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Up-conversion luminescence properties with temperature change of strontium tungstate phosphors

Soung-Soo Yia and Jae-Yong Jung *b

Thermally stable $SrWO_4:[Er^{3+}]/[Yb^{3+}]$ upconversion phosphors were synthesized. X-ray diffraction analysis indicated a crystalline inorganic phosphor material with a tetragonal structure having a clear peak in the (112) phase, which is the main peak. The upconversion phosphor was synthesized using a precursor prepared by co-precipitation and sintered at 800 °C. When the phosphor was excited by a 980 nm laser with a pumping power of 200 mW, a strong green light was emitted. As the concentration of Er^{3+} ions increased, it was observed that the emission intensity decreased due to concentration quenching. The changes in the intensity of luminescence according to the pumping power are due to a two-photon process. As the temperature increased, the green emission intensity of the up-conversion phosphor increased. This was thought to be a phenomenon caused by efficient energy transfer between Yb^{3+} and Er^{3+} ions by the $SrWO_4$ host with negative thermal expansion. A composite was prepared by mixing phosphor powder and PDMS, that could be used for temperature sensing.

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1 Introduction

Up-conversion phosphors are materials that emit light by fusing low-energy photons and converting them into high-energy photons, and these phosphors are attracting attention in various fields such as sunlight, bio-emerging, and phosphor applications. 1,2 Existing down-conversion phosphors are mainly based on Stokes emission, which generates low energy long wavelength visible light from high energy short wavelengths such as the ultraviolet region.3,4 In contrast to this Stokes emission, upconversion phosphors have an anti-Stokesemission mechanism in which long-wavelength photons fuse to produce short-wavelength photons.5,6 By using an upconversion phosphor, light in the infrared region can be converted into visible light, or light in the visible region can be converted into ultraviolet light.7,8 This can be considered a phenomenon that violates the laws of thermodynamics, but the up-conversion phenomenon is possible because it is an emission phenomenon that occurs by the fusion of energy of two or more photons, not by a single photon. 9,10 Research on upconversion phosphors has been actively conducted using inorganic materials doped with rare earth ions. Up-conversion is caused by a luminescence phenomenon, due to the double excitation of photons in inorganic materials with a long lifetime

transition energy region.11,12 By absorbing the primary photon, the excited electron with the transition energy band absorbs an additional photon before falling to the ground state and is excited to a higher energy level. 13,14 Pavani et al. synthesized SrLaAl₃O₇ co-doped with Er³⁺ and Yb³⁺ by the facile Pechini method. The phosphor excited at 980 nm showed strong green emission by the ${}^4\mathrm{I}_{13/2} \to {}^4\mathrm{I}_{15/2}$ transition. In addition, the visible spectrum of 528, 548, and 660 nm was shown, and the upconversion mechanism was reported.15 Lim et al. synthesized a yellow-emitting phosphor when excited at 980 nm by codoping Yb3+ and Ho3+ with LiNaCaLa(MoO4)3 quadruple molybdate as a host, by the microwave sol-gel method.16 Deng et al. doped the GaAlO₃:Er³⁺, Yb³⁺ phosphor with Lu³⁺ and Ga³⁺ ions by co-precipitation. Ga³⁺ is Al³⁺ and Lu³⁺ is Gd³⁺ substituted, and a change in the intensity of the up-conversion green emission according to the structural change in the host was reported.17 Barrera et al. synthesized an up-conversion phosphor by doping Er^{3+} and Yb^{3+} ions into a $KY(WO_4)_2$ host using the Pechini method. The phosphor excited at 980 nm showed emission spectra of 530, 550, and 660 nm. A change in emission intensity according to the change in the concentration of doped rare earth ions, and a change in the intensity of the excitation light, were observed.18 Pandey et al. prepared Y2O3 upconversion phosphors co-doped with Ho³⁺ and Yb³⁺ ions by the combustion route. When excited with a 980 nm diode laser, the color changed according to the doping concentration of Ho3+ ions, as shown in the CIE color coordinates, and a visible light spectrum of strong green and relatively weak red and blue was observed.19 Various synthesis methods and doping with rare earth ions have been performed to synthesize upconverted

^aDivision of Materials Science and Engineering, Silla University, Busan 46958, Republic of Korea

