1. Introduction

Nanoscale materials have long attracted the interest of researchers due to their unique properties, which often differ from the properties of bulk compounds of similar compositions. A vivid example is the appearance of broadband "white" emission (BBWE) in nanoscale dielectric materials when they are excited by intense laser radiation. In most cases, this emission was observed in compounds doped with rare-earth (RE) ions upon excitation into the absorption band of these ions. An analysis of these publications indicates that there are different points of view on the nature of the observed phenomenon and the processes responsible for it. If we generalize the researchers’ opinions regarding the physical nature of this emission, we can conditionally divide them into two groups. The first group of researchers believes that the observed emission is inherently thermal (blackbody). According to the second group of opinions, it represents luminescence and is not associated with sample heating. For example, the authors of attribute the thermal nature to the BBWE observed when the nanosized particles of Y_2O_3:Yb,Er are excited into the absorption band of Yb^{3+} ions. At the same time, broadband emission (BBE) in the visible spectral region, which arises upon excitation of the 2F_5/2 level of Yb^{3+} ions of LiYbP_2O_{12}:Er nanoparticles, is explained by charge transfer luminescence of Yb^{3+} ions.

In our own studies, we demonstrated that the BBWE arising in Y_{1−x}Er_xPO_4 (x = 0–1) nanosized dielectric particles under laser excitation with λ_{exc} = 970 nm, is thermal. Studies of the features of similar phenomenon in Y_{1−x}Er_xVO_4 and La_{1−x}Pr_xGa_{0.5}Sb_{1.5}O_6 (x = 0–1) nanopowders upon their excitation into the absorption bands of Er^{3+} and Pr^{3+} ions also confirmed its thermal nature. The appearance of BBE in the visible spectral range in the compounds studied by us is a result of their strong heating under the impact of intense laser radiation. In our opinion, such a significant heating of the samples is resulted from the interaction of electrons in the conduction band with phonons of the crystal lattice. The transition of electrons to the conduction band is due to the interaction of excited RE ions with each other and with defects in the crystal structure, a significant amount of which are concentrated in the surface layers of nanoscale particles due to uncompensated bonds in many atoms.

According to the mechanism we proposed, in addition to the excitation power density and the concentration of RE ions, the appearance of BBWE in various matrices should be significantly affected by their band gap (E_g), the RE ion absorption value at the excitation wavelength, as well as the presence of structure defects. To clarify proposed mechanism and to identify which of these parameters is dominant, it is necessary to study the features of the BBWE appearance in various nanoscale dielectric materials with RE ions, in which these parameters differ significantly.

The study of Y_{1−x}Er_xPO_4 and Y_{1−x}Er_xVO_4 nanoparticles (x = 0–1) with a close crystal structure but different band gap (E_g = 8.6–9.2 eV [ref. 15 and 16] and 3.4–3.8 eV [ref. 17 and 18], respectively) revealed differences in conditions necessary for the BBWE appearance in them. For this reason, one of the criteria for choosing compounds for the present study was the value of their band gap, which should differ from values for the materials we have already studied. The next criterion was
the presence of defects in the structure, which would be confirmed experimentally.

Compounds CaF$_2$-x mol% ErF$_3$ and ZrO$_2$-x mol% Er$_2$O$_3$ (x = 0–25) satisfy the proposed criteria, are characterized by the same type of crystal structure, different band gap and have a number of features. Compounds of the CaF$_2$-ReF$_3$ type belong to the structural type of fluoride with a cubic crystal lattice and are wide-gap dielectrics with $E_g$ = 12 eV. A characteristic feature of such materials is their tendency to form clusters of RE ions at their concentrations of 0.1 at% and higher. At high concentrations of RE ions, the percolation effect is observed for these compounds, which consists in the interaction of clusters with each other. It should also be noted that in most studies, BBWE was detected in oxide nanosized particles doped with RE under laser excitation. To date, we have found only one such study for fluoride nanosized particles (for LiYbF$_4$ compounds). However, studies on the occurrence of BBE in CaF$_2$-x mol% ReF$_3$ compounds were not carried out.

ZrO$_2$-M$_2$O$_3$ solid solutions (where M = Y, RE ions) are also cubic and are characterized by $E_g$ = 4.6–5.8 eV (x = 8–9.5 mol%). The features of these compounds are their low thermal conductivity and the presence of defects in the structure (oxygen vacancies) due to heterovalent substitution of Zr$^{4+}$ ions with Y$^{3+}$ or Re$^{3+}$ ions. BBE in the ZrO$_2$-Y$_2$O$_3$-Yb$_2$O$_3$-Tm$_2$O$_3$ (YZS:Tm,Yb), ZrO$_2$-Y$_2$O$_3$, and Y$_{1.03}$Yb$_{0.07}$Zr$_{0.12}$O$_3$ compounds and the prospects for its practical application in photovoltaics were reported in ref. 11, 12 and 31. However, the physical mechanisms leading to the occurrence of this emission are not presented in the above papers, except that the authors attribute its occurrence to multiphonon relaxation. A deeper understanding of the physical processes causing the described phenomenon will expand the scope of its application, and will also be of fundamental importance.

Thus, summarizing the currently available experimental facts about BBWE in nanoscale dielectric particles with RE ions when they are excited by intense laser radiation into the absorption bands of these ions, we can state the ambiguity of views on the nature of its occurrence and the expediency of further studies in this direction.

