A-site doped $BiFe_{0.95}Mn_{0.05}O_3$ Nanoparticles for Photocatalytic Applications

Astita Dubey[1]*, Chin Hon Keat,[1] Marianela E. Castillo[1], Vladimir V. Shvartsman[1], Doru C. Lupascu[1]

[1] Institute for Materials Science and Center for Nanointegration Duisburg-Essen (CENIDE), University of Duisburg-Essen, Universitätsstrasse 15, D 45141 Essen, Germany

*Presenting Author: astita.dubey@uni-due.de

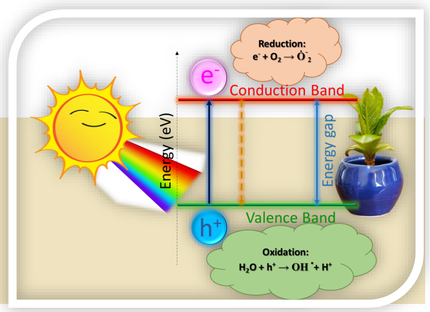
UNIVERSITÄT DUISBURG ESSEN

Offen im Denken

CENIDE CENTER FOR NANOINTEGRATION DUISBURG-ESSEN

INTRODUCTION

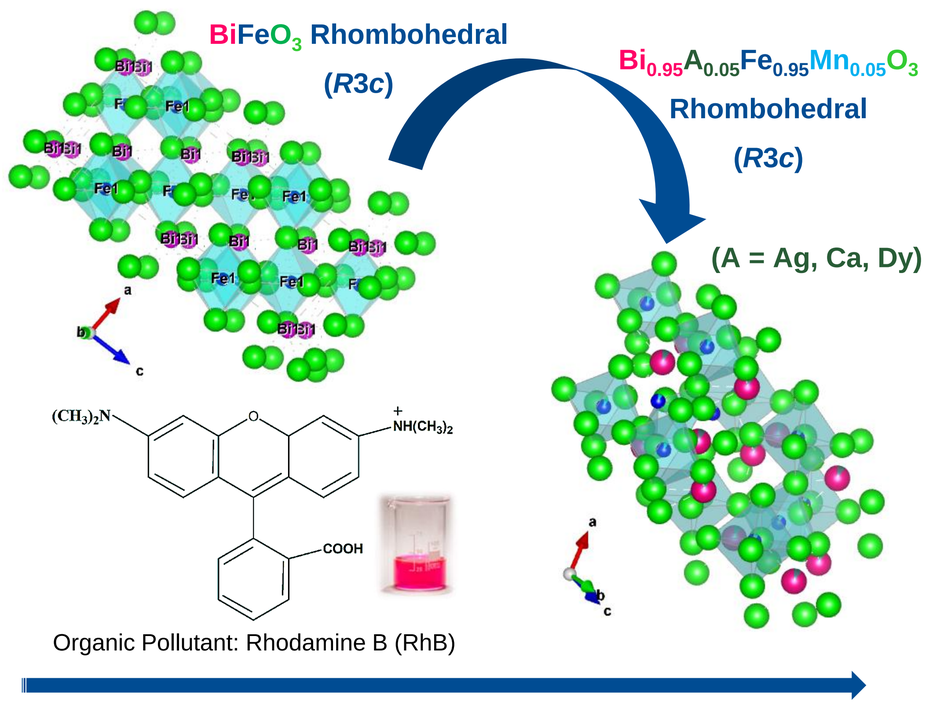
Organic pollutants like dyes used in textile industries are the major sources of water contamination. Photocatalysis is one of the technique for degrading such harmful environmental waste. Perovskites like Bismuth Ferrite (BFO: $BiFeO_3$ = ABO_3) Nanoparticles (NPs) with suitable band gap are attractive multiferroic material due to the coexistence of ferroic orders at room temperature.[1] BFO can be used as a photocatalyst and it also provides a broad research area to exploit its photocatalytic properties via doping. The effect of A-site doping on ferroelectric properties of BFO NPs is also interesting for studying its role in photocatalysis.



