

NOVEL HETEROSTRUCTURE $\text{Ba}_x\text{TiO}_3\text{-Zn}_x\text{Fe}_2\text{O}_4$ NANOCOMPOSITE: A QUANTITATIVE STUDY

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ABSTRACT

A novel Barium Titanate-Zinc ferrite ($\text{Ba}_x\text{TiO}_3\text{-Zn}_x\text{Fe}_2\text{O}_4$) heterostructure nanocomposites are synthesized at temperatures less than 500°C which is the major theme of the present research. The synthesis technique is adapted in such a way that the size of the particle is governable. In this research two dissimilar ratios of BTO (hard-site) and ZFO (soft-site) composites are synthesized (H-S 90:10, H-S 60:40) and quantitatively analyzed for their exclusive structural, textural, spectroscopic, and optical properties. With XRD data, structural refinement has been carried out showing 49 % of harder-BTO phase (Triclinic) and 51% of softer-ZFO phase (Cubic) for H-S 90:10 and similarly 78% of harder-BTO phase and 22% of softer-ZFO phase in the H-S 60:40 composite respectively. Very small particles of 6nm are found which is confirmed by SEM histogram and sample purity was determined using EDX analysis. Proofs for the formation of nanocomposites and the existence of Tetrahedral and Octahedral phases for each sample were given using FTIR Spectroscopy. From UV spectrometer data, Tauc's plot is used to find the wide energy band gap which is observed to be 2.6651 and 3.1971 eV, thus proving that these composites can present themselves as a budding candidate for nano-level optoelectronic devices and other photovoltaic applications.

Key Words: Barium Titanate, Zinc ferrite, Heterostructure, Nanocomposite, Low Temperature, Wide bandgap Tauc's plot.

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INTRODUCTION

Multifunctional materials have extended their definition to constituents having instantaneous ferromagnetic, ferroelectric, and ferroelastic properties.^{1,2} Electro-magnetic coupling within the nanocomposites enables them to control the electrical phase via magnetism.³ Such composites can also be called Magneto-electric Multiferroics.⁴⁻⁷ In addition, composite multiferroics have countless novel applications.⁸⁻¹⁷ Between numerous ferroelectrics like PbTiO_3 , PZT, PLZT, BaTiO_3 , PVDF, Rochelle salt, etc., Due to the minimum toxic nature compared to Lead (Pb); Barium Titanate (BaTiO_3) is widely used in high-level applications.¹⁸⁻²¹ The purpose of the present research is to develop Barium Titanate based composite at low temperatures and study its optical properties for possible photonic applications. Recently Cobalt Ferrite- Barium Titanate core-shell nanoparticle was synthesized by Hossain *et al.* for application in photo simulation or triggering drug release at a specific absorption band.²²

EXPERIMENTAL

Initially, for the hard site (H), optimum amounts of Chlorides are mixed with Oxalic acid and Barium Titanate is synthesized as shown in Fig.-1.

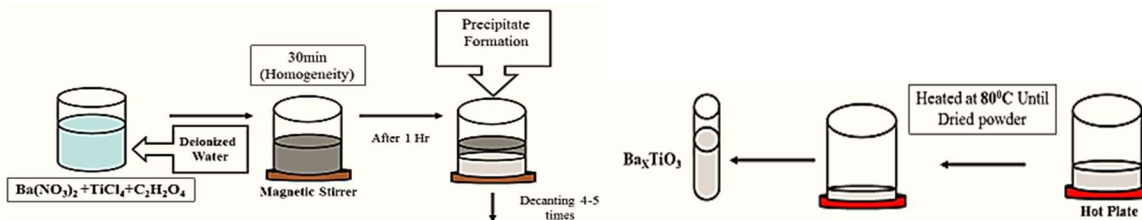


Fig.-1: Preparation of Hard Site (BTO) by Co-Precipitation Method

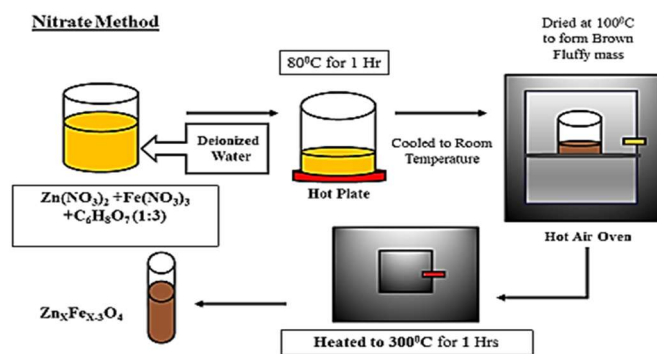


Fig.-2: Preparation of Soft Site (ZFO) by Nitrate Method

Similarly, for the soft site (S), stoichiometric amounts of Nitrates are mixed with Citric acid and a Zinc Ferrite particle is obtained as shown in Fig.-2. The composite materials are prepared by mixing two dissimilar weight ratios of hard and soft metal oxides in a motor and pistol for over 1 hour.

