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# Optical pressure nano-sensor based on lanthanide doped $SrB_2O_4$:$Sm^{2+}$ luminescence – Novel high-pressure nanomanometer

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## ABSTRACT

A new, non-contact optical sensor of pressure based on the $SrB_2O_4$:$Sm^{2+}$ nanoparticles has been successfully synthesized via a simple and low-cost Pechini method. The obtained nanomaterial was thoroughly characterized using powder X-ray diffraction, transmission electron microscopy, and Raman and luminescence spectroscopies, including high-pressure and high-temperature extreme conditions measurements. Compression of the material leads to a significant red-shift of the intraconfigurational $^5D_0 \rightarrow {}^7F_J$ ($J = 0-3$) emission bands, and to an increase of the Raman mode energies, whose shift rates as a function of pressure were determined. The shift of the extremely sharp and the most intense $^5D_0 \rightarrow {}^7F_0$ emission band ($\Delta\lambda \approx 0.24$ nm/GPa; $\Gamma$ (FHWM) $\approx 0.15$ nm) has been used for the determination of the pressure calibration curve. The high-temperature luminescence measurements revealed a desirably weak temperature dependence of the peak spectral position, which was included in the determined pressure calibration curve. The $SrB_2O_4$:$Sm^{2+}$ nanomaterial studied exhibits a negligible temperature-induced emission lines broadening, and relative low thermal quenching of luminescence. The use of such $Sm^{2+}$-based contactless pressure nano-sensor allows a very accurate pressure sensing ( ± 0.01 GPa), in the sub-micro sized regions, both at low and high temperature conditions.

## 1. Introduction

Currently, lanthanide-based functional nanomaterials are being extensively studied, mainly due to their favorable spectroscopic, magnetic and catalytic properties [1–6]. There are many benefits of using nano-sized particles (NPs) instead of their bulk, micro-sized analogues, e.g. for labeling, detection and sensing purposes, i.e. they allow manipulation in nano and sub-micro sized regions, and show high spatial resolution, possibility of using colloidal solutions instead of powders, facile material processing and applications into ultra-small areas [1,7–13].

Materials doped with trivalent (e.g. $Eu^{3+}$, $Tb^{3+}$, $Er^{3+}$, $Tm^{3+}$) and some divalent (e.g. $Sm^{2+}$) lanthanide (Ln) ions exhibit tunable multicolor luminescence in the UV–vis-NIR range, long radiative lifetimes (in the µs-ms range) and narrow absorption peaks or emission bands [14–18]. Such unique spectroscopic properties originate from the forbidden (by Laporte selection rules) *4f*-*4f* transition within the Ln ions, as well as shielding of the *4f* electrons by *5 s* and *5p* ones [19–21]. Their luminescence properties can be modulated by applying pressure and temperature, as well [1,7,22–27]. The NPs doped with Ln ions are resistant to high temperature and photo-degradation, which are important features for application of materials in various fields of science and industry [23,27–29]. Moreover, their cytotoxicity is relatively low, hence they are claimed to be good candidates for bioapplication purposes, as biomarkers and contrast agent [5,6,29–33].

Compression of materials under high-pressure conditions is a very useful technique, since due to the decreasing interatomic distances and bonds shortening may lead to the formation of new structures (phase transitions) and altered crystallinity of the samples [1,18,25,34–38]. Different types of diamond anvil cells (DAC) are commonly used for materials compression, as they allow generation of very high pressure values, usually up-to several tens or even hundreds of GPa [39]. The crucial issue for high-pressure experiments is determination of the pressure value affecting the compressed material. This can be done by different ways, e.g. X-ray diffraction measurements using volume equation of state, sound velocity measurements (via ultrasonic interferometry or Brillouin spectroscopy) using bulk modulus, optical measurements such as Raman or luminescence spectroscopies, etc. [1,18,40–43].

