KSr₄(BO₃)₃:Pr³⁺: a new red-emitting phosphor for blue-pumped white light-emitting diodes

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Abstract. A novel red phosphor KSr₄(BO₃)₃: Pr³⁺ was prepared by using a solid-state reaction method, and its photoluminescence and charge compensator effect (Li⁺) were investigated. The synthesized phosphors were characterized by X-ray diffraction (XRD), scanned electron microscope (SEM) and photoluminescence (PL) spectroscopy. The as-prepared material indicates that Pr³⁺ ions occupy Sr²⁺ sites in the lattice of KSr₄(BO₃)₃ with micron-scale irregular morphology. Their excitation bands at 449, 475 and 487 nm are originated from the transitions of ³H₄→³P₂, ³H₄→³P₁ and ³H₄→³P₀ of Pr³⁺ ion. Under 449 nm excitation, the emission of Pr³⁺ at 587, 606 and 627 nm are attributed to ¹D₂→³H₅, ³P₀→³H₆ and ³P₀→³F₂. The optimized doping concentration of Pr³⁺ in KSr_{4-x}(BO₃)₃: xPr³⁺ is determined to be x=0.015. By codoping Li⁺ in KSr₄(BO₃)₃: Pr³⁺ to compensate the charge unbalance, the intensities of emission spectra at 606 nm can be increased greatly. The nonradiative concentration quenching among two nearest Pr³⁺ ions occurs via dipole-dipole interaction based on the Dexter theory. The Commission Internationale de l'Eclairage (CIE) chromaticity coordinates are (0.645, 0.354) for KSr₄(BO₃)₃: Pr³⁺ and (0.644, 0.355) for KSr₄(BO₃)₃: Pr³⁺, Li⁺, respectively. The decay curves of the selected samples are also studied in detail. The result shows that KSr₄(BO₃)₃: Pr³⁺ is promising candidate for red phosphors in the fabrication of white light-emitting diodes *via* blue LED chips.

Keywords: Phosphor; Photoluminescence; Solid-state reaction method; Charge compensation; KSr₄(BO₃)₃: Pr³⁺

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1. Introduction

White light-emitting diodes (W-LEDs) are considered as the new generation light source because of their high brightness, long lifetime and environment friendliness [1-7]. One approach to get white light is using blue light (around 430-480 nm) chip coated with yellow phosphors. However, this white light, due to the lack of red component, slants cold [8-10]. The other approach is mixed tri-color (red, green and blue) phosphors in which red phosphors have more significant effect on the luminous flux than green and blue [11]. Pr^{3+} -doped materials show intense ${}^3\text{P}_0 \rightarrow {}^3\text{H}_6$ emission in the red spectral region, which have been widely adopted as red emitting phosphors [12-17]. For example, the Pr^{3+} -doped β -SiAlON red phosphor was synthesized by gas pressure sintering under 1950 °C for 2 h, and the phosphor holds the superior characteristics of nitride compounds [15]. Luminescence spectra of β -SiAlON/ Pr^{3+} under high hydrostatic pressure have also been investigated by S. Mahlik and R.S. Liu, et al [16], and they found there is a weak dependence of the Pr^{3+} emission on applied pressure. In addition, novel efficient phosphors on the base of Mg and Zn co-doped SrTiO_3 : Pr^{3+} were synthesized by I.V. Kityk, et al [17], and they found the Zn^{2+} and Mg^{2+} ion doping in the phosphor generates deep traps, which results in slightly longer decay time. In recent years, the Pr^{3+} doped borates have drawn abundant interest among the researchers for their use in various optical and optoelectronic devices [18-22]. Especially, the Pr^{3+} doped $\text{KSr}_4(\text{BO}_3)_3$ compound may be a potential phosphor due to its excellent chemical stable, environmental friendliness and easily productive at temperature below 900 °C in air. Several methods such as solution combustion synthesis method [23] and solid state reactions [24] have been used to prepared rare-earth ions doped borate phosphors.

