Bismuth Pyromangenate: Hydrothermal and Solid State Synthesis, Characterization and Optical Properties

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ABSTRACT

$Bi_2Mn_2O_7$ nano-powders were synthesized via hydrothermal method involving astoichiometric1:1Bi to Mn molar ratio at 180°C for 48 h in a 1M NaOHaqueous solution,and solid state method,using$Bi(NO_3)_3.5H_2O$ andMnO_2as raw materials. The synthesized materials were characterized by powder X-ray diffraction (PXRD) technique. Also, the rietveld analysis was performedin FullProf in profile matching mode.It was found that $Bi_2Mn_2O_7$ crystallizes in a cubic crystal structure with space group$Fd\bar{3}m$ .The size and morphologies of the synthesized materials were studied by transmission electron microscopy (TEM)and field emission scanning electron microscopy (FESEM), respectively. Also, BET-BJH analysis was carried outfor determination of pore size, pore volume, average particle size, pore width and surface area of the obtained materials. Also, photoluminescence spectra of the obtained materials were studied.The FESEM images showed that the synthesized $Bi_2Mn_2O_7$hasrod like structurein hydrothermal method and a mixture ofrod and particle structuresin solid state method.

1. Introduction

Oxides and fluorites with the general formula of $A_2B_2O_7$ (where A is a medium-large cation and B is an octahedrally coordinated, high-charge cation) havebeen widely studied for their great technological potential owing to their ferroelectric and/or magnetic, ionic conductors, catalysts, phosphors, radiation resistant properties [1-5]. Pyrochlore materials have attracted great interest due to their ability to form substituted and defective structures, permitting interesting physical properties [6]. $Bi_2Mn_2O_7$hasalready been prepared by a conventional solid state reactionmethod [7] and has been reported to have catalytic ability for oxygen reduction [8]. The unit cell of this structure is usually face centered cubic with space group $Fd\bar{3}m$ with eight molecules per unit cell (Z = 8) [9].In the present study, a hydrothermal route was employedto synthesize nanostructured $Bi_2Mn_2O_7$ powders using$Bi(NO_3)_3.5H_2O$, MnO_2 and$NaOH$ for the first time.Asolid state synthesis in a system of $Bi(NO_3)_3.5H_2O$, MnO_2 was also achieved. To the best of our knowledge, there is no report on the synthesis of nanostructured$Bi_2Mn_2O_7$by these methods. BET-BJH analysesand photoluminescence spectra of the obtained materials were also studied.

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2. Experimental

All chemicals including $Bi(NO_3)_3.5H_2O$, MnO_2 and NaOH were of analytical gradeand were obtained from commercial sources (Merck Company) and used without further purifications. The materialsS_1 and S_2were synthesized via hydrothermal and solid state methods, respectively. Phase identifications were performed on a powder X-ray diffractometer D5000 (Siemens AG, Germany) using Cu-Kα radiation. The morphology of the obtained materials was examined with byfield emission scanning electron microscopy(Hitachi FE-SEM S-4160). Photoluminescence spectra were recorded on a Perkin Elmer LF-5 spectrometer (PerkinElmer Inc., Waltham, USA). The surface area and pore volume and average nanoparticles size were calculated using the Brunauer-Emmett-Teller (BET) equation. Pore size distributions, pore volume and pore surface area were calculated by the Barrett-Joyner-Halenda (BJH) method. BET surface areas were acquired on a Beckman Coulter SA3100 surface area analyzer. The rietveld analysis was carried outin FullProf with a Chi^2 of 6.7 in profile matching mode.

