



# Photoluminescence properties of Pr<sup>3+</sup> doped Bi<sub>2</sub>ZnOB<sub>2</sub>O<sub>6</sub> microcrystals and PMMA-based composites



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## ABSTRACT

Photoluminescence properties of red-emitting Pr<sup>3+</sup>-doped Bi<sub>2</sub>ZnOB<sub>2</sub>O<sub>6</sub> microcrystalline powder and PMMA-based composite materials were reported. Bi<sub>2</sub>ZnOB<sub>2</sub>O<sub>6</sub>:Pr<sup>3+</sup> powders were synthesized by means of the modified Pechini method. The morphology and crystallographic structure of Bi<sub>2</sub>ZnOB<sub>2</sub>O<sub>6</sub>:Pr<sup>3+</sup> microcrystals were investigated by XRD and HRTEM. The PMMA-based composite materials were prepared by embedding of Bi<sub>2</sub>ZnOB<sub>2</sub>O<sub>6</sub>:Pr<sup>3+</sup> powder in the PMMA matrix. The vibrational properties of the powder and composite systems were investigated by  $\mu$ -Raman spectroscopy. Emission spectra of the samples were measured under blue (451.6 nm) and UV (320 nm) excitation. Both, the powder and composite samples show enhancement of red emission (<sup>1</sup>D<sub>2</sub> → <sup>3</sup>H<sub>4</sub>) and quenching of greenish-blue luminescence from <sup>3</sup>P<sub>0</sub> level of Pr<sup>3+</sup> ions after excitation in UV and VIS caused by the <sup>3</sup>P<sub>0</sub> ~ <sup>1</sup>D<sub>2</sub> non-radiative relaxation of Pr<sup>3+</sup> ion by low-lying charge transfer state and non-radiative de-excitation through Pr<sup>3+</sup>–Bi<sup>3+</sup> energy transfer. The response of the powder and composite samples to pulsed excitation at 451.6 nm was measured by monitoring emission from the <sup>1</sup>D<sub>2</sub> level (595 nm/<sup>3</sup>P<sub>0</sub> → <sup>3</sup>H<sub>6</sub> transition). The determined lifetimes  $\tau_1$  and  $\tau_2$  of the red emission at 595 nm (<sup>1</sup>D<sub>2</sub> → <sup>3</sup>H<sub>4</sub> transition) of the composite are significantly longer in comparison to powder samples. Moreover, because of the good nonlinear optical properties of the Bi<sub>2</sub>ZnOB<sub>2</sub>O<sub>6</sub> crystals and effective luminescence of the Pr<sup>3+</sup>-doped Bi<sub>2</sub>ZnOB<sub>2</sub>O<sub>6</sub> powders and composites, they can be very useful as bi-functional materials in the new generation of optoelectronic devices.

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## 1. Introduction

Significant progress in the research of the luminescent and nonlinear optical properties of nano- and microcrystals is the result of intense investigations of new multifunctional systems [1,2]. There is still the demand for novel, compact, efficient and low cost materials for many optoelectronic applications including optical switching devices [3], integrated optical circuits [4] as well as widely used light emitters [5]. Among various new materials the polymer-based composites containing optically active and

nonlinear optical (NLO) nano- or microcrystals have very desirable features, which make them a good alternative for presently used materials [6,7]. In some bi-functional materials the luminescence effect of optically active ions and NLO phenomena occur in the same host [8]. The polymer-based composite systems obtained on the basis of such a bi-functional materials present an excellent light propagation properties as a result of the polymer matrix and micro- or nanoparticles optical properties, which makes them very promising for new optoelectronic applications.

Among various optically active materials rare earth (RE) doped systems arise great interest because of their unique luminescence properties mainly due to sharp and narrow *f-f* transitions on the manifold energy for which shifting of the band position depends slightly on the host matrix. On the basis of these properties such

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materials can be used for a variety of applications such as lasers and optical amplifiers [9], multicore displays [10], scintillators [11], biological labeling [12] and optical frequency converters [13].