In accordance with this, the aim of this work was to study the BBWE regularities in CaF$_2$-x mol% ErF$_3$ and ZrO$_2$-x mol% Er$_2$O$_3$ nanoparticles upon their excitation by laser radiation with $\lambda_{exc}$ = 1550 nm. It was also interesting to conduct a comparative analysis of the obtained results with results for Y$_{1-x}$Er$_x$PO$_4$ and Y$_{1-x}$Er$_x$VO$_4$ (x = 0–1) to clarify the appearance mechanism of the BBWE in nanoscale dielectric particles with RE ions and to identify the most important factors affecting its occurrence.

### 2. Experimental section

Nanosized CaF$_2$-x mol% ErF$_3$ (x = 5, 10, 15, 25) crystalline powders of fluoride structure were obtained by chemical coprecipitation according to the reaction:

$$1 - x\text{CaCl}_2 + x\text{ErCl}_3 + 2 + x\text{NH}_4\text{F}.$$  

As starting compounds for the preparation of samples, we used CaCl$_2$ (Aldrich, 99.9% purity), ErCl$_3\cdot6\text{H}_2\text{O}$ (Aldrich, 99.9% purity), NH$_4$F (Vecton, 99.9% purity) and deionized water. The mass of reagents was determined to the third decimal place. 25 ml of an initial aqueous solution with a concentration of 0.02 M containing calcium chloride ions and an alloying impurity were slowly added dropwise to 25 ml of 0.045 M aqueous solution of ammonium fluoride. The resulted mother solution was aged on a magnetic stirrer for 60 minutes. After that, the particles were centrifuged and washed three times with deionized water. After the reaction and washing, the product had a pink color, the intensity of which increased with increasing concentration of the dopant. After synthesis annealing was carried out in quartz crucibles in air in a SNOL 6/12-B muffle furnace for 1 hour at a temperature of 650 °C. The choice of the maximum ErF$_3$ concentration in these types of compounds was limited by the formation of the single-phase solid solution, since when the ReF$_3$ content is more than 25 mol%, the probability of the formation of an impurity monoclinic phase along with the cubic one is high.

Nanosized crystals of ZrO$_2$-x mol% Er$_2$O$_3$ (x = 5, 10, 15, 25) were synthesized under hydrothermal conditions according to the procedure. As starting reactants were used Zr(NO$_3$)$_2$$\cdot$2xH$_2$O (Sigma Aldrich, 99.99%) and Er(NO$_3$)$_3$$\cdot$5H$_2$O (Acros Organic, 99.9%). All the reactants were analyzed to determine the amount of crystallohydrate water molecules and weighted up to the fourth decimal place. 27 ml of initial water solution with concentration of 0.06 M containing ions of zirconia and the dopant was precipitated with 23 ml of ammonia solution. The resulting suspension was subjected to hydrothermal treatment for 24 hours at a temperature of 200 °C. After the synthesis was complete the mother solution was titrated to prove that no metal ions were left. Absence of impurity phases in the samples proves that the expected amount of dopant has indeed entered the lattice. Yield of the reaction is quantities and the product is white in color. In order to increase the size of the obtained nanoparticles, they were additionally annealed in a muffle furnace at the first stage for 6 hours at a temperature of 800 °C and at the second stage for 6 hours at a temperature of 1200 °C.

The morphology of the synthesized CaF$_2$-x mol% ErF$_3$ and ZrO$_2$-x mol% Er$_2$O$_3$ particles was studied by scanning electron microscopy (SEM) on a three-beam Carl Zeiss NVision 40 workstation with the function of local energy dispersive X-ray analysis (EDX) and a transmission electron microscope (TEM) (Carl Zeiss Libra 200 MC).

X-ray diffraction was used for the phase analysis of the samples. It was carried out using an Empyrean PANalytical B.V. diffractometer (CuK$_\alpha$ radiation, $\lambda = 1.5414$ Å) with a vertical goniometer and an XFlash 3D detector (for CaF$_2$-x mol% ErF$_3$) and a Bruker D8 Advance diffractometer (CuK$_\alpha$ radiation, Ni-filter and LYNXEYE detector, for ZrO$_2$-x mol% Er$_2$O$_3$). Phases were identified using database of International Centre for Diffraction Data (ICDD). Coherent scattering domain size was calculated with the help of Sherrer formula.
The lattice parameters were calculated using Topas R software (Bruker AXS, Karlsruhe, Germany) and HighScore Plus (PANalytical).

To record the diffuse reflectance spectra, suspensions consisting of nanopowders and silicate glue were applied to one side of the glass slides, the second side of the glass was covered with several layers of white paper. Diffuse reflectance spectra were measured with a 150 mm integrating sphere, which is an accessory to the Lambda 950 PerkinElmer spectrophotometer.

Spectral-luminescent studies were performed using an automated setup based on the MDR-23 monochromator. An Er:6.0 fiber erbium laser with $\lambda_{\text{exc}} = 1550$ nm was used as an excitation source. An FEU-79 photomultiplier was used as a radiation detector.

Images showing the color dynamics of the emission from the samples were obtained by extracting frames from a video (25 frames per second).