2. 1. Hydrothermal and solid state synthesis of $Bi_2Mn_2O_7$

In typical synthetic experiments in both methods, 1.00 g (2.06 mmol) of $Bi(NO_3)_3.5H_2O$ (Mw = 485.07 $gmol^{-1}$) and 0.18 g (2.06 mmol) of MnO_2(Mw = 86.94 $gmol^{-1}$) were used. In hydrothermal method, the raw materials were added to 70 mL of hot aqueous solutions of 1M NaOHunder magnetic stirring at 80°C. The resultant solution was stirred for further 15 min and transferred to a 100-mL Teflon lined stainless steel autoclave. The autoclave was sealed and heated at 180°C for 48 h. When the reaction was completed, it was immediatelycooled down to room temperature by water. The prepared powder was washed with distilled water and dried at 110°C for 20 min under normal atmospheric conditions anda cream - white powder was collected.In the solid state synthesis, the raw materials were added to a 25 mL crucible and treated at 550°C for 8h. Then the product was normallycooled downto room temperaturein the oven. The obtained powder was collected for further analyses.

3. Result and discussion

3. 1. Powder X-ray diffraction analysis

The X-ray diffraction patterns of the $Bi_2Mn_2O_7$ samplesare reported in fig. 1 (a and b) as data points, together with the result of the profile matching analysis (full lines). Fig.1a shows the X-ray diffraction (XRD) patternof the $Bi_2Mn_2O_7$ sample obtained in the θ-2θ geometry with Cu-Kα radiation. Structural analysis was performedthroughthe FullProfprogram by employing profile matching with constant scale factor. The pattern in fig. 1 (a, b)is typical of a cubic structure$Bi_2Mn_2O_7$, reported with space group of$Fd\bar{3}m$ .The red bars are the observed intensities which were obtained from the diffraction data. The black ones are the calculated data, and theblue one is the difference: Yobs-Ycalc. The bars below indicate the Bragg reflections. Since we have two lines of bars, it means that we have two phases. The upper one is $Bi_2Mn_2O_7$ and the lower one shows the Bi_2O_3 reflections. The results demonstratethat the pattern has a main $Bi_2Mn_2O_7$ crystal structure with space groupof$Fd\bar{3}m$. The Bi_2O_3 structure is detected with a space group of $P2_1/c$. Bi_2O_3. Lattice parameters are found as a=5.842770Å, b=8.147644Å, and c=7.498813Å with $\alpha = \gamma = 90°, \beta = 113.024$.

Fig. 1b shows that bychanging the synthesis method to solid state, there is a mixture of three phases including $Bi_2Mn_2O_7$as a main phase, Bi_2O_3 and Mn_2O_3 with space group of Ia-3. The results show that the pattern has a main $Bi_2Mn_2O_7$ crystal structure with space groupof $Fd\bar{3}m$. The Bi_2O_3 structure is detected with a space group of $P2_1/c$. Bi_2O_3 lattice parameters are found as a=5.850432 Å, b=8.290177 Å, and c=7.555346 Å with $\alpha = \gamma = 90°, \beta = 113.158°$. The Mn_2O_3 structure is detected with a space group of $Ia\bar{3}$. The Mn_2O_3 lattice parameters are found as a=b=c=10.672101 Å.

The measured powder XRD data are in agreement with those of reported XRDfor $Bi_2Mn_2O_7$ nanomaterials [7, 8]. In view of

