Promising Er$^{3+}$/Yb$^{3+}$-Codoped GdBiW$_2$O$_9$ Phosphor for Temperature Sensing by Upconversion Luminescence

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ABSTRACT: Yb$^{3+}$/Er$^{3+}$-codoped GdBiW$_2$O$_9$ phosphors are prepared via the solid-state route for application in upconversion temperature sensors. The structural analyses indicate that all phosphors possess a single-phased orthorhombic structure. Upon the excitation of a laser wavelength of 980 nm, Yb$^{3+}$/Er$^{3+}$-codoped GdBiW$_2$O$_9$ phosphors emanate green emission peaks, endorsed to the emission to the $^4I_{15/2}$ state from the $^4S_{3/2}$ and $^2H_{15/2}$ states, respectively, and the weak emission (red) from the $^4F_{9/2}$ state to the $^4I_{15/2}$ state of Er$^{3+}$ ion. The upconversion mechanism has been elucidated via the scheme of energy levels conferred from the pump power-induced upconversion characteristics. The temperature-dependent upconversion of GdBiW$_2$O$_9$ phosphors was investigated in detail along with the estimation of the stability and repeatability of the measurement. The obtained sensitivity data for the present materials with the corresponding sensing parameters show their probable outlook in temperature sensing applications.

1. INTRODUCTION

With the advancement of technology from macrodimension to micro- and nanoelectronics, the temperature in reduced dimensionality because of the Joule heating effect becomes non-negligible and severe to degrade the device performance.1−5 Therefore, the assessment of temperature in micro/nano aspects with an elevated precision is an immense confrontation to avert these thermal spikes.6−8 As the enormity and spot of these temperature spikes mainly depend on the device design and the accuracy of the integrated circuits, it is difficult to get the idea about the location of these hotspots. Moreover, different physical properties including refractive index and optical gain, which control the performance of the devices, are strongly temperature-dependent and hence can influence their utility, even leading to irretrievable smash up.9,10 This requires thermometry at micro-/nanoscale for the electronic devices during real operating conditions. However, the conventional thermometers, based on the expansion of metal or liquid with temperature, are unfeasible to be used in the micro-/nanoelectronic devices.1,11 Therefore, the recent development of noninvasive thermometers including nanoscale thermocouples, IR thermometers, and thermometers based on Raman spectroscopy, which can be incorporated into different micro-/nanoelectronic devices to provide the obligatory thermal information, has quickly become a reality.12−17 In recent years, thermometers based on luminescence are extensively used as noncontact thermometers, owing to their own advantages.

To date, several research works have been conceded on the temperature sensors based on luminescence thermometry, that is, the association between temperature and luminescence characteristics to accomplish thermal sensing.18−22 However, there exist two different approaches to quantify the temperature sensing performance of luminescent materials,23,24 including the measurement of fluorescent intensity ratio (FIR) and the decay time. On the basis of these approaches, various quantum dot materials, organic materials, pigments and dyes, and rare-earth ions were used to develop luminescent thermometers. Recently, FIR-based temperature sensors of the Er$^{3+}$/Yb$^{3+}$-doped luminescent materials, which exhibit efficient upconversion (UC) green emissions to the $^4I_{15/2}$ state from the $^4S_{3/2}$ and $^2H_{11/2}$ states, draw a lot of research attention.25−27 Various research works are available with Er$^{3+}$/Yb$^{3+}$-codoped materials for the thermal sensing properties with different hosts such as glass materials and phosphor materials. Yi et al.25 reported the influence of Er$^{3+}$/Yb$^{3+}$ codoping of the NaYF$_4$ host matrix for temperature sensing applications. Dong et al.28 reported the efficient temperature sensitivity of the CaF$_2$ host. All these researches obtained efficient temperature sensing with relative thermal sensitivity in the range of 1−2.1% K$^{-1}$. However, the temperature range for this temperature sensing was as low as 293−318 K. Liao et al.29 developed Gd$_2$TiO$_5$ phosphors for thermometry applications and obtained maximum sensitivities as $40.76 \times 10^{-4}$ K$^{-1}$ at 565 K. Y$_2$WO$_6$ crystals were synthesized by the hydrothermal method for thermometry applications by Chen et al.30 Other researchers reported the relative temperature sensitivity of the phosphor materials doped with rare-earth ions as 2−3% K$^{-1}$ (333−375
K), and to date, the utmost relative sensitivity was obtained as 5.53\% °K⁻¹.\(^{28,31,32}\) Some recent researches by the author’s group on different glass materials and oxide-based phosphors for temperature sensing applications were reported, and the optimum relative sensitivity was observed as 2.22\% °K⁻¹ in the temperature range 300–550 K.\(^{33}\) Though the temperature range of operation is elevated, still the relative sensitivity requires a large modification. Therefore, the present research work aims to develop new Er\(^{3+}/\)Yb\(^{3+}\)-based luminescent materials for temperature sensor applications.