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**Table 1** Lattice parameters ($a$, $c$), unit cell volume ($V$) and the microstrain values ($\varepsilon$) of ZrO$_2$-$x$ mol% Er$_2$O$_3$ and CaF$_2$-$x$ mol% ErF$_3$ compositions

| $x$, mol% | ZrO$_2$-$x$ mol% Er$_2$O$_3$ | CaF$_2$-$x$ mol% ErF$_3$ |
|----------|-------------------|-------------------|
| $a$, Å    | $c$, Å            | $V$, Å$^3$        | $a$, Å | $V$, Å$^3$ |
| 5        | 3.609             | 5.171             | 67.35  | 5.464 | 163.13 |
| 10       | 3.617             | 5.167             | 67.61  | 5.47  | 163.67 |
| 15       | 5.13              | 135.01            | 5.485  | 165.02 |
| 25       | 5.14              | 135.79            | 5.493  | 165.7  |

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**Fig. 1** XRD patterns of ZrO$_2$-$x$ mol% Er$_2$O$_3$ (PDF-01-072-2742 – cubic phase$^{35}$ PDF-01-088-1007 – tetragonal phase$^{35}$) (a) and CaF$_2$-$x$ mol% ErF$_3$ (PDF-01-071-4110 – cubic phase$^{35}$) (b) ($x = 5$–25) concentration series.

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**Fig. 2** Particle size distribution for samples of ZrO$_2$-$x$ mol% Er$_2$O$_3$ (a) $x = 5$; (b) $x = 25$ pre-annealing. TEM-images of ZrO$_2$-$x$ mol% Er$_2$O$_3$ ($x = 5$) before (c) and after (d) annealing at a temperature of 1200 °C.

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vacancies formation induced by the presence of dopant ions. The nonlinearity of the concentration–parameter relation is caused by the heterovalent nature of the substitution and vacancies formation induced by the presence of dopant ions.

The coherent scattering domain size (CSD) for all ZrO₂−ₓ mol% Er₂O₃ samples was estimated before annealing with the help of Sherrer formula. It can be noted that the CSD slowly decreases from 9 nm at 5 mol% to 5 nm at 25 mol% with dopant concentration increasing. This data is in agreement with the particle size distribution that is based on TEM photos (Fig. 2). SEM data (Fig. 3) shows that a change in the selected range of Er₂O₃ concentrations. Particles with x = 15 have large sizes (~300 nm), which, apparently, is associated with annealing conditions. The particles consist of separate blocks average size of which was evaluated based on the CSD and turned out to be around 60–70 nm independently of erbium concentration. The microstrain values (ε) ranged from 2 to 6 × 10⁻⁴.

Structural analysis of CaF₂-x mol% ErF₃ also showed lattice parameter increasing with rise of erbium content (Table 1). Average CSD size was around 90 nm and the microstrain values (ε) ranged from 1 to 5 × 10⁻⁴ independently of erbium concentration. Analysis of the SEM-images of CaF₂-25 mol% ErF₃ samples (x = 5, 10, 15, 25) showed that the average nanoparticle size is about 200 nm and does not depend on the value of x (Fig. 4) with the exception of sample with x = 15 which average particle size is smaller and equal to about 100 nm. Since in synthesis method the dropping of the chloride solution was carried out manually, a certain deviation of the particle sizes from the average is normal.

Thus, CaF₂-x mol% ErF₃ and ZrO₂-x mol% Er₂O₃ solid solutions are characterized by close values of the average particle size.

Excitation of CaF₂-x mol% ErF₃ samples (x = 5–25) to the 4I₁₃/₂ level of Er³⁺ ions by continuous laser radiation with λexc = 1550 nm and power density J = 0.15 kW cm⁻² led to upconversion luminescence of Er³⁺ ions due to transitions from excited levels of ²H₉/₂, ²S₉/₂, ⁴P₉/₂, ⁴I₉/₂ on the ground state ⁴I₁₅/₂ of these ions. A similar luminescence was observed for samples with x = 5–15 with an increase in J to 1.93 kW cm⁻² (Fig. 5). In this case, the luminescence intensity ratio for the ²H₉/₂ → ⁴I₁₅/₂, ⁴S₉/₂ → ⁴I₁₃/₂ (500–570 nm) transitions and the ⁴P₉/₂ → ⁴I₁₅/₂ transition (630–700 nm) increases with increasing erbium content in the sample (x = 5–10). At x = 15, the relative line intensity decreases in the region of 500–570 nm, and a broad…
The concentration of RE ions in them. The difference in the particle sizes of the sample with \( x = 15 \) did not lead to significant differences in its emission spectra from the spectra of samples with \( x = 10 \) and \( 5 \). Analysis of emission spectra for samples with \( x = 5-25 \) can reveal small changes in the ratio of peak intensity for the main emission band \( \left( ^{4}F_{9/2} \to ^{4}I_{15/2} \right) \). As mentioned in the introduction, the formation of RE ion clusters is characteristic of this type of compounds. In samples with different contents of RE ions, the cluster structure will have some differences, which, in turn, can lead to observed differences in spectra.

It should be noted that the buildup time of BBE in CaF\(_2-x\) mol\% ErF\(_3\) \( (x = 25) \) to a maximum intensity is more than 9 seconds (Fig. 6), which significantly exceeds the buildup time \( (0.2 \text{ s}) \) for ErPO\(_4\) nanoparticles. In this case, at the initial stages after switching on the excitation source, a red glow was observed, which is characteristic of the luminescence of Er\(^{3+}\) ions due to the \( ^{4}F_{9/2} \to ^{4}I_{15/2} \) transition. A similar character of buildup was noted earlier in ref. 5 and by us in ref. 7 and 8. After correcting the BBE spectrum of the CaF\(_2-25\) mol\% ErF\(_3\) sample for instrumental response, the color temperature \( T_c \) of this emission was estimated using the method described in ref. 35 and was about 1800 K. It should be noted that regions with traces of melting were observed on the surface of the CaF\(_2-25\) mol\% ErF\(_3\) sample after exposure to laser radiation with \( J = 1.93 \text{ kW cm}^{-2} \). This indicates local heating of CaF\(_2-25\) mol\% ErF\(_3\) particles to the melting temperature \( (1691 \text{ K}) \). In CaF\(_2-x\) mol\% ErF\(_3\) \( (x = 1-15) \) samples, no traces of melting were found after a same irradiation.

