

Proceedings of the International Conference on Oxide Materials for Electronic Engineering, May 29–June 2, 2017, Lviv

Synthesis and Luminescence Properties of Pr³⁺-Doped BiPO₄ Polycrystals

V.P. CHORNI^{a,*}, S.G. NEDILKO^a, K.L. BYCHKOV^a, K.V. TEREBILENKO^a,
M.S. SLOBODYANIK^a AND V.V. BOYKO^b

^aTaras Shevchenko National University of Kyiv, 64/13 Volodymyrska Str., 01601 Kyiv, Ukraine

^bNational University of Life and Environmental Sciences of Ukraine, 15 Geroiv Oborony Str., 03041 Kyiv, Ukraine

The results of synthesis, crystal structure characterization and luminescence properties study of the Pr³⁺-doped bismuth orthophosphate, BiPO₄, polycrystals are reported. It was found that doping of bismuth orthophosphate with praseodymium of concentration more than 1% leads to phase transition of BiPO₄ from so-called “high-temperature monoclinic” to “low-temperature monoclinic” structure. At room temperature studied samples revealed intensive red luminescence caused by radiation electronic transitions in the Pr³⁺ ions under their intrinsic $f \rightarrow f$ excitation at $^3H_4 \rightarrow ^3P_1 + ^1I_6$ absorption transition. Influence of phase transformation as well as multi-phonon and cross-relaxation processes on the luminescence of the Pr³⁺-doped BiPO₄ compounds were discussed.

DOI: [10.12693/APhysPolA.133.843](https://doi.org/10.12693/APhysPolA.133.843)

PACS/topics: 78.55.Hx, 81.30.Hd

1. Introduction

Currently the new lighting and display devices such as light-emitting diodes (LEDs), plasma display panels (PDPs), and field emission displays (FEDs) have been demanded by industry, which resulted in great interest to develop novel phosphors for those goals [1, 2]. Due to good physical and chemical properties various oxide compounds have been actively studied as materials for novel devices, in particular as luminescent materials. Although some of oxide compounds manifest characteristic own luminescence [3–6], their intensity and color purity are usually far from these ones required for displays and lighting. In order to overcome this drawback the various activator ions (typically ions of transition or rare-earth (RE) metals) are introduced into oxide host to obtain desirable light performance.

Among oxide compounds the BiPO₄ was numerously reported as excellent host for luminescent RE ions [7–12]. At the same time, to the best of our knowledge there are no reports on BiPO₄ doping with Pr³⁺ ions, so far. From another hand, the Pr³⁺ doped oxide materials including phosphates, aluminates or borates have been widely studied as perspective red emitting phosphors with intense red luminescence of good color purity [13–15]. Therefore one can expect good luminescence properties of Pr³⁺-doped BiPO₄.

Some statements were accounted when we performed the Pr³⁺-doped BiPO₄ study. First, it is well-known that luminescence properties of RE ions are determined by their environment in the crystal lattice, in other words — by crystal structure of host material. Equal charge states of Bi³⁺ and Pr³⁺ ions, as well as a similarity of

their ionic radii allowed us to assume that Pr³⁺ ions occupied the Bi³⁺ cation positions in the BiPO₄ structure. The peculiarities of the BiPO₄ crystal structure were previously studied carefully by many authors during more than half of century [16–19]. It was found that the bismuth orthophosphate can exist in three structural phases: hexagonal-type (BiPO₄ × *n*H₂O), monazite-type (low-temperature monoclinic, LTMP) and SbPO₄-type (high-temperature monoclinic, HTMP). All three phases of BiPO₄ are metastable [19] and moreover it was shown that doping with RE ions can lead to phase transformations of this compound [10, 12]. Second, it is worth noting that for Eu³⁺-doped BiPO₄ intensity of luminescence strongly depends on the type of structural phase and increases in the next set: hexagonal → HTMP → LTMP [20, 21].

The synthesis procedures, peculiarities of incorporation of Pr³⁺ ions into BiPO₄ lattice and photoluminescence (PL) properties of Pr³⁺-doped BiPO₄ polycrystalline powder samples are reported in this work. Dependences of the PL intensity on Pr³⁺ dopant concentration have been measured and discussed.