Recently, tungstate materials have fascinated huge curiosity for luminescence applications because of the strong and broad absorption band of the W–O bond and its chemical and thermal stability.\(^{34–36}\) Owing to this, the tungstate materials including CdWO\(_4\), CaWO\(_4\), and KGe(WO\(_4\))\(_2\) can be used for various applications in the fields of scintillators, phosphors, and laser materials.\(^{37–39}\) However, there is a lack of proper research work reported on the luminescent thermometric characteristics of tungstate-based phosphors. Therefore, in this paper, a new Er\(^{3+}/\)Yb\(^{3+}\)-codoped phosphor based on the GdBiW\(_2\)O\(_9\) host was successfully developed via a solid-state approach, and the structure and UC characteristics were investigated. The influence of temperature on the UC characteristics was used to estimate the sensing parameters, including sensitivity and resolution, for the first time for this phosphor.

2. EXPERIMENTAL SECTION

2.1. Material Preparation. The synthesis of the novel GdBiW\(_2\)O\(_9\)Er\(^{3+}/\)Yb\(^{3+}\) phosphors was carried out by the well-known high-temperature solid-state method using Er\(_2\)O\(_3\), Yb\(_2\)O\(_3\), Gd\(_2\)O\(_3\), Bi\(_2\)O\(_3\), and WO\(_3\) as the starting ingredients. The key ingredients were ground homogeneously using a mortar–pestle, and their stoichiometric ratios were taken. The raw precursors were then transferred to alumina crucibles and were heated in a furnace at 600 °C for 10 h. The samples were cooled to room temperature, ground to fine powder, and again sintered for 8 h at 900 °C.

2.2. Material Characterization. The X-ray diffraction (XRD) patterns of the as-prepared phosphors were recorded by using an X-ray diffractometer (Ultima IV, Rigaku) with Cu K\(\alpha\) radiation. The particle size distributions along with the morphology were explored by using a Hitachi S-800 scanning electron microscope. A continuous-wave 980 nm diode laser was used to excite the phosphors, and the UC spectra were evidenced with a PMT detector directly attached to a monochromator. A heating attachment was linked to this instrument with a temperature controller to measure the temperature-induced UC.

3. RESULTS AND DISCUSSION

3.1. Phase Identification, Structural Analysis, and Morphology. A series of UC phosphors Gd\(_{1-x}\)Er\(_{x}\)BiW\(_2\)O\(_9\) (x = 0.005, 0.01, 0.015, 0.02, 0.025) were synthesized, and to identify the phases of the prepared UC materials, the XRD patterns of the as-prepared Gd\(_{1-x}\)Er\(_{x}\)BiW\(_2\)O\(_9\) were measured, which is shown in Figure 1. All the materials were obtained as single-phased compounds that matched well with the isostructurally similar orthorhombic EuBiW\(_2\)O\(_9\)\(^{40}\) having the ICSD database no. 183444.

