(Ba,Sr)TiO$_3$:RE perovskite phosphors (RE = Dy, Eu): nitrate pyrolysis synthesis, enhanced photoluminescence, and reversible emission against heating

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A series of (Ba,Sr)TiO$_3$ phosphors singly doped with Eu$^{3+}$ and Dy$^{3+}$ were successfully synthesized using the nitrate pyrolysis method at 750 °C. Eu$^{3+}$ or Dy$^{3+}$ single-doped BaTiO$_3$ retained the tetragonal crystal structure of the host, while the Sr$^{2+}$-substituted (Ba,Sr)TiO$_3$:RE$^{3+}$ (RE$^{3+} =$ Eu$^{3+}$ or Dy$^{3+}$) experienced a phase transformation from tetragonal to cubic phase with a unit cell shrinkage. For Eu$^{3+}$ doped phosphors, BaTiO$_3$:Eu$^{3+}$ (x = 0.02–0.10) exhibited red photoluminescence and the highest intensity of emission belonged to the optimal-doped BaTiO$_3$:Eu$^{3+}$ (x = 8 mol%). Moreover, the substitution of 30 mol% Sr$^{2+}$ for Ba$^{2+}$ (that is Ba$_{0.7}$Sr$_{0.3}$TiO$_3$:Eu$^{3+}$, x = 8 mol%) further enhanced the emission intensity of BaTiO$_3$:Eu$^{3+}$ (x = 8 mol%). For Dy$^{3+}$ doped phosphors, BaTiO$_3$:Dy$^{3+}$ (x = 0.02–0.10) showed yellow photoluminescence and the highest light intensity was from the optimal-doped BaTiO$_3$:Dy$^{3+}$ (x = 4 mol%). In addition, the substitution of 20 mol% Sr$^{2+}$ for Ba$^{2+}$ (the phosphor Ba$_{0.8}$Sr$_{0.2}$TiO$_3$:Dy$^{3+}$, x = 4 mol%) induced further increase in emission intensity of BaTiO$_3$:Dy$^{3+}$ (x = 4 mol%). The emission intensities at higher temperature of 100 °C retained about 70% and 90% of the initial values at room temperature (RT) for the optimal BaTiO$_3$:Eu$^{3+}$ (x = 8 mol%) and BaTiO$_3$:Dy$^{3+}$ (x = 4 mol%) phosphors, respectively, while the emission intensities at the temperature of 100 °C retained about 60% and 80% of the initial intensities at RT for the optimal Sr$^{2+}$-substituted Ba$_{0.5}$Sr$_{0.5}$TiO$_3$:Eu$^{3+}$ (x = 8 mol%) and Ba$_{0.8}$Sr$_{0.2}$TiO$_3$:Dy$^{3+}$ (x = 4 mol%) phosphors, respectively. It is worth noting that on cooling down to RT again from 210 °C, the BaTiO$_3$:Dy$^{3+}$ (x = 4 mol%) phosphor exhibited excellent luminescent thermal stability (with a high activation energy of 0.387 eV) and the strongest recovery (~95%) of PL emission among the series of phosphors. The as-prepared phosphors with optimal compositions would be good candidates for the applications in lighting, display, and related fields.

1. Introduction

In recent years, trivalent rare-earth (RE) ions doped phosphors have been developed rapidly because of their gradually widespread applications in many fields, such as field emission displays (FEDs), cathode-ray tubes (CRTs), light-emitting diodes (LEDs), plasma display panels (PDPs), colour televisions, and optical fiber telecommunication. Currently, LEDs are considered as one of the most important solid-state illumination sources owing to their environment-friendly nature, low power consumption, as well as promising applications. In the use of LED devices, heat generates in phosphor materials coated on the LED chip, resulting in the increase in phosphor layer temperature to 120–150 °C. Generally, the luminescence thermal quenching of phosphors occurs at such temperatures, which further decrease the performance of LED devices. It is well known that thermal stability of phosphors is one of the important parameters for evaluating the performance of LEDs, which influences lighting efficiency and colour performance. Thus, the detailed investigation of phosphors’ thermal stability is of great significance for understanding their practical properties and exploring their potential in various applications. Furthermore, more efforts should be made to develop and research some promising phosphors that maintain their emission intensities and colour coordinates at higher temperatures for applications in lighting.

The selection of appropriate host materials as well as dopants (for example rare earth ions), is a crucial for obtaining phosphors with improved photoluminescence properties. Perovskite structured titanate is a traditional material that has been widely used in functional materials fields for its excellent dielectric and ferroelectric properties. Moreover, increasing

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number of researchers have recently begun to pay more attention to the optical properties of perovskite structured titanate due to its low phonon energy and stable physical and chemical properties.\textsuperscript{10,11} The preparation conditions of titanate are not very harsh and hence, titanate phosphors have always been the subject of attention. Concerning dopants, Eu\textsuperscript{3+} is usually selected because of its specific energy level and high radiative recombination rate. Dy\textsuperscript{3+} is also an important dopant in many luminescent materials owing to its various transitions between different energy levels, leading to three special emission bands of blue (480 nm), yellow (575 nm) and red (625 nm). Numerous research reports have exhibited that Dy\textsuperscript{3+} has been applied in phosphors for the purpose of lighting applications.