2. Experimental details

A series of the Bi_{1-x}Pr_xPO₄ ($x = 0.001-0.1$) compounds were synthesized by high temperature solid state reaction method. The starting materials, Bi₂O₃ (99.99%), (NH₄)₂HPO₄ (99.999%), and Pr₆O₁₁ (99.999%) were weighted in stoichiometry ratio, then thoroughly mixed and milled in agate mortar for more than 30 min till they are uniformly distributed. The prepared mixtures have been heated at 450, 500 and 600 °C for 6 h at each temperature with intermediate regrinding in porcelain crucibles, and then have been naturally cooled to room temperature. In order to measure the characteristics of the phosphor the samples were grinded into powder.

*corresponding author; e-mail: vchornii@gmail.com

The phase composition of prepared samples was determined by X-ray powder diffraction (XRD) using SHIMADZU XRD-6000 diffractometer with a linear detector and Cu K_α radiation ($\lambda = 1.5418 \text{ \AA}$). The PL characteristics were measured using DFS-12 double diffraction grating monochromator equipped with photomultiplier FEU-79. Diode-pumped laser ($\lambda_{em} = 473 \text{ nm}$) and powerful Xenon lamp DXeL1000 (1000 W) together with DMR-4 double prism monochromator (working range 220–900 nm) were used as excitation light sources. The PL studies were performed at room temperature. All the PL emission and excitation spectra were corrected on system responses.

3. Results and discussion

3.1. X-ray diffraction study

The most informative part of XRD patterns of $\text{Bi}_{1-x}\text{Pr}_x\text{PO}_4$ ($x = 0.001\text{--}0.1$) samples (2θ range is $16\text{--}55^\circ$) is shown in Fig. 1. The final and the highest annealing temperature (600°C) had to determine bismuth phosphate HTMP structure [22]. However, some LTMP contribution to the sample composition takes place even for the lowest concentration of praseodymium (Fig. 1, curve 1). Besides, the higher RE amount is, the higher amount of the LTMP is in the prepared samples (according to the peaks at $2\theta = 21.4, 27.3, 29.2,$ and 34.6° marked by arrows near curve $x = 0.001$). The fact means that doping of BiPO_4 by praseodymium stabilizes the LTMP in the sample composition. The same behavior was earlier shown for the Eu^{3+} doped bismuth orthophosphate [12]. For the used concentration range all the samples represent mixtures of HTMP and LTMP.

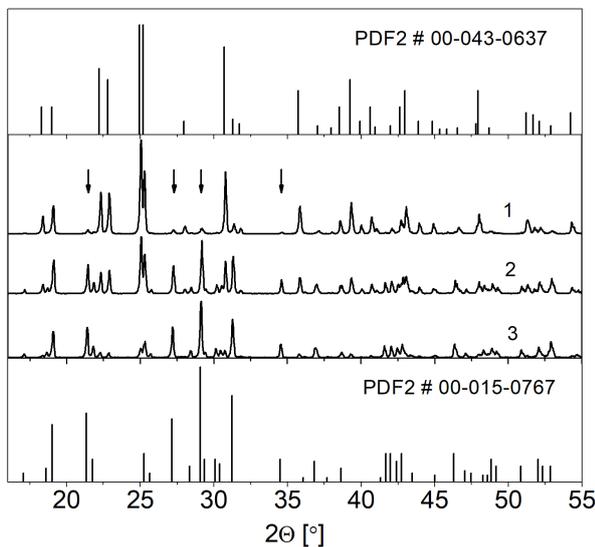


Fig. 1. XRD patterns for $\text{BiPO}_4 : x\text{Pr}^{3+}$ samples ($x = 0.001$ (1), 0.01 (2), 0.1 (3)). Standards for high-temperature monoclinic BiPO_4 (PDF2 card # 00-043-0637) and low-temperature monoclinic BiPO_4 (PDF2 card # 00-015-0767) are shown at the top and at the bottom part of figure.

3.2. Luminescence spectroscopy

Excitation spectra of the Pr-doped BiPO_4 photoluminescence are presented in Fig. 2 in 300–550 nm spectral range. The spectra were measured at various luminescence wavelengths, λ_{em} , and they consist of lines related with transitions from ground 3H_4 level to $^3P_{0,1,2}$ multiplet of Pr^{3+} ion. In fact, the optical band gap of BiPO_4 is near 4.7 eV (264 nm) [5], so only transitions related with dopant' levels in the forbidden band of BiPO_4 can be observed in this spectral range.