To our knowledge, the luminescence properties of Pr^{3+} doped $\text{KSr}_4(\text{BO}_3)_3$ have not been studied yet, though the red luminescence of Pr^{3+} ion has been extensively used in the lighting and laser [13, 14, 25]. Therefore, motivated by the above investigations and the attempt to develop novel phosphors for the promising applications of W-LED, we have investigated the photoluminescence (PL), photoluminescence excitation

(PLE) and color chromaticity properties as well as the structure of $\text{KSr}_4(\text{BO}_3)_3: \text{Pr}^{3+}$ and $\text{KSr}_4(\text{BO}_3)_3: \text{Pr}^{3+}, \text{Li}^+$ phosphors. The optimized concentration, quenching mechanism and decay time of $\text{KSr}_4(\text{BO}_3)_3: \text{Pr}^{3+}$ and $\text{KSr}_4(\text{BO}_3)_3: \text{Pr}^{3+}, \text{Li}^+$ have been simultaneously discussed. The effect of charge compensation (Li^+) is also studied in this paper.

2. Experimental details

2.1 Synthesis of $\text{KSr}_4(\text{BO}_3)_3: \text{Pr}^{3+}$ and $\text{KSr}_4(\text{BO}_3)_3: \text{Pr}^{3+}, \text{Li}^+$

The structure of the host crystal $\text{KSr}_4(\text{BO}_3)_3$ is a noncentrosymmetric space group *Ama2* [24-26]. Until now, quite few phosphors' studies have been published on this compound in spite of the potential interest in many applications [23-27]. Polycrystalline samples of $\text{KSr}_4(\text{BO}_3)_3: \text{Pr}^{3+}$ and $\text{KSr}_4(\text{BO}_3)_3: \text{Pr}^{3+}, \text{Li}^+$ were prepared by a solid-state reaction at high temperature starting from analytical purity K_2CO_3 (A.R.), SrCO_3 (A.R.), H_3BO_3 (A.R.), Li_2CO_3 (A.R.) and high purity Pr_2O_3 (99.99%). Firstly, stoichiometric amount of the raw powders was weighed out, mixed and finely ground together in an agate mortar, and then sintered under ambient atmosphere at 500 °C for 4 h. After this step, the sintered powder mixtures were ground and sintered at 850 °C for 12 h. The products were finally cooled down to room temperature in the furnace, ground, and pulverized for further measurements.

2.2 Characterization

The X-ray powder diffraction (XRD) data for phase identification were collected at ambient temperature by a X-ray diffractometer (Shimadzu XRD-6000) with a Cu $K\alpha$ radiation ($\lambda=0.154056$ nm), operating at 30 kV and 30 mA. The morphology of the typical sample was examined using scanning electron microscopy (SEM; TESCAN MIRA3). The PL and PLE spectra were measured at room temperature using a fluorescence spectrophotometer (Hitachi F-4600) equipped with a 150 W xenon light source. The PL decay curve was recorded using an FLS-980 fluorescence spectrophotometer (Edinburgh Instruments) equipped with both continuous and

pulsed xenon lamps as the light source.