^bResearch and Business Development Foundation, Silla University, Engineering Building, Busan 45985, Republic of Korea. E-mail: eayoung21@naver.com; Tel: +82-51-999-6441

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phosphors and to investigate their luminescence properties. In this study, phosphors were synthesized by co-doping with Er³⁺ and Yb3+ rare earth (RE) ions using strontium tungstate (SrWO₄), which has chemical and thermal stability, as a host. The precursor was prepared by co-precipitation and heattreated at 800 °C. Changes in the crystal structure and luminescence characteristics of the synthesized phosphor after doping with rare earth ions were investigated. In addition, a change in luminescence characteristics according to the power and temperature of the excitation light was observed, and it was suggested that the composite could be used for temperature sensing.

Experimental

2.1. Synthesis of SrWO₄:[Er³⁺]/[Yb³⁺] by co-precipitation and sintering

Starting materials. Barium acetate ((CH₃CO₂)₂Sr, Sigma-Aldrich), sodium tungstate (Na₂WO₄·2H₂O, Sigma-Aldrich), ytterbium(III) nitrate pentahydrate (Yb(NO₃)₃·5H₂O, Yb³⁺), and erbium(III) nitrate pentahydrate (Er(NO₃)₃·5H₂O₃, Er³⁺). 10 mmol of (CH₃CO₂)₂Sr was dissolved in beaker "A" containing 100 ml of distilled water. In beaker "B", 10 mmol of Na₂WO₄·2H₂O was dissolved in 100 ml distilled water (Fig. 1). The solution that was completely dissolved in beaker "B" was slowly poured into a stirring beaker "A" and remained there for about 20 minutes. After that, powder was recovered using a centrifuge (4000 rpm, 5 min), and the powder was prepared by rinsing with distilled water 3 times to remove any remaining sodium. The powder was dried in an oven at 80 °C for 16 hours. The up-conversion phosphor was synthesized with SrWO₄ as a host, the precursor made by simultaneously adding Yb(NO₃)₃·5H₂O and $Er(NO_3)_3 \cdot 5H_2O$ to beaker "A". The prepared precursor was sintered at 800 °C until the SrWO₄:[Er³⁺]/[Yb³⁺] phosphor was synthesized. Rare earth [RE] ions of Yb³⁺ were fixed at 0.5 mmol, and the amount of Er^{3+} (0.05, 0.1, 0.15, 0.2, 0.25, 0.3, 0.4, 0.5 mmol) added changed ($[Er^{3+}]/[Yb^{3+}] \sim 0.1, 0.2, 0.3, 0.4, 0.6, 0.8,$ 1).20,21

2.2. Characterization

The crystal structure of the synthesized phosphor powder was measured using an X-ray diffraction apparatus (XRD, X'Pert PRO MPD, 40 kV, 30 mA) having Cu-Kα radiation (wavelength: 1.5406 Å) at a scan rate of 4° min⁻¹ at a diffraction angle of 10° to 70°. The size and microscopic surface shape of the crystal grains were photographed with a field emission scanning electron microscope (FE-SEM, CZ, MIRA I LMH, TESCAN). To measure the fluorescence spectrum by up-conversion, a semiconductor pulse laser (TCLDM9, Thorlabs) that emitted an output of 200 mW at a wavelength of 980 nm as excitation, and a spectrometer (HR4000, Ocean Optics) with a photomultiplier connected were used to measure the emission spectrum. To analyze the fluorescence mechanism by up-conversion, the energy absorption and energy transfer processes in the excited state were analyzed by changing the intensity of the pulsed laser and measuring the changes in the intensity of the fluorescence.

2.3. Fabrication of a temperature sensing composite

The synthesized SrWO₄:[Er³⁺]/[Yb³⁺] up-conversion phosphors were mixed with 0.1 g each and 1 g of polydimethylsiloxane (PDMS) and cast in a square mold. After curing in an oven at 80 °C for 2 hours, the prepared composite was placed on a hot plate, excited at 980 nm, and the change in luminescence intensity according to temperature change was photographed.