In the case of an optical pressure sensor (P-sensor), which uses the

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pressure-sensitivity of the emission of optically active ions in different host crystals, Tröster [44] has pointed out some ideal requirements that should be fulfilled: I) the spectrum should consist of a single line with no significant broadening or weakening with pressure; II) the emission line should show a large shift with pressure ($d\lambda/dP$); III) the temperature dependent line shift should be as small as possible ($d\lambda/dT$); IV) for high sensitivity and precision, the linewidth $\Gamma$ (FHWM) should be small compared to the line shift ($\Gamma^{-1}\cdot d\lambda/dP$); and V) the host lattice must show a large structural stability at high pressure and temperature conditions. In addition, optically active ions must have absorption bands in those wavelengths used for commercial lasers of low-cost and easy excitation.

The optical determination of pressure in the DAC´s hydrostatic chamber via ruby $R_1$ line fluorescence shift ($d\lambda/dP \approx 0.35$ nm/GPa; $d\Gamma/dP \approx 0.5$–$0.8$ nm/GPa) is the most commonly used method, due to its high sensitivity and spectral resolution, facile measurement using a simple spectrometer and the excitation source in the range of ≈350–600 nm (usually a 532 nm green laser is used), abundance of natural and synthetic ruby microcrystals, and available calibration up to the very high pressure values (above 100 GPa) [42,43,45]. Despite these advantages of ruby, its main drawbacks are strong temperature dependence of the emission line shift ($d\lambda/dT \approx 0.0068$ nm/K), significant broadening and overlapping of the $R_1$ and $R_2$ lines above 573 K, which hamper exact determination of the pressure values in the system [46]. Besides this undesired, strong temperature dependence of ruby emission, the bands overlapping and rapid intensity decrease may occur also at room temperature, at pressure above ~20 GPa, due to the non-hydrostaticity of the most commonly used pressure transmitting media, in this pressure range [47].

Thus, a special attention has been paid to lanthanide-based pressure sensors to overcome the mentioned limitations of the pressure determination at elevated temperature. Luminescence under pressure of $Nd^{3+}$, $Eu^{3+}$, $Sm^{3+}$, $Er^{3+}$ and $Tm^{3+}$ ions have been studied in different hosts as potential optical sensors [1,7,44,48–51]. However, the $Sm^{2+}$ ion, with the same electronic structure of levels as the $Eu^{3+}$ ion, has attracted much interest due to its favorable optical properties at high temperature conditions [52,53]. An optical pressure sensor based on the samarium(II)-doped strontium borate microcrystals, $SrB_4O_7:Sm^{2+}$, has been calibrated and used as a luminescence pressure sensor at high temperature conditions [18,46,47]. Thus, this material exhibits a very narrow ($d\lambda/dP \approx 0.25$ nm/GPa; $\Gamma \approx 0.1$–$0.2$ nm), intense and well separated, single emission line around 685.5 nm, corresponding to the $^5D_0 \rightarrow {}^7F_0$ transition, which is almost insensitive to temperature changes ($d\lambda/dT \approx 0.0001$ nm/K) [18,46]. However, the currently used $SrB_4O_7:Sm^{2+}$ sensor is commonly synthesized in a form of microcrystals impured with a second phase of $SrB_2O_4$, or a mixture of meta- and tetra-borate phases [18,46,47,54,55]. These issues may contribute to the apparent discrepancies in its calibration, discouraging the potential researchers from using the $Sm^{2+}$-doped materials as an alternative to the existing ruby sensor. Another pressure sensor based on the samarium(II) 0–0 emission line shift is $SrFCl:Sm^{2+}$. This compound exhibits outstanding sensitivity ($d\lambda/dP \approx 1.1$ nm/GPa). However, it reveals quite strong temperature dependence of its emission line shift ($d\lambda/dT \approx 0.0023$ nm/K), and unfortunately a very significant pressure-induced intensity decrease, limiting its use as a sensors to a low pressure range, below 20 GPa [44,52].

Recently, some new multifunctional optical pressure sensors based on the up-converting $Ln^{3+}$-doped NPs have been reported, where pressure sensing requires determination of the luminescence lifetimes ($SrF_2:Yb^{3+}$-$Er^{3+}$) [1], and emission line shift or band ratio ($LaPO_4:Yb^{3+}$-$Tm^{3+}$) [7]. The benefits of their use are the possibility of optical temperature sensing under high-pressure conditions, their small size, allowing a facile use in a colloidal form and possibility of pressure sensing in nano-sized areas, the use of NIR light (≈975 nm), which is highly penetrable for many systems, and the time-resolved measurement, which allows to eliminate the potential background radiation/fluorescence. However, these methods have strong temperature dependences and lower accuracy of the pressure determination (± 0.1 GPa) [1,7].