3. Results and discussion

3.1 Crystal structure and morphology

Fig. 1 shows the XRD patterns of $\text{KSr}_4(\text{BO}_3)_3:\text{Pr}^{3+}$ and $\text{KSr}_4(\text{BO}_3)_3:\text{Pr}^{3+},\text{Li}^+$ phosphors. All XRD patterns are found to agree well with that reported in the Inorganic Crystal Structure Database (ICSD 171423) regardless of the contents of dopants, indicating that the doped Pr^{3+} or Li^+ ions do not induce significant changes in the host structure. This agreement indicates that the phosphors $\text{KSr}_4(\text{BO}_3)_3:\text{Pr}^{3+}$ and $\text{KSr}_4(\text{BO}_3)_3:\text{Pr}^{3+},\text{Li}^+$ have been successfully prepared by using the solid-state reaction method. The host crystal structure of $\text{KSr}_4(\text{BO}_3)_3$ belongs to the noncentrosymmetric space group *Ama2*. There are four crystallographic positions of cations in the unit cell: eightfold coordinated K^+ (4b), Sr(1) (4b) and Sr(2) (8c) sites, and nine-fold coordinated Sr(3) (4a) sites. The morphology of the typical samples $\text{KSr}_{3.985}(\text{BO}_3)_3:0.015\text{Pr}^{3+}$ and $\text{KSr}_{3.97}(\text{BO}_3)_3:0.015\text{Pr}^{3+},0.015\text{Li}^+$ are, respectively, presented in Fig. 2 (a) and (b). These particles in Fig. 2 (a) and (b) have good dispersion and crystallinity although the appearance is irregular. The $\text{KSr}_{3.985}(\text{BO}_3)_3:0.015\text{Pr}^{3+}$ sample in Fig. 2 (a) consists of aggregated particles with sizes ranging from 2 to 3 μm . Interestingly, the surfaces of these particles are covered with the filaments. The grains of the selected SEM image of $\text{KSr}_{3.97}(\text{BO}_3)_3:0.015\text{Pr}^{3+},0.015\text{Li}^+$ in Fig. 2 (b) are mainly in the range of 2–5 μm which are smooth surfaces without any fluffs.

3.2 Photoluminescence properties

In Fig. 3, the PLE spectra are recorded which monitored wavelength at 606 nm with a broad excitation band and three sharp peaks from 300 to 500 nm. The strong excitation peak at around 449 nm is attributed to $^3\text{H}_4\text{-}^3\text{P}_2$ transition, and 475 nm is owing to $^3\text{H}_4\text{-}^3\text{P}_1$ transition, and 487 nm is ascribed to $^3\text{H}_4\text{-}^3\text{P}_0$ transition of Pr^{3+} ion. Interestingly, there is a wide charge transfer band of 300-430 nm which is due to the promotion of the orbital redistribution of the charge density transmission from 2p

(O²⁻) to 4p (Sr²⁺) or to 3p (K⁺) state. The strong transfer band also possibly owes to the charge imbalance caused by trivalent Pr³⁺ ions partly replacing divalent Sr²⁺ sites in the KSr₄(BO₃)₃ lattice, thus making (SrO₈)¹⁴⁻ or (SrO₉)¹⁶⁻ cluster absorb energy more efficiently transmits to the Pr³⁺ ion, and significantly enhancing the electronic transition band of 430-500 nm.

The PL spectra have also been shown in Fig. 3 by monitoring at 449 nm. The emission spectrum of KSr₄(BO₃)₃: Pr³⁺ phosphor was characterized which peaked at 587, 606 and 627 nm corresponding to ¹D₂→³H₅, ³P₀→³H₆ and ³P₀→³F₂ transitions of Pr³⁺, respectively. As shown in Fig. 2, there are strong red emission of KSr₄(BO₃)₃: Pr³⁺ at around 600-640 nm.

Fig. 4 shows the PL intensity of KSr₄(BO₃)₃: Pr³⁺ and KSr₄(BO₃)₃: Pr³⁺, Li⁺ phosphors under blue excitation of 449 nm. As shown in Fig. 4, the PL intensity increases from 0 to 1.5 mol.% Pr³⁺, while the luminescence will decrease and then quench owing to the clustering of the Pr³⁺ centers when Pr³⁺ concentrations are higher than 1.5 mol.%. In addition, the light emitting color is one characterization of a fundamental parameter of the material properties [28, 29]. Fig. 5 labels the KSr₄(BO₃)₃: Pr³⁺ and KSr₄(BO₃)₃: Pr³⁺, Li⁺ phosphors in the red region of the CIE chromaticity diagram. Test results demonstrate that when the concentration of Pr³⁺ and Pr³⁺, Li⁺ arrived at 1.5 mol.%, the phosphor's color coordinates (0.645, 0.354) for KSr₄(BO₃)₃: Pr³⁺ and (0.644, 0.355) for KSr₄(BO₃)₃: Pr³⁺, Li⁺ with high purity closed to the ideal red color (0.65, 0.35). Therefore, the novel red phosphors KSr₄(BO₃)₃: Pr³⁺ and KSr₄(BO₃)₃: Pr³⁺, Li⁺ can be used as a new generation of white LED material, and can effectively excite by the blue LED.