3 Results & discussion

Structure and morphology of SrWO₄:[Er³⁺]/[Yb³⁺] upconversion phosphors

Fig. 2(a) shows the XRD patterns of the samples prepared by coprecipitation at room temperature and calcined at 800 °C. The synthesized SrWO₄ was consistent with the ICDD card no. 01-089-2568, and the tetragonal structure (a = 5.40 Å, b = 5.40 Å, c= 11.91 Å, space group $I4_1/a$) could be confirmed. A strong peak at 27.65° was detected, which was the (112) phase, the main peak of SrWO₄. In addition, the phases (101), (004), (200), (211), (204), (220), (116), (312), (224), (008), and (440) were also observed. In the SrWO₄:[Er³⁺]/[Yb³⁺] samples doped with rare earth ions for synthesis as up-conversion phosphors, the main peak (112) phase was also clearly observed. As the amount of rare earth ions increased (Er3+), the detection position of the main peak (112) phase shifted, but no secondary phase was found. Using the change in the detection position of the main peak-in (112), the change in the lattice constant was calculated by substituting it into the Bragg's equation $(2d \sin \theta = n\lambda)^{22}$ and is shown in Fig. 2(b). The lattice constant of pure SrWO₄ was calculated to be 0.2901 nm, and the lattice constant decreased as the added amount of Er3+ ions increased (SrWO4: 0.2901 nm, $SrWO_4:[Er^{3+}]/[Yb^{3+}] \sim 0.1:0.2898 \text{ nm } SrWO_4:[Er^{3+}]/[Yb^{3+}] \sim$ 0.4: 0.2896 nm). Although this is a small change, due to the change in the lattice constant it means that rare earth ions were doped in the lattice. Ortega et al. observed a shift of 2 theta angles on (111), the main peak of CeO2. It was reported that this was due to doping with rare earth ions having a large ionic radius ($Ce^{4+} = 0.97 \text{ Å, } Eu^{3+} = 1.066 \text{ Å, } La^{3+} = 1.16 \text{ Å).}^{23} \text{ Ortega}$ et al. observed a shift of 2 theta angles on (111), the main peak of CeO2. It was reported that this was due to doping of rare earth ions with a large ionic radius. In this study, 2 theta angles on the main peak (112) were shifted by doping rare earth ions with relatively small ionic radii, and the lattice constant was changed, due to co-doping $(Sr^{2+} = 1.18 \text{ Å}, Yb^{3+} = 0.868 \text{ Å}, Er^{3+} =$ 0.89 Å).24,25 Fig. 3 shows the FE-SEM image and energy dispersive X-ray spectroscopy (EDS) component analysis of the synthesized SrWO₄:[Er³⁺][Yb³⁺] sample. The sample had a shape like a dumbbell as it was spread out widely with round ends in the form of a long cylinder. It had a size of about 4.08 µm in the longitudinal direction and about 1.38 µm in the transverse direction. Ryu et al. observed the change in the surface shape of the particles according to the molar ratio of Sr²⁺ and WO₄²⁻when synthesizing crystalline SrWO₄ by the co-precipitation method. As the value of $[WO_4^{2-}]/[Sr^{2+}]$ increased, the rod-like shape changed to dumbbell and spherical shapes. This phenomenon was explained as a process in which the

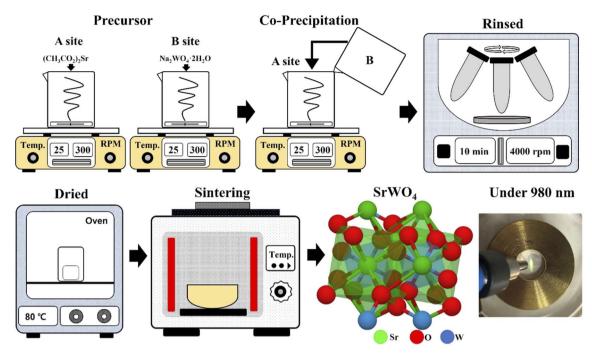


Fig. 1 Experimental procedure for preparing the SrWO₄:[Er³⁺]/[Yb³⁺] up-conversion phosphors.

aggregation and growth directions of particles, etc., started from both ends of the particles and eventually changed to a spherical shape due to the self-assembly reaction. ²⁶