The study of the spectral and luminescent characteristics of ZrO\(_2\)-x mol\% Er\(_2\)O\(_3\) \( (x = 5-25) \) compounds revealed a number differences from the characteristics of CaF\(_2\)-x mol\% ErF\(_3\) \( (x = 1-25) \) under identical excitation conditions. Fig. 5 shows the emission spectra of ZrO\(_2-x\) mol\% Er\(_2\)O\(_3\) \( (x = 5-25) \), recorded upon excitation to the \( ^{4}I_{15/2} \) level of Er\(^{3+}\) ions by laser radiation with \( \lambda_{\text{exc}} = 1550 \text{ nm} \) and \( J = 0.89 \text{ kW cm}^{-2} \).
Fig. 7(a) demonstrates that, at the indicated $J$, upconversion luminescence of Er$^{3+}$ ions is observed for samples with $x = 5, 10$, and intense BBE is observed for samples with $x = 15, 25$. The dip in the 600–650 nm region of the emission spectra of ZrO$_2$–$x$ mol% Er$_2$O$_3$ ($x = 15, 10, 15, 25$) is associated with the features of the recording system, and the dips in the ranges of 500–550, 650–700 and 780–820 nm is due to the reabsorption of radiation by Er$^{3+}$ ions. As $J$ increases to 1.1 kW cm$^{-2}$, BBE is already detected in all ZrO$_2$–$x$ mol% Er$_2$O$_3$ ($x = 5, 10, 15, 25$) samples. The $I(P)$ dependence for BBE in all samples is nonlinear and the slope is 5.8–6.2, as for the previously studied ErPO$_4$ powders.$^8$ As an illustration, this dependence is presented for the ZrO$_2$–25 mol% Er$_2$O$_3$ sample in Fig. 7(b). As in the case of fluoride particles, the morphology and particle sizes of ZrO$_2$–$x$ mol% Er$_2$O$_3$ with $x = 25, 10, 5$ do not differ significantly (Fig. 3), which allows us to relate the differences in the behavior of the emission spectra of these samples (under identical excitation conditions) with different RE ions content in them. As noted in the manuscript, the particle size of the sample with $x = 15$ is slightly different from the rest of the samples, however, its spectral-luminescent properties are close to the properties of the sample with $x = 25$ (Fig. 7).

The buildup character of BBWE in ZrO$_2$–$x$ mol% Er$_2$O$_3$ ($x = 5, 10, 15, 25$) compounds is also similar to that observed in Y$_{0.95(1-x)}$Yb$_{0.05}$Er$_{0.05}$PO$_4$, Y$_{0.95(1-x)}$Yb$_{0.05}$Er$_{0.05}$PO$_4$·0.8H$_2$O nanopowders and is described in ref. 7 and 24. As an illustration, Fig. 8 shows the temporal dynamics of the emission color of the ZrO$_2$–5 mol% Er$_2$O$_3$ sample, the numbers in the figure indicate the time (in seconds) after the laser was turned on.

It can be seen that, at the initial moment after switching on the excitation source with $J = 1.1$ kW cm$^{-2}$, up-conversion luminescence of Er$^{3+}$ ions is observed in nanoscale crystalline powders ZrO$_2$–5 mol% Er$_2$O$_3$. BBE in these compounds appears 0.23 s after switching on the excitation source, and reaches a maximum intensity in 3.6 s, which is almost three times faster than in CaF$_2$–25 mol% ErF$_3$.

After correction the BBE spectra of the ZrO$_2$–$x$ mol% Er$_2$O$_3$ ($x = 5, 10, 15, 25$) concentration series for $J$ equal to 0.89, 1.45, 1.93 kW cm$^{-2}$, we estimated the emission color temperatures $T_c$, which corresponded to the range of 2200–2720 K.

A comparison of BBE spectra of ZrO$_2$–$x$ mol% Er$_2$O$_3$ and the spectrum of the tungsten lamp (color temperature of 2850 K) revealed similarity of their forms. As an illustration, Fig. 9 shows the emission spectra of CaF$_2$–25 mol% ErF$_3$, ZrO$_2$–25 mol% Er$_2$O$_3$ samples and the TRSH-2850 tungsten lamp, as well as the spectra of Y$_{0.75}$Er$_{0.25}$PO$_4$ and Y$_{0.75}$Er$_{0.25}$VO$_4$ (ref. 8) particles without correction for instrumental response.

As noted above, in ref. 7 and 8 we presented an occurrence mechanism of blackbody emission in nanoscale orthophosphate and orthovanadate dielectric particles doped with RE ions. This mechanism includes a number of processes (Fig. 10). When nanoparticles are excited by laser radiation with a high
power density to the absorption band of the RE ions, nonlinear interaction of these ions occurs and leads to population of their high energy levels \( (1) \). Further, ions excited to high energy levels interact with defects in the crystal structure \( (2) \), for example, with surface defects. Then, the electrons pass from the energy levels of defects into the conduction band and their interaction with the lattice phonons \( (3) \) results to the nanoparticle heating, which, in turn, leads to the BBWE appearance. An analysis of the characteristics of this emission for the \( \text{ZrO}_2 \cdot x \text{mol}\% \text{Er}_2\text{O}_3 \) and \( \text{CaF}_2 \cdot x \text{mol}\% \text{ErF}_3 \) particles studied in this work allows us to conclude that the proposed mechanism is also applicable to these particles.