For a better analysis of the crystal structure of the synthesized material, the Rietveld refinement was accomplished for Gd\(_{0.99}\)Er\(_{0.01}\)BiW\(_2\)O\(_9\) by utilizing the crystallographic data of the isotopic single-crystal structure of EuBiW\(_2\)O\(_9\) (ICSD no. 183444) as an initial model with the help of FullProf Suit software\(^{41}\) and is shown in Figure 2. The reliability factors of refinement were converged as R\(_p\) = 7.38\% and R\(_{wp}\) = 9.58\%, and it indicated the quality of the refinement. From the XRD refinement, it was clear that the crystal possessed an orthorhombic phase with the space group Pnma and lattice parameters: a = 31.802 Å, b = 5.594 Å, and c = 3.952 Å. The values of the results were smaller than those reported for the polymorphic EuBiW\(_2\)O\(_9\) of GdBiW\(_2\)O\(_9\). It could be explained on the basis of the difference in the ionic radius of Eu\(^{3+}\) (1.066 Å) and Gd\(^{3+}\) (1.053 Å). When Gd\(^{3+}\) ions are replaced by Eu\(^{3+}\), the volume of the unit cell becomes smaller and hence the lattice parameters.\(^{42}\)

All the refinement data are used to draw the crystal structure of the GdBiW\(_2\)O\(_9\) phase using VESTA software,\(^{43}\) as shown in Figure 3. Figure 3 displays the crystal structure of Gd\(_{0.99}\)Er\(_{0.01}\)BiW\(_2\)O\(_9\) based on the three-dimensional network of alternating (BiO\(_2\))^\(+\) and (Gd\(_3\)W\(_6\)O\(_{12}\))^\(+\) layers. These two layers are connected by the chains of the WO\(_3\) octahedron,
which are linked in the corner. The Gd atoms are coordinated by seven oxygen atoms, as shown in Figure 3b, and formed the GdO$_7$ polyhedra. These polyhedrons are attached to a chain by edge-sharing O atoms. The W atoms are coordinated to five and six oxygen atoms to form a trigonal bipyramidal WO$_5$ and an octahedrally coordinated WO$_6$ polygon, respectively, as shown in Figure 3b. Figure 3b also presents the coordination of Bi atoms with six oxygen atoms to form a distorted triangular prism as BiO$_6$, and multiple BiO$_6$ polygons are interconnected into a (BiO$_2$)$_{-}$ layer. Figure 3c displays the unit cell of the GdBiW$_2$O$_9$ phase.

Figure 4 presents the XRD data of the Yb-codoped Gd$_{0.99}$Er$_{0.01}$BiW$_2$O$_9$, with the Yb concentration varying as 5, 10, 15, 20, and 25 mol %. The XRD patterns were similar to the ICSD pattern no. 183444 and represent a single phase, devoid of any unidentified diffraction peaks from impurity, implying the easy incorporation of Yb$^{3+}$ in the framework of the Gd$_{0.99}$Er$_{0.01}$BiW$_2$O$_9$ phosphor. It was owing to the fact of the similarities of the ionic radii of the host cation to that of the doping cation.

![Figure 3](image)

Figure 3. (a) Crystal structure of Gd$_{0.99}$Er$_{0.01}$BiW$_2$O$_9$; (b) coordination geometry of various elements Gd, Bi, and W; and (c) unit cell structure of the Gd$_{0.99}$Er$_{0.01}$BiW$_2$O$_9$ phosphor.

![Figure 4](image)

Figure 4. XRD patterns of Gd$_{0.99-y}$Er$_{0.01}$Yb$_y$BiW$_2$O$_9$ phosphors for (a) $y$ = 0.05, (b) $y$ = 0.1, (c) $y$ = 0.15, (d) $y$ = 0.2, and (e) $y$ = 0.25.