In the past decades, several reports have been published on the luminescent properties of lanthanide (Ln\textsuperscript{3+} or RE\textsuperscript{3+}) doped BaTiO\textsubscript{3} and SrTiO\textsubscript{3}.\textsuperscript{12-19} Recently, RE\textsuperscript{3+} (Gd\textsuperscript{3+}, Dy\textsuperscript{3+}, Tb\textsuperscript{3+}, Lu\textsuperscript{3+})-doped BaTiO\textsubscript{3}-based phosphors with tetragonal structure were synthesized by a modified solid-state reaction at 1000 °C, and their photoluminescence properties have been studied. It has been found that Gd\textsuperscript{3+} ion doped BaTiO\textsubscript{3} phosphor showed the strongest yellow emission intensity compared to the other phosphors.\textsuperscript{20} The preparation of bulk BaTiO\textsubscript{3}:Pr\textsuperscript{3+} by a solid-state reaction and nanocrystalline BaTiO\textsubscript{3}:Pr\textsuperscript{3+} by a solvothermal method were also studied. It was found that the photoluminescence (PL) intensity of the bulk material was stronger than that of the nanocrystalline BaTiO\textsubscript{3}:Pr\textsuperscript{3+}, which was attributed to more surface defects on nanocrystal powder.\textsuperscript{21} Furthermore, SrTiO\textsubscript{3}:Pr\textsuperscript{3+} phosphors with different morphologies have been synthesized by three different methods: high-temperature solid-state reaction, solvothermal synthesis, and sol-gel synthesis. The red-emitting phosphors possess cubic phase, and the PL intensity of SrTiO\textsubscript{3}:Pr\textsuperscript{3+} synthesized by the solid-state method was the strongest compared to the phosphors synthesized by the other two methods.\textsuperscript{19} However, to the best of our knowledge, there are few reports on the luminescence intensity, thermal stability, and emission recovery against heating/cooling of Ba\textsubscript{1-x}Sr\textsubscript{x}TiO\textsubscript{3}-based phosphors concerning the effects of Sr\textsuperscript{2+} ion substitution and rare earth activators.

In this prospective study, we designed and prepared a series of comparable Eu\textsuperscript{3+} and Dy\textsuperscript{3+} singly-doped (Ba, Sr)TiO\textsubscript{3} phosphors for the first time, and the luminescence thermal stability of phosphors was evaluated systematically. The resultant phosphors exhibited enhanced emission via the substitution of Sr\textsuperscript{2+} for Ba\textsuperscript{2+} in (Ba, Sr)TiO\textsubscript{3}:RE\textsuperscript{3+} (RE\textsuperscript{3+} = Eu\textsuperscript{3+} or Dy\textsuperscript{3+}). Herein, excellent luminescence stability against heating in Dy\textsuperscript{3+} doped BaTiO\textsubscript{3} phosphors was found, presenting a promising phosphor candidate for lighting applications.

2. Experimental

A series of Eu\textsuperscript{3+} and Dy\textsuperscript{3+} singly-doped BaTiO\textsubscript{3}:xEu\textsuperscript{3+} (x = 0.02–0.10), BaTiO\textsubscript{3}:xDy\textsuperscript{3+} (x = 0.02–0.10), Ba\textsubscript{1-x}Sr\textsubscript{x}TiO\textsubscript{3}:xEu\textsuperscript{3+} (y = 0–1.0) and Ba\textsubscript{1-x}Sr\textsubscript{x}TiO\textsubscript{3}:xDy\textsuperscript{3+} (y = 0–1.0) phosphors were designed and synthesized using the nitrate pyrolysis method. Herein, it has to be emphasized that the doping sites of rare-earth Eu\textsuperscript{3+} and Dy\textsuperscript{3+} in the BaTiO\textsubscript{3} host depended on many factors, including the ionic radius, dopant concentration, and electronegativity. In fact, large lanthanide ions such as La\textsuperscript{3+} and Ce\textsuperscript{3+} replaced the Ba\textsuperscript{2+} sites in the BaTiO\textsubscript{3} lattice, whereas small lanthanide ions such as Dy\textsuperscript{3+}, Ho\textsuperscript{3+}, and Er\textsuperscript{3+} showed amphoteric behaviour in the BaTiO\textsubscript{3} lattice and could get incorporated at both Ba\textsuperscript{2+} and Ti\textsuperscript{4+} sites in the lattice with comparable probabilities.\textsuperscript{22-23} In our experiments, the starting raw materials were barium nitrate (Ba(NO\textsubscript{3})\textsubscript{2}, 99.9% purity), strontium nitrate (Sr(NO\textsubscript{3})\textsubscript{2}, 99.9% purity), tetrabutyl titanate (C\textsubscript{4}H\textsubscript{8}O\textsubscript{2}Ti, 98% purity), europium(III) oxide (Eu2O\textsubscript{3}, 99.9% purity), dysprosium(III) oxide (Dy2O\textsubscript{3}, 99.9% purity), acetylacetone (C\textsubscript{6}H\textsubscript{4}CO\textsubscript{2}H), and absolute ethyl alcohol (CH\textsubscript{3}CH\textsubscript{2}OH). During the preparation, titanium solution was obtained by adding appropriate amounts of C\textsubscript{4}H\textsubscript{8}O\textsubscript{2} and CH\textsubscript{3}CH\textsubscript{2}OH to tetrabutyl titanate (the molar ratio of tetrabutyl titanate, CH\textsubscript{3}CH\textsubscript{2}OH, and C\textsubscript{4}H\textsubscript{8}O\textsubscript{2} was 1 : 4 : 0.2). Typically, Eu\textsubscript{2}O\textsubscript{3} and Dy\textsubscript{2}O\textsubscript{3} were dissolved in diluted nitric acid (HNO\textsubscript{3}) solutions with constant stirring and heating to obtain the nitrate solutions of Eu(NO\textsubscript{3})\textsubscript{3} (0.03 mol L\textsuperscript{-1}) and Dy(NO\textsubscript{3})\textsubscript{3} (0.03 mol L\textsuperscript{-1}). Ba(NO\textsubscript{3})\textsubscript{2} (0.04 mol) and Sr(NO\textsubscript{3})\textsubscript{2} (0.04 mol) were separately dissolved in deionized water (200 mL) for dilution. Ba(NO\textsubscript{3})\textsubscript{2} and Sr(NO\textsubscript{3})\textsubscript{2} aqueous solutions were first mixed and then added to the titanium solution to obtain a mixed solution. Eventually, Eu(NO\textsubscript{3})\textsubscript{3} (0.03 mol L\textsuperscript{-1}) or Dy(NO\textsubscript{3})\textsubscript{3} (0.03 mol L\textsuperscript{-1}) was added to the above mixed solution. The amount of each solution added was calculated based on the stoichiometric ratio of the corresponding chemical formula. The solution mixture was then stirred on a magnetic stirrer for 4 hours, followed by drying in a box furnace at 160 °C for 6 h. Following this, the as-obtained mixture was preheated at 600 °C for 4 h in air to decompose the nitrates, and then sintered at certain temperatures for some time in air to derive the final powder products. We tried to optimize the crystallization conditions, including sintering temperature and time, for the purpose of fabricating (Ba, Sr)TiO\textsubscript{3} phosphors at a fixed Eu\textsuperscript{3+} or Dy\textsuperscript{3+} doping concentration. Based on the phase purity and luminescence intensity analyses of samples, the optimal sintering condition was considered as 750 °C for 4 hours to obtain the desired phosphors. As a result, throughout this article, we focussed on the phosphors prepared under the above optimal sintering conditions.

