

Article

Novel Fluoride Matrix for Dual-Range Optical Sensors and Visualization

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Abstract: Novel tetragonal matrix $\text{Ba}_{0.5-x}\text{Ln}_{0.5}\text{Na}_x\text{F}_{2.5-x}$ with $x = 0.08$, doped by Yb^{3+} , Ho^{3+} , Er^{3+} , was synthesized by molten salt synthesis (MSS) from nitrate flux. XRD data show that the tetragonal phase with $a = 4.122(1) \text{ \AA}$, $c = 17.672(1) \text{ \AA}$ is stable in an argon atmosphere up to 960°C . Luminescence spectra recorded in 500–900 nm and 1050–1700 nm upon 974 nm pumping demonstrated the characteristic luminescence at 1550 nm ($^4\text{I}_{13/2} \rightarrow ^4\text{I}_{15/2}$) for Er^{3+} and 1150 nm ($^5\text{I}_6 \rightarrow ^5\text{I}_8$) for Ho^{3+} . The relative thermal sensitivity (S_r) at 296–316 K were $0.3\% \times \text{K}^{-1}$ and $5.5\% \times \text{K}^{-1}$ in shortwave infrared (SWIR) and visible range, respectively. Synthesized luminophores can be used as dual-range optical temperature sensors, which simultaneously operate in visible and SWIR ranges.

Keywords: fluoride matrix; luminescence; thermometry; thermography; molten salt synthesis



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1. Introduction

Luminescent thermometry is an effective way to display the temperature in the analyzed objects. The main advantage of luminescent thermometry is the possibility of contactless temperature measurement [1–5]. This approach is efficiently applied in medicine, biology, detecting catalytic reactions, and other areas, where contact measurement is inconvenient or inapplicable [6–9].

Luminescent nanoprobes are widely used quantum dots [10], organic dyes [11], polymers [12], DNA or protein-conjugated systems [13], transition metal-based materials, or materials doped with rare-earth ions [14]. The latter has many advantages, such as high photostability and narrow luminescence peaks with large shifts between excitation and emission. Moreover, these materials are also capable of converting near-infrared (NIR) excitation to emission in the ultraviolet (UV), visible, or NIR range via a multiphoton excitation process known as upconversion. This feature makes upconverting materials interesting for biological applications where NIR excitation offers several advantages, such as higher penetration depth in biological tissue, negligible autofluorescence, and lower photodamage in comparison to UV.

Temperature measuring using rare-earth (Ln) ions luminescence [15] is based on two main approaches. The first approach is based on the measurement of luminescence intensity ratio (LIR) from two different energy levels that are thermally coupled [16,17]. The energy gap between the thermally coupled levels is so small that, according to Boltzmann's law, an increase in temperature can lead to an increase in the population of the overlying state. In the luminescence spectrum, an increase in the shorter-wavelength peak will be observed.

The second approach was proposed by Sekiyama et al. [18] and is based on temperature-dependent non-resonant energy transfer. In this case, a matrix is doped with three rare-earth

ions [19,20]. One of them (usually Yb^{3+}) acts as a donor, absorbs exciting radiation, and transfers it to two other acceptor ions. Acceptor ions are selected in such way that one of the energy transfers is resonant, its probability does not depend on temperature and this signal is used as a reference. The second transfer is non-resonant and with increasing temperature, its probability increases (phonon-assisted energy transfer). This approach was realized for Yb^{3+} - Er^{3+} - Ho^{3+} -doped NaYF_4 nanoparticles and allows thermometry in the SWIR region.

Pumping was carried out into the absorption band Yb^{3+} (${}^7\text{F}_{7/2} \rightarrow {}^5\text{F}_{5/2}$), followed by energy redistribution between Ho^{3+} and Er^{3+} ions as a result of non-radiative energy transfer. In this case, the energy transfer of $\text{Yb}^{3+} \rightarrow \text{Ho}^{3+}$ is phonon assisted, as a result of which the luminescence intensity of Ho^{3+} ions at the transition ${}^5\text{I}_6 \rightarrow {}^5\text{I}_8$ will depend on temperature, and the energy transfer of $\text{Yb}^{3+} \rightarrow \text{Er}^{3+}$ is resonant, as a result of which the luminescence of Er^{3+} ions at the transition ${}^4\text{I}_{13/2} \rightarrow {}^4\text{I}_{15/2}$ depends on temperature weakly [21]. This makes it possible to measure the relative coefficient of temperature sensitivity by the ratio of the integral intensities of the luminescence bands. The obtained thermal sensitivity was in the range of $1.34\text{--}1.87\% \cdot ^\circ\text{C}$ in the physiological temperature range.