In fact, the influence mechanism of luminescence for earth ions in crystals is quit complex. When the Pr³⁺ ions doped into the KSr₄(BO₃)₃ crystal, the forbidden f-f transitions of praseodymium can be partially or completely removed due to the ligand-field effect, and hence produce the luminescence. It should be pointed out that, for pure KSr₄(BO₃)₃ crystal, there is no any emissions which can be observed during the detection in Fig. 3, i.e., electron-hole pairs with respect to the optics are almost negligible in the host crystal. Considering the ionic radii and electronegativity are

different between the impurity ion (Pr^{3+}) and host ion (Sr^{2+}), the intrinsic cationic defects will exist in the host crystal. Thus, in order to the charge balance of the as-prepared samples, Li^+ ion is introduced in this system. One Pr^{3+} ion plus one Li^+ ion replace two Sr^{2+} ion, i.e., $\text{Pr}^{3+} + \text{Li}^+ \rightarrow 2\text{Sr}^{2+}$, and then the charge is balance. At the same time, the obvious enhanced emissions can be observed in Fig. 3.

The critical energy transfer distance or critical distance (R_c) between the activators in the host can be estimated by Blasse's formula [30],

$$R_c \approx 2 \left[\frac{3V}{4\pi x_c Z} \right]^{1/3} \quad (1)$$

where x_c (1.5 mol.%) is critical concentration; Z is the number of host cations in the unit cell, and V is the volume of the unit cell. For $\text{KSr}_4(\text{BO}_3)_3$ host, Z is 16, V is $910.02 \text{ \AA}^3$ obtained from the XRD refinement results [24]. Thus, the critical distance (R_c) of $\text{KSr}_4(\text{BO}_3)_3: \text{Pr}^{3+}$ is calculated by the Eq. (1) to be about $12.2 \text{ \AA}$.

Dexter theory shows that the concentration quenching of inorganic materials is originated from the electric multipolar interaction or magnetic dipoles interaction among the activator ions [31]. The mechanism of interaction between Pr^{3+} ions can be expressed by the following equation [32],

$$\frac{I}{x} = \frac{k}{1 + \beta(x)^{\theta/3}} \quad (2)$$

where x is the concentration of activator; β and k are the constants for each interaction for a specified host lattice; and $\theta = 6, 8$, and 10 corresponds to dipole-dipole, dipole-quadrupole and quadrupole-quadrupole interactions, respectively. When x is

more than critical concentration, the equation can be simplified to $\frac{I}{x} = \frac{K'}{\beta(x)^{\theta/3}}$. So θ

can be determined from the ratio of $\lg(I/x)$ to $\lg x$. As shown in Fig. 4, θ value can be obtained from the slope of the straight line $(-(\theta/3))$. The slope of the straight line $-(\theta/3) \approx 2$, so that the value of θ is ~ 6 . The result indicates that non-radiative transition between Pr^{3+} ions occur *via* dipole-dipole interaction for the concentration quenching of Pr^{3+} in $\text{KSr}_4(\text{BO}_3)_3$ host.

