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Radiation-Induced Dehydration of $Na_2SO_4.10H_2O$ as Energy Storage Material

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ABSTRACT

This study focus on the effects induced by gamma-(γ) ray and electron beam (EB) irradiation on the thermal behavior, structure, and morphology of $Na_2SO_4.10H_2O$.Thermal dehydration of un-irradiated, gamma (γ), and electron beam (EB)-irradiated samples of $Na_2SO_4.10H_2O$(Glauber's salt) was studied in the nitrogen atmosphere in the temperature range of 22 – 300℃. The TG curve displays a total mass loss percentage of ≅ 55% corresponding to the removal of ten crystalline water molecules. Gamma and electron beam EB irradiation had different effects on the thermal behavior of $Na_2SO_4.10H_2O$ resulting in complete and partial dehydration of water molecules during crystallization, respectively. FT-IR spectra revealed that the characteristic vibration bands of hydrogen bonding of water molecules and SO_4^{-2} anion of $Na_2SO_4.10H_2O$ irradiated by EB were shifted to lower wavenumbers compared to the corresponding bands of pristine and gamma irradiated samples. Electron beam-induced changes in the crystal structure of $Na_2SO_4.10H_2O$ leads to the formation of a new phase of orthorhombic system with space group SG (pmmm) a = 25.0426, b = 4.645, and c = 3.878Å.

INTRODUCTION

Our modern society is becoming increasingly reliant on renewable energy sources, which have a lesser environmental impact than traditional energy sources. The disadvantage of renewable systems is the variability of energy generation and the gap in time between the demand and supply of energy [1]. Latent energy storage is used in the phase change storage process. It has an isothermal or nearly isothermal phase transition, a wide range phase transition temperature, a small volume, and a high energy density. Phase change materials include organic (fatty acids, paraffin, etc.) and inorganic compounds (molten salts, crystalline hydrated salt, etc.) as well as composite materials.

The melting points of salt hydrates from solid to liquid phase are typically well defined and discrete [2], with a moderate phase change temperature of 32.4ºC, a phase change latent heat of energy of about 254 J/g, and non-hazardous nature. Sodium sulfate decahydrate also known as Glauber's salt, $Na_2SO_4.10H_2O$ is an inorganic hydrate salt that is suitable for energy storage [3] or dosage administration [4]

The system exhibits drawbacks such as superconductivity [5] and phase segregation [6], but these can be mitigated by adding nucleating or thickening [7]. Through thermochemical reaction, the system stores heat during dehydration of the salt, thenardite, according to the reaction [8].

$$Na_2SO_4.10H_2O_{(s)} \leftrightarrows Na_2SO_{4(s)} + 10H_2O_{(g)} \quad [1]$$

The phase diagram of sodium sulfate includes two stable phases, mirabilite ($Na_2SO_4.10H_2O$), anhydrous thenardite (V), meta stable phase, Na_2SO_4(III) and $Na_2SO_4.7H_2O$ [9].

We report here the effects induced by gamma-(γ) ray and electron beam (EB) on the thermal behavior, structure, and morphology of $Na_2SO_4.10H_2O$. These characteristics were investigated by different techniques like TG, DTA, DSC, FT-IR, XRD, and SEM.

Experimental: -

Materials

$Na_2SO_4.10H_2O$ (99%) was obtained commercially from alpha Aesor and used without further purification. Table 1 lists the physical and chemical characteristics of the salt.

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Table (1): The physical and chemical characteristics of $Na_2SO_4.10H_2O$ salt

Material	Formula	Molecular weight	Melting point	Solubility	Density (Solid)	Heat of fusion
Sodium sulfate decahydrate (Glauber's salt)	$Na_2SO_4.10H_2O$	322.19 g/mole	32.4 ℃	Soluble in H_2O and glycerin. Insoluble in C_2H_5OH and CH_3OH.	1.49 (10^3 Kg/m^3)	248 (J/g)