3.2. Luminescence characteristics of $SrWO_4{:}[Er^{3+}]/[Yb^{3+}]$ upconversion phosphors

Fig. 4(a) shows the photoluminescence (PL) spectrum of SrWO₄:[Er³+]/[Yb³+] phosphors prepared by co-precipitation at 800 °C. When the sample was excited with a 980 nm semiconductor laser, the pump power was fixed at 200 mW. The synthesized up-conversion phosphor showed a strong green light emission signal at 520–560 nm and a relatively weak red signal spectrum at 640–680 nm. The green emission bands were centered at 529 and 543, corresponding to the $(^2H_{11/2}, ^4S_{3/2}) \rightarrow$

 $^4I_{15/2}$ transitions, and the red emission band was centered at 657 nm, corresponding to the $^4F_{9/2} \rightarrow ^4I_{15/2}$ transitions of Er^{3+} ions. 27,28 It is well known that Yb^{3+} and Er^{3+} rare earth ions codoped into a $SrWO_4$ host are absorbed by the Yb^{3+} ions of 980 nm from the outside, and then energy is transferred to the Er^{3+} ions, with emission peaks in the green and red spectrum, respectively, from the Er^{3+} ions. 29 Yb^{3+} ions are suitable coactivators because of their large absorption cross-sectional area and the high concentration at which quenching occurs, and most of the infrared energy is absorbed by Yb^{3+} ions. In Fig. 4(b), when $[Er^{3+}]/[Yb^{3+}] \sim 0.1$, the integrated area of the PL spectrum was the highest, and thus strong emissions were shown. As the concentration of Er^{3+} ions increased, PL intensity decreased, and it is considered that the energy absorbed due to the concentration quenching caused by excessive rare earth

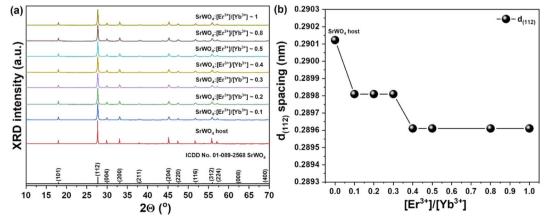


Fig. 2 (a) XRD patterns of synthesized SrWO₄ and SrWO₄: $[Er^{3+}]/[Yb^{3+}]$ powders and (b) change in $d_{(112)}$ spacing.

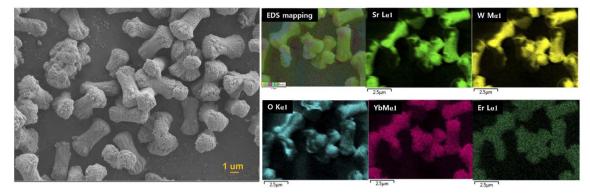


Fig. 3 FE-SEM image and EDS analysis of the SrWO₄:[Er³⁺]/[Yb³⁺] powder.

doping is caused by inefficient transfer. The $[\mathrm{Er}^{3+}]/[\mathrm{Yb}^{3+}] \sim 0.1$ sample, which showed the strongest up-conversion luminescence at a laser power of 980 nm at 200 mW, exhibited a change in up-conversion luminescence characteristics according to the change in laser power, and is shown in Fig. 5(a). The laser power was varied from 75 to 280 mW. A band of strong green emission was still observed, and the intensity of the emission spectrum also increased as the laser power increased (Fig. 5(b)). The upconversion process induces an energy transfer (ET) process, in which energy absorbed by Yb³⁺ ions is transferred to Er³⁺ ions, and an excited state absorption (ESA) process by the transfer of additional energy to the excited Er3+ ions. The ESA process occurs in a single ion, while the ET process occurs when two rare earth ions are involved. The SrWO₄[Er³⁺]/[Yb³⁺] ~ 0.1 phosphor to which Er3+ and Yb3+ ions are added absorbs photons from a 980 nm laser, and Yb^{3+} ions at the ${}^2F_{7/2}$ level are excited to the ²F_{5/2} level. The excited Yb³⁺ ions are adjacent to Er³⁺ ions, which excite the Er³⁺ ions to the ⁴I_{11/2} level through ET $\left(^{2}F_{5/2}\left(Yb^{3+}\right)+{}^{4}I_{15/2}\left(Er^{3+}\right)\to{}^{2}F_{7/2}\left(Yb^{3+}\right)+{}^{4}I_{11/2}\left(Er^{3+}\right)\right)\text{ and return}$ to the ground state. 30-32 When an up-conversion phosphor with a wavelength of 980 nm is pumped by an excitation source, the Er³⁺ ions are excited to the ⁴I_{11/2} level through the ET₁ process,