Table-1: Characterization Tools Involved

S. No.	Instrumentation	Specification	Purpose
1.	X-ray diffractometer (XRD)	3rd generation Empyrean, Malvern Panalytical with Copper K-Alpha(α) ($\lambda=1.540598 \text{ \AA}$) radiation	Structural mapping of composites
2.	Scanning Electron Microscopy (SEM equipped with EDX)	Joel JSM 6390model for elemental analysis	To analyze texture, purity, and particle size distribution
3.	Fourier transform infrared spectra (FTIR)	Shimadzu, IR affinity 1A spectra to record a spectrometer in the range of 4000-400 cm^{-1}	To confirm the formation of composites and the presence of spinel, M-type hexaferrite, and metal-oxygen bond
4.	UV analysis	UV-2400PC Series 1.0nm -360 nm	To calculate the band gap via Tauc's Plot

Tab,e-2: Cell Parameter and Volume Calculated With JCPDS Comparison for H-S 90:10 and H-S 60:40

Lattice parameters			a	b	c	α	β	γ	Cell Volume
Calculated results	H-S 90:10	H	7.3485	14.4357	13.1038	95.157	75.063	85.939	1329.76
		S	8.4248	-	-	90	90	90	1366.05
	H-S 60:40	H	7.459	14.1692	13.3259	93.6084	77.195	85.836	1366.01
		S	8.4433	-	-	90	90	90	602

Table-3: Average Crystallite Size of Nano H-S Composite Tabulated using Scherrer's Equation

Sample %	The average size in nm	Phase Coexistence (%)	
90:10	7.04	H site (BTO) 58.63	S site (ZFO) 41.37
60:40	6.01	H site (BTO) 91.89773	S site (ZFO) 8.102269

Table-4: Quantitative tabulation of EDAX Spectral Data of both Nano H-S Composite

Chemical	Ba	Ti	Zn	Fe	O
H-S 90:10					
The concentration of chemicals (%)	7.83	2.73	2.00	2.14	9.36
Atomic Percentage	8.02	7.72	4.37	5.51	74.38
H-S 60:40					
The concentration of chemicals (%)	8.04	2.62	3.71	3.48	9.96
Atomic Percentage	7.53	6.76	7.39	8.10	70.22

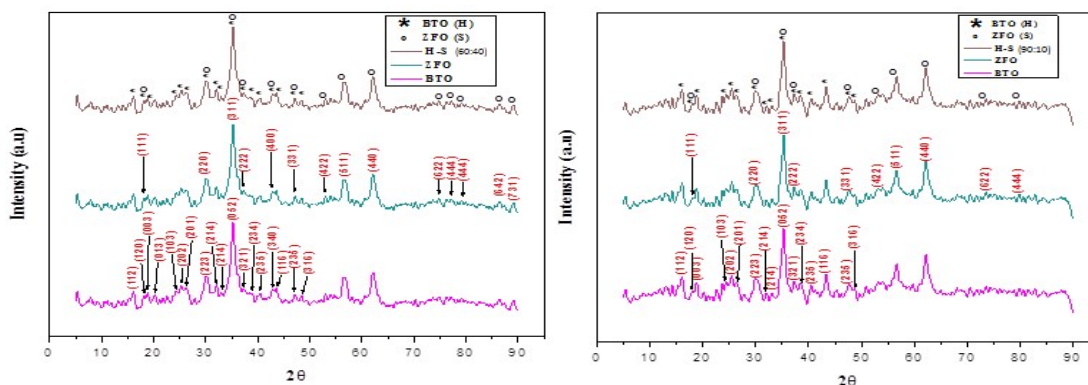


Fig.-3: Crystalline Structure Mapping of H-S 90:10 and H-S 60:40 Respectively using XRD Results