INSTRUMENTATIONS

Thermal dehydration of $Na_2SO_4.10H_2O$ samples was studied by thermogravimetric techniques using LINSEIS STA PT 1000 (TG / DTA / DSC) in nitrogen atmosphere. The average mass of the sample was approximately 4mg and the flow rate was maintained at 40mL/min. Under the dynamic (non-isothermal) conditions, four linear heating rates (2.5, 5, 7.5, and 10℃/min) were applied in the temperature range of (25-600℃). X-ray powder diffraction patterns were performed on Philips model PIV 1710 with Cu K_α radiation (λ=1.54Å) and operating at 30mÅ. The scan mode was the continuous speed of 0.06deg/min. The diffraction patterns were analyzed using Match software program. FT-IR analysis was performed in the transmission mode. For the hydrate salt, the use of KBr was unsuitable because a large amount of water escaped during the vacuum process, therefore the Nujol technique was employed in this investigation.

Irradiation Facilities

Gamma-ray and Electron-beam irradiations (100 KGy total absorbed doses for each sample) were performed at the National Centre for Radiation Research and Technology (NCRRT), Egyptian Atomic Energy Authority (EAEA), Cairo, Egypt. For γ-irradiation, the sample of $Na_2SO_4.10H_2O$ was subjected to gamma cell type 4000Å, India source, at ambient air, humidity, and room temperature. The dose rate was 1.3kGy/h. For Electron-beam irradiation, the sample was subjected to an electron accelerator (3Mev and 25 kW). The conveyor speed was adjusted at 20mm/min. The dose rate was estimated by the FWT-60-00 dosimeter that was calibrated using the Ceric/Cerous dosimeter.

RESULTS AND DISCUSSION

Thermal analysis

Using thermal analysis techniques, the structural changes of un-irradiated, gamma–irradiated, and EB -irradiated samples of $Na_2SO_4.10H_2O$ were subsequently examined. Figure 1 shows typical TG/DTG profiles obtained in a nitrogen atmosphere in the temperature range of 22-300°C at a heating rate of 7.5 C/min. The TG curve displays a total mass loss percentage of ≅ 55% corresponding to the removal of ten crystalline water molecules (55.9% theoretical value). The DTG curve exhibits inflection points and reveals six hidden reactions, indicating that the dehydration of $Na_2SO_4.10H_2O$ is a complex process. The DTG data were supported by the asymmetric profiles of the DTA and DSC curves shown in Figure 2. Detailed studies on the kinetics of the dehydration process of un-irradiated $Na_2SO_4.10H_2O$ using solid-state reaction kinetics are in progress in our laboratory and will be published in a separate publication.

Figure 3 displays the TG curves of γ-irradiated and EB-irradiated samples of $Na_2SO_4.10H_2O$ (10^2 kGy total absorbed dose for each study). Complete dehydration of the sample was achieved upon γ-irradiation. The TG curve of EB-irradiated sample showed partial (≅25%) dehydration. Complete dehydration of γ-irradiated sample led to the formation of the pure phase of anhydrous sodium sulfate (thenardite structure). Partial dehydration by EB-irradiation offered a new phase of structure, as will be discussed in the X-ray study section.

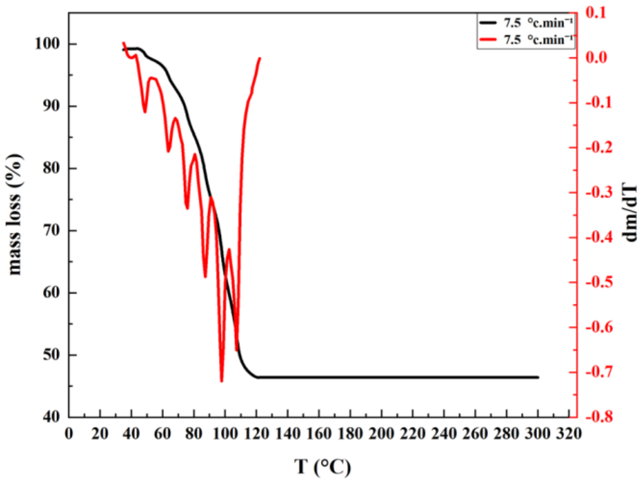

Fig. (1): TG/DTG curves of un-irradiated $Na_2SO_4.10H_2O$ (Glauber's salt) in a nitrogen atmosphere at a heating rate of 7.5°C/min

