institutional facilities and encouragement. Thanks are also due to Mr. Deepak, Mr. Anoop Khare and Mr. Mohd. Shafique, CSIR- AMPRI for analysis of sample on FESEM and providing XRD data of sample. Cali labs, Bhopal for Infra red studies and Carrier Institute of Medical Sciences, Bhopal for initial qualitative testing of the developed sample are also acknowledged.

References

1 Loiseau A, Launois-Bernede P, Petit P, Roche S & Salvetat J P, *Understanding Carbon Nanotubes From Basics to Applications*, (Springer), 2006.

2 Kim H M, Kim K, Lee C Y, Joo J, Cho S J & Yoon H S, *Appl Phys Lett*, 84 (2004) 589.

3 Verma S, Amritphale S S & Das S, *Mater Sci Appl*, 7 (2016) 192. http://dx.doi.org/10.4236/msa.2016.74019

4 Chiang W H, Huang S J & Jang G W, *Radiation shielding composite material including radiation absorbing material and method for preparing the same* WO 2014121717 A1, 2014.

5 Fujimori T, Tsuruoka S, Fugetsu B, Maruyama S, Tanioka A, Terrones M, Dresselhaus M S, Endo M & Kaneko K, *Mater Exp*, doi:10.1166/mex. (2011) 1043.

6 Karimi L, Zohoori S & Amini A, *New Carbon Mater*, 29 (2014) 380.

7 Chlor alkali process - Wikipedia, the free encyclopedia https://en.wikipedia.org/wiki/Chloralkali_process Accessed on 9/17/2014.

8 CPCB Report on ‘Review of Environmental standards of Caustic Soda industry (Membrane cell) and preparation of COINDS on Caustic Soda’, 9 (2013).

9 Garg M & Pundir A, *J Waste Manag*, Article ID 389316, (2014) 1.

10 Kappe C O, Dallinger D & Murphree S S, *Practical Microwave Synthesis for Organic Chemists - Strategies, Instruments, and Protocols,* ISBN-10-3-527-32097-0, (Wiley-VCH, Weinheim) 2009.

11 Sharma A K & Mishra A K, *Adv Mater Lett*, 1 (2010) 59.

12 Sharma K, Singh R, Fahmi N & Singh R V, *Spectrochim Acta*, 75 (2010) 422.

13 IS, “Methods of chemical analysis,” IS 4032-2005, Bureau of Indian Standards, New Delhi, India, 2005.

14 XRD Powder Diffraction File, Alphabetical Index Inorganic Phases, (*JCPDS International Centre for Diffraction Data 1601, Park Lane Swarthmore, Pennsylvania 19081 USA*), 1984.

15 Socrates G, Infrared and Raman Characteristic Group Frequencies: Table and Charts, 3rd Edn, John Wiley & Sons Inc, New York, 287 (2004).

16 Nakamoto K, *Infra Red and Raman Spectra of Inorganic and Coordination Compounds*, 6th Edn, John-Wiley & Sons, Hoboken, (2009) 766.