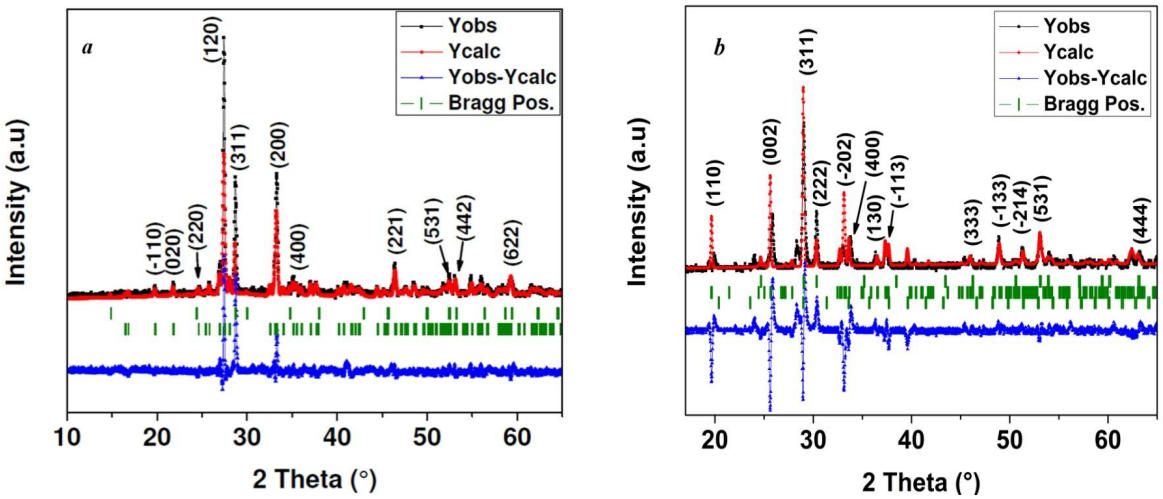

Fig. 1. PXRD patterns of the a) hydrothermally and b) solid state synthesized $Bi_2Mn_2O_7$ nanomaterials

theoretical calculations, pyrochlore oxides are found to be stable when the radius ratio (r_A/r_B) of the cations lies in the range of 1.46–1.78. Oxides of general formula $A_2B_2O_7$ crystallize in ordered pyrochlore (cubic, $Fd\bar{3}m$) and defect fluorite (cubic, Fm3m) structures when the radius ratio (r_A/r_B) is in the upper or lower limits of the above range. In the present investigation, the radius ratio (r_A/r_B) for$Bi_2Mn_2O_7$ is higher than 1.78 and the obtained stable phase is isostructural with $Bi_2Mn_2O_7$ (space group $Fd\bar{3}m$) (radius of Bi^{3+} cations is about 1.17Å and Mn^{4+} 0.53 Å) [10-13], whichis in agreement withthe rietveld analysis data. Compared to the nanomaterials of the hydrothermally synthesized $Bi_2Mn_2O_7$ (S_1), the diffraction lines in the powder XRD patterns of the solid state synthesized $Bi_2Mn_2O_7$ (S_2) nanomaterials has shifted to lower 2θ values and therefore to higher d values. So,byusing the peak with miller indices 311, a blue diffraction line shift of $\Delta 2\theta = 28.58°$ (S_2) – $28.64°$ (S_1) = $-0.06°$ ($\Delta d = 3.121$ Å (S_2) - 3.114 Å (S_1) = 0.07 Å) are calculated via Bragg's equation. So there is an expansion in the unit cell.

3. 2. Morphology of the materials

Fig. 2 shows the typical FESEM images of the hydrothermally synthesized $Bi_2Mn_2O_7$ nanomaterials. From the typical FESEM images of S_1, at low magnification in fig. 2 (a and b), we can see that the morphology of the obtained materials is in rod-like form. At higher magnification in fig. 2 (c and d), it is clear that the materials are composed of rods with different lengths and thicknesses.

Fig. 3 shows the typical FESEM images of the solid state synthesized $Bi_2Mn_2O_7$ nanomaterials. From the typical FESEM images of S_2, at low magnification in fig. 3 (a and b) we can see that the morphology of the obtained materials isa mixture of rod and spherical particle forms. At higher magnification in fig. 3 (c and d), it is clear that the materials are composed of rods with different lengths and thicknesses.

Fig.4 shows the TEM images of the obtained materials via hydrothermal method. It shows that the structure of the materials is rod like that is in agreement with those of fig.2. Fig. 4 (b and c) shows that the thicknesses of the rod structures are between60-150 nm (fig.4b) and 84 nm (fig.4c). With high magnification in fig.4 f, the thickness of the material was observedto be about 73 nm.