Now we analyze the effect of some physical characteristics and geometric factors of \( \text{CaF}_2 \cdot 25 \text{mol}\% \text{ErF}_3, \text{ZrO}_2 \cdot 25 \text{mol}\% \text{Er}_2\text{O}_3, Y_{0.75}\text{Er}_{0.25}\text{PO}_4, Y_{0.75}\text{Er}_{0.25}\text{VO}_4 \) (ref. 8) nanoparticles on the conditions of the BBE appearance in them and its characteristics.

Since BBWE is observed in dielectric nanoparticles doped with RE ions when they are excited by laser radiation of a certain intensity in the absorption bands of these ions, the conditions for its occurrence may depend on the absorption and scattering coefficients of the radiation at an excitation wavelength. However, evaluative studies using diffuse optical spectroscopy revealed that there are no cardinal differences at the excitation wavelength in the absorption spectra of \( \text{CaF}_2 \cdot 25 \text{mol}\% \text{ErF}_3, \text{ZrO}_2 \cdot 25 \text{mol}\% \text{Er}_2\text{O}_3, Y_{0.75}\text{Er}_{0.25}\text{PO}_4, Y_{0.75}\text{Er}_{0.25}\text{VO}_4 \) samples. As confirmation, Fig. 11 shows the diffuse reflection spectra of these samples converted using the Kubelka–Munk formula.  

The next feature of nanoparticles, which can affect their spectral and luminescent properties, is a high surface to volume ratio. This feature leads to an increase in the fraction of near-surface RE ions with an environment different from the environment of ions inside the particle. However, for our studied particle size range, such an effect will be insignificant. As noted above, the average particle sizes of \( \text{CaF}_2 \cdot 25 \text{mol}\% \text{ErF}_3 \) are \( 200 \text{ nm} \), \( \text{ZrO}_2 \cdot 25 \text{ mol}\% \text{Er}_2\text{O}_3 \) are \( 100 \text{–} 200 \text{ nm} \), and the particle sizes of \( Y_{0.75}\text{Er}_{0.25}\text{PO}_4 \) and \( Y_{0.75}\text{Er}_{0.25}\text{VO}_4 \) correspond to ranges \( 20 \text{–} 50 \text{ and } 40 \text{–} 100 \text{ nm} \).

In ref. 8, we also suggested that the material band gap \( (E_g) \) affects the appearance of thermal emission. The band gap affects the number of transitions that an electron must undergo in order to get into the conduction band. In order to be at the high energy level corresponding to the energy level of the structural defect, the electron will need to overcome a larger number of transitions in a compound with large \( E_g \) than in a compound with a smaller \( E_g \). For clarity, Table 2 shows the band gap values \( (E_g) \) and melting temperatures \( (T_m) \) of the materials, the threshold power density of the exciting radiation \( (J_{\text{thr}}) \), as well as BBWE color temperatures \( (T_c) \). The threshold power density of the exciting radiation \( (J_{\text{thr}}) \) was estimated from the \( (P) \) dependence.

The table shows that the smallest \( J_{\text{thr}} \) value corresponds to \( Y_{0.75}\text{Er}_{0.25}\text{VO}_4 \) with the narrowest band gap. As noted in ref. 8, with a further increase in \( J \), the BBWE arising in these materials became unstable. This fact, apparently, is associated with the particle recrystallization as a result of significant heating in the region of BBWE occurrence. With increasing \( E_g \), the value of \( J \) also increases.

Excitation of compounds with RE ions can lead not only to luminescence of these ions, but also to nonradiative relaxation processes, which will lead to additional heating of the samples. As noted in the introduction, some authors\(^ {39,41} \) attribute the occurrence of thermal “white” emission precisely to these processes. In our case, when erbium-containing nanoparticles are excited to the \( ^4I_{13/2} \) level of \( \text{Er}^{3+} \) ions, the probability of nonradiative relaxation from this level to the \( ^4I_{15/2} \) ground state is close to zero, since the energy gap between these levels \( (6500 \text{ cm}^{-1}) \) is several times higher than vibrational quantum \( \nu \) (Table 2). Excitation of \( \text{Er}^{3+} \) ions to the \( ^4I_{13/2} \) level also leads to population of higher levels, the probability of nonradiative relaxation from which is nonzero. In ref. 8, we directly excited to one of these levels \( (^2H_{11/2}) \), but no BBWE was observed. This allowed us to conclude that nonradiative relaxation does not play a major role in its appearance. If nonradiative relaxation from excited levels of RE ions played a significant role in