1. MOTIVATION

Visible light absorber BFO NPs are potential materials in the field of optoelectronics, hydrogen production and photocatalysis due to their narrow band gap (2.18 eV) and robustness towards humidity and light unlike halide perovskites. Nevertheless, the photocatalytic activity of BFO NPs is far behind than well established TiO_2 cause of faster recombination of charge carriers and formation of defect assisted trap states. To overcome these issue, molecular engineering is one of the tool to tailor such properties and increase the photocatalytic activity. Therefore, we study the effect of A-site doping in $BiFe_{0.95}Mn_{0.05}O_3$ NPs on the degradation of organic Pollutant i.e. Rhodamine B (RhB).

Fig.1: Schematic Representation of BFO and codoped BFO crystal structure in rhombohedral fashion



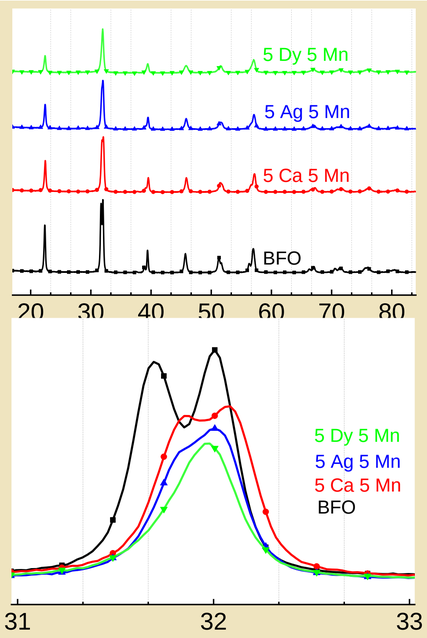
Organic Pollutant: Rhodamine B (RhB)

2. SYNTHESIS

BFO and codoped BFO NPs were synthesized via a modified sol-gel route as shown in Fig.2. The calcined NPs were washed with dilute nitric acid and were milled at 400 rpm for 5 h to remove unwanted byproducts and to avoid agglomeration.

Fig.2: sol-gel route

3. STRUCTURAL CHARACTERIZATION



- Powder diffraction pattern unveils *R*3*c* (Fig 1.) crystal structure for all undoped and doped NPs
- Doublet peak between 31° and 33° start to merge after A-site doping and also shifts to higher angle
- The lattice parameters alters that results in distortion of pristine BFO's crystal structure due to doping of mono, di and trivalent cations of different size (Table 1.)
- SEM images and PFM images reveals size of codoped NPs in following order

60 nm > BFO > Ag+Mn > Ca+Mn > Dy+Mn

Ions	Bi^{+3}	Ag^{+}	Ca^{+2}	Dy^{+3}	Fe^{+3}	Mn^{+4}	O^{-2}
Ionic radius (Å)	1.45	1.38	1.34	1.18	0.645	0.53	1.40
Coordination Number	12	12	12	12	6	6	6

