Spectroscopic characterization of SrB₄O₇:TM²⁺, a potential laser material and optical temperature sensor

Piotr Solarz, Jarosław Komar, Michał Głowacki, Marek Berkowski and Witold Ryba-Romanowski

Polycrystalline samples of SrB₄O₇:1% Tm²⁺ were prepared in air by a solid state reaction method. High resolution spectra and decay curves for infrared luminescence related to the intraconfigurational 2F⁵/₂ → 2F⁷/₂ transition and for visible luminescence related to the interconfigurational transition between the lowest energy state of the 4f²5d configuration and the ground 2F⁷/₂ state of the 4f¹³ configuration of Tm²⁺ were recorded as a function of temperature between 5 and 350 K. Energies of crystal field levels of the 2F⁵/₂ and 2F⁷/₂ multiplets and the 2F⁵/₂ lifetime value were determined from low temperature measurements. With these data room temperature emission and absorption spectra were calibrated in the cross-section units. It was found that the infrared emission in SrB₄O₇:Tm²⁺ is long-lived with a lifetime value of 9.5 ms and its spectrum indicates that stimulated emission near 1.18 nm may be feasible. Examination of recorded decay curves for the visible luminescence revealed that the lifetime of the lowest energy state of the 4f²5d configuration depends weakly on temperature in the region 5–280 K and then shows a steep decrease when the temperature grows from about 290 K to 350 K. The evaluated values of the thermal sensitivity parameter S for SrB₄O₇:Tm²⁺ in the region 300–330 K (27–57 °C) exceed 3.9% per K with a peak at 320 K (47 °C) equal to 6.30% per K. The S value is the highest reported thus far for luminescence thermometers operating in physiological temperatures.

1 Introduction

There is a long lasting interest in rare earth-doped crystals and glasses. In the past attention has been directed mainly toward finding new laser crystals and designing laser devices. In an enormous number of published papers, laser operation for Nd³⁺, Ho³⁺, Er³⁺, Tm³⁺ and Yb³⁺ in a variety of host crystals has been reported and solid state lasers employing some of these systems are now commercially available. Physicochemical and laser properties of these materials have been reported in several review works, e.g., an exhaustive review by Kaminskii. The search for new laser active crystals is continuing and is directed mainly toward finding better and cheaper laser hosts. Crystals doped with divalent rare earth ions have been studied, too. Interest in these systems resulted from an expectation that owing to low energies of the 4f⁶−⁵d excited configurations the broad and intense absorption bands related to parity allowed inter-configurational transitions in divalent rare earth ions would be beneficial for optical pumping. This expectation has not been corroborated, however. In early works the alkaline fluoride host crystals have been chosen and laser operation has been demonstrated in CaF₂:Sm²⁺, SrF₂:Sm²⁺ and CaF₂:Dy²⁺ (ref. 9–11) and CaF₂:Tm³⁺, 12,13 but only at cryogenic temperatures. Attempts to achieve room temperature laser operation in crystals doped with Sm²⁺ or Dy²⁺ were unsuccessful because their luminescence bandwidths were found to grow adversely with increasing temperature. Room temperature laser operation in CaF₂:Tm³⁺ could not be achieved as a consequence of an adverse ground state absorption of Tm³⁺ ions (about 80% of thulium ions in CaF₂ host was present in the trivalent state).

Recently, a considerable interest has been directed to optical temperature sensing that offers a possibility to measure the temperature remotely. Numerous papers published during last decade have been devoted to elaborate various methods of temperature sensing and potential sensors that may be employed for this purpose. A variety of thermometers for thermal sensing based on organic fluorophores, quantum dots, bio-molecules and rare earth-doped systems have been described and their sensing capabilities compared. Achievements and current knowledge in this field are presented in valuable review works published recently e.g., Phosphor thermometers based on luminescent rare earth ions in inorganic hosts are especially attractive because they offer rich energy level structures and are able to show luminescence transitions in a vast spectral region

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1 Institute of Low Temperature and Structure Research, Polish Academy of Sciences, al. Okłina 2, 50-422 Wroclaw, Poland. E-mail: solarz@int.pan.wroc.pl; Fax: +48-71-3444102; Tel: +48-71-3455201
2 Institute of Physics, Polish Academy of Sciences, al. Lotników 32/46, 02-668 Warsaw, Poland
from UV to near infrared. Phosphor thermometers investigated thus far contained trivalent luminescent rare earth ions Nd$^{3+}$, Eu, Dy, Ho, Er, Tm.