Fig. 5 shows the TEM images of the obtained materials via hydrothermal method. It shows that the structure of the material is a mixture of rod and particle like, which is in agreement with those of in fig. 3. Fig. 5 (a-c) shows that the thickness of the rod structure is about 240 nm and fig. 5 (d-f) shows that the particle size is about 41 nm.

3. 3. BET and BJH texture analysis

The synthesized powders were characterized in

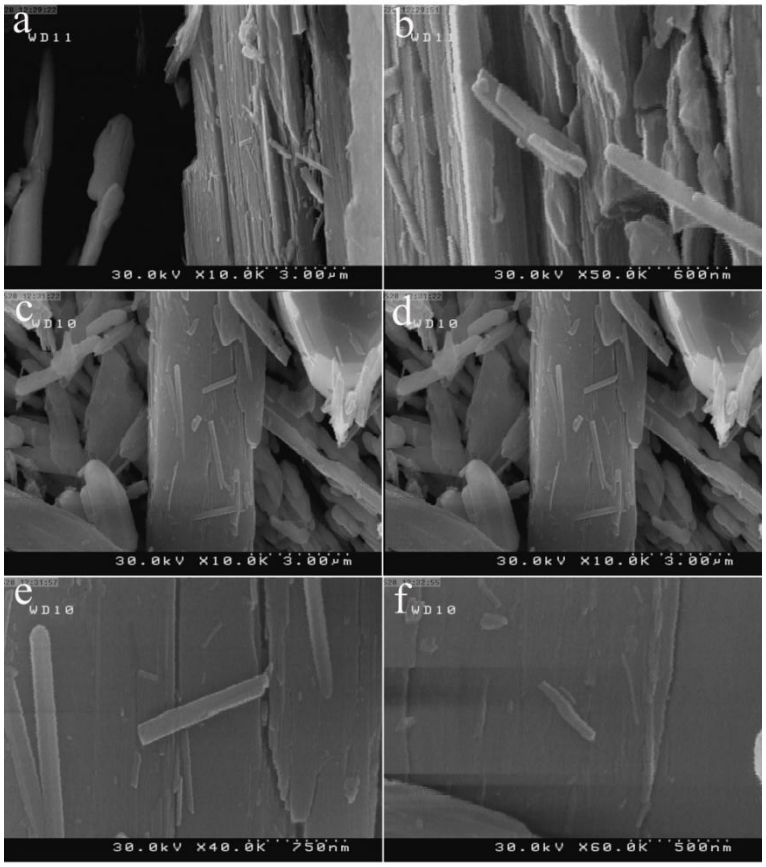

Fig. 2. SEM images of the hydrothermally synthesized $Bi_2Mn_2O_7$ nanomaterialsin1M NaOH solution

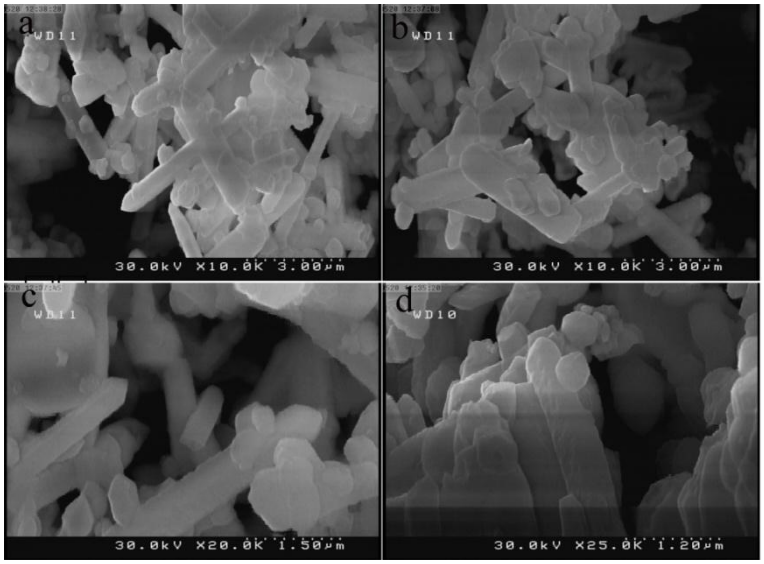

Fig. 3. SEM images of the solid state synthesized $Bi_2Mn_2O_7$ nanomaterials at 550 °C for 8h