Table.1: Ionic radii trend

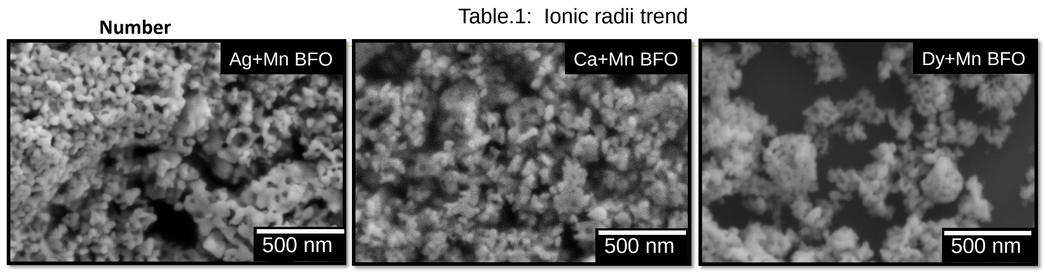


Fig.3: Scanning Electron Microscopy (SEM) images of co-doped BFO NPs

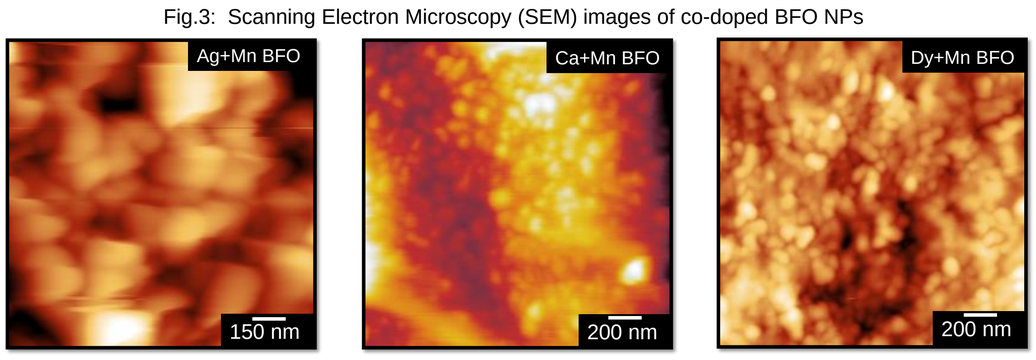
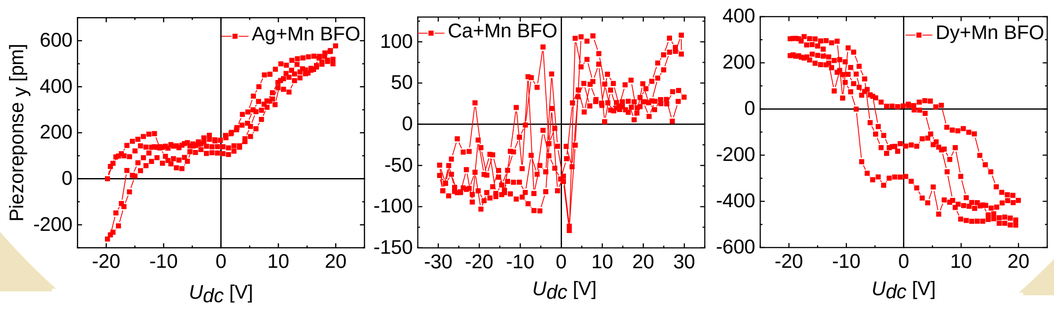
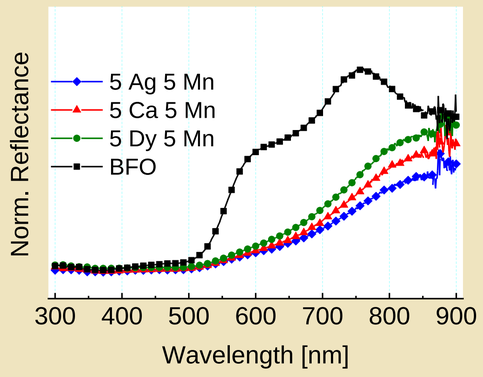


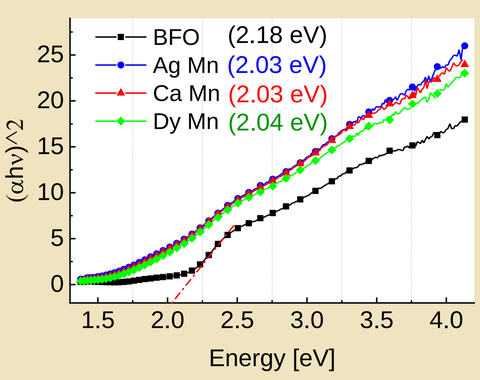
Fig.4: Piezoresponse Force Microscopy (PFM) images of co-doped BFO NPs



4. OPTICAL CHARATERIZATION



- The reflectance spectra show no significant effect of A-site cations
- The spectrum is more affected due to Mn doping in BFO NPs
- The Tauc plot also show no difference in band gap energies for codoped NPs, however band gap is lower than pristine BFO NPs
- We speculate that A site cations doping alters the defect levels and trap states than the band gap