Figure 5a,b shows the scanning electron microscopy (SEM) images of the Er$^{3+}$-ion-doped and Er$^{3+}$/Yb$^{3+}$-ion-codoped GdBiW$_2$O$_9$ phosphors synthesized via the solid-state reaction route. The distribution of particle size for both phosphors indicated the presence of particles less than 1 $\mu$m with agglomerated morphology. Figure 5c displays the transmission electron microscopy (TEM) image of the Er$^{3+}$/Yb$^{3+}$-ion-codoped GdBiW$_2$O$_9$ phosphor, and the inset image indicates the corresponding diffraction pattern of the visible crystal. Figure 5d displays the high-resolution TEM (HRTEM) image of the corresponding crystal. In the HRTEM and diffraction patterns, the well-crystallized phosphors are clearly visible, and the calculated interplanar spacing was obtained as 0.32 nm. It corresponds to the lattice constants of the customary GdBiW$_2$O$_9$ materials in the (111) plane.

![Figure 5](image)

Figure 5. SEM images of (a) Gd$_{0.99}$Er$_{0.01}$BiW$_2$O$_9$ and (b) Gd$_{0.84}$Er$_{0.01}$Yb$_{0.15}$BiW$_2$O$_9$ phosphors. (c) TEM image of the Gd$_{0.84}$Er$_{0.01}$Yb$_{0.15}$BiW$_2$O$_9$ phosphor; inset: corresponding TEM diffraction pattern. (d) HRTEM image of the Gd$_{0.84}$Er$_{0.01}$Yb$_{0.15}$BiW$_2$O$_9$ phosphor.

3.2. Room-Temperature UC and Energy-Level Diagram.

The UC spectra of the GdBiW$_2$O$_9$:Er$^{3+}$ phosphors excited via a 980 nm laser display several emission peaks around 525, 545, and 655 nm, as presented in Figure 7a. The emission band in the green region peaking at 525 nm (G1 band) and 545 nm (G2 band) is owing to the transition to the $^4I_{15/2}$ level from the $^2H_{11/2}$ and $^2S_{3/2}$ states of Er$^{3+}$ ions, respectively, and the band in the red region peaking at 655 nm (R band) is due to the $^4F_{9/2}$ $\rightarrow$ $^4I_{15/2}$ transition. With an
increasing Er\textsuperscript{3+} concentration, the UC intensity increased up to 1 mol % and then decreased, owing to the self-concentration quenching.\textsuperscript{45} Figure 7b shows the corresponding CIE coordinate, and it reveals the invariance of the color coordinate with the Er\textsuperscript{3+} concentration. When the Yb\textsuperscript{3+} ions are codoped in the optimized GdBiW\textsubscript{2}O\textsubscript{9}:Er\textsuperscript{3+} phosphors, the UC intensity increased manifold, owing to the Yb\textsuperscript{3+} ion to Er\textsuperscript{3+} ion energy transfer. However, the G1 band enhanced about 70 times, G2 band about 1.3 times, and R band enhanced about 60 times. The UC intensity of the Er\textsuperscript{3+}/Yb\textsuperscript{3+}-coactivated phosphor was seen to increase with the Yb\textsuperscript{3+} concentration up to the Er\textsuperscript{3+}/Yb\textsuperscript{3+} ratio of 1/15 and then decreased, as shown in Figure 7c. The increase in UC intensity pointed to the presence of more population in the excited levels from the ground-state level. The population might be increased because of the energy transfer from the Yb\textsuperscript{3+} to Er\textsuperscript{3+} ions. The decrease in UC intensity with the increase in the Er\textsuperscript{3+}/Yb\textsuperscript{3+} ratio over 1/15 could be explained with the concentration quenching phenomenon. The corresponding CIE coordinates (Figure 7d) indicated that the color coordinate position remained about the same with the variation of the Yb\textsuperscript{3+} concentration. However, the reason behind the dissimilar variation of different emission bands can be discussed on the basis of the energy-level scheme.

