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Enhanced photocatalytic activity in Zn/Mn substituted $BiFeO_3$ nanoparticles

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KEYWORDS

BFO, Nanostructure, Cycloid magnetic order, Optical properties, Photocatalysis

SHORT SUMMARY

Pure and Mn/Zn-doped BFO nanopowders were synthesized using a hydrothermal process. The homogeneity and purity have been achieved by X-ray diffraction (XRD) and Raman spectroscopy. Transmission electron microscopy (TEM) images revealed that all powders consist of agglomerated nanoparticles with sizes less than 10 nm. Mössbauer spectrometry (MS) measurement reveals that substituting Fe atoms by Mn/Zn destabilizes the cycloidal modulation to lead to a homogenous antiferromagnetic state. The main substitution causes an important modification in the crystal field and the band structure, clearly seen in the plotted Kubelka-Munk function. It, mainly, reduces the band gap value. Thus, the photocatalytic activity of doped samples for the degradation of Methylene blue (MB) under solar irradiation is found to be remarkably better than that of pure BFO.

EXTENDED ABSTRACT

Investigating the concert of nanoscale multiferroic materials is a noteworthy challenge since the physical properties of these materials vary noticeably on this scale and depend closely on the method of synthesis [1-3].

In this work, $BiFe_{(1-x-y)}Mn_xZn_yO_3$ nanopowders (x= 0, 0.02 / y= 0, 0.02) were prepared by a facile hydrothermal synthesis. X-ray diffraction (see figure1) and Raman studies confirmed the presence of the typical rhombohedral symmetry (*R3c*) structure of Bi_2FeO_3 (BFO) [4] for all the samples.

Also, they revealed an expected structure distortion for doped and co-doped samples. As doping atoms were added, the principle doubly pics in the vicinity of 2θ= 32 of XRD pattern (figure 1 b) shows a shift and the Jahn–Teller effect was clearly distinguished in the Raman spectra indicating the successful substitution of Fe ions (i.e., oxygen octahedra distortion). Transmission electron microscopy study showed agglomerated nanoparticles with sizes less than 10 nm as presented in Figure 2. The main size is in agreement with size values estimated by the Scherrer equation and deduced from XRD patterns.

Mossbauer spectrometry measurements revealed that the spectacular magnetic cycloidal order known for BFO [5] was destabilized after doping. As a result of magnetic anisotropy due to magnetoelastic and surface-confinement effects, the cycloid is unstable as only a slight amount of substitution is enough to destroy it and lead to a homogenous antiferromagnetic state. Compared to the pure BFO, doped samples present remarkable changes in band structure and structure field as shown in plotted Kubelka-Munk function [6], which fit well with the obtained structure results.

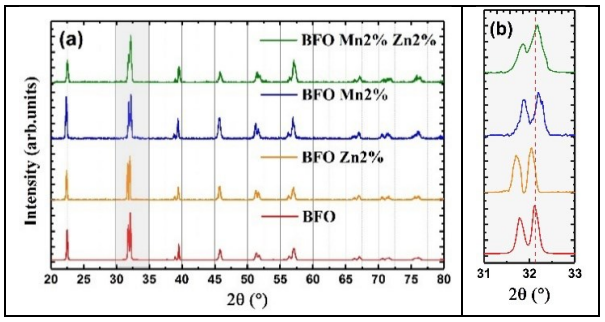

Figure 1 X-ray diffraction patterns of synthesized samples; (a) overview, (b) enlarged part in the vicinity of 2θ= 32.