The X-ray diffraction (XRD) data were collected by a Bruker D8 Advance diffractometer (Cu K\textalpha radiation, \(\lambda = 1.5405\) Å) in the 2\(\theta\) range from 20° to 80° to characterize the crystal phase. The phosphors used for the XRD analysis were pressed into a thin disc on a quartz slide before testing. The morphology of the powder samples was observed using a S-4800 Field Emission Scanning Electron Microscope (SEM) (Hitachi, Tokyo, Japan). For SEM observation, the phosphors were processed by ultrasonically dispersing in ethanol and then putting the drops on an aluminum substrate. Photoluminescence (PL), PL excitation (PLE) spectra, and temperature-dependent luminescence properties (from room temperature to 210 °C) were measured by a Hitachi F-4600 fluorescence spectrophotometer, equipped with a 150 W Xe lamp as the excitation source. The scan speed was fixed at 240 nm min\textsuperscript{-1}, and the excitation slit as well as the emission slit width were set as 2.5 nm. In PL spectrum tests, the
size of the powder container was kept constant in the Hitachi F-4600 fluorescence spectrophotometer. Hence, the amount of phosphor powder put into the container was the same which ensured that the test results were comparable. Also, the comparison of luminescence intensities of different samples was carried out by calculating the integral area under the emission peak of each phosphor. The decay times of Eu$^{3+}$-doped phosphors (monitored at 615 nm with the 465 nm excitation) and Dy$^{3+}$-doped phosphors (monitored at 573 nm with the 452 nm excitation) were measured with a FLS 980 fluorescence spectrofluorometer equipped with photonics µF2 (Edinburgh Instruments, UK).

3. Results and discussion

3.1 Morphology, crystal structure, and photoluminescence of BaTiO$_3$:RE phosphors

The representative SEM morphology images of undoped BaTiO$_3$, BaTiO$_3$:$xEu^{3+}$ (x = 8 mol%), and Ba$_{0.7}$Sr$_{0.3}$TiO$_3$:$xEu^{3+}$ (x = 8 mol%) phosphors indicated the irregular morphology of particles consisted of agglomerated short-rod-like sub-particles, as shown in Fig. 1. The average particle sizes of BaTiO$_3$, BaTiO$_3$:$xEu^{3+}$ (x = 8 mol%), and Ba$_{0.7}$Sr$_{0.3}$TiO$_3$:$xEu^{3+}$ (x = 0 = 8 mol%) phosphors were almost the same with the agglomerated irregular morphology.

The XRD patterns of Eu$^{3+}$ and Dy$^{3+}$ singly-doped BaTiO$_3$ samples with different doping concentrations are shown in Fig. 2a and b, respectively. In all the samples doped with different Eu$^{3+}$ concentrations, a tetragonal main phase of BaTiO$_3$ (JCPDF #79-2264, with lattice constants a = b = 3.9998 Å, c = 4.018 Å) was observed due to the appearance of all the standard XRD peaks of the tetragonal phase. The diffraction patterns of Dy$^{3+}$ doped BaTiO$_3$ phosphors also agreed well with the literature values of tetragonal BaTiO$_3$ (JCPDF #79-2264, with lattice constants a = b = 3.9998 Å, c = 4.018 Å), and there was no detectable impurity or shifting of XRD peaks after doping rare-earth ions into the BaTiO$_3$ host.

Room temperature PL and PLE spectra of BaTiO$_3$:$xEu^{3+}$ (x = 0.02–0.10) phosphors are depicted in Fig. 3. As shown in the figure, the PL spectra of BaTiO$_3$:$xEu^{3+}$ under excitation at 394 nm are indicated in Fig. 3a. With the increase in Eu$^{3+}$ content up to 8 mol%, the emission intensity increased to a maximum and then decreased with the further increase in concentration of Eu$^{3+}$, which was attributed to the concentration quenching effect. At the same time, the dependence of the emission intensity on the concentration of Eu$^{3+}$ is shown in the inset of Fig. 3a. As shown in Fig. 3a, in the spectral range from 560 nm to 680 nm, there are four peaks centred at 580, 593, 615 and 655 nm, which were assigned to the transitions from the higher excited state (5D$_0$) to the lower states (7F$_0$, 7F$_1$, 7F$_2$, 7F$_3$) of Eu$^{3+}$ owing to the splitting of the 4f energy level of Eu$^{3+}$.