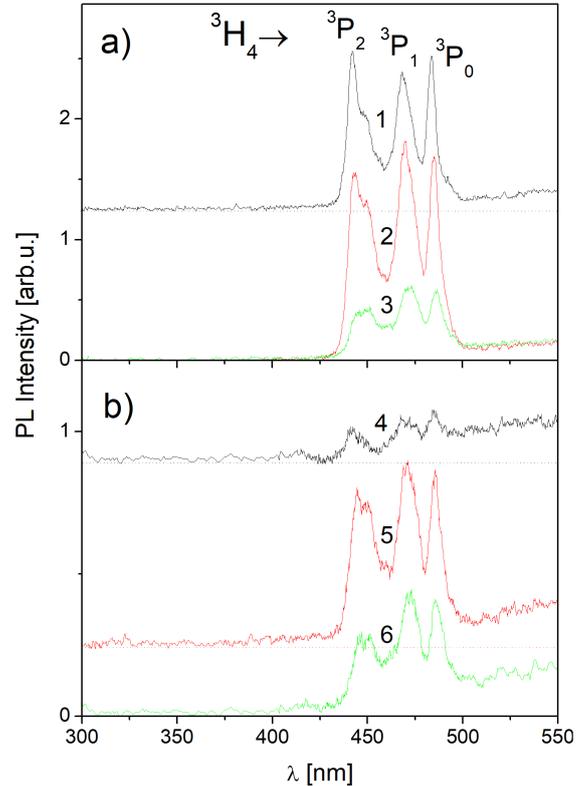


Fig. 2. The PL excitation spectra of $\text{BiPO}_4 : x\text{Pr}^{3+}$ ($x = 0.001$ (1, 4), 0.01 (2, 5), 0.1 (3, 6)) polycrystals; $\lambda_{em} = 611.5$ (a) and 642.8 nm (b); $T = 300 \text{ K}$. Zero intensity levels for spectra 1, 4 and 5 are shown by dotted straight lines.

Figure 3 shows the PL spectra of Pr^{3+} -doped BiPO_4 samples under direct excitation from ground state 3H_4 to $^3P_1 + ^1I_6$ levels of Pr^{3+} ions ($\lambda_{ex} = 473 \text{ nm}$). The most intensive PL lines are related with radiation transitions from 3P_0 to 3H_4 (483 nm), 3H_6 ($\approx 615 \text{ nm}$), 3F_2 (640 nm), and to 3F_4 levels (728 nm) and also from 1D_2 to 3H_4 ($\approx 595 \text{ nm}$) levels of Pr^{3+} ions. Some of lines related with $^1D_2 \rightarrow ^3H_4$ transitions are overlapped with those for $^3P_0 \rightarrow ^3H_6$ transitions and therefore complex structured wide band in $570\text{--}635 \text{ nm}$ spectral range was formed (roughly bands in $570\text{--}600 \text{ nm}$ range can be attributed mainly to $^1D_2 \rightarrow ^3H_4$ transitions; e.g. curve 1 in Fig. 3).

The PL spectra obviously depend on the RE content (Fig. 3). The most prominent changes appear when con-

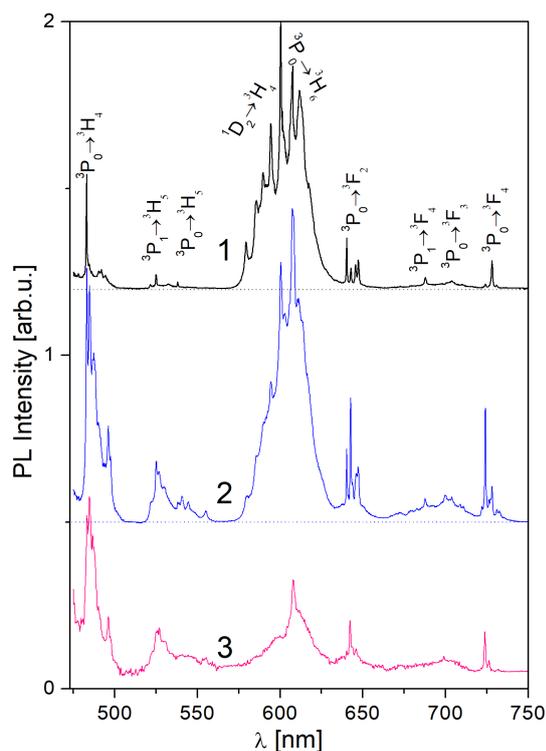


Fig. 3. The PL spectra of $\text{BiPO}_4 : x\text{Pr}^{3+}$ ($x = 0.001$ (1), 0.01 (2), 0.1 (3)); $\lambda_{ex} = 473$ nm, $T = 300$ K. Zero intensity levels for the spectra 1 and 2 are shown by dotted straight lines.