To date, the active search for new thermal sensors continues. The main tasks are to expand the range of operating temperatures and the range of excitation and emission wavelengths, as well as to increase thermal sensitivity. The sensitivity between 0.5 and $1.5\% \text{ K}^{-1}$ at around 300 K is typically for Er^{3+} [22]. In the paper [23], it was proposed to use silica coating to expand the thermometry range to 900°C ; the relative sensitivity was from $1.02\% \text{ K}^{-1}$ at 300 K to $0.13\% \text{ K}^{-1}$ at 900°C . The use of Nd^{3+} ions allows a shift of the operating wavelength range into NIR and obtains a relative sensitivity of $1.1\% \text{ K}^{-1}$ for $\text{NaYF}_4:0.1\%\text{Nd}^{3+}$ [24]. For $\text{Nd}^{3+}/\text{Tm}^{3+}/\text{Yb}^{3+}/\text{Gd}^{3+}$ four-doped NaYF_4 nanoparticles the relative sensitivity was significantly higher and reached $2.89\% \text{ K}^{-1}$ in the temperature range of $333\text{--}553 \text{ K}$ [25].

Thus, using thermally coupled levels, taking into account resonant and non-resonant energy transfer channels from the sensitizer, it is possible to expand the range of wavelengths in which thermometry can be performed, as well as increase the thermal sensitivity.

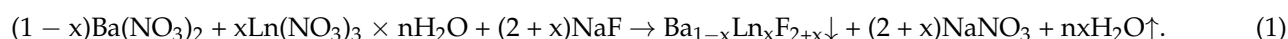
Fluoride matrices such as NaYF_4 [26], NaGdF_4 [27], and MF_2 , where $\text{M} = \text{Ca}, \text{Sr}, \text{Ba}$ [28], have proven to be effective photonics materials [29]. It is known that an increase in matrix molecular weight leads to a decrease in multi-phonon relaxation and usually increases the luminescence energy yield [30,31]. In this connection, the purpose of the study is to search for new “heavy” matrices based on fluorides and recognize their spectral and luminescent characteristics for luminescent nanothermometers. As part of the study, a method was developed for the synthesis of a new “heavy” matrix $\text{Ba}_{0.5-x}\text{Ln}_{0.5}\text{Na}_x\text{F}_{2.5-x}$ ($x = 0.08$) and phosphors based on it for testing as a dual-band luminescent thermometer.

2. Materials and Methods

2.1. Synthesis of Luminophores

We synthesized the samples by crystallization from a solution in a sodium nitrate melt according to the method [32]. Sodium fluoride (Reagent grade, Chimmed) was used as a fluorinating agent, and sodium nitrate (Reagent grade, Chimmed) was used as a solvent. The reagents were used without additional purification steps. The weights of the initial reagents are given in Table S1.

The synthesis is described by the following reaction equation:



The samples of barium nitrate (specialty grade 10-2, Reachem) and nitrate hydrates of rare earth elements (99.99% purity in terms of cation impurity, Lanhit) were homogenized in an agate mortar for 10 min and then added to the samples of fluoride and sodium nitrate. After homogenization, the mixture was transferred to a porcelain glazed crucible and annealed at a temperature of 500°C for 1 h with a heating rate of 10°C per minute. After natural cooling to room temperature, the sinter was removed from the crucible and

washed three times with double-distilled water in a polypropylene reactor until a negative reaction of a solution of diphenylamine in sulfuric acid to nitrate anions. The samples were dried under an IR lamp at a temperature of 40–60 °C for 6 h.

2.2. Characterization of Luminophores

The samples were characterized by X-ray phase analysis (XRD) (Bruker, D8 Advance with CuK α irradiation, Karlsruhe, Germany), scanning electron microscopy (SEM) (Carl Zeiss, Nvision 40, Oberkochen, Germany), energy dispersion analysis (EDX) (Oxford Instruments, X-Max 80 mm², Abingdon, UK), differential scanning calorimetry (DSC) (Netzsch, STA 449 F3 Jupiter, Selb, Germany). All samples were analyzed as prepared.

2.3. Temperature-Dependent Luminescence Spectra Measurements

Luminescent spectroscopy of the samples was performed on an installation consisting of a laser with a wavelength of 974 nm, a spectrometer (StellarNet, DWARF-Star) in the SWIR range of 1000–1700 nm, a spectrometer (BIOSPEC, LESA-01-BIOSPEC) in the visible range of 300–900 nm, and a thermal infrared camera (CEDIP, JADE MWIR SC7300M) for temperature measurements in the range from 24 to 44 °C [21]. Heating was carried out using a Primelab PL-R-basic H heated magnetic stirrer (Primelab, Mytischci, Russia) with 0.1 °C temperature heating sampling. Luminescence intensity ratio (LIR) was used to quantify the dependence of luminescence spectra on temperature in the SWIR range:

$$\text{LIR} = I_{\text{Ho}}/I_{\text{Er}} \quad (2)$$

where I is the integral luminescence intensity calculated as the area under the luminescence peak in the corresponding wavelength range. For SWIR the area was calculated under the peak in the 1100–1250 nm range for $\text{Ho}^{3+} {}^5\text{I}_6 \rightarrow {}^5\text{I}_8$ transition and the 1450–1650 nm range for $\text{Er}^{3+} {}^4\text{I}_{13/2} \rightarrow {}^4\text{I}_{15/2}$ transition. In visible range we use luminescence in green range, 520–570 nm range, which corresponds to $\text{Er}^{3+} {}^2\text{H}_{11/2}, {}^4\text{S}_{3/2} \rightarrow {}^4\text{I}_{15/2}$, and in red range, 625–675 nm, which probably includes both the Er^{3+} and Ho^{3+} luminescence, transitions ${}^4\text{F}_{9/2} \rightarrow {}^4\text{I}_{15/2}$ and ${}^2\text{F}_5 \rightarrow {}^5\text{I}_8$, correspondingly.

The relative coefficient of temperature sensitivity (S_r) was calculated using the following formula:

$$S_r = \frac{\text{LIR}_{T1} - \text{LIR}_{T2}}{T_2 - T_1} * 100\% \quad (3)$$

3. Results

In the course of our work, we synthesized samples in the $\text{BaF}_2\text{-GdF}_3$ system doped with Yb, Ho, and Er. The nominal composition and composition determined according to the EDX data of the samples obtained, as well as the practical yield of the synthesis reaction are shown in Table 1. EDX results show that the crystal lattice of synthesized samples contains sodium in an amount of up to 8 mol. %, regardless of the content of the rare earth element. Apparently, this value corresponds to solubility limit of sodium in this solid solution. The content of rare earth elements was overestimated compared to the initial charge, and the content of barium was underestimated.

Figure 1 shows the X-ray diffraction patterns of prepared samples.

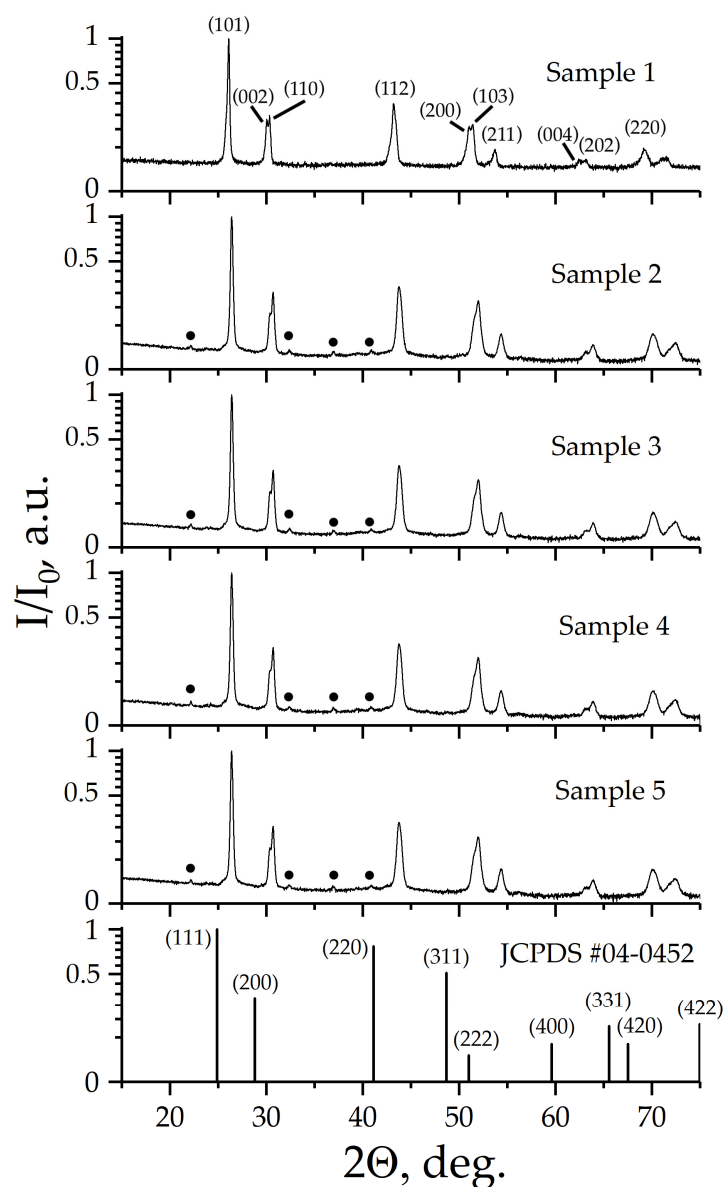
According to X-ray diffraction patterns, Samples 1–5 are single phase, and have a structure derived from the fluorite structure in which BaF_2 crystallizes. The X-ray pattern of Sample 1 is characterized by a fine splitting of the main X-ray diffraction reflexes and is indicated in the tetragonal crystallographic system in a space symmetry group (SSG) $I4$. X-ray pattern of Samples 2–5 also indexed in SSG $I4$. It is worth noting that X-ray diffraction patterns of Samples 2–5 contain superstructural peaks, which are well described when the crystal lattice parameter “ c ” is increased three times. The Supplementary Materials, Tables S2–S6, show the results of indexing of X-ray patterns. For all samples, the estimated values of the coherent scattering regions D were more than 100 nm. The lattice parameters of Samples 1–5 and the calculated X-ray density (D_x) values are given in Table 2.