The triply ionized praseodymium ions ( $\text{Pr}^{3+}$ ) were used as an activator in a variety of host materials useful in many phosphors [14,15] for different types of light emitting devices. In particular, the luminescence properties of  $\text{Pr}^{3+}$ -doped materials were extensively investigated for many potential application including fiber optical communication [16], LEDs [17], field-emission display devices and photoluminescence devices [18]. Depending on the concentration of  $\text{Pr}^{3+}$  ions and the host matrix properties the  $\text{Pr}^{3+}$  ions can emit in the visible (VIS) and the near infrared (NIR) spectral range [19].  $\text{Pr}^{3+}$  ions possess the specific electronic energy level structure with several optical transitions in VIS spectral range. The  $4f^2$  electronic configuration of  $\text{Pr}^{3+}$  ions consists of:  $^3\text{H}_{4,5,6}$ ,  $^3\text{F}_{4,3,2}$ ,  $^1\text{G}_4$ ,  $^1\text{D}_2$ ,  $^1\text{I}_6$ ,  $^3\text{P}_{2,1,0}$  and  $^1\text{S}_0$  electronic energy levels. The greenish-blue and red emission of the  $\text{Pr}^{3+}$  ions originates from excited  $^3\text{P}_0$  and  $^1\text{D}_2$  levels upon the UV or VIS excitation [20].

In many oxide-based host materials, the  $\text{Pr}^{3+}$  ions exhibit a prominent red luminescence from  $^1\text{D}_2$  level under blue or UV excitation accompanied by a total or partial quenching of the emission from the  $^3\text{P}_0$  level. Several non-radiative pathways were proposed to explain quenching of  $^3\text{P}_0$  luminescence of  $\text{Pr}^{3+}$  ion in oxide-based lattices: multiphonon relaxation, cross-relaxation, intersystem crossing through low-lying  $4f^15d^1$  levels, energy transfer between  $\text{Pr}^{3+}$  and metal ions as well as charge transfer (CT) mechanism [21]. The CT between active ions and the host lattice results in the formation of the charge transfer state CTS. The energetic position of the CTS depends on the nature of the host lattice and for the oxide-based crystals is typically located around excited states of rare earths. Partial or total quenching of  $^3\text{P}_0$  emission of  $\text{Pr}^{3+}$  ions depend on the relative energetic position of the CTS with respect to the  $^3\text{P}_0$  and  $^1\text{D}_2$  levels. The possible CT mechanism, very probable for oxide-based host lattices is ligand-to-metal charge transfer (LMCT) [19]. The LMCT state was previously reported for  $\text{BZBO}:\text{Eu}^{3+}$  phosphors [22].

Recently new RE-doped  $\text{Bi}_2\text{ZnOB}_2\text{O}_6$  materials (abbreviated as BZBO) in the form of single crystals [23], powders [23] as well as glasses [24,25] and polymer-based composites [7] are gathering important attention because of their promising optical properties and consequently numerous potential applications. BZBO crystals are also known as effective nonlinear optical materials [26], which possess high laser damage tolerance. Moreover, they may be efficiently doped with rare earth ions resulting in effective luminescence [22,27–29]. Depending on the host material, the structure of the energetic levels of the  $\text{Bi}^{3+}$  ions may change. Particularly, for oxide-based lattices the structure of electronic levels of  $\text{Bi}^{3+}$  ions strongly depends on configuration of the nearest oxygen surrounding of  $\text{Bi}^{3+}$  ions [30]. In the BZBO structure the  $\text{Bi}^{3+}$  ions are located at 4c positions ( $\text{C}_1$  symmetry) and occur in octahedral coordination  $\text{BiO}_6$  being six-coordinated by the oxygen atoms forming the  $\text{BiO}_6$  octahedra [31] and the lowering of the excited states energy is typically observed in comparison to the structure of electronic levels of isolated  $\text{Bi}^{3+}$  ions [30]. The BZBO is an optically positive biaxial optical crystal [40]. The experimentally determined band gap of BZBO single crystal is equal to 3.444 eV ( $27777.72 \text{ cm}^{-1}$ ) [32]. The ultraviolet cutoff absorption edge of the  $\text{BZBO}:\text{Pr}^{3+}$  single crystal was reported to be about 350 nm [27]. The vibrational and some spectroscopic properties of  $\text{BZBO}:\text{Pr}^{3+}$  single crystals have been already reported [31]. This system is particularly interesting because it is characterized with the large values of nonlinear optical coefficients as well as the effective luminescence of excited  $\text{Pr}^{3+}$  ions, which make this system an excellent candidate for NIR to VIS laser converters [27].