In the present paper we deal with spectroscopic features of divalent thulium ions in SrB$_4$O$_7$ host. Currently, the interest in oxide crystals doped with divalent rare earth ions is stimulated by the search for efficient phosphors able to convert the radiation of blue light emitting diodes (LED) into white light, providing thereby new sources for lighting purposes. The discovery of Sn$^{4+}$ ions in SrB$_4$O$_7$ host doped with Eu$^{3+}$ (ref. 18) and with Sm$^{3+}$ ions$^{20}$ has proved that oxide host crystals are worth considering. In fact, numerous visible phosphors based on Eu$^{3+}$-doped hosts have been recently fabricated and characterized, e.g.: Ca$_2$SiO$_4$·Eu$^{3+},^{20}$ CaSrSiO$_4$·Eu$^{2+},^{21}$ Ba$_2$SiO$_4$·N$_2$:Eu$^{2+}$(ref. 22) and many sulphides.$^{23}$

Considerable less attention has been paid to Sm$^{2+}$-doped systems. Nevertheless, recent papers dealing with the SrB$_4$O$_7$:Sm$^{2+}$ phosphor have demonstrated its suitability for application as optical pressure sensors at high temperatures.$^{24-26}$ Peculiarities of emission spectra related to the intra-configurational transitions of Sm$^{2+}$ in SrB$_4$O$_7$:Sm$^{3+}$ have been reported in ref. 27–29. Effect of temperature on intensities of inter- and intra-configurational transitions and on luminescence lifetime of SrB$_4$O$_7$:Sm$^{2+}$ have been studied in ref. 30 and 31. Just recently it has been demonstrated that SrB$_4$O$_7$:5%Sm$^{3+}$ system is promising for application as an optical sensor characterized by a high relative decay time temperature sensitivity in a wide temperature region with a record value of 3.36% per K at 550 K.$^{32}$

The search for phosphors based on divalent thulium ions is hampered by the fact that these ions are less stable than Eu$^{2+}$ and Sm$^{2+}$ ions. As far as we know only two papers published in the past provide fundamental information on luminescence of Tm$^{2+}$ ions in oxide crystals. The paper by Schipper et al.$^{33}$ has reported the first observation of the 4f$^{12}5d \rightarrow 4f^{13}$ emission of Tm$^{2+}$ in SrB$_4$O$_7$ powder samples prepared by a solid state reaction in a reducing atmosphere consisting of 25% H$_2$ and 75% N$_2$. Authors have analysed and interpreted emission and excitation spectra recorded at 4.2 K and proposed mechanisms governing the excited state relaxation dynamics in the temperature region between 4.2 K and 300 K. In the paper by Peterson et al.$^{34}$ the room temperature diffuse reflectance spectra of SrB$_4$O$_7$:Tm$^{2+}$ powders fired at temperatures ranging from 650 °C to 900 °C in air or in Ar/H$_2$ atmosphere have been recorded and analysed. Authors have shown that the reduction from Tm$^{3+}$ to Tm$^{2+}$ in SrB$_4$O$_7$ occurred also for samples fired in air though a significant fraction of incorporated thulium ions still was present in the trivalent state.$^{34}$ The outstanding feature of the SrB$_4$O$_7$:RE$^{3+}$ (RE = Eu, Sm, Tm) stems from the stability of oxidation state of incorporated rare earth ions combined with a large transparency region of the host crystal stretching from UV to about 3000 nm.$^{35}$

Intention of the present work is to determine spectroscopic properties of the SrB$_4$O$_7$:Tm$^{2+}$ system that are relevant to its potential for practical application. First, spectral and temporal characteristics of transitions within the 4f$^{13}$ configuration of Tm$^{2+}$ are analysed to assess the feasibility of resonantly pumped infrared laser operation near 1.2 μm. Second, the effect of temperature on spectra and decay of visible luminescence related to the inter-configurational 4f$^{12}5d \rightarrow 4f^{13}$ transition of Tm$^{2+}$ is investigated aiming at assessment of utility of the SrB$_4$O$_7$:Tm$^{2+}$ as an optical temperature sensor.