concentration of Pr^{3+} reaches $x = 0.01$. In particular, the lines of ${}^3P_0 \rightarrow {}^3H_4$ transitions, which were observed as a shoulder (480–500 nm range) (Fig. 3, curve 1), became more intensive. Intensity of the ${}^3P_{0,1} \rightarrow {}^3H_5$ (510–575 nm range) and ${}^3P_0 \rightarrow {}^3F_4$ transitions (715–740 nm range) also increased if x increased up to 0.01. Some redistribution of the lines intensity also appears when moving from the lowest value $x = 0.001$ to $x = 0.01$ and higher. For example, it can be seen for the ${}^3P_0 \rightarrow {}^3F_2$ radiation transitions (630–660 nm spectral range).

Figure 4 shows dependence of the total PL intensity as well as dependences of selected transitions intensity on Pr^{3+} concentration. Total intensity and intensities of selected transitions were calculated as area under spectra in the spectral ranges 475–750 nm (total), 475–500 nm (${}^3P_0 \rightarrow {}^3H_4$), 570–630 nm (${}^1D_2 \rightarrow {}^3H_4$; ${}^3P_0 \rightarrow {}^3H_6$), and 635–650 nm (${}^3P_0 \rightarrow {}^3F_2$), respectively. It can be seen if concentration of the Pr^{3+} is low ($x < 0.01$) total intensity and dependence are determined by ${}^1D_2 \rightarrow {}^3H_4$ and ${}^3P_0 \rightarrow {}^3H_6$ transitions. For higher Pr^{3+} concentrations the PL intensity of short-wavelength side of band in 575–630 nm range (possibly related with transitions from 1D_2 level) greatly decreases (Fig. 3) and overall the PL spectra become to be determined mostly by transitions from 3P_0 level. Thus, from viewpoint of luminescence intensity the samples with concentration of Pr^{3+} near $x = 0.01$ are the most attractive for phosphor applications.

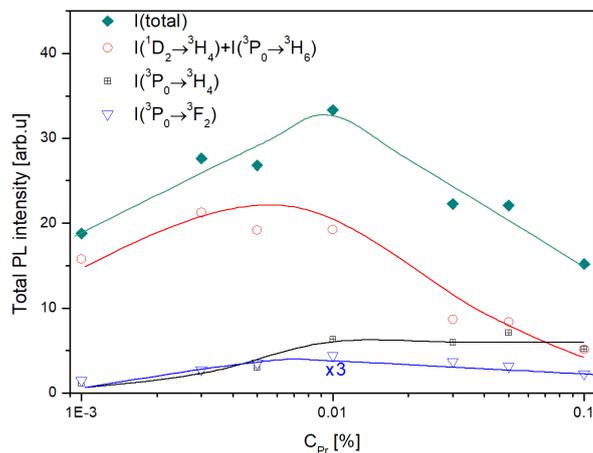


Fig. 4. Dependences of integrated PL intensity on Pr^{3+} concentration, x . (Solid lines are only guide for eyes.)

Described changes in the PL spectra and intensity can be related with impact of several processes. There can be BiPO_4 phase transformations, multi-phonon radiationless relaxation and cross-relaxation processes. It is well known that spectra and intensity of the RE ions luminescence depend on their neighbor surround. As for RE ions in BiPO_4 host we can point data about luminescence of the Eu^{3+} -doped BiPO_4 [20, 21], which showed the most intensive luminescence for LTMP phase among all possible BiPO_4 phases. Therefore, we are able to assume that similar behavior can take place for the Pr^{3+} -doped BiPO_4 crystals and increase of the LTMP content in the row of Pr^{3+} concentration contributes to the increase of the total PL intensity. On the other hand, it had been previously reported that ${}^3P_0 \rightarrow {}^3F_2$ transition is hypersensitive and should strongly depend on symmetry of position occupied by the Pr^{3+} -ion [23]. Our data showed that HTMP \rightarrow LTMP transformation did not led to increase of ${}^3P_0 \rightarrow {}^3F_2$ bands intensity but only redistribution of the Stark component intensity of mentioned transitions occurred (Fig. 3). Therefore, increase of total intensity with increase of Pr^{3+} concentration (curve 1 in Fig. 4) unlikely noticeably related with phase transformation, but this dependence is mainly determined by the increase of the Pr^{3+} ions content.