Table 1. The nominal composition of the samples, the composition according to EDX data, and the practical yield of the sample synthesis reaction.

Samples	Nominal Composition	Composition according to EDX Data ^{1,2}	Reaction Yield, %
1	Ba _{0.67} Gd _{0.33} F _{2.33}	Ba _{0.51(1)} Gd _{0.45(1)} Na _{0.04(2)} F _{2.41}	60.1
2	Ba _{0.600} Gd _{0.304} Yb _{0.080} Ho _{0.012} Er _{0.004} F _{2.4}	Ba _{0.44(1)} Gd _{0.40(1)} (Yb, Ho, Er) _{0.11(1)} Na _{0.05(2)} F _{2.46}	70.5
3	Ba _{0.600} Gd _{0.300} Yb _{0.080} Ho _{0.012} Er _{0.008} F _{2.4}	Ba _{0.43(1)} Gd _{0.38(1)} (Yb, Ho, Er) _{0.11(1)} Na _{0.08(2)} F _{2.41}	67.7
4	Ba _{0.600} Gd _{0.306} Yb _{0.080} Ho _{0.010} Er _{0.004} F _{2.4}	Ba _{0.42(1)} Gd _{0.37(2)} (Yb, Ho, Er) _{0.13(2)} Na _{0.08(1)} F _{2.42}	70.3
5	Ba _{0.600} Gd _{0.304} Yb _{0.080} Ho _{0.008} Er _{0.008} F _{2.4}	Ba _{0.40(1)} Gd _{0.30(4)} (Yb, Ho, Er) _{0.22(5)} Na _{0.08(2)} F _{2.44}	74.0

¹ Fluorine content was calculated by cations based on the assumption of electroneutrality of the solid solution.

² EDX method does not have sufficient sensitivity to separate the signals of neighboring rare earth elements.

**Figure 1.** XRD patterns of prepared samples. ●—superstructural reflections.

SEM micrographs were obtained for all samples (Figure 2).