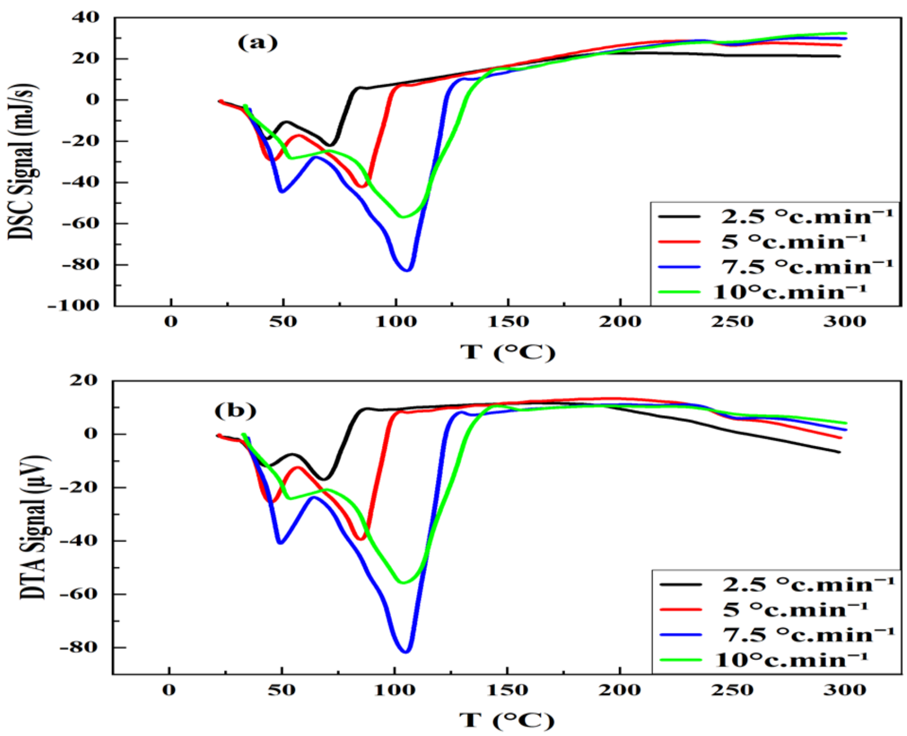

Fig. (2): DSC (a) and DTA (b) curves of the thermal dehydration of un-irradiated $Na_2SO_4.10H_2O$ (Glauber's salt) at different heating rates of 2.5, 5, 7.5, and 10°C/min

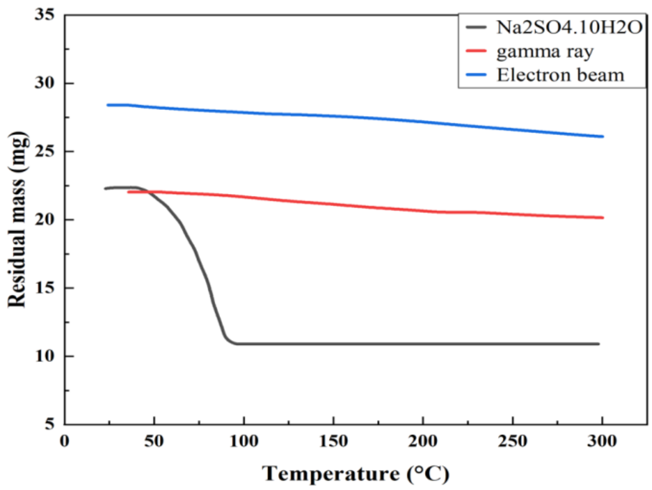

Fig. (3): TG curves of un-irradiated, γ-irradiated, and EB-irradiated salts in nitrogen atmosphere at the heating rate of 5 °C/min