The decay times of Pr^{3+} ions in crystals are of particular interest for various

researchers [13, 33]. These investigations found that the principal role of Pr^{3+} doped borates begins to play phonon subsystem and multi-photon processes [33]. Experimental and theoretical spectroscopic study of Pr^{3+} doped SrAl_2O_4 phosphors have also been studied in detail [34]. Fig. 6 shows the typical fluorescence decay pattern of $\text{KSr}_{3.985}(\text{BO}_3)_3: 0.015\text{Pr}^{3+}$ and $\text{KSr}_{3.97}(\text{BO}_3)_3: 0.015\text{Pr}^{3+}, 0.015\text{Li}^+$. The decay curve is nonexponential and well fitted into a three-exponential function [35, 36]

$$I = A_1 \exp(-t / \tau_1) + A_2 \exp(-t / \tau_2) + A_3 \exp(-t / \tau_3) \quad (3)$$

in which τ_1 , τ_2 and τ_3 are time constants and A_1 , A_2 and A_3 are coefficients. The three exponential behavior is due to the possibility of coexistence of three sites occupancies of Pr^{3+} in $\text{KSr}_4(\text{BO}_3)_3: \text{Pr}^{3+}$ or $\text{KSr}_4(\text{BO}_3)_3: \text{Pr}^{3+}, \text{Li}^+$. In this study, all the decay curves can be fitted well by three exponential equation, which confirm the above experimental scheme that Pr^{3+} will occupy Sr^{2+} sites and have three different substitutional sites, i.e., Sr(1), Sr(2) and Sr(3) sites. Furthermore, the average lifetime can be calculated by using the formula [35, 36]

$$\langle \tau \rangle = \frac{A_1 \tau_1^2 + A_2 \tau_2^2 + A_3 \tau_3^2}{A_1 \tau_1 + A_2 \tau_2 + A_3 \tau_3} \quad (4)$$

As can be seen in Fig. 6, the fitting results are in good agreement with the experimental findings. The average lifetime in $\text{KSr}_{3.985}(\text{BO}_3)_3: 0.015\text{Pr}^{3+}$ is 27.92 μs and in $\text{KSr}_{3.97}(\text{BO}_3)_3: 0.015\text{Pr}^{3+}, 0.015\text{Li}^+$ is 31.52 μs which is caused by the radiation relaxation channels and reduction of the $^3\text{P}_0$ lifetime in the phosphors. The lifetime of the sample containing the charge compensator Li^+ is longer than that without the Li^+ ions, which indicates Li^+ can enhance the fluorescence intensity of $\text{KSr}(\text{BO}_3)_3: \text{Pr}^{3+}$.

4. Conclusions

In summary, Li^+ undoped and doped $\text{KSr}(\text{BO}_3)_3: \text{Pr}^{3+}$ red emitting phosphors have been successfully synthesized through a solid-state reaction. The doped Pr^{3+} ions do not change the host structure. The PL and PLE spectra of $\text{KSr}(\text{BO}_3)_3: \text{Pr}^{3+}$ and $\text{KSr}(\text{BO}_3)_3: \text{Pr}^{3+}, \text{Li}^+$ phosphors indicate that the phosphors can be efficiently excited

by blue-LED, and emit red light with the wavelength at around 606 nm. The emission intensity of $\text{KSr}(\text{BO}_3)_3: \text{Pr}^{3+}$ increases with the increase of the doped Pr^{3+} concentration until reaching a maximum value at $x=1.5$ mol.%, and then decreases with increasing Pr^{3+} content because of concentration quenching. The concentration quenching mechanism occurs *via* electric dipole-dipole interactions according to Dexter theory. The emission intensities are enhanced with Li^+ co-doped $\text{KSr}(\text{BO}_3)_3: \text{Pr}^{3+}$. The decay curves indicate that charge compensator Li^+ can evoke the longer fluorescent lifetimes and higher efficiency of the emission. Thus, the red emitting phosphors contained charge compensator have great potential application in white LEDs.