In this work we report for the first time the result of structural

and spectroscopic investigation of the  $\text{BZBO}:\text{Pr}^{3+}$  microcrystalline powder and the  $\text{BZBO}:\text{Pr}^{3+}/\text{PMMA}$  polymer composite. The synthesis of pure and  $\text{Pr}^{3+}$ -doped BZBO microcrystals and their XRD, HRTEM and spectroscopic characterization are presented. In particular the result of the Raman spectroscopy measurements, photoluminescence (PL) and photoluminescence excitation (PLE) spectra and the fluorescence decay profiles for  $\text{BZBO}:\text{Pr}^{3+}$  microcrystals and  $\text{BZBO}:\text{Pr}^{3+}/\text{PMMA}$  composites are presented and discussed.

## 2. Experiment

### 2.1. Synthesis of $\text{BZBO}:\text{Pr}^{3+}$ powder

Polycrystalline samples of pure and  $\text{Pr}^{3+}$ -doped BZBO phases were synthesized by means of modified Pechini method [33]. The starting materials were:  $\text{Bi}_2\text{O}_3$  (ALFA, 99.999%),  $\text{Pr}_6\text{O}_{11}$  (ALFA, 99.95%),  $\text{ZnO}$  (REACHIM, 99.5%),  $\text{H}_3\text{BO}_3$  (STENMARK, 99.5%),  $\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$  (POCH, 99.4%, complexing agent) and  $\text{C}_6\text{H}_8(\text{OH})_6$  (CHEMDREAMLAND, 99.5%, polymeric agent). First, the stoichiometric amounts of Bi, Zn metal precursors were dissolved in the minimal amount concentrated  $\text{HNO}_3$  in the presence of citric acid monohydrate ( $\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$ ) under continuous heating ( $75^\circ\text{C}$ ) and stirring to complex the cations. In case of Pr-doped powder, the equivalent amounts of  $\text{Pr}_6\text{O}_{11}$  were additionally dissolved in  $\text{HNO}_3$  solution. The overall molar ratio between metal ions and citric acid was set to be 1:3, respectively. When the homogeneous and clarified solution was obtained, an excess (10% molar) of boric acid ( $\text{H}_3\text{BO}_3$ ) was charged into solution. This excess of boron source is needed due to volatilization of  $\text{B}_2\text{O}_3$  at higher temperatures during the synthesis. After all the reagents were completely dissolved, the pH value of the solution was set to about  $8 \div 9$  using ammonia solution. Next, the proper amount of mannitol ( $\text{C}_6\text{H}_8(\text{OH})_6$ ) was added into vessel to enable creation of rigid and volumetric polyester. Citric acid and mannitol were taken in the molar ratio 1:2, respectively. The temperature was then raised up to  $90^\circ\text{C}$  and kept under constant stirring for 2 h to initiate the polyesterification reaction. Then the solution was transferred into alumina crucible, put inside furnace and kept at  $140^\circ\text{C}$  for 20 h to evaporate the solvents. In consequence of polyesterification the brown foamy-like viscous gel was formed. The temperature was then raised to  $350^\circ\text{C}$  for 3 h to eliminate the residuals of solvents and to dry the gel until it turns into black resin. To start the pyrolysis process and burn out the organic part, the temperature was rapidly increased to  $640^\circ\text{C}$ . After 72 h the crucible content was crushed and grounded in agate mortar and very fine, white powders of undoped BZBO and doped  $\text{BZBO}:\text{Pr}^{3+}$  were obtained. The content of  $\text{Pr}^{3+}$  ions in  $\text{BZBO}:\text{Pr}^{3+}$  powder was equal to 2.5% at.

### 2.2. $\text{BZBO}:\text{Pr}^{3+}/\text{PMMA}$ composite

Polymeric matrix was prepared of methyl methacrylate ( $(\text{C}_5\text{O}_2\text{H}_8)_n$  purchased from Sigma-Aldrich. In the first step methyl methacrylate was purified via distillation performed at  $130^\circ\text{C}$  in oil bath and inhibitor of polymerization (monomethyl ether hydroquinone - MEHQ) was removed. Appropriate amount of investigated powder were added to purified  $(\text{C}_5\text{O}_2\text{H}_8)_n$ . Polymerization process was initiated by addition of benzoyl peroxide (Sigma-Aldrich) to the pure MMA, 10 mg of benzoyl peroxide to 10 ml MMA were added. Polymerization process is described with the equation of chemical reaction showed in Fig. 1. Polymerization was performed at  $80^\circ\text{C}$  with mechanical shaking thus uniform samples of powders in PMMA matrix were obtained. The content of  $\text{BZBO}:\text{Pr}^{3+}$  microcrystals in PMMA was equal to 20% at.

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