Temperature Effects on Luminescent Properties of $\text{Sr}_2\text{CeO}_4:\text{Eu}^{3+}$ Nanophosphor: a Machine Learning Approach

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In this paper we analyze possibilities of application of $\text{Sr}_2\text{CeO}_4:\text{Eu}^{3+}$ nanopowder for temperature sensing using machine learning. The material was prepared by simple solution combustion synthesis. Photoluminescence technique has been used to measure the optical emission temperature dependence of the prepared material. Principal Component Analysis, the basic machine learning algorithm, provided insight into temperature dependent spectral data from another point of view than usual approach.

Key words: Photoluminescence, New materials, Thermographic phosphors

1. INTRODUCTION

Nowadays, nano materials have more and more advantages over bulk materials. Nano science inevitably entered our world [1]. Thermographic nano phosphors are widely used in many applications [2-7]. They typically consist of a ceramic host and rare-earth dopant. The temperature dependency of their luminescence is used for remote temperature sensing. For obvious reasons, non contact measurements have many advantages. Thermographic remote monitoring of laser

cleansing is described in [8].

Strontium cerium oxide (Sr_2CeO_4) nano phosphors doped with europium ions (Eu^{3+}), $\text{Sr}_2\text{CeO}_4:\text{Eu}^{3+}$ are described in many scientific papers. As shown in [9], emission color change in a wide range of temperatures proves a great potential of $\text{Sr}_2\text{CeO}_4:\text{Eu}^{3+}$ nanocrystals for industrial applications, particularly in nanothermometric technology. Moreover, additional application possibilities for this material are provided by the fact that the samples with different grain sizes are characterized by various luminescence colors [9]. The possibility of application of this nanophosphor in single-color and two-color fluorescence thermometry techniques in temperature range of 303–523 K has been proposed in [10]. In [11] it was shown that the Eu^{3+} doped Sr_2CeO_4 phosphors emitting white light (by combining blue, green and red emissions) has potential

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applications not only in the fields of lamps and display devices under 280 nm excitation, but also in the field of LEDs under near UV (350 nm) excitation. $\text{Sr}_2\text{CeO}_4:\text{Eu}^{3+}$ considered as a source of anti-stokes white light generated under near infrared excitation was analyzed in [12]. Various methods of synthesis and studies of structural and luminescent characteristics of nanophosphors based on $\text{Sr}_2\text{CeO}_4:\text{Eu}^{3+}$ or non-doped Sr_2CeO_4 are reported in [9-13], and references therein.

In this study, we analyze $\text{Sr}_2\text{CeO}_4:\text{Eu}^{3+}$ nanoparticles, efficiently prepared using a solution combustion synthesis (SCS) method [14,15]. The main characteristics of this process are simplicity and low cost. The structure of prepared materials has been confirmed and characterized using X-ray powder diffraction (XRD), scanning electron microscope (SEM) and photoluminescence (PL) techniques [15]. The most of europium luminescence comes from transitions from the $^5\text{D}_0$ and $^5\text{D}_1$ state; and they are usually used for fluorescence intensity ratio technique for remote temperature sensing.

In our recent publication [16] we have shown that $\text{Sr}_2\text{CeO}_4:\text{Eu}^{3+}$ made by solution combustion synthesis could be used as a red phosphor. In [15] we have studied the possibility of using the synthesized $\text{Sr}_2\text{CeO}_4:\text{Eu}^{3+}$ for temperature measurements, using usual approach of calculating the calibration curves.

However, availability of more and more fast computers, capable of machine learning, gave us an idea of different approach. Here, we analyze the possibilities of training the computer to recognize optical emission spectra of $\text{Sr}_2\text{CeO}_4:\text{Eu}^{3+}$ at different temperatures. So, this paper describes extension of our work presented in [15].

2. EXPERIMENTAL PROCEDURE

The preparation of samples

Europium doped Sr_2CeO_4 nanopowders were prepared by solution combustion method, similarly as described in [14,15]. Stoichiometric quantities of starting chemicals $\text{Sr}(\text{NO}_3)_2$, $\text{CH}_4\text{N}_2\text{O}$, $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, and $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ with the purity of 99.99% were chosen to obtain the Eu^{3+} concentration in Sr_2CeO_4 of 2.5 at.% ($\text{Sr}_{2-0.05}\text{Eu}_{0.05}\text{CeO}_4$). The used chemicals were purchased from ABCR, and urea, $(\text{NH}_2)_2\text{CO}$, from Sigma-Aldrich.