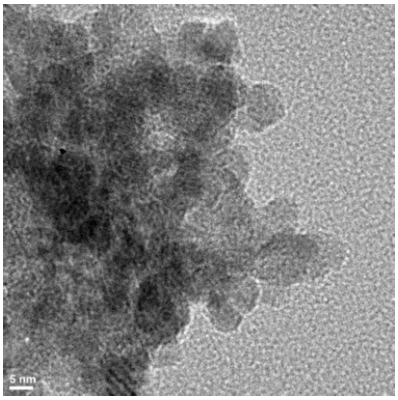

Figure 2 Transmission electron microscopy image of pure BFO nanopowders

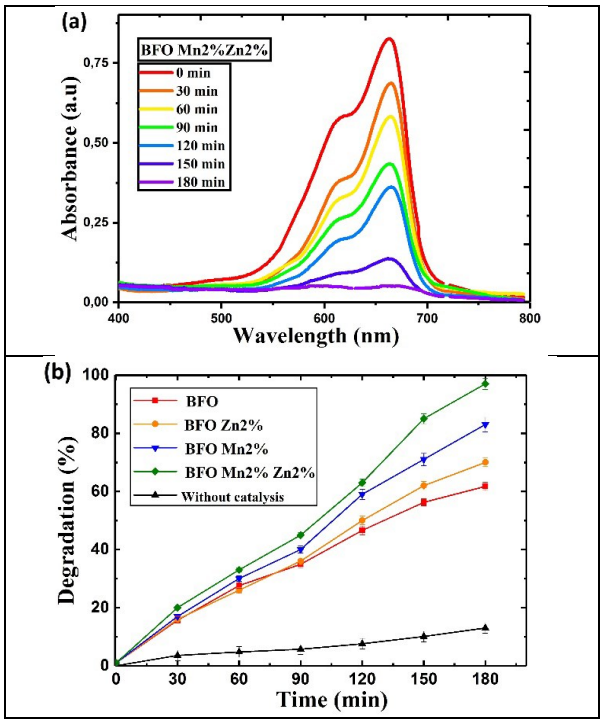

Figure 3 (a) Absorption spectrum of MB dye exposed under visible-light irradiation in the presence of BFO Mn2% Zn2% powders, (b) Photocatalytic degradation efficiency.

Direct optical bandgap determined from Tauc plot showed an important decrease in value: it shifts from 2.2 to 1.9 eV for pure BFO and $BiFe_{(0.96)}Mn_{0.02}Zn_{0.02}O_3$ respectively). Such Band gap value reduction makes BFO more suitable for photoinduction applications. the evolution of the energy values reminds the effect of the pressure [7]. The photocatalytic activity of the pure and the doped samples was evaluated by the degradation of the methylene blue dye (MB) under visible light irradiation. The activity of the doped samples was found to be higher than that of $BiFeO_3$ as expected.

After 3 hours of sunlight irradiation, the degradation efficiency increases from 61% to 97% for $BiFeO_3$ and $BiFe_{0.96}Mn_{0.02}Zn_{0.02}O_3$, respectively (see figure 3). The optimized specific surface and the reduced band gap value after substitution are considered the principal important causes of the obvious enhanced photocatalytic activity.

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References

[1] J. Zhang, Z. H. Liu, Z. F. Liu, Novel WO3/Sb2S3, "Heterojunction photocatalyst based on WO3 of different morphologies for enhanced efficiency in photoelectrochemical water splitting", *ACS Appl. Mater. Interfaces*, 2016

[2] K. Kocı, L. Obalova, L. Matejova, D. Placha, Z. Lacny, J. Jirkovsky, O. Solcova, "Effect of TiO_2 particle size on the photocatalytic reduction of CO_2", *Appl. Catal. B*, 2009

[3] P. Suresh, S. Srinath, "Effect of synthesis route on the multiferroic properties of BiFeO3: A comparative study between solid state and sol–gel methods", *Journal of Alloys and Compounds*, 2015

[4] W. B. Taazayet, I. M. Zouari, N. Hosni, B. Dkhil, and N. T. Mliki, "Facile synthesis of pure $BiFeO_3$ and $Bi_2Fe_4O_9$ nanostructures with enhanced photocatalytic activity", *J Mater Sci: Mater Electron*, 2021

[5] I. M. Zouari, W. B. Taazayet, J.-M. Grenèche, L. Bessais, B. Dkhil, N. T. Mliki, "Field-induced spin cycloidal modulation to antiferromagnetic transition and possible flexomagnetic effect in $BiFeO_3$ nanoparticles", *Journal of Alloys and Compounds,* 2023

[6] W. Ben Taazayet, I. Mallek Zouari, P. Gemeiner, B. Dkhil, and N. Thabet Mliki, "Effect of Zn Substitution on the Structural, Optical Properties and Photocatalytic Activity of $BiFeO_3$ Nanopowders," *Physica Rapid Research Ltrs*, 2022

[7] F. Meggle, J. Ebad-Allah, J. Kreisel, C. A. Kuntscher, Optical spectroscopy on the photoresponse in multiferroic $BiFeO_3$ at high pressure, *J. Appl. Phys*, 2019.