Effect of Bi^{2+} ions on the photoluminescence properties of $\text{BaTiO}_3:\text{Dy}^{3+}$ perovskite phosphors for LEDs application

ARULMOZHI A (✉ arulsiva79@gmail.com)

St.Joseph's College of Engineering <https://orcid.org/0000-0003-3131-1461>

K. Vishista

Anna University Chennai

G.Suba Lakshmi

Theivanai Ammal College for Women

Research Article

Keywords: Luminescence, Dy^{3+} , Solid state reaction, Commission International De L'Eclairage (CIE), Correlated Color Temperature (CCT)

Posted Date: February 15th, 2021

DOI: <https://doi.org/10.21203/rs.3.rs-176522/v1>

License: © ⓘ This work is licensed under a Creative Commons Attribution 4.0 International License.
[Read Full License](#)

Abstract

A series of $(\text{Ba}_{1-x}\text{Bi}_{0.01})\text{TiO}_3$ doped with Dy^{3+} ions of varying concentrations is prepared by single step solid state reaction that promulgates solid state lighting device applications. The cubic phase perovskite structure of the prepared samples is determined by the Powder X-ray diffraction results. The emission spectra show evidence of intensive peaks at 572 nm attributing to the $^4\text{F}_{9/2}$ to $^6\text{H}_{15/2}$ of Dy^{3+} ions. Dy^{3+} doped phosphors $(\text{Ba}_{1-x}\text{Bi}_{0.01})\text{TiO}_3: x\text{Dy}^{3+}$ ($x = 0, 0.01, 0.03, 0.05$ and 0.07) exhibit yellow emission and the highest intensity of emission demarcates the optimum concentration of $\text{Ba}_{1-x}\text{Bi}_{0.01}\text{TiO}_3:0.05\text{Dy}^{3+}$.

SEM studies to assess the surface morphologies alongside the elemental analyses from Energy dispersion spectroscopy (EDS) extensively for optimal concentration have been ventured. The Commission International De l'Eclairage (CIE) and Correlated Color Temperature (CCT) analyses authenticate the present phosphor genuine for fabricating light emitting diodes.

1. Introduction

Researchers and lighting industries are drawn to Solid State Lighting (SSL) based devices, quite recently, due to their prominence in science and technology. The environmental friendly SSL devices are efficacious energy conservationists [1]. The rapid evolution of the superior SSL device enhanced w-LEDs are at the helm of affairs because of their longer life span, compact size, high efficiency and less energy consumption [2]. The selection of apt base materials and dopants (e.g., rare earth ions), is crucial to fabricate phosphors of intense photoluminescence. Of late, Perovskite fabricated titanate exhibiting optical properties has been the centre of attention to most researchers on account of its low phonon energy, stable physical as well as chemical traits [3]. Enhancement of the efficacies of perovskite LEDs has experienced dramatic progress in the recent decades. Barium titanate (BaTiO_3), a remarkable ferroelectric oxide that is transparent to the naked-eye and infrared light has strong electro-optic co-efficiency drawing active as well as active optical components [4, 5]. Rare earth (RE) ions, more particularly, Ba sites in $(\text{Ba}_{1-x}\text{Bi}_{0.01})\text{TiO}_3$ host are a natural trivalent compounds. RE ions are widely studied as the unique 4f transition levels of lanthanide ions, shielded by the outer 5s and 5p electron orbitals feature charming optical personality [6]. They are ineffectually dependent on the coordination environs resulting in feeble or sturdy emission peaks. Trivalent dysprosium (Dy^{3+}) with $^4\text{F}_9$ electronic configuration, of all the RE ions, is an eminent candidate for visible spectral region between its f-f transitions [7]. The photoluminescence (PL) spectra of Dy^{3+} ions comprising extended yellow emission in the 570–600 nm region is indicative of the transitions $^4\text{F}_{9/2} \rightarrow ^6\text{H}_{15/2}$ levels [8]. These rare earth Dy^{3+} ions as white light emitting sources with blue LEDs chip are a noteworthy electron trapping material and are used in mercury free luminescence lamps [9]. Despite the innumerable traditional methods available in the preparation of phosphors composition the current study prioritises solid state reaction process accounting for its single step synthesis route [10]. The prime concern of Dy^{3+} doping is to strengthen the host material useful for optical applications with illuminating light and display techniques that effect the WLED function [11]. The present study is, thus inspired to prepare the Dy^{3+} doped $(\text{Ba}_{1-x}\text{Bi}_{0.01})\text{TiO}_3$