5. PHOTOCATALYSIS

Average Photocatalytic Trend: **Dy+Mn > Ag+Mn > Ca+Mn > BFO**

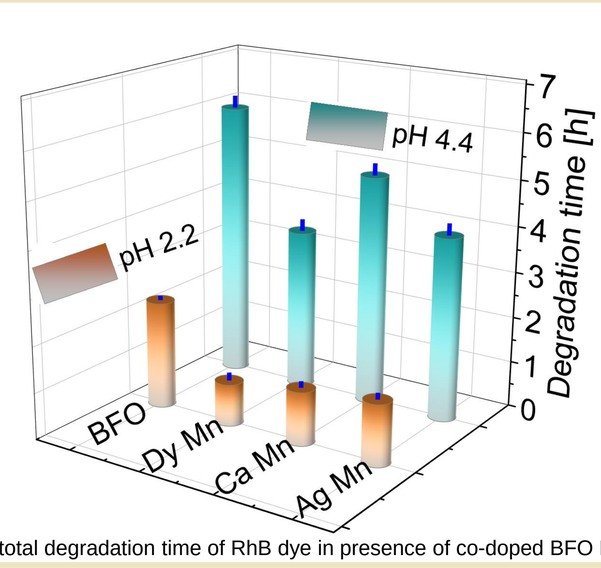


Fig.5: total degradation time of RhB dye in presence of co-doped BFO NPs

6. PIEZORESPONSE

- The local Piezoresponse profile show ferroelectric nature of these codoped NPs, Piezoresponse trend: Ag+Mn > Dy+Mn > Ca+Mn
- Dy+Mn combination shows best degradation in normal and acidic medium, as its able to degrade RhB completely in 55 minutes
- The rate constant increases by three times comparative to pristine BFO

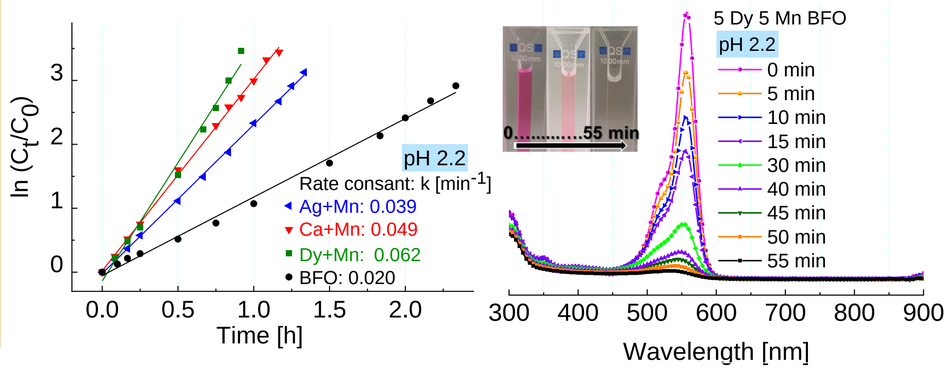


Fig.6: Photocatalytic activity of co-doped BFO NPs in acidic medium

7. SUMMARY

- Phase pure co-doped BFO NPs were successfully synthesized via Sol-gel route
- RhB dye was completely degraded in the presence of codoped BFO NPs under UV+Vis light (solar simulator)
- The photocatalytic activity increases in acidic medium, where Dy+Mn combination shows best photocatalytic activity in normal and acidic conditions
- Dy+Mn one has smallest particle and crystallite size and also largest surface area
- A-site substitution no significant effect on band gap of Mn doped BFO NPs, whereas A site doping distorts crystal structure and alters particle size, piezoresponse of pristine
- PFM images unveil the existence of local piezoresponse and hence ferroelectric behavior for all codoped BFO NPs
- Best photocatalyst i.e. Dy+Mn, is due to large surface area, best solubility and good ferroelectric

ACKNOWLEDGEMENTS

We kindly acknowledge Mr. Tobias Bochmann for the SEM measurements and Mrs. Claudia Schenk for the BET measurements.

DFG Deutsche Forschungsgemeinschaft [Project No: Lu 729/21-1]

UDEMAT Institut für Materialwissenschaft Universität Duisburg-Essen