The dry mixture of 10.32 g (48.75 mmol) of $\text{Sr}(\text{NO}_3)_2$, 15.015 g (250 mmol) of $\text{CH}_4\text{N}_2\text{O}$, 10.86 g (25 mmol) of $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and 0.558 g (1.25 mmol) of $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ was combined with the mixture of 4.8 g (60 mmol) of ammonium nitrate and 3.003 g (50 mmol) of urea which were used as organic fuels.

The prepared starting reagents were combusted with the flame burner at approximately 500 °C, yielding a voluminous foamy pink powder in an intensive exothermic reaction. After the solution combustion synthesis, the nanopowder was annealed for 2 hours, in air atmosphere, at 900 °C. The annealing of the material is needed to achieve optimal optical characteristics of synthesized material.

Experimental details

As an excitation source for photoluminescence measurements we used the output of the optical parametric oscillator (Vibrant OPO), continuously tunable over a spectral range from 320 nm to 475 nm. Laser pulse duration is about 5 ns, at a repetition rate of 10 Hz. Time-resolved streak images of the luminescence response of $\text{Sr}_2\text{CeO}_4:\text{Eu}^{3+}$ nanopowder excited by the OPO system were acquired by Hamamatsu streak camera equipped with a spectrograph.

Emission spectra of $\text{Sr}_2\text{CeO}_4:\text{Eu}^{3+}$ were also acquired using Ocean Optics USB2000 and AVANTES AvaSpec 2048TEC USB2 spectrometers and continuous laser diode excitation at 405 nm. The experimental setup for luminescence measurement as a function of temperature is described in [17].

For machine learning simulation experiments we have used Solo software package (Version 8.8, Eigenvector Research Inc, USA).

3. RESULTS AND DISCUSSION

The structure of material was confirmed by XRD patterns and SEM images, see [15].

The streak image of the time resolved photoluminescence spectrum of the $\text{Sr}_2\text{CeO}_4:\text{Eu}^{3+}$ using the 330 nm excitation is presented in Figure 1. Horizontal scale of streak image corresponds to wavelength, vertical scale shows development of spectra in time. Images are presented in pseudocolor, where different colors mean different optical intensities.

The $^5\text{D}_1-^7\text{F}_3$ transition (583 nm), located closely between the $^5\text{D}_0-^7\text{F}_0$ (582 nm) and the $^5\text{D}_0-^7\text{F}_1$ (587 nm) transitions is easy to identify on the time resolved image. Its time integrated peak has a comparable intensity to the intensities of peaks originating from nearby $^5\text{D}_0$ levels (see the line profile denoted by a red curve in Fig. 4).

The luminescence spectra presented in publications usually do not have the time resolution, so it is hard to guess which transitions are short lived. Streak image presented in Figure 1 shows clearly that the $^5\text{D}_1-^7\text{F}_3$ transition (583 nm) has a much higher intensity and a much shorter lifetime than nearby transitions from $^5\text{D}_0$ state.

Figure 1 - Streak image of the photoluminescence spectrum of $\text{Sr}_2\text{CeO}_4:\text{Eu}^{3+}$ nanophosphor. (OPO excitation at 330 nm).

The temperature dependency of intensity ratio of spectral lines

The luminescence of samples was measured both using pulsed (OPO) and continuous excitation. The measured luminescence spectra of Eu^{3+} doped Sr_2CeO_4 at various temperatures are presented in Figure 2. The spectra were obtained by using continuous laser diode excitation at 405 nm.

Figure 2 - Luminescence spectra of Eu^{3+} doped Sr_2CeO_4 at various temperatures. (Continuous laser diode excitation at 405 nm).

The fluorescence intensity ratio (FIR) of spectral line intensities from the $^5\text{D}_0$ and $^5\text{D}_1$ transitions depend on two physical processes: the thermalization of the $^5\text{D}_1$ level with rising temperature, where the energy difference to populate the $^5\text{D}_1$ level from the $^5\text{D}_0$ level is fully covered by phonons; and the nonradiative quenching of the $^5\text{D}_0$ and $^5\text{D}_1$ levels through the charge transfer state. Looking at Figure 2 we can see that intensity ratio between lines at 614 nm and 537 nm is temperature dependent.