and the GSA process, as shown in Fig. 5(c). The lifetime of the ⁴I_{11/2} level is long enough that electrons are occupied at the ⁴F_{7/2} level of the Er^{3+} ion by the $ET_3(^2F_{5/2}(Yb^{3+}) + ^4I_{11/2}(Er^{3+}) \rightarrow ^2F_{7/2}$ $(Yb^{3+}) + {}^4F_{7/2}(Er^{3+})$) process and the ESA₁ process by the Yb³⁺ ion excited by the absorption of another photon.33 Another way electrons can be occupied at the 4F7/2 level is the crossrelaxation process that occurs between adjacent Er3+ ions. One of the two Er³⁺ ions in the ⁴I_{11/2} level interacts with an adjacent ion to gain energy and move to ${}^{4}F_{7/2}$, and the other ion loses energy and transitions to the ground state 4I15/2 level.34 By this process, two green lights are emitted at a wavelength of 529 nm by the ${}^{2}H_{11/2} \rightarrow {}^{4}I_{15/2}$ transition and 543 nm by the ${}^{4}S_{3/2}$ \rightarrow ${}^{4}I_{15/2}$ transition. In the observed red spectrum, electrons are occupied at the 4I13/2 level by non-radiative transition from the ⁴I_{11/2} level, and the electrons are occupied at the ⁴F_{9/2} level through the ET2 and ESA2 processes. Then, red light of 657 nm is emitted by ${}^4F_{9/2} \rightarrow {}^4I_{15/2}$ transition.³⁵ The intensity of fluorescence by up-conversion is related to the fluorescence intensity of pump excitation light by the following equation:³⁶

$$I \propto P^n$$
 (1)

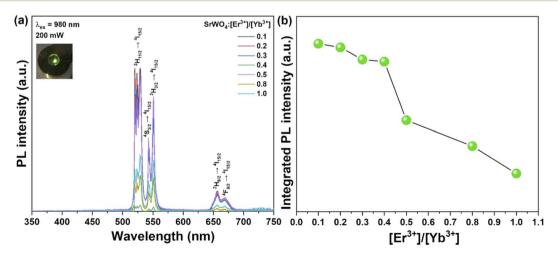


Fig. 4 (a) PL spectra under 980 nm and (b) change in PL intensity according to Er³⁺ concentration at 200 mW in the SrWO₄:[Er³⁺]/[Yb³⁺] upconversion phosphors.

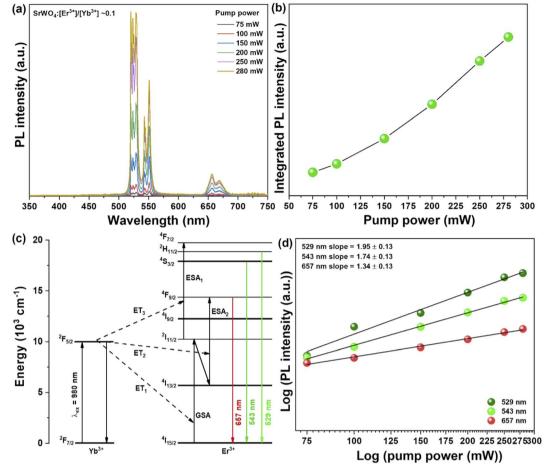


Fig. 5 (a) PL spectra, (b) change in PL intensity, (c) schematic energy transfer process, (d) linear fitting 529 nm, 543 nm, and 657 nm intensity according to pump power under 980 nm of $SrWO_4$:[Er^3+]/[Yb^3+] ~ 0.1 up-conversion phosphors.

where, I is the up-conversion emission intensity, P is the laser power intensity, and n is the number of pumping photons required to excite the upper emitting state. The n is the number

of excitation photons involved in the upward conversion process for fluorescence emission, and it can be obtained from the slope of the graph by the logarithm of the pumping light

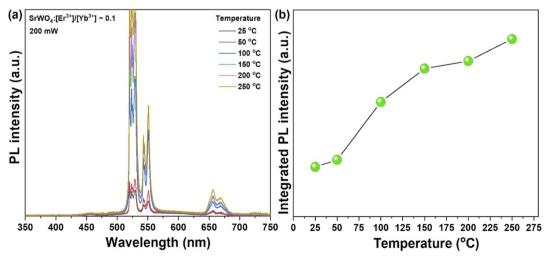


Fig. 6 (a) PL spectra of changing temperature and (b) integrated PL intensity under 980 nm at 200 mW of SrWO₄:[Er³⁺]/[Yb³⁺] ~ 0.1 upconversion phosphors.