To explicate the UC phenomena and the energy plot, the UC emission of the optimized GdBiW\textsubscript{2}O\textsubscript{9}:Er\textsuperscript{3+},Yb\textsuperscript{3+} phosphor was evidenced with the variation of pump power (P), as viewed in Figure 8a. The corresponding CIE coordinate is shown in Figure 8b. It indicated that the pump power had a negligible effect on the CIE color coordinates. This was owing to the consistent doping and successful energy transfer from Yb\textsuperscript{3+} to Er\textsuperscript{3+} in the host. It demonstrated the stability of UC emission from the present host materials. The integral intensity (I) follows the relation I \propto P^n, where n is the number of incident photons involved in the present UC.\textsuperscript{46} From the logarithmic plot of integral UC intensity with pump power, the n value can be calculated. Figure 8c displays the linear variation for three UC emission bands, including G1, G2, and R. The n value for the G1 and G2 transitions were calculated as 1.97 and 2.27, and for
the R emission band, it was estimated as 2.04. These results exhibited the contribution of two-photon excitation in the UC mechanism.

Figure 8d displays the schematic diagram of the energy-level scheme for the GdBiW2O9:Er3+/Yb3+ phosphor based on the two-photon mechanism. Initially, the electrons from the ground-state 4I15/2 in the Er3+ ions were stimulated to the higher excited state 4I11/2, with the help of ground-state absorption. It is accomplished via the Yb3+ to Er3+ ion energy transfer. Then, the electrons were moved to the 4F7/2 level from the 4I11/2 state via excited state absorption as well as via the energy transfer route. Then, nonradiative relaxation to the lower levels of 4S3/2 and 2H11/2 occurred, which thereby influenced the 2H11/2 → 4I15/2 (G1) and 4S3/2 → 4I15/2 (G2) transitions. The probability of nonradiative relaxation to the 4S3/2 and 4H11/2 levels secures the emission intensity of the G1 and G2 bands. However, the population of the 2H11/2 level increased more than that of the 4S3/2 level after the codoping of the GdBiW2O9 host matrix.

Figure 9. (a) UC spectra of Gd0.84Er0.01Yb0.15BiW2O9 phosphors, varying the temperature from 303 to 498 K; (b) corresponding CIE coordinate diagrams of Gd0.84Er0.01Yb0.15BiW2O9 phosphors; (c) variation of the FIR value with temperature. The blue line indicates the Boltzmann fitting, and (d) logarithmic plot of the FIR value with the inverse of temperature for Gd0.84Er0.01Yb0.15BiW2O9 phosphors.
the Yb\(^{3+}\) ions, which results in the higher variation of G1 band compared to the G2 band. Therefore, a dissimilar variation of different emission bands was observed. The electron which relaxed to the \(^{4}I_{15/2}\) level and then stimulated to the \(^{4}F_{9/2}\) level can help in the \(^{4}F_{9/2} \rightarrow ^{4}I_{15/2}\) transition (R).

3.3. Luminescence Thermometry and Temperature Sensing. To check the dependence of the temperature on UC, a series of UC spectra were recorded with the optimized GdBiW\(_2\)O\(_9\):Er/Yb materials (Gd\(_{0.84}\)Er\(_{0.01}\)Yb\(_{0.15}\)BiW\(_2\)O\(_9\)) as a temperature function and displayed in Figure 9a. It is observed that with an increase in temperature from 303 to 498 K (30–225 °C), the intensity of the G1 band and the G2 band changed in opposite ways, whereas the peak positions remained unchanged. At room temperature (303 K), the intensity of the G1 band corresponding to the \(^{2}H_{11/2} \rightarrow ^{4}I_{15/2}\) transition was comparable to the G2 band intensity corresponding to that of the \(^{4}S_{3/2} \rightarrow ^{4}I_{15/2}\) transition. As the temperature increases, the luminescent intensity of the G1 band at about 525 nm shows a gradual increase, whereas the corresponding intensity of the G2 band first increases and then slightly decreases. It is owing to the low transition rate of \(^{2}H_{11/2} \rightarrow ^{4}I_{15/2}\) compared to \(^{4}S_{3/2} \rightarrow ^{4}I_{15/2}\) at high temperatures. The integral intensity of the phosphor decreased because of the increased lattice vibration, and, therefore, the upconverted green emission shows a small variation with a change in temperature. The variation in color emission with temperature was clearly observed in the CIE color coordinate diagram, as shown in Figure 9b. The integral intensity ratio between the 525 and 545 nm transitions [(\(^{2}H_{11/2} \rightarrow ^{4}I_{15/2}\))/\(^{4}S_{3/2} \rightarrow ^{4}I_{15/2}\)], generally known as fluorescence intensity ratio (FIR), was also measured with different temperatures and shown in Figure 9c. It is well-known that the \(^{2}H_{11/2}\) and \(^{4}S_{3/2}\) energy states are very close and separated by a very low energy gap (699 cm\(^{-1}\)), thus being thermally coupled.