The Principal Component Analysis of temperature dependent $\text{Sr}_2\text{CeO}_4:\text{Eu}^{3+}$ spectra

Principal component analysis (PCA) finds combinations of variables, or *factors*, that describe major trends in the data [18].

If X is a data matrix with m rows and n columns, each variable being a column and each sample a row,

PCA decomposes X as the sum of $r\mathbf{t}_i$ and $\mathbf{p}_i$, where r is the rank of the matrix X :

$$X = \mathbf{t}_1\mathbf{p}_1^T + \mathbf{t}_2\mathbf{p}_2^T + \dots + \mathbf{t}_k\mathbf{p}_k^T + \dots + \mathbf{t}_r\mathbf{p}_r^T$$

where $r \leq \min\{m, n\}$

The $\mathbf{t}_i$, $\mathbf{p}_i$ pairs are ordered by the amount of variance captured. The $\mathbf{t}_i$ vectors are known as scores and contain information on how the samples relate to each other. The $\mathbf{p}_i$ vectors are known as loadings and contain information on how the variables relate to each other.

For analysis presented here, we use luminescence spectra of Eu^{3+} doped Sr_2CeO_4 at temperatures between 300 and 400 K, measured with the step of 5 K. About a half of the spectral data (measured at 300, 310, 320 ... K) are used to train the PCA algorithm. Another half of the spectral data (measured at 305, 315, 325 K) are used to test the obtained PCA model.

Scores on first two principal components of measurement data of temperature dependence of luminescence of $\text{Sr}_2\text{CeO}_4:\text{Eu}^{3+}$ nanophosphor are shown in Figure 3. It could be seen that scores on PC 1 gradually move along the x axis, while scores on PC 2 oscillate along the y axis.

Figure 3 - Scores on first two principal components of measurement data of temperature dependence of luminescence of $\text{Sr}_2\text{CeO}_4:\text{Eu}^{3+}$ nanophosphor.

We see that the predictions for future measurements are well within the 95% confidence level. However, it should be noted that this approach is different, and not necessarily better, than usual method based on fitting the temperature sensing calibration curve. Namely, the machine is trained on restricted size of training data set. The remote temperature estimation is based on classification of newly obtained data in regard the calibrated data. The classification is implemented by comparing the scores distances between the calibrated data and the newly measured ones. So, the larger the training set, the better is resolution of the remote temperature sensing.

4. CONCLUSION

In this paper we have applied the Principal Component Analysis, the basic machine learning algorithm, on temperature dependent $\text{Sr}_2\text{CeO}_4:\text{Eu}^{3+}$ spectral data. We have shown that the machine could be trained to differentiate spectral data obtained on different temperatures. However, the resolution of this remote temperature sensing technique depends on the size of spectral data training set. For relatively small training set, the predicted data are well within the confidence level of 95 %.