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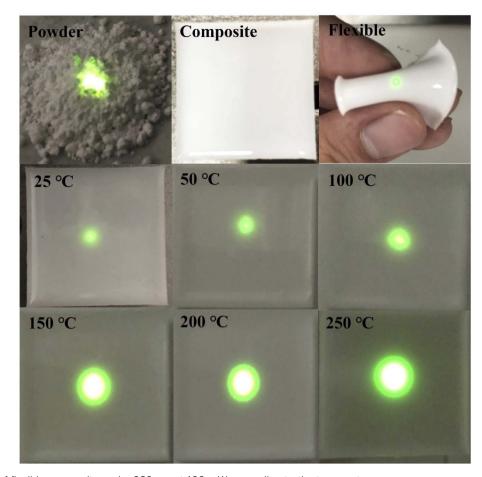


Fig. 7 Photograph of flexible composite under 980 nm at 100 mW, according to the temperature.

intensity and the logarithmic value of the fluorescence intensity. As shown in Fig. 5(d), the slope values of 529 nm (1.95) and 543 nm (1.74) of green emission were greater than 1. This is because the emission of green fluorescence is due to a twophoton process involving two excitation photons. The slope of 657 nm of red fluorescence is 1.34. After the above-mentioned ground state electron absorbs the first photon, it is excited to the ⁴I_{11/2} level, and then occupies the ⁴I_{13/2} level by non-radiative transition, and through the ET2 process. This is a two-photon process that emits red light with a transition of ${}^4F_{9/2} \rightarrow {}^4I_{15/2}$ by an ESA2 process that absorbs a second photon.37,38

3.3. SrWO₄:[Er³⁺]/[Yb³⁺] up-conversion phosphors applied for temperature sensing

0.1 g of the synthesized up-conversion SrWO₄:[Er³⁺]/[Yb³⁺] \sim 0.1 phosphor powder was placed in a copper holder and immersed in a silicone oil bath. The silicone oil bath was placed on a hot plate and the temperature was raised (25-250 °C). After checking the temperature of the powder with an infrared thermometer, a change in luminescence intensity according to temperature change was observed. The spectrum and integrated up-conversion photoluminescence intensity are shown in Fig. 6(a) and (b). In general, it has been reported that the luminescent properties of up-conversion and down-conversion

phosphors are reduced due to thermal quenching by external temperature. Ju et al. synthesized a down-converted phosphor doped with Sm3+ rare earth ions using SrWO4 as a host, and observed a change in luminescence properties by heating it from room temperature to 200 °C. As the temperature increased, the thermal quenching phenomenon was observed very weakly. It was observed that the luminescence intensity rather increased at 190 °C, and it was reported that SrWO₄ is an excellent material as a thermally stable host.39 Liao et al. synthesized the Sc₂(MoO₄)₃:Yb/Er up-conversion phosphor, and reported the change in luminescence characteristics according to temperature increase, to be negative thermal expansion of the host.40 This phenomenon is caused by the radiative trapping of Yb3+. This is because lattice shrinkage shortens the distance of Yb3+/Er3+ at high temperatures and promotes the radiative trapping of Yb3+. In phosphorescent materials co-doped with Yb³⁺/Er³⁺, Yb³⁺ acts not only as a radiation trap to store energy, but also as a sensitizer to transfer energy to Er³⁺. These radiation traps may promote the release of Er³⁺. Also, the distance of Yb3+/Er3+ becomes shorter as the temperature rises. The ET process between the sensitizer (Yb3+) and the activator (Er3+) is usually thought to be caused by dipole interactions. Its ET efficiency is proportional to r^{-6} (where r is the donor-acceptor distance). Therefore, ET efficiency can be significantly improved