2 Experimental

Synthesis

SrB$_4$O$_7$ polycrystalline samples were prepared by a solid state reaction method. As starting materials SrCO$_3$ (4N5), B$_2$O$_3$ (4N), and Tm$_2$O$_3$ (5N) were used. Powders were dried for 10 hours and then their appropriate amounts were weighted to obtain following molar composition: Sr$_{0.99}$Tm$_{0.01}$B$_2$O$_7$. Mixed SrCO$_3$ and B$_2$O$_3$ were formed into pellets and heated in air for 10 hours in 300 °C and 10 hours in 800 °C. First step of heating is necessary to avoid melting of B$_2$O$_3$ before getting in reaction with strontium carbonate. When reaction begins the CO$_2$ is starting to volatilize and heated pellets begins to swell. Second step of heating causes complete removal of CO$_2$ from the material. Thoroughly grounded and formed into pellets materials were heated in air again for 24 hours in 800 °C to remove other SrO–B$_2$O$_3$ phases and obtain pure SrB$_4$O$_7$ phase. Then 1% of Tm$_2$O$_3$ was added and mixture was heated for the third time for 24 hours in 800 °C. To perform spectroscopic measurement the polycrystalline pellets 17 mm in diameter and 2 mm thick were prepared.

Spectroscopic measurements

High resolution emission spectra were recorded upon ion argon laser excitation 488 nm line with DongWoo Opton setup composed of 750 mm focal length monochromator DM711 (1 cm$^{-1}$ spectral resolution FWHM for 0.02 mm slits), and detection systems: (VIS) PDS-1 with photomultiplier tube R3896 (Hamamatsu) or (IR) PS/TC-1 controller with InGaAs detector model IGA-030-TE2-H Electro-Optical Systems Inc Kinetic measurements were taken employing an experimental set-up consisting of a tunable optical parametric oscillator (OPO) pumped by a third harmonic of a Nd:YAG laser, a double grating monochromator with a 1000 mm focal length, a detection unit incorporating a photomultiplier operating in the visible or a cooled InSb detector operating in near infrared and a Tektronix MDO 4054B-3Mixed Domain Oscilloscope. The OPO source delivered a train of light pulses with duration of 7 ns and pulse energy of several mJ (depending on wavelength within the 430–600 nm region) with the repetition rate of 20 Hz. The same apparatus was employed to record excitation (PLE) spectra. To perform measurements at low temperature, the samples were installed in a continuous flow liquid helium cryostat equipped with a temperature controller.

Crystallographic structure determination

Phase analysis and structural refinement were performed with a Siemens D5000 diffractometer (Ni-filtered CuKα radiation). Data were collected in the range 20–100° with a step of 0.02° and averaging time of 10 s per step. XRD pattern (Fig. 1) shows pure SrB$_4$O$_7$ phase (JCPDS Card No. 15-0801) for undoped sample. In
thulium doped SrB₄O₇ beside the main tetraborate phase there is a little amount of metaborate (JCPDS Card No. 15-0779) phase visible.

3 Results and discussion

Luminescence of Tm²⁺ ions in crystals may be related to vibronic inter-configurational transitions between the lowest energy state of the 4f²5d configuration and the ground 3F₇/₂ state of the 4f⁴ configuration and to an intra-configurational 3F₅/₂ → 3F₇/₂ transition. The spectral region of the latter transition is close to that of the 2²F₅/₂ → 2²F₇/₂ transition of isoelectronic Yb³⁺ ions and depends weakly on the host crystal. Resulting luminescence band in CaF₂:Tm²⁺ system has been observed near 1.12 μm and the low temperature laser operation at 1.116 μm has been obtained in the past.¹²⁻¹³ Peculiarities of the 2²F₅/₂ → 2²F₇/₂ luminescence for the SrB₄O₇:Tm²⁺ system have not been determined in previously reported study because weak luminescence lines could not be separated from the background.¹³ Also, the room temperature absorption (diffuse reflectance measurement) spectrum recorded for the 2²F₅/₂ → 2²F₇/₂ transition in SrB₄O₇:Tm²⁺ did not provide reliable information because of superposed absorption of residual Tm³⁺ ions.¹⁴ It will be shown in the following paragraph that spectra and decay curves recorded in a wide temperature region are able to provide new information on the 2²F₅/₂ → 2²F₇/₂ infrared luminescence in SrB₄O₇:Tm²⁺.