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REFERENCES

- [1] Uskokovic V, Nanoscience: Whence it entered our World, *Tehnika*, Vol. 22, pp 795-803, 2013.
- [2] Jaque D, Vetrone F, Luminescence nanothermometry, *Nanoscale*, Vol. 4, pp 4301-4326, 2012.
- [3] Brites C. D. S, Lima P. P, Silva N. J. O, Millan A, Amaral V. S, Palacio F, Carlos L. D, Thermometry at the nanoscale, *Nanoscale*, Vol. 4, pp. 4799-4829, 2012.
- [4] Aldén M, Omrane A, Richter M, Särner G, Thermographic phosphors for thermometry: A survey of combustion applications, *Progress in Energy and Combustion Science*, Vol. 37, pp. 422-461, 2011.
- [5] Allison S. W, Gillies G. T, Remote thermometry with thermographic phosphors: Instrumentation and applications, *Rev. Sci. Instrum*, Vol. 68, pp 2615-2650, 1997.
- [6] Goss L. P, Smith A. A, Post M. E, Surface thermometry by laser-induced fluorescence, *Rev. Sci. Instrum*, Vol. 60, pp 3702-3706, 1989.
- [7] Heyes A. L, On the design of phosphors for high-temperature thermometry, *Journal of Luminescence*, Vol. 129, pp 2004-2009, 2009.
- [8] Ristic S, Polic S, Knjezevic D, Radojkovic B, Linic S, Jegdic B, Termografija u kontroli efikasnosti i bezbednosti laserskog čišćenja, *Tehnika*, Vol. 28, pp 623-629, 2019.
- [9] Stefanski M, Marciniak L, Hreniak D, Strek W, Size and temperature dependence of optical properties of $\text{Eu}^{3+}:\text{Sr}_2\text{CeO}_4$ nanocrystals for their application in luminescence thermometry, *Mat. Res. Bull.*, Vol. 76, pp 133-139, 2016.
- [10] Shi L, Zhang H, Li C, Su Q., Eu^{3+} doped Sr_2CeO_4 phosphors for thermometry: single-color or two-color fluorescence based temperature characterization, *RSC Advances*, Vol. 1, pp. 298-304, 2011.
- [11] Suresh K, Poornachandra Rao N. V, Murthy K. V. R, Photoluminescent properties of $\text{Sr}_2\text{CeO}_4:\text{Eu}^{3+}$ and $\text{Sr}_2\text{CeO}_4:\text{Eu}^{2+}$ phosphors suitable for near ultraviolet excitation, *Bull. Mater. Sci.*, Vol. 37, pp 1191-1195, 2014.
- [12] Stefanski M, Lukaszewicz M, Hreniak D, Strek W, Laser induced white emission generated by infrared excitation from $\text{Eu}^{3+}:\text{Sr}_2\text{CeO}_4$ nanocrystals, *Jour. Chem. Phys.*, Vol. 146, pp 104705-1-7, 2017.
- [13] Stefanski M, Marciniak L, Hreniak D, Strek W, Influence of grain size on optical properties of Sr_2CeO_4 nanocrystals, *Jour. Chem. Phys.*, Vol. 142, pp 184701-1-7, 2015.
- [14] Rabasovic M. S, Sevic D, Krizan J, Terzic M, Mozina J, Marinkovic B. P, Savic Sevic S, Mitric M, Rabasovic M. D, Romcevic N, Characterization and luminescent properties of Eu^{3+} doped $\text{Gd}_2\text{Zr}_2\text{O}_7$ nanopowders, *J. Alloys and Compounds* Vol. 622, pp 292-295, 2015.
- [15] Vlasic A, Sevic D, Rabasovic M. S, Krizan J, Savic-Sevic S, Rabasovic M. D, Mitric M, Marinkovic B. P, Nikolic M. G, Effects of temperature and pressure on luminescent properties of $\text{Sr}_2\text{CeO}_4:\text{Eu}^{3+}$ nanophosphor, *Journal of Luminescence*, Vol. 199 pp 285-292, 2018.
- [16] Rabasovic M. S, Krizan J, Gregorcic P, Rabasovic M. D, Romcevic N, Sevic D, Time-resolved luminescence spectra of Eu^{3+} doped YVO_4 , Sr_2CeO_4 and $\text{Gd}_2\text{Zr}_2\text{O}_7$ nanopowders, *Optical and Quantum Electronics*, Vol. 48, pp163-1-4, 2016.
- [17] Rabasovic M. D, Muric B. D, Celebonovic V, Mitric M, Jelenkovic B. M, Nikolic M. G, Luminescence thermometry via the two-dopant intensity ratio of $\text{Y}_2\text{O}_3:\text{Er}^{3+}, \text{Eu}^{3+}$, *J. Phys. D: Appl. Phys.*, Vol. 49, pp 485104-1-6, 2016.
- [1] Hotelling H, Analysis of a Complex of Statistical Variables into Principal Components. *Journal of Educational Psychology*, Vol. 24, 417-441, 1933.

REZIME

TEMPERATURNNA ZAVISNOST LUMINESCENTNIH OSOBINA $\text{Sr}_2\text{CeO}_4:\text{Eu}^{3+}$ NANOFOSFORA: PRISTUP MAŠINSKIM UČENJEM

U ovom radu analizirali smo mogućnosti primene $\text{Sr}_2\text{CeO}_4:\text{Eu}^{3+}$ nanopraha za merenje temperature primenom mašinskog učenja. Materijal je pripremljen jednostavnom metodom sinteze sagorevanja rastvora. Fotoluminescentna tehnika je korišćena za merenje temperature zavisnosti optičke emisije pripremljenog materijala. Analiza ključnih faktora omogućila nam je uvid u temperaturnu zavisnost spektralnih podataka sa drugačije tačke gledišta nego što je uobičajeni pristup.

Ključne reči: fotoluminescencija, novi materijali, termografski fosfori