XRD analysis

Sodium sulfate is polymorphic and undergoes the following transformation [10]:

$$Na_2SO_4(V) thenadrite \xleftrightarrow[160-180°C]{} Na_2SO_4(IV) \xleftrightarrow[185°C]{} Na_2SO_4(III) \xleftrightarrow[241°C]{} Na_2SO_4(I) \quad (2)$$

Figure 4 shows XRD of un-irradiated, γ- irradiated, and EB-irradiated (c) samples of $Na_2SO_4.10H_2O$. Crystal structure of un-irradiated pristine sample was indexed to monoclinic system SG ($P2_1/c$) (JCPDF: 96 – 210 – 5959) [11, 12] as reported in the literature. Due to the dehydration process occurring by γ- irradiation, the anhydrous salt was indexed to the pure phase of thenadrite structure (anhydrous $Na_2SO_4(V)$) with orthorhombic space group SG (fddd), (JCPDF: 96 – 900 – 4093) [13]. Electron beam-induced changes in the crystal structure of $Na_2SO_4.10H_2O$ leads to the formation of a new phase of orthorhombic system with space group SG (pmmm) a = 25.0426, b = 4.645, and c = 3.878Å. Figure 5 shows Retiveld refinement of XRD pattern of EB-irradiated sample performed using Fullprof software program.

FTIR study

Figure 6 shows FT-IR spectra of un-irradiated, γ-irradiated, and EB-irradiated samples of $Na_2SO_4.10H_2O$ compounds. One noticeable band is obtained at 3510 cm^{-1}. It can be assigned to the O–H stretching mode of water molecule. The frequency of this band is significantly greater than the values for the crystallization of water in the typical inorganic salts [14]. It must be due to the free water molecules where, hydrogen bonding generally lowers the stretching frequency. The band observed at ≅ 2930 cm^{-1} is probably attributed to hydrogen bonding and was detected as very weak band in the FT-IR spectrum of EB-irradiated sample of

$Na_2SO_4.10H_2O$ [15]. The position of the band at ≅ 1650 cm^{-1} assigned to $\nu_2(H_2O)$ bending mode of vibration. The characteristic bands of water molecule were shifted to lower frequency upon EB-irradiated sample. The three bands at $\nu = 1113$, 1130, and $1145 cm^{-1}$ can be assigned to ν_3 (SO_4^{-2}) and the ν_4 (SO_4^{-2}) band is split into two peaks at 616 and 634 cm^{-1} [3, 16]. These bands were also shifted to lower frequencies by EB-irradiation and showed degree of symmetry in case of EB-irradiated compared with un-irradiated and γ- irradiated samples.