terms oftheir surface area, average pore size and average pore volume. Prior to the N_2-physical adsorption measurement, the samples were degassed at 150 °C for 120 min in the nitrogen atmosphere. So, the specific surface area (S_{BET}) of the obtained materials was determined with adsorption-desorption isotherms of N_2 at 77 K. The surface area, pore volume, and average pore diameter of the synthesized materials are summarized in

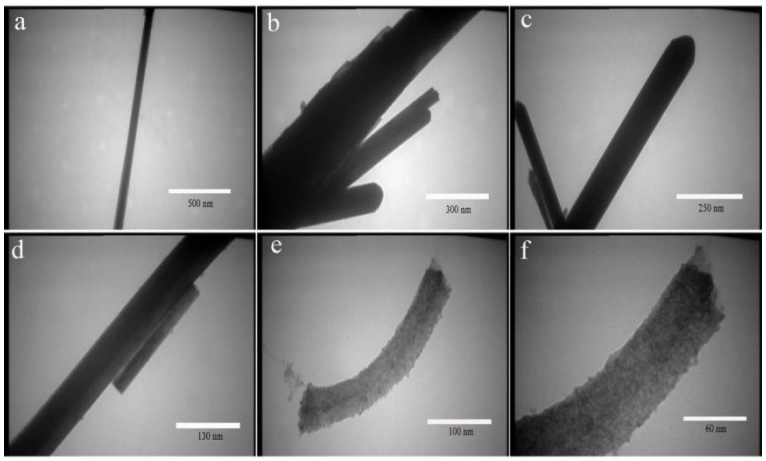

Fig. 4. TEM images of the hydrothermally synthesized $Bi_2Mn_2O_7$ nanomaterials after 48h at 180 °C

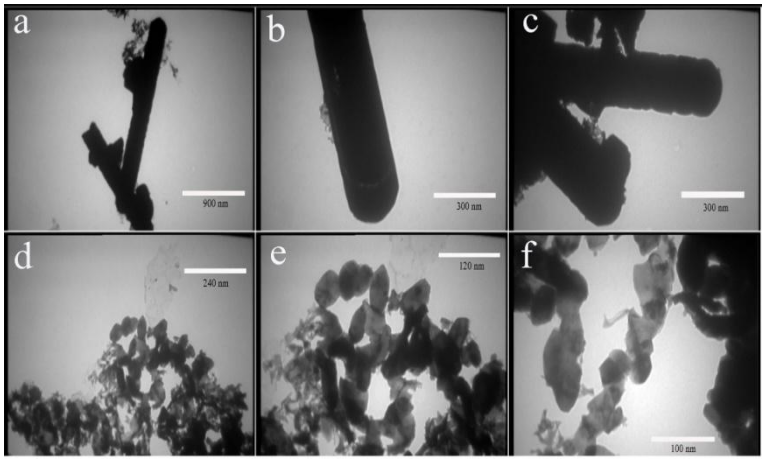

Fig. 5. TEM images of the solid state synthesized $Bi_2Mn_2O_7$ nanomaterials after 48h at 550°C

Table 1. BET data for $Bi_2Mn_2O_7$ showing the textural properties of the obtained materials

Sample	BET surface area (m^2g^{-1})	Pore size (Å)	Pore volume (cm^3g^{-1})	Average particles size (nm)
S_1	0.35	126.11	0.002	6954
S_2	0.74	139.06	0.003	8133