Therefore, the electron population on these levels can be governed by Boltzmann’s distribution. However, with the rise in temperature, the population of the \(^{2}H_{11/2}\) and \(^{4}S_{3/2}\) levels changes in a different manner because of which the intensity ratio of FIR transitions might vary. The variation of this ratio is generally described as per the Boltzmann formula. It is in complete agreement with the present results. The variation of FIR shows a gradual increase with temperature, following the Boltzmann behavior according to the equation\(^{38}\)

\[ \text{FIR} = B \exp \left( \frac{-\Delta E}{kT} \right) \]  

(1)

where B is a constant factor (pre-exponential), \(\Delta E\) is the energy gap involving the two levels, T is the temperature (K), and k is the Boltzmann constant.

It can be understood from this equation that FIR is only temperature-dependent, therefore making the phosphor a suitable material for temperature sensing applications. The plot of FIR with the inverse of temperature (Figure 9d) gives a near-linear curve, thus verifying the phosphor’s suitability in the temperature sensing field.

The slope of the linear plot was obtained as \(-1091.71\) K and further used for the calculation of the \(\Delta E\) value. It was obtained as \(752\) cm\(^{-1}\), which was close to the energy gap sandwiched between the \(^{2}H_{11/2}\) and \(^{4}S_{3/2}\) levels, as observed from the emission energy-level diagram in the present case.

To know more about the sensing ability of the GdBiW\(_2\)O\(_9\):Er,Yb phosphor, the temperature-induced variation of the rate of FIR (R)\(^{3,4}\)

\[ S = \left| \frac{\partial R}{\partial T} \right| = R \frac{\Delta E}{kT^2} \]  

(2)

In the present case, it was estimated to be 0.0107 K\(^{-1}\). This value was seen to increase to 0.0174 K\(^{-1}\), with an increase in temperature up to 450 K, and then decreased.

The variation of sensitivity with temperature is shown in Figure 10a. Various researches were reported on luminescence-based thermometry, and Table 1 summarizes the results with the present research. These comparisons indicate the suitability of the present phosphor for temperature sensing applications. The sensitivity value is used further to estimate the relative sensor sensitivity via the normalization of the temperature-dependent sensitivity as follows\(^3\)

![Table 1. List of Materials with Maximum Sensitivity and Temperature Range](Image)