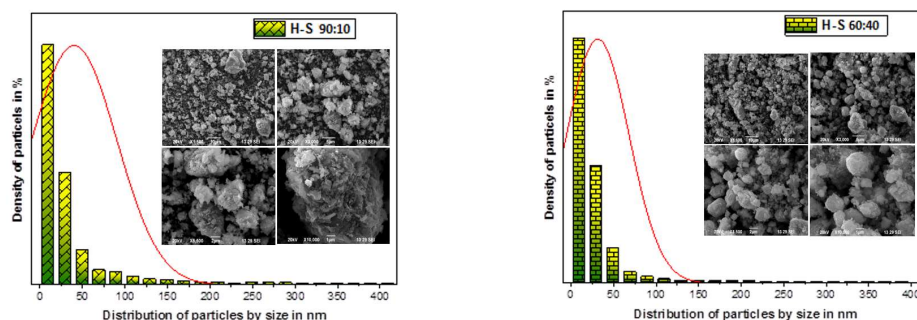


Fig.-4: Histogram and Scanning Electron Micrograph of Nano H-S 90:10 and H-S 60:40 Composite

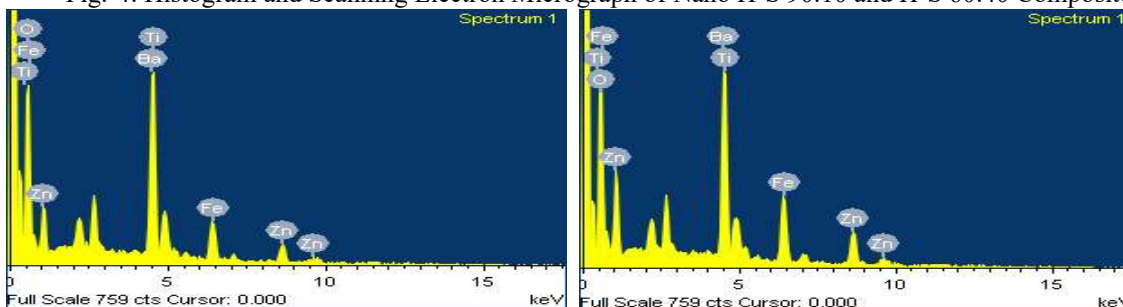


Fig.-5: EDAX analysis for both H-S Samples Highlighting the Elemental Weight %.

RESULTS AND DISCUSSION

As shown in Table-2 the cell parameters and volume are calculated in comparison with the standard JCPDS card data which shows that all lattice parameters and angles decrease with a decrease in H material except b & γ . Also, from the graph more definite sharper peaks are found in H-S 60:40 compared to H-S 90:10 which may be due to the increased concentration of H material sample that is even 1.16nm for H-S 90:10 and 1.19nm for H-S 60-40 concluding that crystal size decreases with an increase in H site concentration.