Similarly, decrease of the PL intensity if $x > 0.01$ also is not determined by structural transformation of the crystal lattice, but it is a manifestation of concentration quenching. In the case of Pr^{3+} ions excitation to the 3P_1 level, a non-radiative relaxation leads to population of the below lying 3P_0 or 1D_2 levels. The depopulation of the 3P_0 level can occur either via radiation transitions to ${}^3H_{4,5,6}$ and ${}^3F_{2,3,4}$ (the PL emission) or via non-radiation relaxation to 1D_2 level. Two possible ways for the 1D_2 level population through the 3P_0 usually had been discussed. There are multi-phonon relaxation and phonon-assisted [${}^3P_0, {}^3H_4$] \rightarrow [${}^3H_6, {}^1D_2$] cross-relaxation processes [24]. Taking into account rela-

tively small energy gap between 3P_0 and 1D_2 levels (less than 4200 cm^{-1}) and presence of high energy phonons in the BiPO_4 host (1160 cm^{-1} , generated by asymmetric stretching vibration of the P–O bond [25]) the multi-phonon relaxation is possible. Its probability as well as probability of multi-phonon radiationless relaxation from the 1D_2 level determine quantum yield of the Pr^{3+} ions luminescence, but they do not depend on the Pr^{3+} concentration.

As for the cross-relaxation, we note that for low Pr^{3+} ions concentrations, average distances between RE ions, $d = (4\pi N/3)^{-1/3}$ (N is Pr^{3+} concentration in ions/ cm^3) [26], in the BiPO_4 compounds are too large for effective realization of this mechanism (e.g. $d = 26.89\text{ \AA}$, if $x = 0.001$). In fact, critical distance between RE ions that ensures efficient energy transfer is near 10 \AA [27, 28], so cross-relaxation could play significant role only if x is above 0.01 ($d = 12.07\text{ \AA}$). Decreasing of $^3P_0 \rightarrow ^3H_6$ transitions intensity for concentrations $x > 0.01$ is related with cross-relaxation of the $[^3P_0, ^3H_4] \rightarrow [^3H_6, ^1D_2]$ type. Energy gap between 1D_2 level and next lower lying energy level 1G_4 is large (about 6800 cm^{-1}), therefore the multiphonon relaxation between these levels is of low probability because at least 6 phonons are needed to do it. Therefore, radiationless depopulation of the 1D_2 level should occur mostly due to the $[^1D_2, ^3H_4] \rightarrow [^1G_4, ^3F_{3,4}]$ cross relaxations.

Thus, luminescence properties of $\text{BiPO}_4 : x\text{Pr}^{3+}$ are dependent on RE ions concentration and three processes are responsible for observed luminescence behavior. These are phase transformations of BiPO_4 host, multiphonon relaxation, and cross-relaxation, too.

4. Conclusions

Doping of the BiPO_4 with praseodymium promotes transformation of the $\text{Bi}_{1-x}\text{Pr}_x\text{PO}_4$ crystal from so-called high-temperature monoclinic phase to low-temperature monoclinic phase. This transformation was observed even for low Pr^{3+} concentrations, $x = 0.001$.

Pr^{3+} -doped BiPO_4 compounds revealed intensive red luminescence under direct excitation of Pr^{3+} ions by $f \rightarrow f$ electronic transitions. Concentration quenching of the luminescence was found and maximum of total luminescence intensity was observed at praseodymium concentration $x = 0.01$.

Multi-phonon relaxation is responsible for population of 1D_2 level, while concentration quenching of luminescence from 1D_2 and 3P_0 levels were ascribed to $[^1D_2, ^3H_4] \rightarrow [^1G_4, ^3F_{3,4}]$ and $[^3P_0, ^3H_4] \rightarrow [^3H_6, ^1D_2]$ cross-relaxation processes, respectively.