3.1 Effect of temperature on the intra-configurational 2²F₅/₂ → 2²F₇/₂ infrared luminescence

Fig. 2 compares luminescence spectra of Tm²⁺ in the near infrared region, recorded at several different temperatures in the region of 5–300 K.

The site symmetry for Tm²⁺ ions in this host is lower than cubic, therefore four crystal field components for the ground 3F₇/₂ multiplet and three crystal field components for the 2²F₅/₂ excited multiplet are predicted. Since the population of the crystal field components is governed by the Boltzmann statistics the luminescence spectra are expected to be temperature dependent. It can be seen in Fig. 2 that at 5 K the luminescence spectrum consists of four well separated lines located at 1131.6 nm (8837 cm⁻¹), 1141.3 nm (8762 cm⁻¹), 1152.95 nm (8673 cm⁻¹) and 1180 nm (8475 cm⁻¹). We assign these lines to...
transitions from the lowest crystal field component of the \( ^2F_{5/2} \) excited multiplet to four crystal field components of the ground state. Accordingly, the line located at 1131.6 nm is related to the transition ending on the lowest crystal field component of the ground multiplet (0-0 line) and remaining lines are related to transitions ending on the higher crystal field components located at 75, 164 and 362 cm\(^{-1}\). In the spectrum of the 50 K luminescence an additional line related to transition from the second higher energy component of the initial \( ^2F_{5/2} \) multiplet appears at 1120.25 nm (8927 cm\(^{-1}\)). Above 200 K a weak line peaking at 1093.3 nm (9147 cm\(^{-1}\)) contributes to the spectrum. Assuming that it is related to transitions from the highest energy component of the initial state we locate components of the \( ^2F_{5/2} \) excited multiplet at 8837, 8927 and 9147 cm\(^{-1}\). At higher temperatures the transitions from all crystal field levels of the \( ^2F_{5/2} \) multiplet contribute to luminescence band and recorded spectra do not show significant differences.

The \( ^2F_{5/2} \rightarrow ^2F_{7/2} \) infrared luminescence of Tm\(^{3+}\) in SrB\(_4\)O\(_7\) is found to be long-lived. Decay curves of this luminescence were recorded at different temperatures in the 5–450 K region. All of them were consistent with a single exponential time dependence providing thereby a set of reliable lifetime values. A plot of measured luminescence lifetimes versus temperature is shown in Fig. 3.

Observed increase of the lifetime with growing temperature is due to a lengthening effect of self-absorption, commonly encountered during investigation of the \( ^2F_{5/2} \rightarrow ^2F_{7/2} \) emission in crystals doped with Yb\(^{3+}\). Therefore we consider the value of 9.5 ms determined from a decay curve recorded at 5 K to be actual \( ^2F_{5/2} \) lifetime.

In principle the relaxation of the \( ^2F_{5/2} \) metastable level of Tm\(^{3+}\) in SrB\(_4\)O\(_7\) is governed by radiative transitions and nonradiative multiphonon transitions. The rate of multiphonon relaxation is expected to be low since a simultaneous emission of six phonons with the highest energy of about 1400 cm\(^{-1}\) that are available in the host would be needed to bridge the energy difference of about 8400 cm\(^{-1}\) between the \( ^2F_{5/2} \) and \( ^2F_{7/2} \) levels. Having this in mind we assume that the measured luminescence lifetime of 9.5 ms is close to the \( ^2F_{5/2} \) radiative lifetime and we calibrate the \( ^2F_{5/2} \rightarrow ^2F_{7/2} \) emission band in units of emission cross-section \( \sigma_{em}(\lambda) \) employing the Füchtbauer-Ladenburg relation:

\[
\sigma_{em}(\lambda) = \frac{\beta I(\lambda)}{8\pi c n^2 \tau_{rad}} \int I(\lambda) d\lambda
\]