It is generally accepted that the strongest peak at 615 nm (red emission) corresponds to the electric dipole transition 5D$_0$ → 7F$_2$ and its intensity is strongly influenced by the ligand ions around Eu$^{3+}$ in the host. The second strong emission peak at 593 nm belongs to the magnetic dipole transition 5D$_0$ → 7F$_1$. Interestingly, the intensity ratio of (5D$_0$ → 7F$_2$)/(5D$_0$ → 7F$_1$) is usually regarded as a measurement of the site symmetry around Eu$^{3+}$ in the host. If Eu$^{3+}$ occupies an inversion symmetry, a dominant red-orange emission will be obtained according to the magnetic dipole transition 5D$_0$ → 7F$_1$. In contrast, red emission will predominate in the spectra due to the electric dipole transition 5D$_0$ → 7F$_2$. In this study, we can see that the (5D$_0$ → 7F$_2$)/(5D$_0$ → 7F$_1$) ratio increases with the increase in x value up to 0.08 and then decreases, as shown in Fig. 4. When more Eu$^{3+}$ ions were doped, the distortion of the ligand ions around Eu$^{3+}$ was severe, indicating that more Eu$^{3+}$ ions occupied the non-inversion symmetry sites in the host. The intensity of the electric dipole transition 5D$_0$ → 7F$_2$ was more sensitive to the forthcoming distortion than the magnetic dipole transition 5D$_0$ → 7F$_1$. Therefore, the increase in the (5D$_0$ → 7F$_2$)/(5D$_0$ → 7F$_1$) ratio could be witnessed with the increasing x value up to 0.08. Furthermore, the PL intensity started to decrease on 8 mol% Eu$^{3+}$ doping. The reduction in intensity is mainly attributed to the non-radiative transition, which contributed to the concentration quenching. The PLE spectra (monitored at 615 nm) are shown in Fig. 3b. A strong excitation peak is centred...
at 465 nm, which corresponds to the $^7F_0 \rightarrow ^5D_2$ (f-f) transition of Eu$^{3+}$. The other excitation peaks belonged to different f-f transitions: $^7F_0 \rightarrow ^5D_4$ (360 nm), $^7F_0 \rightarrow ^5L_6$ (394 nm), $^7F_0 \rightarrow ^5D_3$ (412 nm), and $^7F_0 \rightarrow ^5D_1$ (532 nm). The PLE spectrum consists of two regions of charge transfer transitions (CTT): (i) between the host and Eu$^{3+}$ ions and (ii) f-f intra-transition in Eu$^{3+}$. However, in the present research, the charge transfer (O$_2$p orbitals of O$_2$ and the partially filled f orbitals of Eu$^{3+}$ in the perovskite BaTiO$_3$) was not found explicitly in the region of 230–320 nm, which was possible due to the weak covalent bonding between BaTiO$_3$ host were designed and prepared to cause crystal field changes to enhance the emission.

3.2 Crystal structure and photoluminescence of Sr$^{2+}$-substituted (Ba,Sr)TiO$_3$:RE phosphors

Based on the fixed optimal doping content of activator Eu$^{3+}$ (8 mol%) or Dy$^{3+}$ (4 mol%) in BaTiO$_3$ (mentioned in the Section 3.1), phosphors with smaller Sr$^{2+}$ ions incorporated into the BaTiO$_3$ host were designed and prepared to cause crystal field changes to enhance the emission.

The XRD patterns of the as-prepared Ba$_{1-y}$Sr$_y$TiO$_3$:xEu$^{3+}$ (x = 8 mol%) and Ba$_{1-y}$Sr$_y$TiO$_3$:xDy$^{3+}$ (x = 4 mol%) (y is the substitution value of Sr$^{2+}$ for Ba$^{2+}$, y = 0.0–1.0) phosphors with different Sr$^{2+}$ contents are presented in Fig. 6a and 7a, respectively. In addition, Fig. 6b and 7b show the magnified diffraction peaks, in which the value of 2$\theta$ is 45–49° for all the samples. From Fig. 6b and 7b, it is clear that there exists a clear diffraction peak shifting towards the high-angle direction, which suggests that the lattice parameter gradually decreased with the increase in substitution of Sr$^{2+}$ for the Sr-substituted (Ba,Sr)TiO$_3$:RE$^{3+}$ (RE$^{3+} = $Eu$^{3+}$, Dy$^{3+}$) phosphors. This also suggested that the substitution of Sr$^{2+}$ was achieved in BaTiO$_3$:RE$^{3+}$ phosphors. From Fig. 6b and 7b, it could be seen that the (002)

Fig. 5a. It is clearly observed that the PL intensities increased when x ≤ 0.04, and then suddenly decreased when the content of Dy$^{3+}$ is more than 4 mol% due to concentration quenching, as mentioned for the BaTiO$_3$:xEu$^{3+}$ phosphors. Thus, the optimal doping concentration of Dy$^{3+}$ in the BaTiO$_3$ host to gain the strongest PL emission intensity was obtained, viz., 4 mol%.

Fig. 5 shows the PL and PLE spectra of BaTiO$_3$:xDy$^{3+}$ (x = 0.02–0.10) phosphors. In Fig. 5a, a broad peak can be seen in the yellow light emission region centred at 573 nm, corresponding to the $^7F_0 \rightarrow ^5D_2$ (f-f) transition of Eu$^{3+}$. The dependence of the emission intensity on the content of Dy$^{3+}$ is illustrated in the inset of

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peak and the (200) peak of the tetragonal phase at around $2\theta = 46^\circ$ gradually converted into a single (200) peak of the cubic phase, illustrating that the crystal structure transformed from the tetragonal phase (indexed as JCPDF #79-2264, with lattice constants $a = b = 3.9998$ Å, $c = 4.018$ Å) to the cubic phase (JCPDF #74-1296, with lattice constants $a = b = c = 3.905$ Å) as the concentration of Sr$^{2+}$ increased for either Ba$_{1-y}$Sr$_y$TiO$_3$:xEu$^{3+}$ ($x = 8$ mol%) or Ba$_{1-y}$Sr$_y$TiO$_3$:xDy$^{3+}$ ($x = 4$ mol%) powder. The main reason for the above phenomena is the replacement of larger Ba$^{2+}$ ions ($r = 1.35$ Å) by smaller Sr$^{2+}$ ions ($r = 1.18$ Å), since both the BaTiO$_3$:xEu$^{3+}$ ($x = 8$ mol%) and BaTiO$_3$:xDy$^{3+}$ ($x = 4$ mol%) powder retained the tetragonal crystal structure without Sr$^{2+}$ substitution, as indicated in Fig. 2. In order to clearly understand the phase transformation from tetragonal to cubic phase, the calculation of fractions of cubic and tetragonal phases was performed and the proportions of the cubic phase were 32.92% and 19.70% for the compositions of Ba$_{0.7}$Sr$_{0.3}$TiO$_3$:xEu$^{3+}$ ($x = 8$ mol%) and Ba$_{0.8}$Sr$_{0.2}$TiO$_3$:xEu$^{3+}$ ($x = 4$ mol%) powder respectively. The compositions of both Ba$_{1-y}$Sr$_y$TiO$_3$:xDy$^{3+}$ ($x = 8$ mol%), Ba$_{0.8}$Sr$_{0.2}$TiO$_3$:xDy$^{3+}$ ($x = 4$ mol%), and Ba$_{0.8}$Sr$_{0.2}$TiO$_3$:xEu$^{3+}$ ($x = 4$ mol%) were nearly at the critical line of the phase transformation, as shown in Fig. 6b and 7b.