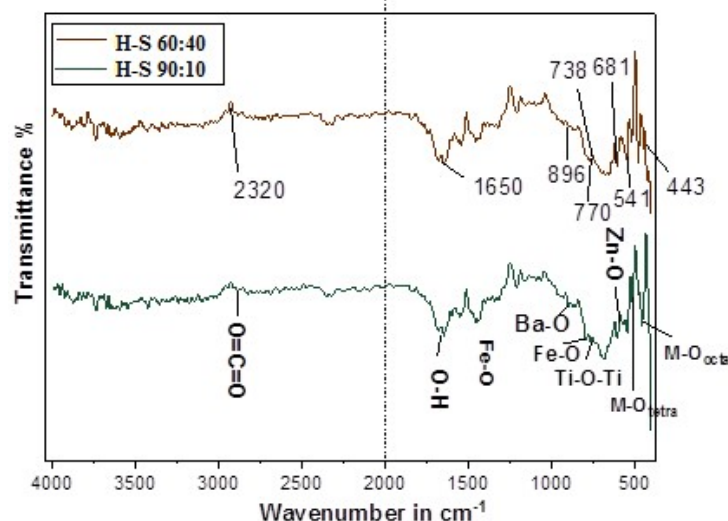


Fig.-6: Spectroscopic Graph of H-S 90:10 and H-S 60:40

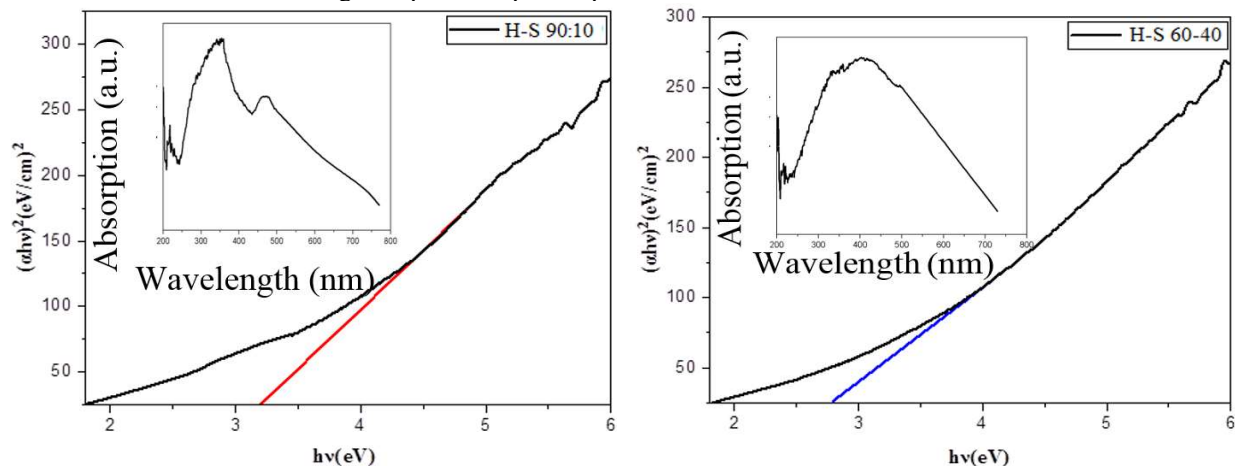


Fig.-7: Energy Gap Determination with Tauc's plot for H-S 90:10 and H-S 60:40 using UV Data

With the aid of XRD data structural refinement has been carried out which showed 49 % of Harder BTO phase (Triclinic) and 51% of softer ZFO phase (Cubic) for H-S 90:10 and similarly 78% of harder BTO phase and 22% of softer ZFO phase in the H-S 60:40 composite respectively.

Morphology and Elemental (Purity) Determination

In both samples' the histogram confirms the homogeneous distribution of particles that have spherical nanostructure. The average size of grains is calculated to be larger than the size of particles which might be due to the agglomeration of individual crystals to form grains.¹ The EDX confirms the purity of the sample.

Spectroscopic Analysis

The spectroscopic investigation via the FTIR spectrum showed various bands representing different complexes (Tetrahedral at 543- 544 cm^{-1} and octahedral at 423- 424 cm^{-1}). The successful formation/ hard-soft coupling of ferrite composites in the samples is confirmed by a peak at wavenumber 603 cm^{-1} and

1677 cm^{-1} , where 681 cm^{-1} represents the characteristic Zn-O band. Since the precursors are Barium Chloride and Titanium Tetrachloride, a C-Cl stretching is observed at 852 cm^{-1} (strong) and similarly, 2347 cm^{-1} reflects C-O stretching due to atmospheric CO_2 presence during FTIR experimentation.

Optical Analysis for Energy Gap Determination

Visible light absorption across Tauc's Plot for the samples is graphed which serves as an indication of the Energy gap. On calculating $(\alpha h\nu)^{1/2}$ and the photon energy on the abscissa the energy gap for H-S 90:10 is 3.1971 eV and for H-S 60:40 is 2.6651 eV. This indicates that the energy gap decreases with an increase in S-site weight percentage which might be due to the larger radius of barium titanate atom compared to zinc ferrite. The bandgap result may be because TiO_2 has a 3.0 eV absorbing UV region and Fe_2O_3 has a 2.2 eV absorbing wavelength less than 550 nm. Also, when the weight percentage (concentration) increases, the number of molecules increases which form narrow valence and conduction bands with an increased energy gap.

CONCLUSION

As a result, the nanoscale composites possess better textural, structural, and Optical behaviors related to other oxide-nano level-based composites. The significance is that these characteristic behaviors were observed at just 0.1 % chemical concentrations on both the H-site and S-site of composites. Thus, further studies can be carried out to develop these materials for nanoelectronic devices including wide bandgap semiconductors.