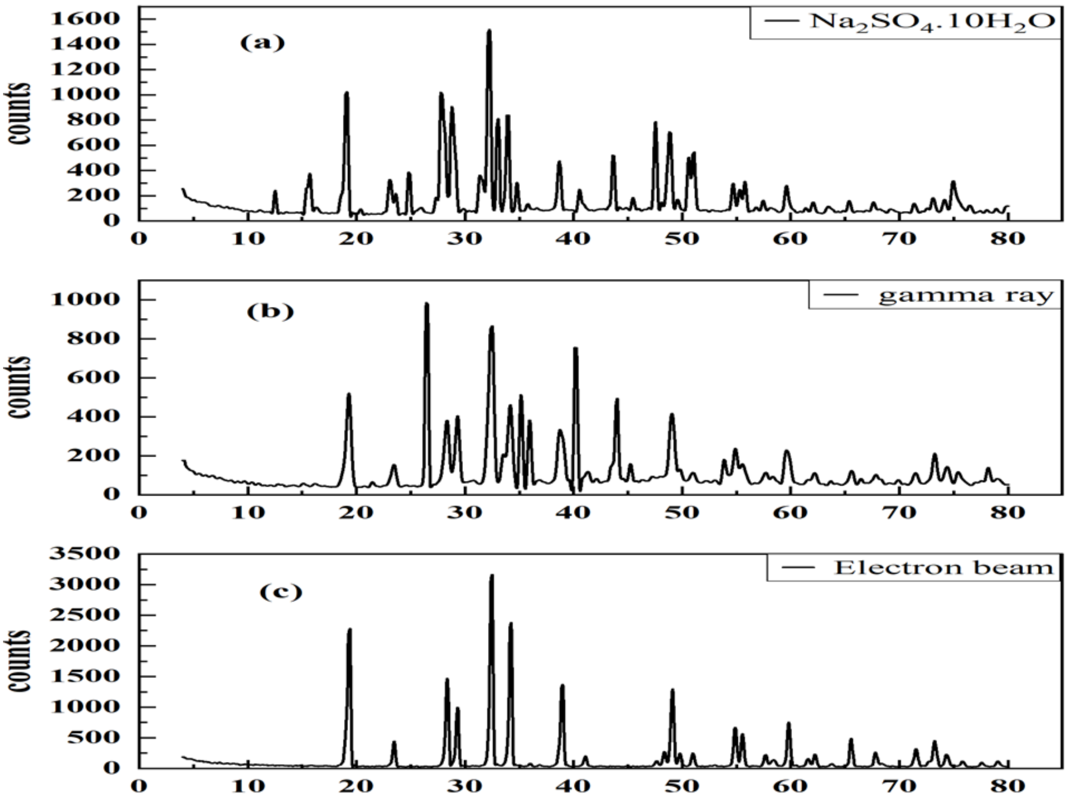

Fig. (4): Powder X-ray diffraction of un-irradiated (a), γ-irradiated (b), EB-irradiated (c) of $Na_2SO_4.10H_2O$ (Glauber's salt)

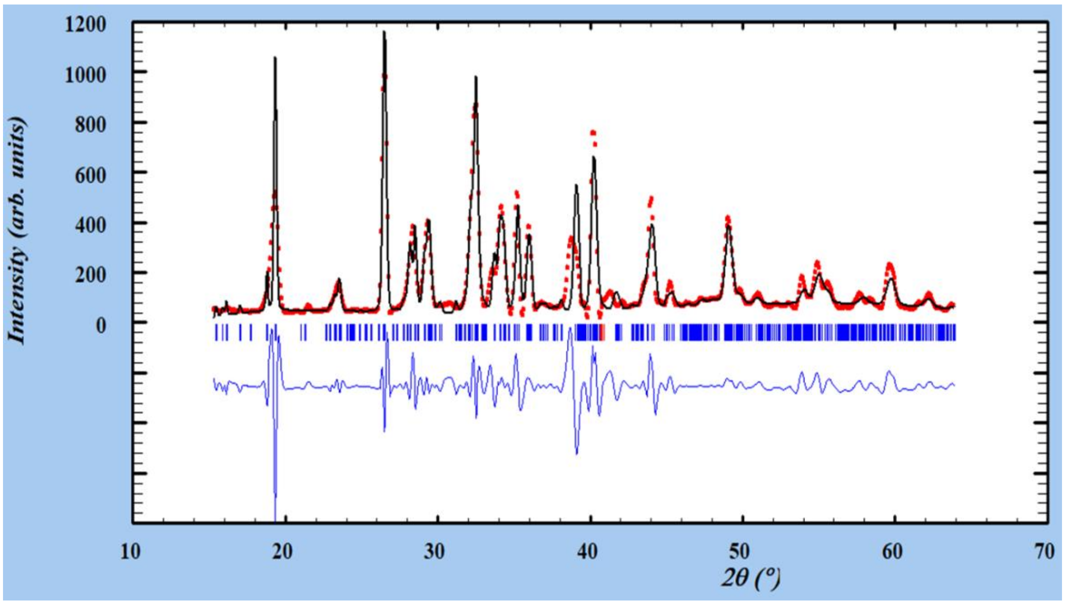

Fig. (5): Retiveld refinement of XRD pattern of anhydrous Na_2SO_4 SG (pmmm)