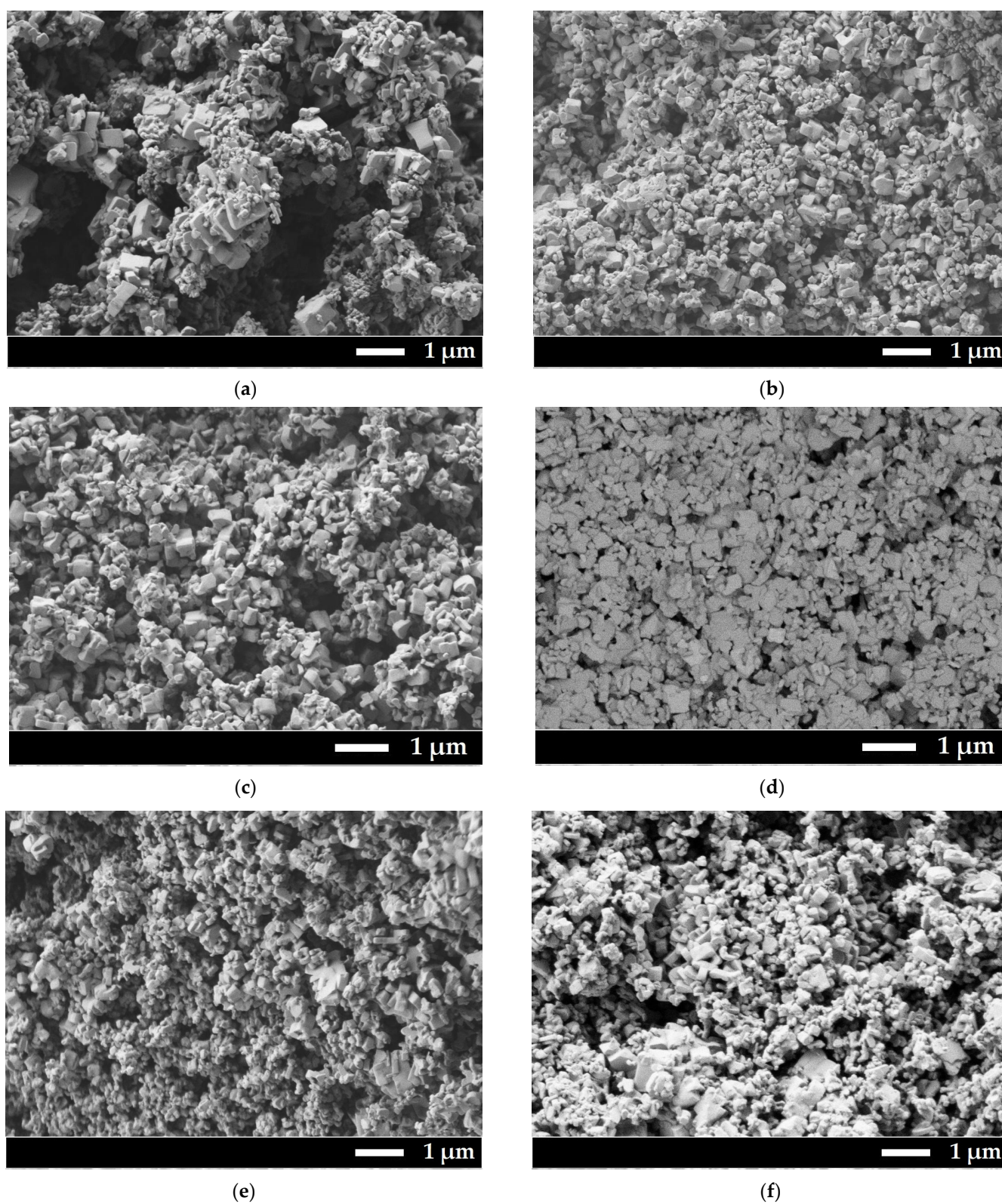


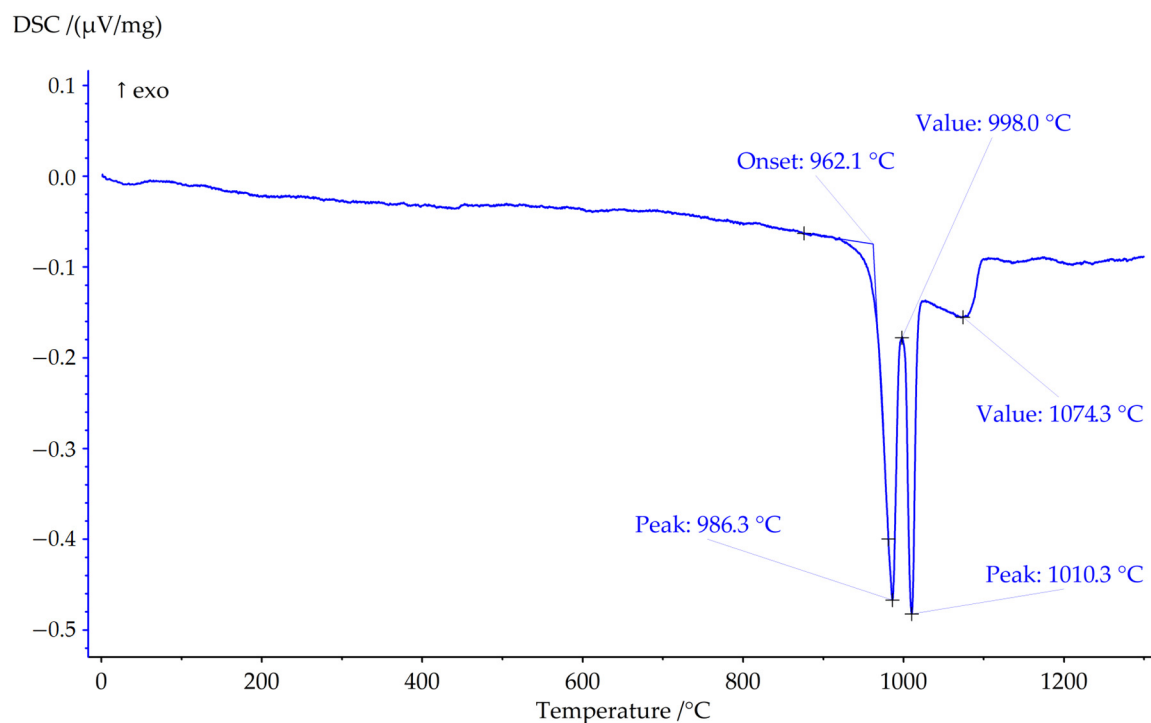
Figure 2. SEM microphotography of prepared samples. (a) Sample 1; (b) Sample 2; (c) Sample 3; (d) Sample 3 (detector of backscattered electrons was used for elemental contrast); (e) Sample 4; (f) Sample 5.

Table 2. Crystal lattice parameters and sample density.

Sample №	a , Å	c , Å	V , Å ³	D_x , g/cm ³
1	4.164 (1)	5.946 (1)	103.09 (2)	6.039
2	4.122 (1)	17.672 (1)	300.30 (3)	6.310
3	4.122 (1)	17.674 (1)	300.37 (1)	6.150
4	4.124 (1)	17.682 (1)	300.69 (1)	6.167
5	4.123 (1)	17.683 (1)	300.61 (1)	6.242

All powders have submicron sizes with a bimodal particle size distribution. The first maximum is about 200 nm, and the second is about 700 nm. Histograms of particle size distribution can be found in Supplementary Materials, Figure S1. Detection of backscattered electrons showed that the particles in Sample 3 are homogeneous in composition, there is no contrast in microphotographs. It has to be mentioned that corrosion of the glazed porcelain crucible and additional phases in SEM microphotographs were not observed. The presence of aluminum or silicon as the main elements of the crucible was not detected in EDX analysis. Buchinskaya et al. [33] also showed that there is no interaction between the sodium nitrate melt and the porcelain glazed crucible.