where \( \beta \) is the luminescence branching ratio (equal to 1 for this transition), \( I(\lambda) \) is the emission spectrum intensity, \( \tau_{rad} \) is the radiative lifetime of the \( ^2F_{5/2} \) level and \( n \) denotes the index of refraction of the crystal. Solid line in Fig. 4 represents the resulting \( \sigma_{em}(\lambda) \) spectrum for the experimental \( ^2F_{5/2} \rightarrow ^2F_{7/2} \) infrared luminescence band recorded at 300 K. The peak value for the emission cross section of \( 3.5 \times 10^{-20} \text{ cm}^2 \) is advantageously high. However, the terminal level of this transition is the ground state and an actual ability of the system for light amplification will be markedly smaller due to an adverse effect of self-absorption. To assess quantitatively this shortcoming we calculate the spectrum for the \( ^2F_{7/2} \rightarrow ^2F_{5/2} \) absorption cross-section employing a so called reciprocity relation. The method is based on the relation between absorption cross-section \( \sigma_{abs}(\lambda) \) and emission cross-section \( \sigma_{em}(\lambda) \):

\[
\sigma_{em}(\lambda) = \frac{Z_{low}}{Z_{up}} \sigma_{abs}(\lambda) \exp(\frac{E_l - E(\lambda)}{k_B T}) \tag{2}
\]

where \( Z_{low}, Z_{up} \) are the partition functions for the lower and upper levels, respectively, defined as:

\[
Z_{low} = \sum_{i=1}^{n} g_{i} \exp(\frac{-E_i}{k_B T}); \quad Z_{up} = \sum_{i=1}^{n} g_{i} \exp(\frac{-E_j - E(\lambda)}{k_B T}) \tag{3}
\]

where \( g_i \) and \( (g_j) \) are the degeneration of a crystal field level having the \( E_i \) and \( (E_j) \) energy, respectively. \( E_d \) is energy difference between lowest crystal field components of the upper and lower multiplets and \( k_B \) is the Boltzmann constant. Inserting

![Fig. 3](image_url)  
**Fig. 3** Lifetime of the \( ^2F_{5/2} \) multiplet of Tm\(^{3+}\) in SrB\(_4\)O\(_7\) host plotted versus temperature.
values for energies of crystal field levels determined above to
eqn (2) and (3) we obtain the spectrum for the absorption cross
section $\sigma_{\text{abs}}$ represented by a dashed line in Fig. 4.

It can be seen that the curve of emission cross-section
dominate significantly that of absorption cross-section in the
spectral region between 1150 and 1230 nm pointing thereby at
positive values of optical amplification coefficient. To predict
the wavelength of a potential laser operation the effective
emission cross-section function $\sigma_{\text{em}}^{\text{eff}}(\lambda)$ was evaluated according to the relation:

$$\sigma_{\text{em}}^{\text{eff}}(\lambda) = K\sigma_{\text{em}}(\lambda) - (1 - K)\sigma_{\text{abs}}(\lambda)$$

(4)

where $K$ is the population inversion parameter defined as the
density of excited Tm$^{2+}$ ions divided by the overall density of
Tm$^{2+}$ ions in the crystal host. Resulting $\sigma_{\text{em}}^{\text{eff}}(\lambda)$ spectra cal-
culated for several reasonable values of $K$ are shown in the inset to
Fig. 4. It follows from these spectra that the laser operation in
SrB$_4$O$_7$:Tm$^{2+}$ at 1180 nm can be feasible for low $K$ values. It is
worth noticing here that an excited state absorption (ESA) due
to allowed transitions from the metastable level to states of the
$4f^{12}5d$ configuration (ESA), detrimental for stimulated emis-
sion in SrF$_2$:Sm$^{3+}$, cannot affect the emission around 1180 nm
in SrB$_4$O$_7$:Tm$^{2+}$ because of a large $3F_{5/2}$-$4F^{15}d$ energy gap.

3.2 Effect of temperature on the $4f^{2}5d \rightarrow 4f^{13}$ visible
luminescence

In contrast to the $2F_{5/2}$ level of the $4f^{13}$ configuration considered
above, the lowest energy state of the $4f^{12}5d$ configuration of
Tm$^{2+}$ ions depends strongly on the host. Based on careful
analysis of low temperature luminescence spectrum it has been
located at 17 210 cm$^{-1}$ SrB$_4$O$_7$:Tm$^{2+}$ system, that is markedly
higher than about 14 000 cm$^{-1}$ found in the past for CaF$_2$:Tm$^{2+}$
system. Due to larger energy gap between the bottom of the
$4f^{12}5d$ configuration and the next lower energy $2F_{5/2}$ state the
nonradiative relaxation is suppressed in SrB$_4$O$_7$:Tm$^{2+}$ system
and an efficient visible emission related to the $4f^{12}5d \rightarrow 4f^{13}$
($^2F_{7/2}$) transition is observed.