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REFERENCES

1. D. Zhang, J. Cheng, J. Chai, J. Deng, R. Ren, Y. Su, H. Wang, C. Ma, C. S. Lee, W. Zang and G. P. Zheng, *Journal of Alloys and Compounds*, **740**, 1067(2018), <https://doi.org/10.1016/j.jallcom.2018.01.081>
2. L. Lin, H. Ning, S. Song, C. Xu, and N. Hu, *Composites Science and Technology*, **192**, 108102(2020), <https://doi.org/10.1016/j.compscitech.2020.108102>
3. R. Samad, M. D. Rather, K. Asokan, and B. Want, *Journal of Alloys and Compounds*, **744**, 453(2018), <https://doi.org/10.1016/j.jallcom.2018.01.403>
4. M. VijatovicPetrovic, J.D. Bobic, and B.D. Stojanovic, *Magnetic, Ferroelectric, and Multiferroic Metal Oxides*, Vol. Metal Oxides. Amsterdam: Elsevier Publisher (2018).
5. O. Condurache, I. Turcan, L. Curecheriu, C. Ciomaga, P. Postolache, G. Ciobanu, L. Mitoseriu, *Ceramics International*, **43(1)**, 1098(2017), <https://doi.org/10.1016/j.ceramint.2016.10.047>
6. R.Grigalaitisa, M. M. Vijatovic Petrovic, J. D. Bobic, A. Dzunuzovic, R. Sobiestianskas, A. Brilingas, B. D. Stojanovic, J. Banys, *Ceramics International*, **40(4)**, 6165(2014), <https://doi.org/10.1016/j.ceramint.2013.11.069>
7. A. Jain, A. K. Panwar, A. K. Jha, and Y. Sharma, *Ceramics International*, **43(13)**, 10253(2017), <https://doi.org/10.1016/j.ceramint.2017.05.053>
8. Y. Wang D. Gray, D. Berry, J. Gao, M. Li, J. Li, D. Viehland, *Advanced Materials*, **23(35)**, 4111(2011), <https://doi.org/10.1002/adma.201100773>
9. Y. Wang, J. Gao1, M. Li1, D. Hasanyan, Y. Shen, J. Li1, D. Viehland, and H. Luo, *Applied Physics Letters*, **101**,2(2012), <https://doi.org/10.1063/1.4733963>
10. Z. Chu, W. Shi, H. Shi, Q. Chen, L. Wang, M. J. PourhosseiniAsl, C. Xiao, T. Xie, S. Dong, *Advanced Materials Technologies*, **4**, 3(2019), <https://doi.org/10.1002/admt.201800484>
11. M. J. PourhosseiniAsl, X. Gao, S. Kamalishahroudi, Z. Yu, Z. Chu, H. Y. Lee, and S. Dong, *Nano Energy*, **70**, (2020), <https://doi.org/10.1016/j.nanoen.2020.104506>
12. J. Zhai, S. Dong, Z. Xing, J. Li, and D. Viehland, *Applied Physics Letters*, **89**,8(2006), <https://doi.org/10.1063/1.2337996>

13. Y. H. Chu, L. W. Martin, M. B. Holcomb, M. Gajek, S. J. Han, Q. He, N. Balke, C. H. Yang, D. Lee, W. Hu, and Q. Zhan, *Nature Materials*, **7**(6), 478(2008), <https://doi.org/10.1038/nmat2184>
14. J. M. Hu, Z. Li, L. Q. Chen, and C. W. Nan, *Nature Communications*, **2**, 1(2011), <https://doi.org/10.1038/ncomms1564>
15. A. Kumar, S. H. Kim, M. Peddigari, D. H. Jeong, G. T. Hwang, and J. Ryu, *Electronic Materials Letters*, **15**(3), 323(2019), <https://doi.org/10.1007/s13391-019-00124>
16. H. Wu, A. Tatarenko, M. I. Bichurin, and Y. Wang, *Nano Energy*, **83**, (2021), <https://doi.org/10.1016/j.nanoen.2021.105777>
17. S. Hajra, V. Vivekananthan, M. Sahu, G. Khandelwal, N. P. M. Joseph Raj, and S. J. Kim, *Nano Energy*, **85**, (2021), <https://doi.org/10.1016/j.nanoen.2021.105964>
18. G. Liu, Y. Li, B. Guo, M. Tang, Q. Li, L. Yu, K. Yu, Y. Yan, D. Wang, L. Zhang, H. Zhang, Z. He, and L. Jin, *Chemical Engineering Journal*, **398**, (2020), <https://doi.org/10.1016/j.cej.2020.125625>
19. H. Chandrasekar, T. Razzak, C. Wang, Z. Reyes, K. Majumdar, and S. Rajan, *Advanced Electronic Materials*, **6**, 8(2020), <https://doi.org/10.1002/aelm.202000074>
20. K. GireeshBaiju, B. Murali, and D. Kumaresan, *Solar Energy*, **224**, 93(2021), <https://doi.org/10.1016/j.solener.2021.05.063>
21. T. Jin and P. Lin, *IEEE Journal of Selected Topics in Quantum Electronics*, 1(2020).
22. S. Hossain, S. Hossain, *IEEE Transactions on Nanotechnology*, **21**, 172(2022), <https://doi.org/10.1109/tnano.2022.3160349>

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