The results of thermal analysis are shown in Figures 3 and 4.

**Figure 3.** DSC curve of Sample 3 in argon at heating rate 20 K×min^{−1}.

DSC analysis of Sample 3 in argon atmosphere was made up to 1300 °C (Figure 3). Peaks with maximums at 986 °C and 1010 °C correspond to phase reactions, and the effect with a maximum at 1074 °C corresponds to the end of melting of the sample (liquidus point). DSC data show that Sample 3 is stable in the flow of argon until 962.5 °C.

Thermal stability in air also was investigated (Figure 4). Sample 3 starts to lose weight at approximately 290 °C. The endothermal peak around 80 °C may be attributed to dehydration of adsorbed water. There are two exothermal peaks that could be attributed to the chemical reaction of pyrohydrolysis [34]. However, the X-ray pattern of Sample 3 did not change after this DSC experiment.

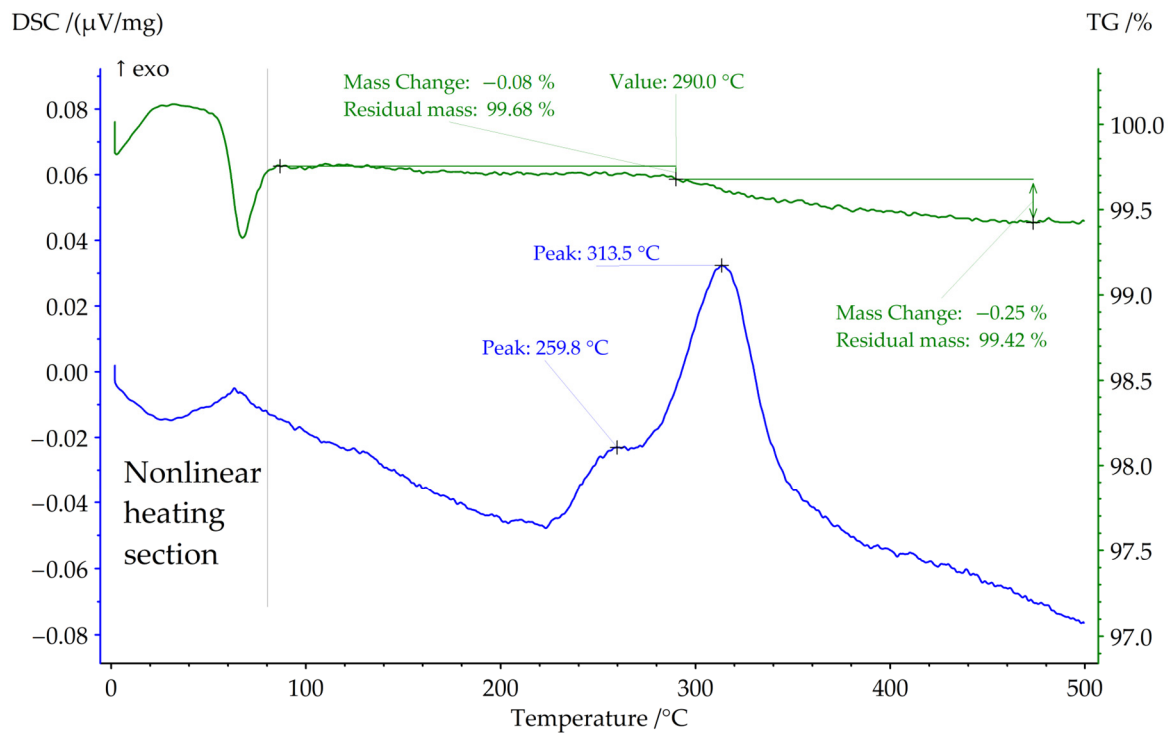


Figure 4. DSC curve of Sample 3 in air at heating rate $20 \text{ K} \times \text{min}^{-1}$.

Figure 5 shows the luminescence spectra in the visible range for Sample 5 at different temperatures (Figure 5a) and in the SWIR range for Samples 3 and 5 at a temperature of 296 K (Figure 5b).