The substitution of Sr$^{2+}$/Ba$^{2+}$ in hosts can change the crystal field and the covalence portion of the host. Therefore, the photoluminescence of BaTiO$_3$-based phosphors could be fine-tuned by the partial substitution of the host lattice cation Ba$^{2+}$ by Sr$^{2+}$ ions. To discern the luminescent properties of Ba$_{1-y}$Sr$_y$TiO$_3$:xEu$^{3+}$ ($x = 8$ mol%) phosphors, the PL and PLE spectra are shown in Fig. 8. As shown in Fig. 8a, the profiles of the PL spectra of the phosphors with different Sr$^{2+}$ contents are similar, and the emission peaks remained at the same positions as those of the BaTiO$_3$:xEu$^{3+}$ ($x = 8$ mol%) phosphor without Sr$^{2+}$ (Fig. 3). A previous study showed that the crystal structure transition only affects the PL/PLE intensity in BaTiO$_3$ based phosphors doped by Li$^+$ and Er$^{3+}$; thus, the position of PL/PLE remains unchanged. Furthermore, the PL intensity increased until the Sr$^{2+}$ content reached $y = 0.3$ and then, an abrupt decreasing trend could be observed on continually increasing the substitution concentration of Sr$^{2+}$, as shown in the inset of Fig. 8a. Generally, the phase transition of (Ba,Sr)TiO$_3$ occurs when the substitution of Sr$^{2+}$ is about 40%. With the structure variation from tetragonal to cubic, the structure symmetry increases, inducing higher site symmetry surrounding Eu$^{3+}$ ions. Hence, the probability of f-f ($^5D_0 \rightarrow ^7F_J$) transitions decreases, which further reduces the emission intensity because the electric dipole transition between f-f levels is forbidden when a rare-earth ion is located at a high centrosymmetric site, according to the quantum mechanical selection rules. When $y \leq 0.3$, the probability of f-f transitions increases due to the lower portion of cubic phase and low local point symmetry, which improves the luminescence intensity of Ba$_{1-y}$Sr$_y$TiO$_3$:xEu$^{3+}$ ($x = 8$ mol%). To sum up, the intensity of luminescence mainly depends on the concentration of Eu$^{3+}$ and the proportion of tetragonal phase in phosphors with Sr$^{2+}$ substitution. Clearly, the emission intensity was much stronger than the other Ba$_{1-y}$Sr$_y$TiO$_3$:xEu$^{3+}$ ($x = 8$ mol%) when the substituting concentration of Sr$^{2+}$ was at $\sim$30 mol%, and the crystal structure of the Ba$_{1-y}$Sr$_y$TiO$_3$:xEu$^{3+}$ ($x = 8$ mol%) phosphors with $y \leq 0.3$ was dominated by the tetragonal phase. Therefore, the optimum substitution concentration of Sr$^{2+}$ in the series of (Ba,Sr)TiO$_3$:xEu$^{3+}$ ($x = 8$ mol%) phosphors was considered to be 30 mol%. Fig. 8b shows the Sr$^{2+}$-content-dependent PLE spectra of Ba$_{1-y}$Sr$_y$TiO$_3$:xEu$^{3+}$ ($x = 8$ mol%) phosphors. As shown in the figure, the excitation intensity of the Sr$^{2+}$-totally-substituted SrTiO$_3$:xEu$^{3+}$ ($x = 8$ mol%) phosphor, particularly the broadband peaks at around 380 nm, is the highest among others, due to the band gap absorption of the SrTiO$_3$ cubic phase host.

Fig. 9 shows the Sr$^{2+}$-content-dependent PL and PLE spectra of Ba$_{1-y}$Sr$_y$TiO$_3$:xDy$^{3+}$ ($x = 4$ mol%) phosphors. Clearly, all the PL and PLE spectra had the same profiles. From the inset in Fig. 9a, we could see that the optimal substitution content of Sr$^{2+}$ was $y = 0.2$ (tetragonal phase dominated) for obtaining the strongest emission intensities among the series of Ba$_{1-y}$Sr$_y$TiO$_3$:xDy$^{3+}$ ($x = 4$ mol%) phosphors. Fig. 9b shows the Sr$^{2+}$-content-dependent PLE spectra of Ba$_{1-y}$Sr$_y$TiO$_3$:xDy$^{3+}$ ($x = 4$ mol%) samples. There are several typical Dy$^{3+}$ excitations, and all the PLE spectra present similar shapes with the increase in Sr$^{2+}$ content. Given the above information, moderate substitution of Ba$^{2+}$ by Sr$^{2+}$ in the BaTiO$_3$ host can improve the luminescence intensity of Eu$^{3+}$ and Dy$^{3+}$ singly-doped (Ba,Sr)TiO$_3$ phosphors because of the partial formation of cubic phases in the tetragonal BaTiO$_3$ crystal structure. As mentioned in case of BaTiO$_3$:xEu$^{3+}$ ($x = 8$ mol%), enhanced electric dipole transition ($^5D_0 \rightarrow ^7F_J$) relates to the degree of distortion or the non-centrosymmetry of Eu$^{3+}$’s local symmetry groups in the BaTiO$_3$ host. In other words, when the partial formation of highly symmetrical cubic phases occurs in the Sr-substituted
tetragonal (Ba,Sr)TiO₃ host crystal structure, the distortion of the Eu³⁺’s local site symmetry groups aggravates because of the mixed structure with a co-existing bi-phase and then, the emission intensity increases accordingly. The situation is the same as that in the ⁴F₉/₂ → ⁶H₁₃/₂ electric dipole transition in (Ba,Sr)TiO₂ₓDy³⁺ (x = 4 mol%) phosphors after substituting larger Ba²⁺ by smaller Sr²⁺. With the further addition of Sr²⁺, the phase transformation from tetragonal to cubic phase completes, the degree of distortion or the non-centrosymmetry of RE³⁺’s local symmetry groups in (Ba,Sr)TiO₃:RE³⁺ reduces and then, the emission intensity from electric dipole transition declines for both ⁵D₀ → ⁷F₂ of Eu³⁺ and ⁴F₉/₂ → ⁶H₁₃/₂ of Dy³⁺. Therefore, the optimal Sr²⁺ substitution content was considered to be 30 mol% for (Ba,Sr)TiO₂ₓEu³⁺ (x = 8 mol%) and 20 mol% for (Ba,Sr)TiO₂ₓDy³⁺ (x = 4 mol%) phosphors, respectively.