### Table 2 Parameters of BBE in different studied matrices

| Compound                  | \( E_g \), eV | \( J_{\text{thr}} \), kW cm\(^{-2} \) | \( T_c \), K | \( T_m \), K | \( \nu \), cm\(^{-1} \) |
|---------------------------|---------------|------------------------------------|------------|------------|----------------|
| \( \text{CaF}_2 \cdot 25 \text{mol}\% \text{ErF}_3 \) | 12 (ref. 19)  | 1.93                               | 1800       | 1691 (ref. 36) | 443 (ref. 40) |
| \( Y_{0.75}\text{Er}_{0.25}\text{PO}_4 \)        | 8.6–9.2 (ref. 15 and 16) | 1.39 (ref. 8)                               | 2400 (ref. 8) | 2173 (ref. 41) | 1061 (ref. 42) |
| \( \text{ZrO}_2 \cdot 25 \text{mol}\% \text{Er}_2\text{O}_3 \) | 4.6–4.7, 5.49–5.8 (ref. 27 and 30) | 0.89                               | 2200       | 2973 (ref. 43) | 625 (ref. 44) |
| \( Y_{0.75}\text{Er}_{0.25}\text{VO}_4 \)        | 3.4–3.8 (ref. 17 and 18) | 0.52 (ref. 8)                               | 1800 (ref. 8) | 2083 (ref. 45) | 891 (ref. 20) |

Fig. 11 Diffuse reflection spectra of \( \text{CaF}_2 \cdot 25 \text{mol}\% \text{ErF}_3, \text{ZrO}_2 \cdot 25 \text{mol}\% \text{Er}_2\text{O}_3, Y_{0.75}\text{Er}_{0.25}\text{PO}_4, Y_{0.75}\text{Er}_{0.25}\text{VO}_4 \).
increasing the temperature of the samples, then thermal emission would be most pronounced for compounds with a large value of $\nu$ and would be less pronounced for materials with small $\nu$. However, as follows from Table 2, despite the fact that $\nu$ values for ZrO$_2$-25 mol% Er$_2$O$_3$ and Y$_{0.75}$Er$_{0.25}$PO$_4$ are two times different, the BBWE color temperatures in these compounds are close. Apparently, the presence of defects in the crystal structure, in particular, oxygen vacancies, is a more important factor affecting the conditions for the appearance of BBWE in ZrO$_2$-x mol% Er$_2$O$_3$ nanopowders.

The influence of defects on the conditions for the appearance of thermal emission is clearly seen in the analysis of its features in ZrO$_2$-25 mol% Er$_2$O$_3$ nanoparticles. Fig. 7 shows that the BBWE in ZrO$_2$-25 mol% Er$_2$O$_3$ has the highest relative intensity, while in CaF$_2$-25 mol% ErF$_3$, Y$_{1-x}$Er$_x$PO$_4$, Y$_{1-x}$Er$_x$VO$_4$ ($x = 0.25$) it has a background character. Moreover, the considered emission appeared in ZrO$_2$-x mol% Er$_2$O$_3$ even at low $x$ values (5, 10), which was not observed for other samples in the available range of $J$. As noted in the introduction, heterovalent substitution of Zr$^{4+}$ ions by Er$^{3+}$ ions leads to the appearance of oxygen vacancies in ZrO$_2$-$M_2$O$_3$, structural defects, which are characterized by energy levels near the conduction band. 27–10,40,47 According to studies, the energy levels of oxygen vacancy is located at 2.5–2.6 eV (19 600–20 300 cm$^{-1}$), 3.3–3.8 eV (∼25 800–29 700 cm$^{-1}$) and 4–5 eV (∼31 200–39 000 cm$^{-1}$). 27,28,47 X-ray phase analysis of the ZrO$_2$-x mol% Er$_2$O$_3$ ($x = 5–25$) concentration series confirmed (Fig. 1) that synthesized nanoparticles are single-phase and correspond to the structural types which are typical for ZrO$_2$–$M_2$O$_3$ compounds with similar RE content. Consequently, the synthesized compound will possess typical features for this structure, in particular, it will be characterized by the presence of defects. The presence of a significant number of such defects ZrO$_2$-25 mol% Er$_2$O$_3$ and their interaction with Er$^{3+}$ ions excited to high energy levels will greatly contribute to the appearance of electrons in the conduction band.

It should be noted that an important role in the population of the upper energy levels of Er$^{3+}$ ions is played by the resonances in the energy level system, as well as the interaction probability of ions with each other. This probability increases with decreasing distance between ions and with increasing their concentration. In addition, the interaction processes will proceed more intensively with an increase in the excitation power density. The effective interaction of Er$^{3+}$ ions in all samples studied both in this work and earlier is evidenced by the presence of upconversion luminescence of these ions. Also, a clear dependence of the BBWE occurrence on the RE ions content is observed for all the studied samples. This is due to the fact that, at low concentrations of these ions, the processes of interaction between them and with defects are not intense enough to transfer a significant number of electrons into the conduction band. In CaF$_2$-x mol% ErF$_3$ compounds, the described interaction will be more effective due to the clustering of RE ions. 21,22 Nevertheless, according to the results presented above, the process of the appearance of BBWE in these compounds is less pronounced in comparison with other compounds. This fact is an additional confirmation that the value of $E_g$ is a significant factor.

To summarize, we can list the main factors affecting the conditions for the BBWE appearance in dielectric nanoparticles doped with RE ions when they are excited by intense laser radiation. These include the band gap of the material and the presence of defects in its crystal structure. Also, one cannot exclude the effect of the RE ions absorption at the excitation wavelength.