References

- [1] C.C. Lin, A. Meijerink, R.-S. Liu, *J. Phys. Chem. Lett.* **7**, 495 (2016).
- [2] M. Janulevicius, P. Marmokas, M. Misevicius, J. Grigorjevaite, L. Mikoliunaite, S. Sakirzanovas, A. Katelnikovas, *Sci. Rep.* **6**, 26098 (2016).
- [3] Yu. Hizhnyi, O. Gomenyuk, S. Nedilko, A. Oliynyk, B. Okhrimenko, V. Bojko, *Radiat. Meas.* **42**, 719 (2007).
- [4] Y. Hizhnyi, V. Chornii, S. Nedilko, M. Slobodyanik, I. Zatovsky, K. Terebilenko, V. Boyko, *Radiat. Meas.* **56**, 397 (2013).
- [5] Yu.A. Hizhnyi, S.G. Nedilko, V.P. Chornii, M.S. Slobodyanik, I.V. Zatovsky, K.V. Terebilenko, *J. Alloys Comp.* **614**, 420 (2014).
- [6] S. Nedilko, V. Chornii, Yu. Hizhnyi, M. Trubitsyn, I. Volnyanskaya, *Opt. Mater.* **36**, 1754 (2014).
- [7] B. Sanyasi Naidu, B. Vishwanadh, V. Sudarsan, R. Kumar Vatsa, *Dalton Trans.* **41**, 3194 (2012).
- [8] M. Zhao, L. Li, J. Zheng, L. Yang, G. Li, *Inorg. Chem.* **52**, 807 (2013).
- [9] S.Q. Yan, *J. Mater. Sci. Mater. Electron.* **25**, 1868 (2014).
- [10] X. Shi, Y. Liu, J. Zhang, K. Zhang, J. Li, H. Zuo, P. Li, *Ceram. Int.* **41**, 6683 (2015).
- [11] J. Zhang, Z. Yu, J. Guo, W. Yan, W. Xue, *J. Alloys Comp.* **703**, 156 (2017).
- [12] Y. Zheng, L. Li, M. Zhao, J. Zheng, G. Li, E. Yang, X. Zhang, *Cryst. Eng. Commun.* **16**, 5040 (2014).
- [13] O. Antonenko, O. Chukova, Yu. Hizhnyi, S. Nedilko, V. Scherbatskyi, *Opt. Mater.* **28**, 643 (2006).
- [14] O. Chukova, S. Nedilko, *Opt. Mater.* **35**, 1735 (2013).
- [15] X. Yang, F. Huang, Z. Huang, F. Cao, J. Zhang, *RSC Adv.* **6**, 65311 (2016).
- [16] R.C.L. Mooney-Slater, *Z. Kristallogr.* **117**, 371 (1962).
- [17] O. Müller, R. Roy, *Z. Kristallogr.* **138**, 237 (1973).
- [18] B. Romero, S. Bruque, M.A.G. Aranda, J.E. Iglesias, *Inorg. Chem.* **33**, 1869 (1994).
- [19] S.N. Achary, D. Errandonea, A. Muñoz, P. Rodríguez-Hernández, F.J. Manjón, P.S.R. Krishna, S.J. Patwe, V. Grover, A.K. Tyagi, *Dalton Trans.* **42**, 14999 (2013).
- [20] M. Zhao, G. Li, J. Zheng, L. Li, H. Wang, L. Yang, *Cryst. Eng. Commun.* **13**, 6251 (2011).
- [21] P. Arunkumar, C. Jayajothi, D. Jeyakumar, N. Lakshminarasimhan, *RSC Adv.* **2**, 1477 (2012).
- [22] K.L. Bychkov, K.V. Terebilenko, R.P. Linnik, N.S. Slobodyanik, *Solid State Phenom.* **230**, 62 (2015).
- [23] V.K. Tikhomirov, S.A. Tikhomirova, *J. Non-Cryst. Solids* **274**, 54 (2000).
- [24] A. Watras, I. Carrasco, R. Pazik, R.J. Wiglusz, F. Piccinelli, M. Bettinelli, P.J. Deren, *J. Alloys Comp.* **672**, 45 (2016).
- [25] V.D. Nithya, L. Vasylechko, R. Kalai Selvan, *RSC Adv.* **4**, 65184 (2014).
- [26] D.F. de Sousa, F. Batalioto, M.J.V. Bell, S.L. Oliveira, L.A.O. Nunes, *J. Appl. Phys.* **90**, 3308 (2001).
- [27] Y.V. Mal'yukin, A.A. Masalov, P.N. Zhmurin, N.V. Znamenski, E.A. Petrenko, T.G. Yukina, *Phys. Status Solidi B* **240**, 655 (2003).
- [28] J. Collins, M. Geen, M. Bettinelli, B. Di Bartolo, *J. Lumin.* **132**, 2626 (2012).