phosphor and scrutinise its authenticity. The current research attempts the preparation of yellow emitting $(\text{Ba}_{1-x}\text{Bi}_{0.01})\text{TiO}_3:\text{x}\text{Dy}^{3+}$ phosphor by solid state reaction method with its novel advancement in luminescence dynamics. The structural, optical absorption, luminescent parameters along with energy mechanism and CIE, CCT of $(\text{Ba}_{1-x}\text{Bi}_{0.01})\text{TiO}_3$ doped Dy^{3+} ($x = 0, 0.01, 0.03, 0.05$ and 0.07) phosphors are discussed in detail.

2. Experimental

2.1 Materials

The precursor chemicals BaCO_3 (Sigma-Aldrich, 99.99%), Bi_2O_3 (Sigma-Aldrich, 99.99%), TiO_2 (Sigma-Aldrich, 99.99%), Dy_2O_3 (Merck, 99%) are used to initiate the formation. An analytical grade reagents are used directly without further refining process while ethanol for grinding and acetone for cleaning purposes are implemented.

2.2 Preparation of phosphors sample

The initial components of BaCO_3 , Bi_2O_3 , TiO_2 and Dy_2O_3 ($x = 0, 0.01, 0.03, 0.05$ and 0.07) are taken in the stoichiometric composition. An agate mortar is used to grind the sample for 1 hour to obtain the fine form through ethanol as a grinding agent and acetone, for cleaning process. Then, the formed powder is transferred into the alumina crucible held in a Muffle furnace maintained at 600°C for 6 hours in air atmosphere for the removal of the water organic impurities in the substance. Afterwards, the Muffle furnace is cooled naturally till it reaches the environment temperature. Subsequently, the sample is transferred to the agate mortar with the help of spatula. Then the sample treated with ethanol agent is fed into the alumina crucible for calcination process. The sample, on attaining fine powder is taken out after 18 hours at 1200°C with grinding intervals on completion of the calcination process. Further, the manufactured materials are taken out and held into the final grinding process for characterization studies. Thus, the host and Dy^{3+} doped $(\text{Ba}_{1-x}\text{Bi}_{0.01})\text{TiO}_3$ samples are prepared by similar procedure for altered doping concentrations.

2.3 Characterization

The phase purity of the samples is determined by X-ray diffraction (XRD) patterns investigated on PAN analytical X'Pert Pro with Cu-K α radiation (wavelength = 0.15405 nm) at 45 kV generator voltage and 40 mA tube current in the range of 20° and 60° as the X-ray source. The collected data for the procedure with 0.02 step size of continuous scan type are duly tabulated. Cary Eclipse Fluorescence Spectrometer equipped with xenon lamp excitation source observes the photoluminescence (PL) spectra. HRSEM (FEI Quanta FEG 200) evaluates the morphological structure of the material while the Energy-dispersive spectrum (EDS) analysis assesses elemental presence in the sample material. MATLAB activated CIE (a 1931 software program) determines the chromaticity colour coordinates of the prepared compounds. All the characterization studies are accomplished at atmospheric temperature only.