Fig. 5 shows spectra of visible luminescence in the SrB$_4$O$_7$: Tm$^{2+}$
system recorded at several sample temperatures in the
300–5 K temperature region. At 300 K the spectrum has
a maximum at 595.4 nm and consists of a single broad and
smooth band, typical for vibronic transitions. Decrease of
temperature down to 110 K affects little the shape of the lumines-
cence band but it brings about a monotonic shift of the band
maximum to about 601.2 nm.

During further decrease of temperature the position of
maximum is arrested but the intensity of a structure on the
short wavelength side of the band, hardly visible at 110 K, grows
steadily and eventually at 5 K a group of narrow lines contrib-
utes to the spectrum. Details of the 5 K luminescence spectrum
shown in Fig. 5 are consistent with those recorded at 4.2 K and
reported in the work by Schipper et al. proving thereby that we
are dealing with the same material. According to the assign-
ment proposed in the structure that appears in the low
temperature spectrum of the $4f^{12}5d \rightarrow 4f^{13}$ transition of Tm$^{2+}$
in SrB$_4$O$_7$ consists of zero phonon lines and related
progressions. Measurement of the excited state relaxation
dynamics was performed when changing the sample tempera-
ture in a vast region 5–360 K. It was found that the decay curves
of luminescence follow a single exponential time dependence
for all temperature points considered. Fig. 6 shows a plot of
evaluated time constants (luminescence lifetime values) versus
sample temperature.

It can be seen that initially the lifetime values decrease gently
with increasing temperature and then at about 290 K a very
steep decrease occurs. Eventually at 360 K the lifetime value of 5
us was measured. Observed change of lifetime induced by
variation of the temperature points at the potential of the
system under study for optical thermometry. Commonly, the
quality of optical sensors based on temperature-dependent
luminescence lifetime is assessed employing a thermal sensi-
tivity parameter $S$ defined by the relation:

$$S = \frac{\int_0^\infty \frac{1}{T} \frac{d\tau}{dT} \, dT}{\tau}$$

(5)

where $\tau$ denotes the lifetime value and $T$ denotes the
temperature.
The sensitivity parameter was calculated according to eqn (5) above and plotted versus temperature in Fig. 6.

The evaluated values of thermal sensitivity parameter $S$ for the SrB$_4$O$_7$:Tm$^{3+}$ system in the 300–330 K (27–57 °C) region exceed 3.9% per K with a peak value of 6.30% per K at 320 K (47 °C). It can be seen that in the temperature region between 10 °C and 47 °C the luminescence lifetime values are advantageously high and the $S$ parameter depends linearly on the temperature.

In addition, the SrB$_4$O$_7$:Tm$^{3+}$ system shows a broad and intense absorption band stretching from 450 nm to 550 nm favouring thereby an efficient excitation. Moreover, the PLE spectra recorded at 15 °C, 25 °C and 40 °C and compared in Fig. 7 indicate that the excitation efficiency is weakly affected by the temperature in this region. It is worth mentioning that in contrast to crystals doped with trivalent rare earth ions the ion–ion energy transfer processes do not affect significantly spectra and excited state relaxation dynamics of Tm$^{3+}$ ions in SrB$_4$O$_7$.

Indeed, low temperature luminescence spectra and lifetime of inter-configurational transition reported for SrB$_4$O$_7$:0.5% Tm$^{3+}$ in ref. 33 do not differ from those presented above for SrB$_4$O$_7$:1% Tm$^{3+}$. All these features indicate that the SrB$_4$O$_7$-Tm$^{3+}$ system may be a promising optical sensor operating in the physiological temperature region.