The obtained results are not only of fundamental importance, but can also be used in practice, for example, in dermato-logy, to remove skin neoplasms. Currently, infrared (IR) lasers are the most common in this area, and their radiation is delivered to the tissue via optical fiber, which allows both contactless and contact effects on biological tissue to be realized. 48–54 To increase the thermal effect during contact exposure and increase the efficiency of the procedure, “blackening” of the fiber end face is proposed. 21 Such a modification does not provide for the reuse of fiber and increases the cost of the procedure. Coating the biological tissue with ZrO$_2$-x mol% Er$_2$O$_3$ nanoparticles, which are bioinert, can act as an alternative way of enhancing the thermal effect of the contactless IR irradiation. This method will also allow the use of radiation sources with a relatively low power (∼1–2 W), which will positively affect the cost of the procedure.

4. Conclusion

In this work, we studied the features of broadband “white” emission in CaF$_2$-x mol% ErF$_3$ and ZrO$_2$-x mol% Er$_2$O$_3$ nanoparticles upon their excitation by laser radiation with $\lambda_{exc} = 1550$ nm. In CaF$_2$-x mol% ErF$_3$ nanoparticles, this emission arose at an erbium concentration of 25 mol% and an excitation power density $J$ equal to 1.93 kW cm$^{-2}$ and had a background character with respect to the luminescence bands of Er$^{3+}$ ions due to $^2$H$_{15/2}$, $^4$S$_{3/2}$, $^4$F$_{9/2}$, $^4$I$_{15/2}$ transitions to the ground state $^4$I$_{15/2}$ of these ions. In ZrO$_2$-x mol% Er$_2$O$_3$ nanoparticles (15, 25), the indicated emission was observed at a lower value of $J$ (0.89 kW cm$^{-2}$), and when $J$ increased to 1.1 kW cm$^{-2}$, it also appeared in samples with $x = 5, 10$.

Comparison of the results obtained in this study with those obtained earlier for erbium-containing particles of orthophosphates and orthovanadates, 8 confirmed the nature and the mechanism of the appearance of “white” emission that we proposed. We have revealed the dependence of the threshold excitation power density necessary for its appearance on the band gap of the material and found that this parameter is one of the dominant ones. Also, by the example of ZrO$_2$-x mol% Er$_2$O$_3$ nanoparticles, it was demonstrated that the presence of crystal structure defects is the next key factor contributing to the appearance of thermal emission.

Conflicts of interest

There are no conflicts to declare.
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References