3.3 Temperature-dependent luminescence and reversible emission against heating in the series of phosphors

Generally, in the process of the application of phosphors in LED, the phosphor’s emission intensities are reduced against the temperature as the result of the thermal phonon-assisted relaxation between the excited states and the ground states. In fact, the temperature of the phosphor can be increased to about 150 °C during the operation of a LED. Therefore, the thermal quenching properties are of great significance to phosphors. For example, it has considerable effects on the output of light and the colour rendering index. To evaluate the effect of temperature on luminescence, the temperature dependent emission spectra for our four different samples were measured and are shown as follows.

Fig. 10a and c show the temperature-dependent PL spectra of BaTiO₂ₓEu³⁺ (x = 8 mol%) and BaTiO₂ₓDy³⁺ (x = 4 mol%), respectively. As shown in the figures, the PL profiles of the Eu³⁺-optimal-doped BaTiO₂ₓEu³⁺ (x = 8 mol%) as well as Dy³⁺-optimal-doped BaTiO₂ₓDy³⁺ (x = 4 mol%) phosphors are similar at different temperatures. The PL intensities of both phosphors decreased with the increase in temperature from RT to 210 °C. In addition, the CIE chromaticity coordinates of the optimal BaTiO₂ₓEu³⁺ (x = 8 mol%) phosphors gradually moved from (0.624, 0.370) to (0.567, 0.419), while the color coordinates of the optimal BaTiO₂ₓDy³⁺ (x = 4 mol%) phosphor were stable at (0.390 ± 0.01, 0.571 ± 0.007) with the increase in temperature, which are also clearly shown in Fig. 11 and Table 1. The curves of relative PL intensities of these two optimal phosphors as a function of temperature are illustrated in Fig. 10b and d. While heating the BaTiO₂ₓEu³⁺ (x = 8 mol%) phosphor up to 100 °C and 150 °C, it retained about 70% and 50% of its initial PL intensity at RT, respectively, because of the non-radiative transitions from the excited state to the ground state under heating. While cooling down to RT again from 210 °C, the phosphor retained 83% of its initial PL intensity, and is known as thermal degradation. However, while heating the BaTiO₂ₓDy³⁺ (x = 4 mol%) phosphor up to 100 °C and 150 °C, it retained about 90% and 60% of its initial PL intensity at RT, respectively. While cooling down to the room temperature again from 210 °C, the PL intensity of the BaTiO₂ₓDy³⁺ (x = 4 mol%) phosphor could be reserved at ~95% of its initial intensity. The above results indicated that the BaTiO₂ₓDy³⁺ (x = 4 mol%) phosphor possessed superior thermal stability than the BaTiO₂ₓEu³⁺ (x = 8 mol%) phosphor, and it could be a good candidate for applications in lighting.

In principle, the effect of luminescence thermal quenching is put down to the non-radiative relaxation between the excited and ground state through the crossing points of configuration coordinate diagram of RE³⁺ electrons in host. The most important factor affecting non-radiative transition is the

![Fig. 10](https://example.com/figure10.png)  
(a) Temperature-dependent PL spectra of the BaTiO₂ₓEu³⁺ (x = 8 mol%) phosphor (λ_ex = 465 nm). (b) The relative PL intensity of BaTiO₂ₓEu³⁺ (x = 8 mol%) as a function of temperature. Inset is the linear fitting of the calculated activation energy for thermal quenching. (c) Temperature-dependent PL spectra of the BaTiO₂ₓDy³⁺ (x = 4 mol%) phosphor (λ_ex = 452 nm). (d) The relative PL intensity of BaTiO₂ₓDy³⁺ (x = 4 mol%) as a function of temperature. Inset is the linear fitting of the calculated activation energy for thermal quenching.

![Fig. 11](https://example.com/figure11.png)  
CIE chromaticity diagram of BaTiO₂ₓEu³⁺ (x = 8 mol%) and BaTiO₂ₓDy³⁺ (x = 4 mol%) phosphors at elevated temperatures.
temperature. The relationship between the emission intensity and the temperature can be described by the following Arrhenius equation:  

$$\frac{I(T)}{I_0} = \frac{1}{1 + A \exp(-\Delta E/kT)}$$  

(1)

where $I_0$ is the PL intensity of the phosphor at room temperature, $I(T)$ is the PL intensity at a given temperature $T$, $A$ is a constant, $\Delta E$ is the activation energy for thermal quenching, and $k$ is the Boltzmann constant ($8.629 \times 10^{-5}$ eV K$^{-1}$). According to the Arrhenius equation, the plot of $\ln[I_0/I(T)-1]$ versus $1/kT$ yielded a straight line, which is displayed in the insets of Fig. 12b and d. The activation energy $\Delta E$ was obtained from the slope of the fitting line. For the BaTiO$_3$:Eu$^{3+}$ ($x = 8$ mol%) phosphor, the activation energy was calculated to be 0.272 eV, which was lower than that of BaTiO$_3$:Dy$^{3+}$ ($x = 4$ mol%) (0.387 eV). This indicates that the thermal stability of rare earth doped BaTiO$_3$ phosphors depends largely on the rigid structure or the chemical bonding of phosphors, the nature of rare earth ions, and the effect of the doping concentration of the rare earth on the change of crystal field. The chemical bonding of Dy–O is stronger than that of Eu–O due to the lanthanide contraction; so, the Dy$^{3+}$ doped phosphors possess higher thermal stability (or activation energy). The higher the doping concentration of rare earth ions, the fiercer is the non-radiative transition (caused by collisions among ions) of rare earth ions during the heating process.