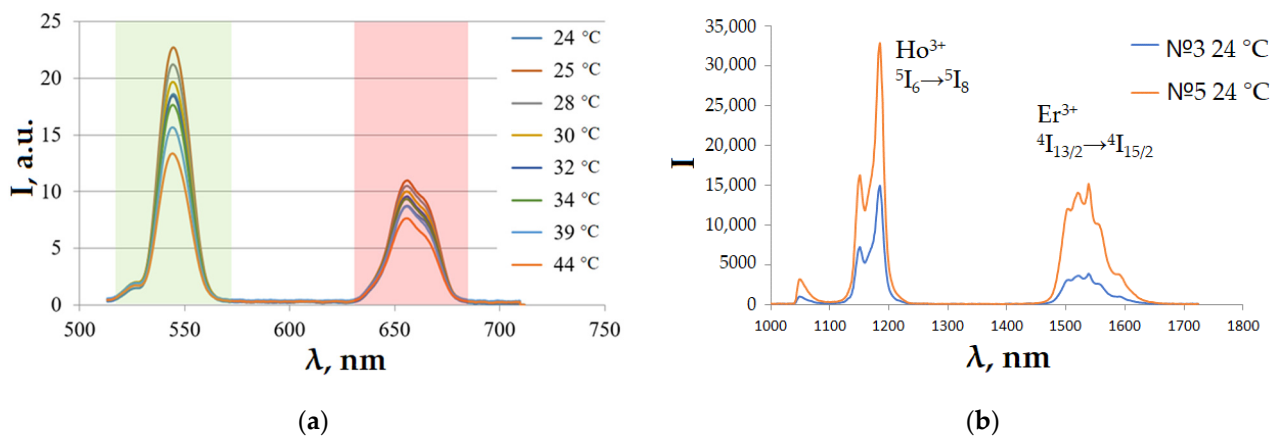


Figure 5. Luminescence spectra (a) Sample № 5, visible range; (b) Sample №3 and 5, SWIR range.

The peak in the SWIR region at 1150 nm wavelength corresponds to Ho^{3+} ($^5\text{I}_6 \rightarrow ^5\text{I}_8$), and the peak at 1550 nm corresponds to Er^{3+} ($^4\text{I}_{13/2} \rightarrow ^4\text{I}_{15/2}$).

The temperature dependences of the ratio of the intensities of the red and green luminescence bands for the visible range of the spectrum are shown in Figure 6a, and the intensity ratios of the erbium and holmium luminescence bands for the SWIR range are shown in Figure 6b.

From the dependences presented in Figure 6, the relative coefficients of temperature sensitivity in the temperature range from 24 to 44 °C are determined: $S_r = 5.55\% \times \text{K}^{-1}$ in the visible range and $S_r = 0.34\% \times \text{K}^{-1}$ in the SWIR range.

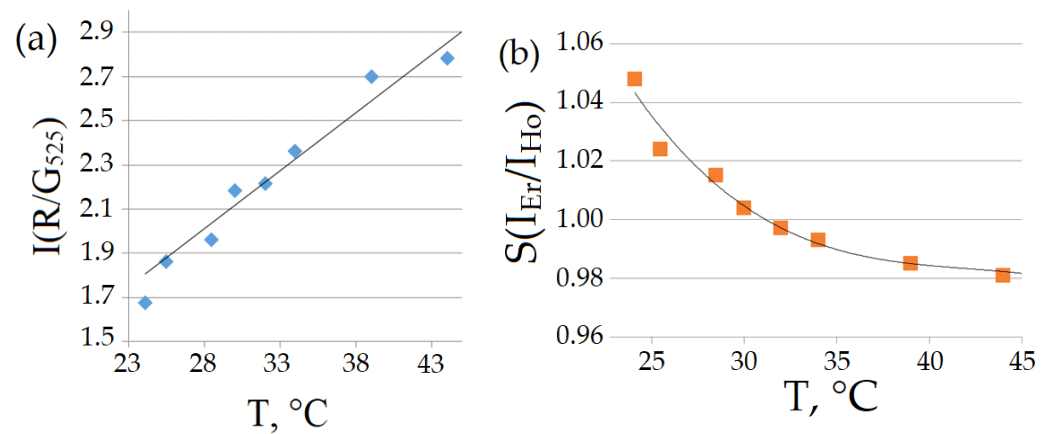


Figure 6. Temperature dependences of the ratio of the integral intensities of the luminescence bands (LIR) for Sample 5. (a) The wavelengths are 625–675 nm and 520–570 nm. (b) The wavelengths are 1450–1650 nm and 1100–1250 nm.

4. Discussion

According to the XRD data, the synthesized samples crystallize in a tetragonal crystallographic system with the spatial symmetry group $I4$. Comparing the data obtained with the well-known phase diagram of the $\text{BaF}_2\text{--GdF}_3$ system, as presented in Figure 7, makes it obvious that the samples prepared by us correspond to a high-temperature T phase having a similar composition [35]. This phase with a fluorite-derived structure is characterized by a tetragonal cell, SSG $I4$, with the parameter “ c ” increased three times. The cause of tetragonal distortion is the ordered arrangement of clusters of defects in a fluorite-type lattice. The synthesis of the phase of such a structure at a low synthesis temperature of 500 $^\circ\text{C}$ is apparently explained by the entry of sodium into the lattice of synthesized samples, leading to the stabilization of the high-temperature phase.