| phosphor | sensitivity (k^-1) | temperature range (K) | refs |
|----------|-------------------|-----------------------|------|
| Gd\(_{0.84}\)Er\(_{0.01}\)Yb\(_{0.15}\)BiW\(_2\)O\(_9\) | 0.0039 | 300–900 | 50 |
| Na\(_2\)Y\(_2\)O\(_3\):Er\(_{3+}\)/Yb\(_{3+}\) | 0.0026 | 288–328 | 51 |
| Na\(_2\)Y\(_2\)O\(_3\):Er\(_{3+}\)/Gd\(_{3+}\)/Nd\(_{3+}\) | 0.0029 | 93–673 | 52 |
| Na\(_2\)Y\(_2\)O\(_3\):Er\(_{3+}\)/Yb\(_{3+}\) | 0.0028 | 300–690 | 33 |
| Na\(_2\)Gd\(_2\)O\(_2\):Er\(_{3+}\)/Yb\(_{3+}\) | 0.0037 | 303–543 | 53 |
| Ca\(_2\)O\(_2\):Ho\(_{3+}\)/Yb\(_{3+}\)/Mg\(_{2+}\) | 0.0066 | 303–543 | 54 |
| Y\(_2\)O\(_3\):Er\(_{3+}\)/Yb\(_{3+}\) | 0.0117 | 302–582 | 55 |
| Ca\(_2\)O\(_2\):Ho\(_{3+}\)/Yb\(_{3+}\) | 0.005 | 303–923 | 56 |
| La\(_2\)CaZn\(_2\):Er\(_{3+}\)/Ho\(_{3+}\)/Yb\(_{3+}\) | 0.00625 | 303–573 | 47 |
| GdB\(_2\)W\(_2\)O\(_9\) | 0.0174 | 303–498 | this work |
Er3+/Yb3+ ions were synthesized by the solid-state method. The structural refinement analysis indicated that the phosphors crystallized in an orthorhombic crystal system and the doping/codoping of RE ions keep the crystal structure unchanged. The energy exchange mechanism between the Er3+ and Yb3+ ions. The contribution of two-photon absorption was verified from the measured 4I15/2 → 4I11/2 transitions of Er3+ ions, respectively, which were enhanced manifold after the codoping of Yb3+, and the explanation was given on the basis of the energy exchange mechanism between the Er3+ and Yb3+ ions. The contribution of two-photon absorption was verified from the measured 4I15/2 → 4I11/2 transitions of Er3+ ions, respectively, which were enhanced manifold after the codoping of Yb3+.

\[ S_r = \left( \frac{1}{S} \frac{\partial S}{\partial T} \right) \times 100\% \]  

(3) The variation of relative sensitivity with temperature is shown in Figure 10b.

The reproducibility and stability of the sensors are the indispensable parts of sensitivity estimation.\(^{(4)}\) The variations of the FIR value with the increase in temperature from 300 to 500 K and the corresponding decrease in temperature from 550 to 300 K for the consecutive two cycles are shown in Figure 11a.

An insignificant hysteresis behavior was found in the present case. It indicated an exceptional reversible character of the present phosphor. The FIR values were also recorded at 303, 398, and 498 K incessantly for the 120 min cycle test with 20 min intervals. During this time, the sample position was kept undisturbed.

The FIR value remained about the same throughout the 2 h experiment time and is shown in Figure 11b. These two characteristics also vouch for the use of the present phosphor as a suitable material for practical appliances.

4. CONCLUSIONS

In summary, GdBiW2O9 phosphors doped with Er3+ ions and Er3+/Yb3+ ions were synthesized by the solid-state method. The structural refinement analysis indicated that the phosphors crystallized in an orthorhombic crystal system and the doping/codoping of RE ions keep the crystal structure unchanged. Using the laser excitation of 980 nm, the Er3+ phosphor exhibited strong green UC emissions from the \(^{2}H_{11/2} \rightarrow \) \(^{4}S_{3/2} \) transitions of Er3+ ions, respectively, which were enhanced manifold after the codoping of Yb3+, and the explanation was given on the basis of the energy exchange mechanism between the Er3+ and Yb3+ ions. The contribution of two-photon absorption was verified from the measured 4I15/2 → 4I11/2 transitions of Er3+ ions, respectively, which were enhanced manifold after the codoping of Yb3+, and the explanation was given on the basis of the energy exchange mechanism between the Er3+ and Yb3+ ions. The contribution of two-photon absorption was verified from the measured 4I15/2 → 4I11/2 transitions of Er3+ ions, respectively, which were enhanced manifold after the codoping of Yb3+.
In the document, the author discusses the use of optical thermometry in various applications. The text highlights the use of luminescence thermometry, which involves using materials that emit light at different temperatures to measure temperature. The author references several studies on the development of novel optical thermometers using nanoparticles and nanomaterials.

For example, the author mentions the development of optomechanical luminescence thermometers using nanoparticles. These thermometers can be self-calibrated and provide highly penetrative fluorescence bioimaging. They are particularly useful for in vivo imaging and diagnostics.