3. Results And Discussion

3.1 Phase structure

XRD patterns of $(\text{BaBi}_{0.01})\text{TiO}_3$ and $(\text{Ba}_{1-x}\text{Bi}_{0.01})\text{TiO}_3$ doped Dy ions are calcined at 1200°C (Fig.1). The phase pure and rare earth composition of the as-synthesized $(\text{Ba}_{1-x}\text{Bi}_{0.01})\text{TiO}_3:\text{Dy}^{3+}$ ($x=0,0.01,0.03,0.05$ and 0.07) phosphors producing peaks are indicated in the XRD pattern. The sharp and intense diffraction peaks formed seem to be in good agreement with the patterns confirming the sample materials consign well with the pure Barium Titanate phase. These phases are consistent with the standard JCPDS file no. 89-2475. The synthesized phosphors of the cubic phase perovskite structure with lattice parameters belong to $a=b=c=4.017$ and Pm mm space group. The BaTiO_3 perovskite structure is designed into a framework of corner-linked TiO_6 octahedra with centrally occupied Ba^{2+} ions [12, 13]. These phases are indexed with miller indices (hkl) and compared with the standard JCPDS data as depicted in Fig.1. The maximum intensity is recorded for (110) plane that is in close agreement with JCPDS: 89-2475. The radii of Dy^{3+} ions are similar to those of Ba^{2+} ions present in the host, thus enhancing it to occupy the position of Ba^{2+} ions present in the host. No other crystalline phase has been detected, indicating that all the prepared samples are in single phase state and there appears to be no impact of activator (Dy^{3+}) and co-activator (Bi^{2+}) in the phase of BaTiO_3 . This signifies that the pure and rare earth doped $(\text{Ba}_{1-x}\text{Bi}_{0.01})\text{TiO}_3$ composite are fruitfully prepared by this simple solid state method and the Dy^{3+} ions have been efficiently occupied in the $(\text{Ba}_{1-x}\text{Bi}_{0.01})\text{TiO}_3$ host by substitution process.

3.2 Absorption spectrum

The optical absorption spectrum of $(\text{Ba}_{1-x}\text{Bi}_{0.01})\text{TiO}_3$ doped Dy^{3+} phosphors is recorded for the wavelength range 200-700 nm and represented in Fig. 2. The $(\text{Ba}_{1-x}\text{Bi}_{0.01})\text{TiO}_3:\text{Dy}^{3+}$ shows thick absorption band in UV-Vis region due to host absorption and also accounts for the charge transfer band between Dy^{3+} ions and O^{2-} ions [14]. The charge transfer phenomenon is effected as the consequence of O- 2p electron transition to 4f orbital of Dy^{3+} ion the empty shell [15]. This can be achieved on exciting the electrons from the ground level to the excited level. An absorption shoulder is presented in the UV-Vis region and its location displays tiny changes due to their variation in the doping concentration. This indicates the Dy^{3+} ions can be incorporated into the host lattice without change in the structure of the synthesized compounds.

3.3 Morphology structure of $(\text{Ba}_{1-x}\text{Bi}_{0.01})\text{TiO}_3:0.03\text{Dy}^{3+}$ phosphors

SEM micrographs of $(\text{Ba}_{1-x}\text{Bi}_{0.01})\text{TiO}_3:\text{Dy}^{3+}$ phosphors shown in Fig.3. Display the SEM photographs at three different resolutions. The obtained micrographs show agglomerated and irregular morphology for $x=0.03$. The elemental analysis on the synthesized products is performed using energy dispersive X-ray analysis (EDX) technique. EDX mapping for the elemental distribution of Ba, Ti, Dy, Bi and O has revealed that Bi_2O_3 and Dy_2O_3 are highly dispersed in the BaTiO_3 matrix.

3.4 Photoluminescence analysis

Photoluminescence spectra of $(\text{Ba}_{1-x}\text{Bi}_{0.01})\text{TiO}_3:\text{Dy}^{3+}$ ($x=0.01, 0.03, 0.05$ and 0.07) phosphors at room temperature is shown in Fig. 4. The photoluminescence spectra of $(\text{Ba}_{1-x}\text{Bi}_{0.01})\text{TiO}_3:\text{Dy}^{3+}$ excited under the 387 nm wavelength. On increasing the Dy^{3+} content up to $x=0.05$, the emission intensity is enhanced to the maximum value that diminishes on any further increase in the concentration of Dy^{3+} ions. This indicates the quenching effect concentration of Dy^{3+} ions as well as its dependence on the concentration of rare earth element, which further reduces the emission intensity. Such an experience may be attributed to one of the Quantum Mechanic rules that the location of rare earth ion at a high centrosymmetric rate forbids the f-f levels of electric dipole transition [16,17]. In the photoluminescence spectra, broad peak can be seen in the yellow light emission region centred at 572 nm corresponding to the $^4\text{F}_{9/2}$ to $^6\text{H}_{13/2}$ transition of Dy^{3+} ions [18, 19]. Such a forced electric dipole transition is allowed only at low symmetries without any inversion centres in the host crystal structure, suggestive of dominant occupation of Dy^{3+} at Ba^{2+} sites. Thus, the optimal doping concentration of Dy^{3+} in the $(\text{Ba}_{1-x}\text{Bi}_{0.01})\text{TiO}_3$ host is facilitated to gain the strongest PL emission intensity, which is obtained at $x=0.05$.