at high temperatures.⁴⁰ Desgreniers *et al.* observed changes in Raman signals by giving CaWO₄, SrWO₄, and BaWO₄ changes in temperature (10–300 K) and pressure (910 kbar). As the temperature and pressure increased, no significant change was observed in the high frequency region. However, in the WO₄(Z)-WO₄(Z) stretching region, CaWO₄ shifted in phonon energy and frequency due to external environmental factors. However, SrWO₄ did not react sensitively, and the frequency shift hardly shifted by about 1–2 cm⁻¹. Using this change, the thermal expansion of the crystal was calculated using the equation below,⁴¹

$$\frac{\mathrm{d}\omega}{\mathrm{d}T} = \left(\frac{\partial\omega}{\partial T}\right)_{v} - \frac{\alpha}{\beta} \left(\frac{\partial\omega}{\partial P}\right)_{T} \tag{2}$$

where α and β stand for the thermal expansion and isothermal compressibility of the solid. For crystals of SrWO₄, the thermal expansion was calculated to be negative. Because the ionic bond between the covalent bonds within the tetrahedron. Furthermore, anomalous temperature behavior for the least energetic stretching vibrations is revealed through negative values and cannot be explained by the hierarchy of bonds theory.

The SrWO₄:[Er³⁺]/[Yb³⁺] up-conversion phosphor synthesized in this work is also considered to have a stronger luminescence intensity as the temperature increases due to efficient energy transfer between rare earth ions by negative thermal expansion to a thermally stable SrWO4 host. To check whether the synthesized up-conversion phosphor could be used as a temperature sensor, a composite was prepared by mixing PDMS and the phosphor powder. The prepared composite was placed on a hot plate, the temperature was raised, and a 980 nm laser was fixed at 200 mW and irradiated. The temperature was checked with an infrared thermometer on the composite. The produced composite was easily bent by fingers, and it was confirmed that the size of the laser circle reflected on the surface became clearer as the temperature increased, and its size gradually increased. Not only in the powder state, but also in the composite made by mixing with the polymer, the luminescence intensity increased with the rise in temperature. These characteristics suggest the potential for a device that can directly emit a visual danger signal with an increase in temperature (Fig. 7).

4 Conclusion

The precursor was prepared at room temperature by coprecipitation, and crystalline $SrWO_4$ calcined at 800 °C was synthesized. In order to synthesize an up-conversion phosphor material, $SrWO_4$:[Er^{3+}]/[Yb^{3+}] were synthesized using the same experimental procedure, by co-doping with rare earth ions Yb^{3+} and Er^{3+} using $SrWO_4$ as a host. The synthesized powder exhibited a main peak (112) phase in the X-ray diffraction analysis and had a tetragonal structure. Doping with rare earth ions shifted the 2 theta position of the main peak and decreased the lattice constant. With these changes, it was possible to confirm the change in the crystal structure due to the addition of rare earth ions. The surface of the long cylindrical shaped synthesized powder sample was observed by FE-SEM in the

longitudinal direction, and particles with a size of about 4 µm were confirmed. When the synthesized phosphor powder was excited with a 200 mW pump power of a 980 nm laser, a strong green spectrum (529 nm, 543 nm) was confirmed. A relatively weak red spectrum at 657 nm was also observed. As the concentration of Er3+ ions increased, the luminescence intensity decreased due to the concentration quenching phenomenon. When the intensity of the laser pumping energy was changed, a green fluorescence emission was observed, indicating a two-photon process through an excited state absorption process and an energy transfer process. In addition, the SrWO₄:[Er³⁺]/[Yb³⁺] up-conversion phosphor showed an increase in luminescence intensity according to the increase in temperature. The host SrWO4 showed thermal stability due to negative thermal expansion, and energy transfer between Yb3+ and Er3+ was efficient. It is a phenomenon that has been formed. For application as a temperature sensor, it was confirmed that when a composite was produced by mixing with PDMS and then subjected to a thermal change, as with the powder, the luminescence intensity increased as the temperature increased, so that it could be used as a material for a temperature sensor that could be identified by the naked eye.

Data availability

The data presented in this study are available on request from the corresponding author.

Conflicts of interest

The authors declare no conflict of interest.

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