Generally, the thermal stability of nitride phosphors with strong covalent bonds is higher than that of oxide phosphors, while the thermal stability of oxide phosphors is higher than that of sulphide phosphors. Luminescence thermal stability is also related to the unavoidable defects in/on imperfect phosphors (such as dangling bonds, and oxygen defects, introducing extra defect energy levels), which can induce non-radiative transitions during the heating or cooling process. Although the unavoidable defects in/on the imperfect phosphors are difficult to be detected at present, these defects would affect the luminescence properties. Singh et al. reported that the $\Delta E$ of Eu$^{3+}$-K co-doped Ba$_{1-x-y}$TiO$_3$:Eu$^{3+}$,K$^+$ was only 0.088 eV, which indicated that the BaTiO$_3$:Dy$^{3+}$ ($x = 4$ mol%) phosphor prepared by our group possesses much higher activation energy and better thermal stability.

With the replacement of Ba$^{2+}$ by Sr$^{2+}$ for phosphors (Ba, Sr) TiO$_3$:RE$^{3+}$ (RE = Eu, Dy), there were some differences in thermal stabilities compared to the initial unsubstituted BaTiO$_3$:RE$^{3+}$ (RE = Eu, Dy). Clearly, the PL intensities of both Sr$^{2+}$-substituted phosphors Ba$_{0.7}$Sr$_{0.3}$TiO$_3$:Eu$^{3+}$ ($x = 8$ mol%) and Ba$_{0.4}$Sr$_{0.4}$TiO$_3$:Dy$^{3+}$ ($x = 4$ mol%) decreased with the increase in temperature and there was no evident shift in the emission wavelengths of these two phosphors at higher temperatures (Fig. 12a and c). Furthermore, as shown Fig. 12b and d, when the temperature of the phosphors increases to 100 °C and 150 °C, the PL intensity drops to about 60% and 40%, and 80% and 50% of its initial intensity for Ba$_{0.7}$Sr$_{0.3}$TiO$_3$:Eu$^{3+}$ ($x = 8$ mol%) and Ba$_{0.8}$Sr$_{0.2}$TiO$_3$:Dy$^{3+}$ ($x = 4$ mol%), respectively. While cooling down to the RT again, the PL intensities of these two phosphors were irreversible, indicating thermal degradation. The measured PL intensities after cooling to RT from 210 °C were approximately 85% of the values at the RT before heating up. As shown in the insets of Fig. 12b and d, the calculated activation energy of Ba$_{0.8}$Sr$_{0.2}$TiO$_3$:Eu$^{3+}$ ($x = 8$ mol%) was 0.266 eV, which was lower than that of Ba$_{0.7}$Sr$_{0.3}$TiO$_3$:Dy$^{3+}$ ($x = 4$ mol%) (0.322 eV), calculated according to the Arrhenius equation.

The thermal stability of Sr$^{2+}$-substituted Ba$_{1-x}$Sr$_x$TiO$_3$:RE$^{3+}$ (RE$^{3+}$ = Eu$^{3+}$, Dy$^{3+}$) phosphors decreased compared to the unsubstituted phosphors (BaTiO$_3$:RE$^{3+}$, RE$^{3+}$ = Eu$^{3+}$, Dy$^{3+}$), and the results are summarized in Table 2. Upon the comparison of two phosphors BaTiO$_3$:Eu$^{3+}$ ($x = 8$ mol%) and Ba$_{0.7}$Sr$_{0.3}$TiO$_3$:Eu$^{3+}$ ($x = 8$ mol%), the reduction of the calculated activation energy for thermal quenching of the Sr-substituted phosphors was 0.094 eV, indicating much better thermal stabilities compared to the initial unsubstituted BaTiO$_3$:Eu$^{3+}$ phosphor. The results of the calculated activation energy for thermal quenching of the Ba$_{0.7}$Sr$_{0.3}$TiO$_3$:Eu$^{3+}$ ($x = 8$ mol%) phosphor prepared by our group possesses much higher activation energy and better thermal stability.

Table 1. CIE chromaticity coordinates of BaTiO$_3$:Eu$^{3+}$ ($x = 8$ mol%) and BaTiO$_3$:Dy$^{3+}$ ($x = 4$ mol%) phosphors at different temperatures

| Temperature, (°C) | BaTiO$_3$:Eu$^{3+}$ ($x = 8$ mol%) | BaTiO$_3$:Dy$^{3+}$ ($x = 4$ mol%) |
|-------------------|---------------------------------|---------------------------------|
| 30                | X = 0.624, Y = 0.370            | X = 0.390, Y = 0.571            |
| 50                | X = 0.621, Y = 0.373            | X = 0.390, Y = 0.571            |
| 70                | X = 0.616, Y = 0.377            | X = 0.389, Y = 0.572            |
| 90                | X = 0.611, Y = 0.381            | X = 0.388, Y = 0.572            |
| 110               | X = 0.605, Y = 0.386            | X = 0.386, Y = 0.573            |
| 130               | X = 0.598, Y = 0.392            | X = 0.384, Y = 0.575            |
| 150               | X = 0.590, Y = 0.399            | X = 0.382, Y = 0.576            |
| 170               | X = 0.582, Y = 0.406            | X = 0.382, Y = 0.576            |
| 190               | X = 0.574, Y = 0.412            | X = 0.380, Y = 0.577            |
| 210               | X = 0.567, Y = 0.419            | X = 0.380, Y = 0.578            |

Fig. 12 (a) Temperature-dependent PL spectra of the Ba$_{0.7}$Sr$_{0.3}$TiO$_3$:Eu$^{3+}$ ($x = 8$ mol%) phosphor ($\lambda_{ex} = 465$ nm). (b) Relative PL intensity of the phosphor as a function of temperature. Inset: the linear fitting of the calculated activation energy for thermal quenching of the Ba$_{0.7}$Sr$_{0.3}$TiO$_3$:Eu$^{3+}$ ($x = 8$ mol%) phosphor. (c) Temperature-dependent PL spectra of the Ba$_{0.7}$Sr$_{0.3}$TiO$_3$:Dy$^{3+}$ ($x = 4$ mol%) phosphor ($\lambda_{ex} = 452$ nm). (d) Relative PL intensity of the phosphor as a function of temperature. Inset: the linear fitting of the calculated activation energy for thermal quenching of the Ba$_{0.7}$Sr$_{0.3}$TiO$_3$:Dy$^{3+}$ ($x = 4$ mol%) phosphor.
and Ba$_{0.8}$Sr$_{0.2}$TiO$_3$:xDy$^{3+}$ ($x = 4 \text{ mol\%}$), there a similar trend was observed. The decreased thermal stability of Sr$^{2+}$-substituted Ba$_{1-x}$Sr$_x$TiO$_3$:RE$^{3+}$ could be mainly attributed to the fact that a part of larger Ba$^{2+}$ ions were replaced by smaller Sr$^{2+}$, resulting in shrinkage of the unit cell and an increase in lattice defects. It has to be emphasized that while cooling from 210°C, the partial phase transformation of the tetragonal phase of Sr$^{2+}$-substituted Ba$_1$-Sr$_x$TiO$_3$:RE$^{3+}$ may also contribute to the reduced thermal stability because the optimal Sr substitution contents of both Ba$_{0.8}$Sr$_{0.2}$TiO$_3$:xEu$^{3+}$ ($x = 8 \text{ mol\%}$) and Ba$_{0.8}$Sr$_{0.2}$TiO$_3$:xDy$^{3+}$ ($x = 4 \text{ mol\%}$) were around the critical line where the phase transformation occurs (seen in Fig. 6b and 7b). Lattice defects or lattice mismatch induced by phase transformation may influence the thermal stability to some extent by introducing additional defect energy levels.