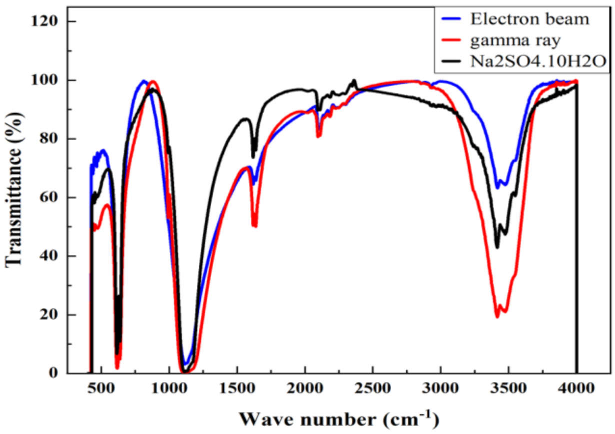

Fig. (6): FT-IR spectra of un-irradiated, γ-irradiated, and EB-irradiated of $Na_2SO_4.10H_2O$ (Glauber's salt)

Morphology study

Figures 7-7.2 display the changes in the morphology of $Na_2SO_4.10H_2O$ before and after irradiation scanned by SEM technique. Un-irradiated sample shows aggregation of big crystallites. The γ-irradiated sample shows different orientations of well-defined shapes of Na_2SO_4 (VI) phase crystals (Thenardite). The morphology of the EB-irradiated sample shows a random distribution of aggregated small crystallites of the Na_2SO_4 (VI) phase.

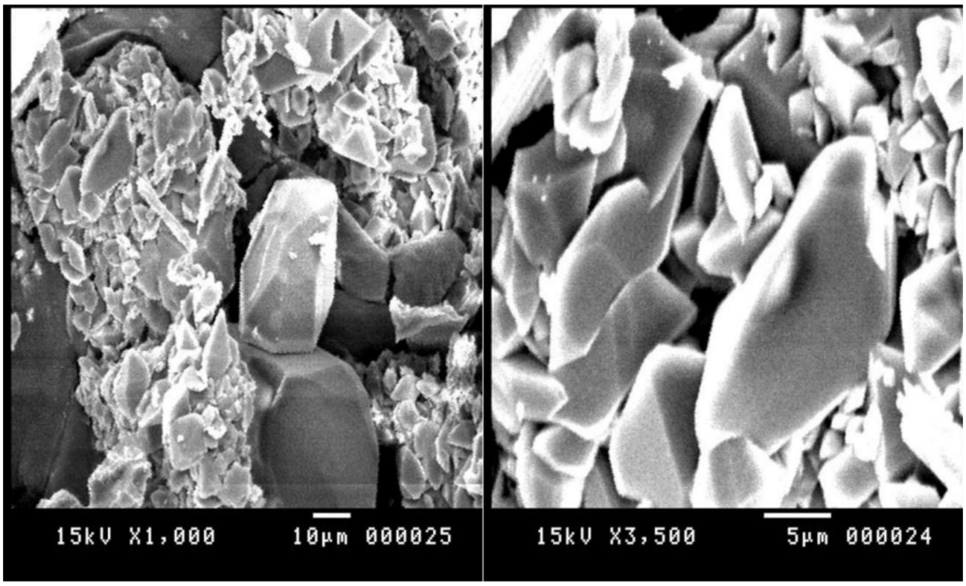

Fig. (7): SEM images of un-irradiated $Na_2SO_4.10H_2O$ (Glauber's salt)