Here we report the use of a novel optical pressure nano-sensor based on the luminescence red-shift of the $SrB_2O_4:Sm^{2+}$ NPs ($d\lambda/dP \approx 0.24$ nm/GPa; $\Gamma \approx 0.15$ nm). Applying a facile synthesis protocol, the pure, single-phase $SrB_2O_4:Sm^{2+}$ nanomaterial has been successfully synthesized and precisely calibrated as a pressure sensor. The shift of the extremely narrow $^5D_0 \rightarrow {}^7F_0$ emission band is linear, at least up to 25 GPa. The very weak temperature dependence of its emission was confirmed. The small size of the obtained NPs guarantees high spatial resolution of the sensor and allows its use in sub-micro sized regions.

## 2. Experimental

### 2.1. Materials

$Sm_2O_3$ (99.99%, Alfa Aesar) was dissolved in HCl (37%, Sigma-Aldrich, ASC grade) to obtain $SmCl_3$, and then evaporated in order to remove an excess of the acid. $SrCl_2*6H_2O$ (Acros Organics, ACS grade, ≥99%), $H_3BO_3$ (Chempur, pure p.a.), citric acid monohydrate (Stanlab, pure p.a.) and ethylene glycol (Chempur, pure p.a.) were used as received. Deionized water was used for the synthesis.

### 2.2. Synthesis of $SrB_2O_4:Sm^{2+}$ 1 mol%

The nanocrystalline $SrB_2O_4:Sm^{2+}$ 1 mol% product was synthesized via a modified Pechini method [56]. Firstly, 1.976 mL of 0.5 M $SrCl_2$ and 0.040 mL of 0.25 M $SmCl_3$ aqueous solutions were mixed together. Subsequently, 2 g of citric acid and 0.25 mL of ethylene glycol were added to the solution of metal ions, acting as chelating and cross linking agents. Afterwards, to the as prepared solution, 5.988 mL of 0.5 M boric acid aqueous solution was added (ratio Sr/B = 1/3). The final solution was transferred onto the hot plate magnetic stirrer, maintaining a vigorous stirring and heating (≈350 K) to evaporate an excess of water and form the white-yellowish resin. After that, the as-prepared resin was transferred to the ceramic crucible and annealed in a furnace, by a two-step process. Namely, at the first step the sample was annealed at 573 K for 2 h, in order to improve the homogeneity and uniformity of the final particles. During the second step, the sample was annealed at 1173 K over 3 h, to remove the organic components and form the nanocrystalline product. Finally, the product was grounded in an agate mortar forming a fine, white powder.

### 2.3. Characterization

Transmission electron microscopy (TEM) measurements were performed with a Hitachi HT7700 microscope, operating at 100 kV. The Powder X-ray diffraction (XRD) pattern was recorded with a Bruker AXS D8 Advance diffractometer using Cu Kα radiation ($\lambda = 1.5406$ Å). Based on the XRD data, the average grain size of the nanocrystals synthesized was estimated using the Scherrer's equation [57]:

$$D = \frac{k\lambda}{\cos\theta\sqrt{\beta^2 - \beta'^2}} \quad (1)$$

where $D$ is grain size, $k$ is a shape factor (0.9 for spherical particles), $\lambda$ is a wavelength of radiation, $\theta$ is an angle of diffraction, $\beta$ is a full width at half maximum (FWHM) and $\beta'$ is an instrumental effect. The excitation spectrum was collected using a Hitachi F-7000 spectrofluorometer, at ambient conditions. Room temperature Raman and emission spectra at high pressure were recorded in a backscattering geometry with a Renishaw InVia confocal micro-Raman system, using a grating with 1800 grooves/mm, and a power-controlled 100 mW 532 nm laser diode. The laser beam was focused using an Olympus x20 SLMPlan N long working distance objective. The emission spectra at high temperature (ambient

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