Table 1. It can be seen that the average surface area and pore volumes are about 0.35 m^2g^{-1} and 0.002 cm^3g^{-1} for S_1 and 0.74 and 0.003 cm^3 g^{-1} for S_2, respectively. Also, for samples S_1 and S_2, the average nanoparticles sizes were measured as 6954 and 8133 nm, respectively. Table 2 shows the textural properties of the as-prepared materials. The data summarized in this tableshow that the specific surface area of the pores of the S_2sample is larger than that of S_1 and the pore width and pore volume of S_2 is larger than that of S_1. So, the investigated results of the BET and BJH measurements suggest that the surface area of S_2 is larger than that of S_1. It also shows that bychanging the reaction method to solid state, the average particle sizes are larger than those of hydrothermal method that is in good agreement with the FESEM images.

3. 4. Optical Properties

Fig. 6 represents the room-temperature emission spectra of the as-synthesized materials under excitation at 200 nm. Strong broad emission bands at 400-650 nm are observed for samples 1 and 2, respectively. These peaks can be related to Bi-Otransitions [14, 15]. The shoulder observed at 650-720 nm can be

Table 2. BJH data for $Bi_2Mn_2O_7$ showing the textural properties of the obtained materials

Property	S_1	S_2
BJH adsorption cumulative surface area of pores between 17 and 3000Å width	0.31 m^2g-1	0.34 m^2g-1
BJH adsorption cumulative volume of pores between 17 and 3000Å width	0.003 cm^3g^{-1}	0.004 cm^3g^{-1}
BJH adsorption average pore width (4V/A)	71nm	69 nm

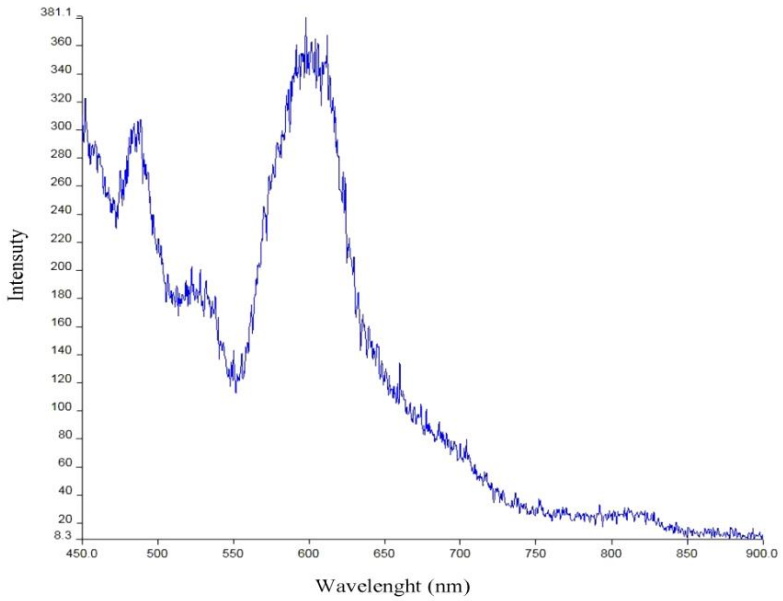

Fig. 6. Photoluminescence spectrum of the hydrothermally synthesized $Bi_2Mn_2O_7$ nanomaterials (λ_{ex} = 200 nm)

attributed to d-d transitions in Mn cations [16].

4. Conclusion

In this work, $Bi_2Mn_2O_7$ nanomaterials were synthesized via hedrothermal and solid state methods. The PXRD patterns showed that the synthesis was sucsessfull. FESEM images showed that the as-synthesized materials are in a rod like and a mixture of rod-particle structures for hydrothermal and solid state methods, respectively. The BET-BJH measurements showed that bychanging the reaction method to solid state, the average particle sizes were larger, which showsgood agreement with those of the TEM images.

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