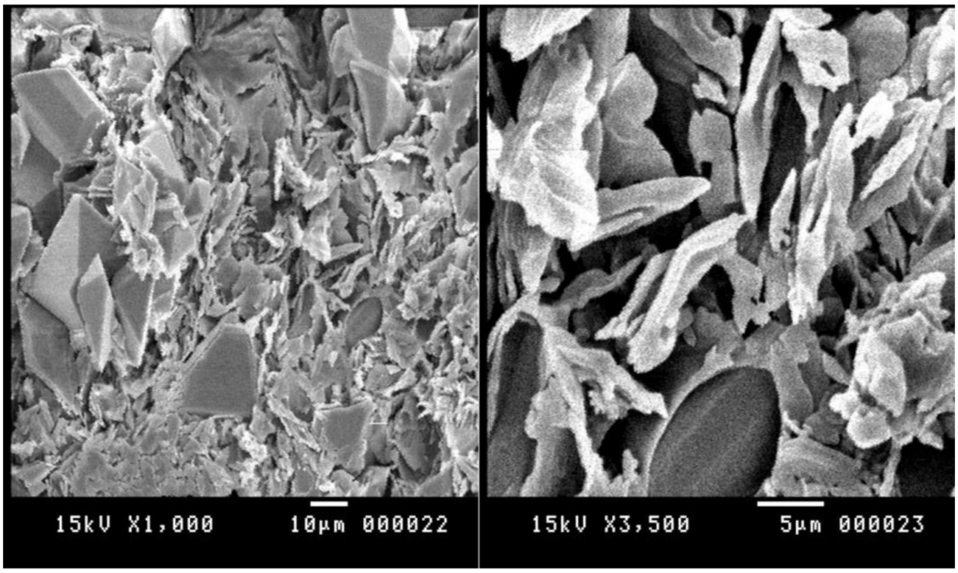

Fig. (7.1): SEM images of γ-irradiated samples of $Na_2SO_4.10H_2O$ (Glauber's salt)

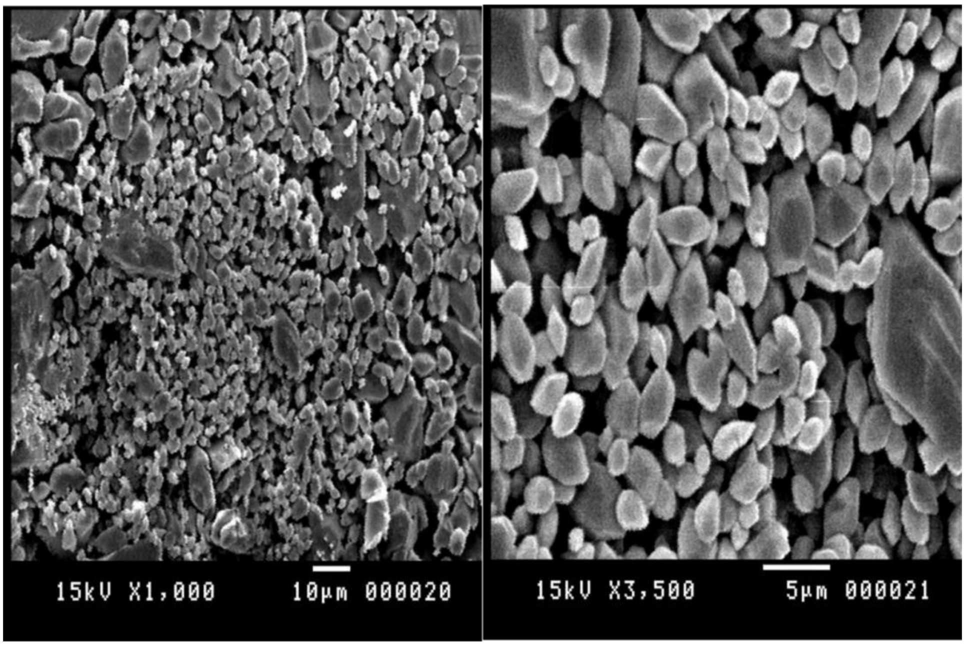

Fig. (7.2): SEM images of EB-irradiated samples of $Na_2SO_4.10H_2O$ (Glauber's salt)

CONCLUSIONS

Complete and partial dehydration of crystalline water was achieved by subjecting pristine$Na_2SO_4.10H_2O$ to gamma and electron beam sources of radiation, respectively. TG study showed that the dehydration of $Na_2SO_4.10H_2O$ was proceed in six dehydration steps with the removal of ten water molecules. γ-irradiated sample with 10^2 kGy total γ-ray led to the formation of pure phase of Thenardite structure (SG *Fddd*). EB-irradiation (10^2 kGy) produces another phase of orthorhombic structure of Na_2SO_4 with SG (Pmmm). Different scanning electron microscopic images were obtained for the different crystal structure phases of the material.

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