### 3.4 Decay times of the series of phosphors

The decay times of the series of phosphors were measured and are shown in Table 3. Additionally, the obtained decay curves were fitted by the double exponential equation:

$$I = I_0 + A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2)$$

(2)

where $I$ is the intensity at time $t$, $A_1$ and $A_2$ are constants, $\tau_1$ and $\tau_2$ are the corresponding decay times. The average decay time for the bi-exponential function can be expressed as follows:

$$\tau_{av} = (A_1\tau_1^2 + A_2\tau_2^2)/(A_1\tau_1 + A_2\tau_2)$$

(3)

As shown in Table 3, the decay time of Dy$^{3+}$-doped (Ba,Sr)TiO$_3$ phosphors was much shorter than that of Eu$^{3+}$-doped (Ba,Sr)TiO$_3$ phosphors. The replacement of Ba$^{2+}$ by Sr$^{2+}$ slightly increased the decay time of phosphors. The detailed investigations on the decay behaviours of our as-prepared phosphors are in progress.

### 4. Conclusions

In summary, a series of (Ba,Sr)TiO$_3$ phosphors singly-doped with Eu$^{3+}$ and Dy$^{3+}$ were successfully prepared by the nitrate pyrolysis method at 750°C. The XRD patterns illustrated that BaTiO$_3$:xEu$^{3+}$ ($x = 0.02$–0.10), BaTiO$_3$:xDy$^{3+}$ ($x = 0.02$–0.10), Ba$_{1-x}$Sr$_x$TiO$_3$:xEu$^{3+}$ ($x = 0.08$, $y = 0.3$), and Ba$_{1-x}$Sr$_x$TiO$_3$:xDy$^{3+}$ ($x = 0.04$, $y = 0.2$) phosphors primarily showed tetragonal phase structure. When the Sr$^{2+}$ substitution content was higher than the optimal value ($y > 0.3$ for Ba$_{1-x}$Sr$_x$TiO$_3$:0.08Eu$^{3+}$ and $y > 0.2$ for Ba$_{1-x}$Sr$_x$TiO$_3$:0.04Dy$^{3+}$), a remarkable phase transformation from tetragonal to cubic phase occurred. In comparison, the photoluminescence intensities of RE$^{3+}$-optimally-doped BaTiO$_3$:0.08Eu$^{3+}$ and BaTiO$_3$:0.04Dy$^{3+}$ phosphors were the highest in the serial phosphors of BaTiO$_3$:xEu$^{3+}$ and BaTiO$_3$:xDy$^{3+}$ ($x = 0.02$–0.10), respectively. Interestingly, the substitution of 30 mol% Sr$^{2+}$ (Ba$_{0.8}$Sr$_{0.2}$TiO$_3$:0.08Eu$^{3+}$) further enhanced the photoluminescence intensity of the BaTiO$_3$:0.08Eu$^{3+}$ phosphor, while the substitution of 20 mol% Sr$^{2+}$ (Ba$_{0.8}$Sr$_{0.2}$ TiO$_3$:0.04Dy$^{3+}$) further enhanced the photoluminescence intensity of the BaTiO$_3$:0.04Dy$^{3+}$ phosphor. Moreover, the appropriate Sr/Ba isomorphic substitution improved the luminescence intensity of the compounds in various degrees, as compared to the luminescence thermal stabilities of Ba$_{1-x}$Sr$_x$-RE$^{3+}$ phosphors without Sr$^{2+}$ substitution. According to curves of the temperature-dependent PL intensity, the calculated activation energies $\Delta E$ were about 0.272 and 0.387 eV for BaTiO$_3$:0.08Eu$^{3+}$ and BaTiO$_3$:0.04Dy$^{3+}$, while they were about 0.266 and 0.322 eV for Ba$_{0.8}$Sr$_{0.2}$TiO$_3$:0.08Eu$^{3+}$ and Ba$_{0.8}$Sr$_{0.2}$ TiO$_3$:0.04Dy$^{3+}$, indicating that the best luminescence thermal stability was obtained in the BaTiO$_3$:0.04Dy$^{3+}$ phosphor. As a result, about 70% and 85% of the emission intensities at 100°C compared to those measured at room temperature is retained for BaTiO$_3$:0.08Eu$^{3+}$ and BaTiO$_3$:0.04Dy$^{3+}$, respectively, while about 60% and 80% is retained for the Sr$^{2+}$-substituted Ba$_{0.8}$Sr$_{0.2}$TiO$_3$:0.08Eu$^{3+}$ and Ba$_{0.8}$Sr$_{0.2}$ TiO$_3$:0.04Dy$^{3+}$, respectively. It has to be emphasized that while cooling from 210°C to room temperature, the BaTiO$_3$:0.04Dy$^{3+}$ phosphor showed the strongest recovery of PL emission (~95% of the intensity measured at room temperature) compared to other phosphors. Thus, BaTiO$_3$:0.04Dy$^{3+}$ phosphor with excellent luminescence stability is a good candidate for applications in lighting, display, and other related fields.

### Conflicts of interest

There are no conflicts to declare.

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