Ability to measure temperature changes in living cells is of paramount importance for the detection of pathological states e.g. of tumour deceases. Therefore numerous papers published during last decade have been devoted to elaborate various methods of temperature sensing and potential sensors that may be employed for this purpose. In an excellent review paper published recently by Tingting Bai and Ning Gu$^{37}$ presenting the state of the art in this topic, thermometers for thermal sensing and imaging of living cells and biological tissues based on organic fluorophores, quantum dots, bio-molecules and rare earth-doped systems are described and their sensing capabilities compared. Reported values of thermal sensitivity parameter $S$ refer to various spans of temperature within the 10–60 °C region. Among non-contact luminescent thermometers the highest values of $S$ parameters have been found for organic fluorophores, e.g. 3.9% per K in the temperature range 32–37 °C for ns decay of “ER thermo yellow” compound$^{37}$ and for rare earth metal complexes, e.g. 2.74% per K in the temperature range 25–50 °C for Eu-TTA.$^{38}$ Evaluated thermal sensitivity parameters for inorganic rare earth-doped thermometers are markedly lower, however$^{39–42}$ with the highest $S$ parameter value of 1.6% per K in the temperature range 10–36 °C reported for NaYF$_4$:Er$^{3+}$,Yb$^{3+}$.$^{43}$ Recently, using a Cr$^{3+}$ to Nd$^{3+}$ emission intensity ratio, the highest 3.48% per K sensitivity has been obtained in the physiological temperature range.$^{44}$ The evaluated values of thermal sensitivity parameter $S$ for the SrB$_4$O$_7$:Tm$^{3+}$ system in the 300–330 K (27–57 °C) region exceed 3.9% per K with a peak value of 6.30% per K at 320 K (47 °C), and to our knowledge they are higher than those reported thus far for other luminescent thermometers operating in this temperature region.

4 Conclusions

Based on analysis of the effect of temperature on luminescence spectrum related to the $^2F_{5/2} \rightarrow ^2F_{7/2}$ intra-configurational transition of Tm$^{3+}$ three crystal field levels of the $^2F_{5/2}$ initial multiplet were located at 8837, 8927 and 9147 cm$^{-1}$ and four crystal field levels of the ground $^2F_{7/2}$ multiplet were located at 75, 164 and 362 cm$^{-1}$ for the SrB$_4$O$_7$:Tm$^{3+}$ system. Observed luminescence is long-lived with a lifetime value of 9.5 ms at 5 K. Comparison of the room temperature $^2F_{5/2} \rightarrow ^2F_{7/2}$ luminescence band calibrated in the cross-section units according to the Füchtbauer–Ladenburg relation to that of the $^2F_{7/2} \rightarrow ^2F_{5/2}$ absorption band derived by a reciprocity method points at a positive value of optical amplification coefficient in a spectral region between 1150 and 1230 nm. Adverse effect of self-absorption was considered and its importance was assessed based on the calculated effective cross-section spectrum. It was also concluded that an excited state absorption (ESA) due to allowed transitions from the metastable level to states of the.

**Fig. 6** Lifetime of the $^{4}I^{13}_{5/2} \rightarrow ^{4}I^{13}_{7/2}$ visible emission (red open circles) and calculated thermal sensitivity parameter $S$ (full blue squares) plotted versus temperature for the SrB$_4$O$_7$:Tm$^{3+}$ system. Lines are only guides for eyes.

**Fig. 7** Excitation spectra of emission at 600 nm recorded at 15, 25, and 40 °C.
4f²→15d configuration (ESA), cannot affect the emission around 1.18 μm in SrB₂O₇:Tm³⁺ because of large 4f⁷→15d → 2F⁵/₂ transition energy gap. In SrB₂O₇:Tm³⁺ system the lifetime (τ) of intense visible emission related to vibronic inter-configuration transitions between the lowest energy state of the 4f⁷15d configuration and the ground 2F⁵/₂ state of the 4f³ configuration of Tm³⁺ changes abruptly when the temperature (T) varies in the region 280–350 K implying utility of this system for luminescence- based thermometry. The evaluated values of thermal sensitivity parameter S for the SrB₂O₇:Tm³⁺ system in the 300–330 K (27–57 °C) region exceed 3.9% per K with a peak value of 6.30% per K at 320 K (47 °C). Therefore, such a phosphor can be used as temperature sensor in biological region of temperatures.

Author contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Funding sources

NCN under project DEC-2013/09/D/ST5/03878.

Abbreviations

4N 99.99%
4N5 99.995%
5N 99.999%
ESA Excited state absorption
Eu-TTA Europium(III) thenoyltrifluoroacetone trihydrate
FWHM Full width at half maximum
IR Infrared
JCPS Joint Committee on Powder Diffraction Standards
LED Light emitting diode
NCN National Science Centre
S Thermal sensitivity parameter
VIS Visible
XRD X-ray diffraction

Acknowledgements

The work was funded by the National Science Centre (NCN) on the basis of the decision number DEC-2013/09/D/ST5/03878.

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