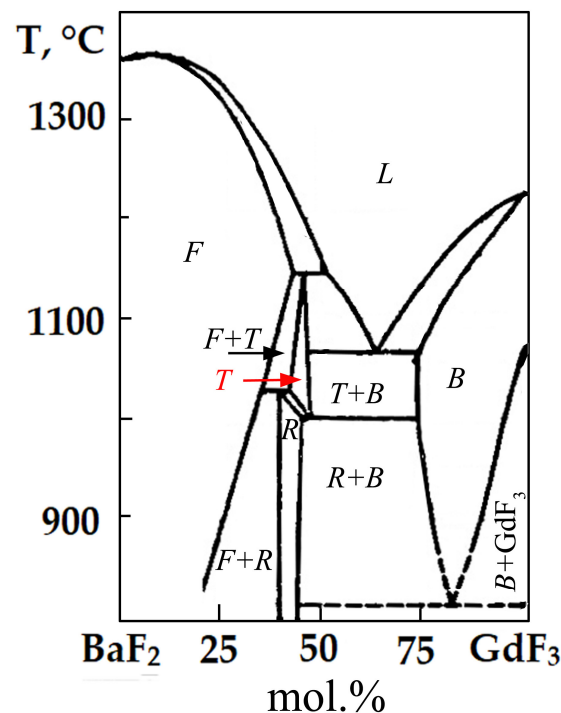


Figure 7. Phase diagram of $\text{BaF}_2\text{--GdF}_3$ system. Phase designations: F —fluorite-type solid solution $\text{Ba}_{1-x}\text{Gd}_x\text{F}_{2+x}$; B —tysonite-type solid solution $\text{Gd}_{1-y}\text{Ba}_y\text{F}_{3-y}$; R —trigonal fluorite-derived phase on the base of $\text{Ba}_4\text{Gd}_3\text{F}_{17}$ compound; T —tetragonal fluorite-derived phase; L —liquid.

As the data in Figure 6 show, the luminescent thermometer synthesized by us can be used to detect temperature in both visible and SWIR ranges. At the same time, the sensitivity in the visible range is high and significantly higher than in the IR range. However, the obtained characteristic of our phosphor is consistent with the analogs described in the literature (Table 3).

Table 3. Comparison of sensitivity of various luminescent IR thermometers in SWIR range.

Matrix	Dopant Ions	Temperature Range, K	$S_r, \% \times K^{-1}$	Bibliography
NaLuF ₄	Yb ³⁺ , Ho ³⁺ , Er ³⁺	293–568	0.21	[20]
β-NaYF ₄	Yb ³⁺ , Ho ³⁺ , Er ³⁺	298–323	0.85	[7]
Sr ₂ LuF ₇	Yb ³⁺ , Ho ³⁺ , Er ³⁺	293–329	0.80	[19]
Ba _{0.51(1)} Gd _{0.45(1)} Na _{0.04(2)} F _{2.41}	Yb ³⁺ , Ho ³⁺ , Er ³⁺	296–316	0.34	This work

5. Conclusions

The synthesis of a heavy matrix based on barium gadolinium fluoride with a density of more than 6 g/cm³ was developed as a result of this study. The entry of sodium into the composition of the samples was recorded using the EDX method. The presence of sodium stabilizes the high-temperature phase of the tetragonal crystallographic system with the general formula Ba_{0.5−x}Ln_{0.5}Na_xF_{2.5−x}.

The relative coefficients of temperature sensitivity (S_r) in the temperature range 296–316 K are equal to $S_r = 5.55\% \times K^{-1}$ in the visible range and $S_r = 0.34\% \times K^{-1}$ in the SWIR range. The samples are not hygroscopic and are stable under air atmosphere up to 200 °C. Thus, a novel dual-range luminescent thermometer of the composition Ba_{0.5}Gd_{0.45}Na_{0.05}F_{2.45}: Yb, Ho, Er has been developed.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/app13189999/s1>, Figure S1: histogram of particle size distribution; Table S1: weights of initial reagents; Table S2: XRD data of Sample 1; Table S3: XRD data of Sample 2; Table S4: XRD data of Sample 3; Table S5: XRD data of Sample 4; Table S6: XRD data of Sample 5.

Author Contributions: Conceptualization, A.A.A., V.K.I. and P.P.F.; methodology, A.A.A., M.V.T. and D.V.P.; validation, S.V.K., V.K.I. and P.P.F.; investigation, A.A.A., L.A.P., D.V.P. and I.D.R.; resources, S.V.K.; writing—original draft preparation, A.A.A.; writing—review and editing, P.P.F.; visualization, A.A.A. and L.A.P.; supervision, V.K.I.; project administration, P.P.F. and M.V.T.; funding acquisition, V.K.I. and P.P.F. All authors have read and agreed to the published version of the manuscript.

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