3.5 Energy Level diagram

The energy level diagram of Dy^{3+} ions depicted in Fig. 5 explains luminescence mechanism of synthesized phosphors. This phosphor is special of its kind as the yellow emission obtained is of high intensity with appropriate doping concentration of Dy^{3+} ions. It is as well conjectured that yellow emissions is suitable for preparing white luminescence with blue LED chip. The emission of white light can be achieved from three different processes: selection of a suitable host composition, changing the concentration of Dy^{3+} ions and, co-doping with appropriate sensitizer [20]. The present work attempts to produce high intensity yellow emission suitable for preparing efficient white LED with blue LEDs chip. The phosphor materials get excited from the ground state ($^6\text{H}_{13/2}$) to excited state of ($^4\text{F}_{7/2}$) [21]. After excitation, the incited electrons relax to the lower energy level by non-radiative (NR) transition lifted from the $^4\text{F}_{7/2}$ state to $^4\text{F}_{9/2}$. In non-radiative transition process, the energy is carried in the form of vibrations or motion of the electron without the luminescence process [22]. On reaching $^4\text{F}_{9/2}$ state the transfer to the ground state occurs by releasing the characteristic emission spectra from the excited state of $^4\text{F}_{9/2}$ to ground state of $^6\text{H}_{13/2}$ [23]. The radiative mechanism is held responsible for the high intensity yellow spectra of Dy^{3+} ions.

3.6 Decay time study

In order to confirm the ET between the Dy^{3+} ions, the luminescence decay profiles are assessed (Fig. 6). The decay time is recorded by exciting the sample material with 387 nm wavelength xenon flash lamp. The monitored emission at 572 nm ($^4\text{F}_{9/2}$ to $^6\text{H}_{13/2}$) reveals that the decay curves seem suitable for bi-exponential fitting [24]:

$$I(t) = A_1 e^{\left(-\frac{t}{\tau_1}\right)} + A_2 e^{\left(-\frac{t}{\tau_2}\right)}$$

$I(t)$ refers to Infer luminescence intensity, A_1 and A_2 indicate the amplitudes and τ_1 & τ_2 signify the decay times of the prepared sample. The Decay time of the synthesized phosphors can be evaluated from the following equation:

$$\tau^* = \frac{A_1 \tau_1^2 + A_2 \tau_2^2}{A_1 \tau_1 + A_2 \tau_2}$$

The decay time range of the $(\text{Ba}_{1-x}\text{Bi}_{0.01})\text{TiO}_3:\text{Dy}^{3+}$ phosphors is 0.04, 0.05, 0.02 and 0.03 ms under 387 nm and 572 nm wavelength for different doping concentrations of Dy ions in the host.

3.7 Photometric analysis:

The stalwart in illumination, Commission Internationale de l'Eclairage (CIE) has chalked out certain chromaticity colour coordinate parameters and colour correlated temperature (CCT) to study the features of the prepared phosphor compound. The chromaticity colour illustration of Dy^{3+} doped $(\text{Ba}_{1-x}\text{Bi}_{0.01})\text{TiO}_3$ phosphor material with varying concentration is explained in Fig.7. The CIE chromaticity coordinates of the synthesized phosphor calculated from the emission spectrum lie in the yellow region. Fig. 7 illustrates the chromaticity image of $(\text{Ba}_{1-x}\text{Bi}_{0.01})\text{TiO}_3$ doped Dy^{3+} for various doping concentrations. It is clearly noticed that by adjusting the concentration of Dy^{3+} ions, the photoluminescence colour is altered in the yellow region. It produces the CIE co-ordinates at $x=0.487, y=0.511$ & $x=0.488, y=0.522$ & $x=0.477, y=0.510$ & $x=0.475, y=0.508$ resulting in the concentrations, 0.01, 0.03, 0.05 and 0.07 respectively. These colour co-ordinates imply the presence of luminescence in the yellow region and its suitability for generating efficient WLEDs with blue LED chip.