The text also discusses the use of optically sensitive materials for temperature sensing, including the use of Eu3+-activated SrZrO3 hollow spheres for nanothermometers. These materials have been used to develop multi-functional nanoprobes for temperature sensing and optical imaging.

Overall, the document provides a comprehensive overview of the advancements in optical thermometry and the potential applications of these technologies in various fields, including medicine and materials science.
(45) Wang, M.; Tian, Y.; Zhao, F.; Li, R.; You, W.; Fang, Z.; Chen, X.; Huang, W.; Ju, Q. Alleviating the Emitter Concentration Effect on Upconversion Nanoparticles via an Inert Shell. *J. Mater. Chem. C* 2017, 5, 1537−1543.

(46) Dissanayake, K. T.; Rabuffetti, F. A. Infrared to-Visible Upconversion Luminescence in Er:Yb:SrFBr Nanocrystals. *J. Mater. Chem. C* 2016, 4, 2447−2451.

(47) Kumar, V.; Som, S.; Dutta, S.; Das, S.; Swart, H. C. Influence of Ho3+ Doping on the Temperature Sensing Behavior of Er3+-Yb3+ Doped La2CaZnO5 Phosphor. *RSC Adv.* 2016, 6, 84914−84925.

(48) Wang, X.-d.; Wolfbeis, O. S.; Meier, R. J. Luminescent Probes and Sensors for Temperature. *Chem. Soc. Rev.* 2013, 42, 7834−7869.

(49) Zheng, K.; Liu, Z.; Lv, C.; Qin, W. Temperature Sensor Based on the UV Upconversion Luminescence of Gd3+ in Yb3+-Tm3+-Gd3+ Codoped NaLuF4 Microcrystals. *J. Mater. Chem. C* 2013, 1, 5502−5507.

(50) Singh, S. K.; Kumar, K.; Rai, S. B. Er3+/Yb3+ Codoped Gd2O3 Nano-Phosphor for Optical Thermometry. *Sens. Actuators, A* 2009, 149, 16−20.

(51) Klier, D. T.; Kumke, M. U. Upconversion NaYF4:Yb:Er Nanoparticles Co-Doped with Gd3+ and Nd3+ for Thermometry on the Nanoscale. *RSC Adv.* 2015, 5, 67149−67156.

(52) Du, P.; Luo, L.; Yu, J. S. Facile Synthesis of Er3+/Yb3+-Codoped NaYF4 Nanoparticles: A Promising Multifunctional Upconverting Luminescent Material for Versatile Applications. *RSC Adv.* 2016, 6, 94539−94546.

(53) Chen, D.; Wan, Z.; Zhou, Y.; Huang, P.; Zhong, J.; Ding, M.; Xiang, W.; Liang, X.; Ji, Z. Bulk Glass Ceramics Containing Yb3+/Er3+:β-NaGdF4 Nanocrystals: Phase-Separation-Controlled Crystallization, Optical Spectroscopy and Upconverted Temperature Sensing Behavior. *J. Alloys Compd.* 2015, 638, 21−28.

(54) Dey, R.; Kumari, A.; Soni, A. K.; Rai, V. K. CaMoO4:Ho3+-Yb3+−Mg2+ Upconverting Phosphor for Application in Lighting Devices and Optical Temperature Sensing. *Sens. Actuators, B* 2015, 210, 581−588.

(55) Mahata, M. K.; Tiwari, S. P.; Mukherjee, S.; Kumar, K.; Rai, V. K. YVO4:Er3+/Yb3+ Phosphor for Multifunctional Applications. *J. Opt. Soc. Am. B* 2014, 31, 1814−1821.

(56) Xu, W.; Zhao, H.; Li, Y.; Zheng, L.; Zhang, Z.; Cao, W. Optical Temperature Sensing through the Upconversion Luminescence from Ho3+/Yb3+ Codoped CaWO4. *Sens. Actuators, B* 2013, 188, 1096−1100.