1 S. M. Redmond, S. C. Rand and S. L. Oliveira, Appl. Phys. Lett., 2004, 85, 5517.
2 L. Marciniak, W. Strek, D. Hreniak and Y. Guyot, Appl. Phys. Lett., 2014, 105, 173113.
3 W. Strek, L. Marciniak, A. Bednarkiewicz, A. Lukowiak, R. Wiglus and D. Hreniak, Opt. Express, 2011, 19, 14084.
4 J. Wang and P. A. Tanner, J. Am. Chem. Soc., 2010, 132, 947.
5 S. Redmond, S. C. Rand, X. L. Ruan and M. Kaviany, J. Appl. Phys., 2004, 95, 4069.
6 J.-F. Bisson, D. Kouznetsov, K.-I. Ueda, S. T. Fredrich-Thornton, K. Petermann and G. Huber, Appl. Phys. Lett., 2007, 90, 201901.
7 S. A. Khrushchalina, P. A. Ryabochkina, V. M. Kyashkin, A. S. Vanetsev, O. M. Gaytko and N. Yu Tabachkova, JETP Lett., 2016, 103, 302–308.
8 S. A. Khrushchalina, P. A. Ryabochkina, M. N. Zharkov, V. M. Kyashkin, N. Yu Tabachkova and I. A. Yurlov, J. Lumin., 2019, 205, 560–567.
9 A. V. Egorysheva, O. M. Gajtko, S. V. Golodukhina, S. A. Khrushchalina, P. A. Ryabochkina, A. D. Taratynova and I. A. Yurlov, Ceram. Int., 2019, 45, 16886–16892.
10 Y. Hikichi, T. Sasaki, K. Murayama, T. Nomura and M. Miyamoto, J. Am. Ceram. Soc., 1989, 72, 1073.
11 M. R. N. Soares, M. Ferro, F. M. Costa and T. Monteiro, Nanoscale, 2015, 7(47), 19958–19969.
12 J. Wang, T. Ming, Z. Jin, J. Wang, L.-D. Sun and C.-H. Yan, Nat. Commun., 2014, 5, 1–8.
13 S. Tabanli, H. Cinkaya Yilmaz, G. Bilir, M. Erdem, G. Ertyurek, B. Di Bartolo and J. Collinse, ECS J. Solid State Sci. Technol., 2018, 7(11), 3199–3210.
14 C. I. Silva Filho, A. L. Oliveira, S. C. F. Pereira, G. F. de Sá, L. L. da Luz and S. Alves Júnior, Dalton Trans., 2018, 48(8), 2574–2581.
15 W. Da-Wei, H. Shi-Hua, Y. Fang-Tian and T. Ye, Chin. Phys. C, 2009, 33, 1019–1022.
16 J. J. Bos, P. Dorenbos, A. Bessière and B. Viana, Radiat. Meas., 2008, 43, 222–226.
17 A. H. Krumpel, E. van der Kolk, E. Cavalli, P. Boutinaud, M. Bettinelli and P. Dorenbos, J. Phys.: Condens. Matter, 2009, 21, 115503.
18 Y. Fujimoto, T. Yanagida, Y. Yokota, V. Chani, V. V. Kochurikhin and A. Yoshikawa, Nucl. Instrum. Methods Phys. Res., Sect. A, 2011, 635, 53–56.
19 H. Shi, R. I. Eglitis and G. Borstel, Phys. Rev., 2005, 72, 045109.
20 S. A. Miller, H. H. Caspers and H. E. Rast, Phys. Rev., 1968, 168, 964.
21 B. P. Sobolev, A. M. Golubev and P. Herrero, Crystallogr. Rep., 2003, 48(1), 141–161.
22 S. A. Kazanskiil, JETP Lett., 1983, 38, 521.
23 N. I. Sorokin and B. P. Sobolev, Phys. Solid State, 2019, 61, 2034.
24 P. A. Ryabochkina, S. A. Khrushchalina, V. M. Kyashkin, A. S. Vanetsev, O. M. Gaytko and N. Yu Tabachkova, JETP Lett., 2016, 103, 743–751.
25 F. Auzel, Chem. Rev., 2004, 104, 139.
26 L. Marciniak, R. Tomala, M. Stefanski, D. Hreniak and W. Strek, J. Rare Earths, 2016, 34, 227–234.
27 N. Nicoloso, A. Löbert and B. Leibold, Sens. Actuators, B, 1992, 8(3), 253–256.
28 E. D. Wachsman, N. Jiang, C. W. Frank, D. M. Mason and D. A. Stevenson, Appl. Phys. A: Solids Surf., 1990, 50(6), 545–549.
29 V. R. PauVerneker, A. N. Petelin, F. J. Crowne and D. C. Nagle, Phys. Rev. B: Condens. Matter Mater. Phys., 1989, 40(12), 8555–8557.
30 C. Ricca, A. Ringuédé, M. Cassir, C. Adamo and F. Labat, RSC Adv., 2015, 5, 13941–13951.
31 F. González, R. Khadka, R. López-Juárez, J. Collins and B. Di Bartolo, J. Lumin., 2018, 198, 320–326.
32 B. P. Sobolev, The Rare Earth Trifluorides. Part 1. The High Temperature Chemistry of the Rare Earth Trifluorides, ed. B. P Sobolev, Barcelona: Institut d’Estudis Catalans, 2000, p. 530, ISBN 84-7283-518-9.
33 P. P. Fedorov and B. P. Sobolev, J. Less-Common Met., 1979, 63(1), 31–43.
34 V. O. Veselova, I. A. Yurlov, P. A. Ryabochkina and A. V. Egorysheva, Russ. J. Inorg. Chem., 2020, 65, in press.
35 A. N. Magnunov, Instrum. Exp. Tech., 2009, 52, 451–472.
36 P. A. Popov, P. P. Fedorov and V. V. Osiko, Phys. Solid State, 2010, 52, 504–508.
37 G. Kortum and J. Vogel, Z. Phys. Chem., 1958, 18, 230.
38 P. C. S. Filho and O. A. Serra, J. Phys. Chem., 2011, 115, 636.
39 H.-D. Nguyen, S.-i. Mho and I.-H. Yeo, J. Lumin., 2009, 129, 1754–1758.
40 K. Tahvildari, M. Esmaeilpour, S. Ghammamy and H. Nabipour, Int. J. Nano Dimens., 2012, 2(4), 269–273.
41 Y. Hikichi and T. Nomura, J. Am. Ceram. Soc., 1987, 70, 252.
42 G. M. Begun, G. W. Beall, L. A. Boattner and W. J. Gregor, J. Raman Spectrosc., 1984, 11, 273–278.
43 V. V. Osiko, M. A. Borik and E. E. Lomonova, Technique Springer Handbook of crystal growth, 2010, ch. 14, vol. 353, pp. 432–477.
44 C. M. Phillippi and K. S. Mazdiyasni, J. Am. Ceram. Soc., 1971, 54(5), 254–258.
45 E. M. Levin, J. Am. Ceram. Soc., 1967, 50(7), 381–382.
46 X. Li, X. Mao, M. Feng, J. Xie, B. Jiang and L. Zhang, J. Eur. Ceram. Soc., 2016, 36(16), 4181–4184.
47 A. S. Foster, V. B. Sulimov, F. Lopez Gejo, A. L. Shluger and R. M. Nieminen, Phys. Rev. B: Condens. Matter Mater. Phys., 2001, 64, 224108.
48 A. Klein, W. B. Umler, M. Landthaler and P. Babila, Int. J. Hyperthermia, 2011, 27(8), 762–770.
49 B. Azadgoli and R. Y. Baker, *Ann. Transl. Med.*, 2016, **4**(23), 452.

50 J. N. Pozner and B. E. DiBernardo, *Clin. Plast. Surg.*, 2016, **43**(3), 515–525.

51 A. V. Belikov, M. L. Gelfond, K. V. Shatilova, S. A. Sosenkova and A. A. Lazareva, *Proc. of SPIE-OSA Biomedical Optics*, 2015, vol. 9542, p. 95420.

52 W. G. Stebbins, C. W. Hanke and J. Petersen, *Dermatol. Ther.*, 2011, **24**, 125–130.

53 A. N. Kassab and A. E. Kharbotly, *Eur. Arch. Oto-Rhino-Laryngol.*, 2012, **269**, 419–423.

54 U. Wollina, *Indian J. Dermatol.*, 2016, **61**(5), 540–544.

55 G. Katz, *J. Am. Ceram. Soc.*, 1971, **54**, 531.

56 J. Malek, L. Benes and T. Mitsuhashi, *Powder Diff.*., 1997, **12**, 96.

57 H. E. Swanson and E. Tatge, *Natl. Bur. Stand. Circ.*, 1953, **539**, 69.