Besides, the studied sample is subjected to CCT investigations and the results are evaluated from the renowned McCamy's relation from the given formula [25]:

$$\text{CCT} = -449n^3 + 3525n^2 - 6823.3n + 5520.33$$

n is equated for $x-0.332/y-0.186$ and x, y stands for colour coordinates of the present sample. The correlated colour temperatures (3081K, 3068K, 3134K and 3146 K) are recorded from the chromaticity colour coordinates by altering the concentration of Dy^{3+} ions. The above referred CCT, 3134 K reads the maximum concentration of Dy^{3+} generating efficacious yellow emission best suited for LED applications. Also, the CCT lower than 4,000 K is noteworthy for fashionable indoor lighting purposes [26].

4. Conclusion

To encapsulate, Bi^{2+} stimulated $\text{Ba}_{1-x}\text{TiO}_3:\text{x}\text{Dy}^{3+}$ yellow phosphor compound is manufactured successfully from single step solid state reaction method. The material is examined for its utility in indoor lighting applications. Changing the concentration levels of Dy^{3+} ions the efficient PL resultant concentration $x = 0.05$ is obtained by photoluminescence spectroscopy analysis. The consequential emission spectra arrived at on excitation at 387 nm generates an emission peak at 572 nm in the yellow region. The 387 nm excitation wavelength exhibits the most intense emission spectrum at $x = 0.05$ for the doping concentration of Dy^{3+} ions when its CIE reads $x = 0.477$, $y = 0.510$. The values are in consensus with the LEDs colour co-ordinate values. The 3134 K CCT calculated for the compound validates its feasibility for indoor lighting purposes. The outcomes of all the analyses conducted authenticate the sample phosphor best suited for yellow colour emission in the visible and naked-eye regions. Hence it is concluded that the compound is a potential candidate for light display and optoelectronic device implementations.

Declarations

Acknowledgments

The authors gratefully acknowledge the Sophisticated Analytical Instrument Facility, Indian Institute of Technology Madras, Chennai for the characterization study.

References

1. K. Munirathnam, G.R. Dillip, Shivanand Chaurasia, S.W. Joo, B. Deva Prasad Raju, N. John Sushma, Journal of Molecular Structure, 1118, 117 (2016).
2. Chun Che Lin, Ru-Shi Liu, J. Phys. Chem. Lett., 2, 1268 (2011).
3. G. Nag Bhargavi, Ayush Khare, Optics and Spectroscopy, 118, 902 (2015).
4. Qi Wang, Xiaoming Wang, Zhi Yang, Ninghkao Zhou, Yehao Deng, Jingjing Zhao, Xun Xiao, Peter Rudd, Andrew Moran, Yanfa Yan & Jinsong Huang, Nature communications, 10, 5633 (2019).
5. Alvaro Rosa, Domenico Tulli, Pau Castera, A.M. Gutierrez, Amadeu griol, Mariano Baquero, Bertrand Vilquin, Felix Eltes, Stefan Abel, Jean Fompeyrine, Pablo Sanchis, Optical materials express 7, 4329 (2017).
6. Abhilasha Jain, Ashwini Kumar, S.J Dhoble, D.R Peshwe, Materials Research Bulletin 70, 980 (2015).
7. Nisha Deopa, A.S. Rao, Journal of Luminescence 192, 832 (2017).
8. T R Jeena, A Moses Ezhil Raj and M Bououdina, Mater. Res. Express 4, 025019 (2017).
9. P. Yasaka, and J. Kaewkhao, AIP Conference Proceedings 1719, 020002 (2016).
10. Narayana Perumal Rajesh, G Subalakshmi, CK Jayasankar, Optical Materials 85 464 (2018).
11. K. Ganesh Kumar, P. Balaji Bhargav , K. Aravinth , Raja Arumugam , P. Ramasamy, Journal of Luminescence 223, 117126 (2020).

12. L.A.Xue , Y.Chen, R.J.Brook, Materials Science and Engineering: B 1, 193 (1988).
13. Dhananjay Kumar Singh, J. Manam, Ceramics International 44, 10912 (2018).
14. Kai Li, Rik Van Deun, ACS Appl. Electron. Mater. 2, 1735 (2020).
15. Yu-Chun Li, Yen-Hwei Changa, Yu-Feng Lin,Yee-Shin Chang, Yi-Jing Lin, Journal of Alloys and Compounds 439, 367 (2007).
16. Abhilasha Jain, Ashwini Kumar, S.J Dhoble, D.R Peshwe, Materials Research Bulletin 70, 980 (2015).
17. Dimple P.Dutta, A.Ballal, J.Nuwad, A.K.Tyagi, Journal of Luminescence 148, 230 (2014).
18. A.N. Yerpude, S.J. Dhoble, Micro & Nano Letters 7, 268 (2012).
19. T R Jeena, A Moses Ezhil Raj and M Bououdina, Mater. Res. Express 4, 025019 (2017).
20. Mengmeng Shang, Chunxia Li and Jun Lin, Chem. Soc. Rev., 43, 1372 (2014).
21. S. Badamasi, Y. A. Tanko, Y. A. Yamusa, N. N. Garba, Musa M. Najamuddeen, Fudma journal of sciences 4, 190 (2020).
22. Z. Burshtein, Opt. Eng. 49, 091005 (2010).
23. V. Himamaheswara Rao, P. Syam Prasad, M. Mohan Babu , P. Venkateswara Rao, T. Satyanarayana , Luís F. Santos , N. Veeraiah, Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 188, 516 (2018).
24. Rajesh Narayana Perumal, G Subalakshmi, CK Jayasankar, Journal of Alloys and Compounds, 732, 1 (2018).
25. S. Pravinraj, M. Vijayakumar, K. Marimuthu, Physica B: Physics of Condensed Matter. 509, 84 (2017).
26. Wonyoung Yang, Jin Yong Jeon, Environment Sustainability 12, 4051 (2020).

Figures

Figure 1

XRD patterns of $(\text{Ba}_{1-x}\text{Bi}_{0.01})\text{TiO}_3:\text{x}\text{Dy}^{3+}$ ($x=0, 0.01, 0.03, 0.05$ and 0.07) ions

Figure 2

Absorbance spectrum of $(\text{Ba}_{1-x}\text{Bi}_{0.01})\text{TiO}_3:\text{x}\text{Dy}^{3+}$ ($x=0, 0.01, 0.03, 0.05$ and 0.07) ions

Figure 3

Morphology structure of $(\text{Ba}_{1-x}\text{Bi}_{0.01})\text{TiO}_3:0.03\text{Dy}^{3+}$ phosphors with EDX analysis

Figure 4

Photoluminescence emission spectrum of $(\text{Ba}_{1-x}\text{Bi}_{0.01})\text{TiO}_3:\text{xDy}^{3+}$ ($x=0, 0.01, 0.03, 0.05$ and 0.07) ions

Figure 5

Schematic energy levels diagram of $(\text{Ba}_{1-x}\text{Bi}_{0.01})\text{TiO}_3:\text{x}\text{Dy}^{3+}$ ($x=0,0.01,0.03,0.05$ and 0.07) phosphors

Figure 6

Luminescence decay times of $(\text{Ba}_{1-x}\text{Bi}_{0.01})\text{TiO}_3:\text{x}\text{Dy}^{3+}$ ($x=0,0.01,0.03,0.05$ and 0.07) phosphors

Figure 7

Chromaticity diagram of $(\text{Ba}_{1-x}\text{Bi}_{0.01})\text{TiO}_3:\text{x}\text{Dy}^{3+}$ ($x=0,0.01,0.03,0.05$ and 0.07) phosphors