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References

- [1] J. Qiao, L. Shen, W. Xiao, X. Qiao, Z. Wang, L. Gao, B. Li, Y. Zhou, X. Zhang, X. Zhang, Photoluminescence and charge compensation effects in $\text{Lu}_3\text{Mg}_3\text{Al}_{5-x-y}\text{Si}_x\text{O}_{12}:\text{Ce}^{3+}$ phosphors for white LEDs, *J. Alloys Compd.* 695 (2017) 567–573.
- [2] Z. Zhang, L. Wang, X. Chu, P. Zhang, Y. Cao, Y. Xi, W. Chen, D. Wang, High-brightness $\text{Ca}_9\text{NaGd}_{0.667(1-x)}(\text{PO}_4)_7:\text{xEu}^{3+}$ red phosphor for NUV light-emitting diodes application, *J. Alloys Compd.* 695 (2017) 3220–3224.
- [3] S. Kaur, M. Jayasimhadri, A.S. Rao, A novel red emitting Eu^{3+} doped Calcium aluminozincate phosphor for applications in w-LEDs, *J. Alloys Compd.* 697 (2017) 367–373.

- [4] Y. Peng, R. Li, H. Cheng, Z. Chen, H. Li, M. Chen, Facile preparation of patterned phosphor-in-glass with excellent luminous properties through screen-printing for high-power white light-emitting diodes, *J. Alloys Compd.* 693 (2017) 279–284.
- [5] L. Wang, Q. Liu, K. Shen, Q. Zhang, L. Zhang, B. Song, C. Wong, A high quenching content red-emitting phosphor based on double perovskite host BaLaMgSbO₆ for white LEDs, *J. Alloys Compd.* 696 (2017) 443–449.
- [6] K. R. Devi, S. D. Meetei, S. D. Singh, Role of Eu²⁺ on the blue-green photoluminescence of In₂O₃: Eu²⁺ nanocrystals, *Mater. Charact.* 114 (2016) 197–203.
- [7] A. Raja, G. Annadurai, D. J. Daniel, P. Ramasamy, Synthesis, optical and thermal properties of novel Tb³⁺ doped RbCaF₃ fluoroperovskite phosphors, *J. Alloys Compd.* 683 (2016) 654–660.
- [8] W. Feng Q. Liu, W. Zhang, L. Lv, Y. Cui, Luminescent properties and crystal-field analysis for novel yellow-green phosphor CaWO₄:Pr³⁺, *Acta Optica Sinica*, 34 (2014) 0416004.1–6.
- [9] C. Yang, Z. Zhang, G. Hu, R. Cao, X. Liang, W. Xiang, A novel deep red phosphor Ca₁₄Zn₆Ga₁₀O₃₅: Mn⁴⁺ as color converter for warm W-LEDs: Structure and luminescence properties, *J. Alloys Compd.* 694 (2017) 1201–1208.
- [10] Q. Shao, L. Wang, L. Song, Y. Dong, C. Liang, J. He, J. Jiang, Temperature dependence of photoluminescence spectra and dynamics of the red-emitting K₂SiF₆:Mn⁴⁺ phosphor, *J. Alloys Compd.* 695 (2017) 221–226.
- [11] W.L. Feng, M.F. Zhao, J.Y. Xue, X.J. Tian, Photoluminescence properties of (Ba_{1-x}Eu_x)WO₄ red synthesized by the coprecipitation/calcination method, *J. Alloys Compd.* 521 (2012) 146–149.
- [12] T.C. Liu, B.M. Cheng, S.F. Hu, and R.S. Liu, Highly stable red oxynitride β-SiAlON:Pr³⁺ phosphor for light-emitting diodes, *Chem. Mater.* 23 (2011) 3698–3705.
- [13] K. Wang, W. Feng, X. Feng, Y. Li, P. Mi, and S. Shi, Synthesis and

- photoluminescence of novel red-emitting ZnWO_4 : Pr^{3+} , Li^+ phosphors, *Spectrochim. Acta A* 154 (2016) 72–75.
- [14] Y. Zhou, J. Liu, X. Yang, X. Yu, and J. Zhuang, A promising deep red phosphor $\text{AgLaMo}_2\text{O}_8$: Pr^{3+} with blue excitation for white LED application, *J. Electrochem. Soc.* 157 (2010) H278–H280.
- [15] T.C. Liu, B.M. Cheng, S.F. Hu, R.S. Liu, Highly stable red oxynitride β -SiAlON: Pr^{3+} phosphor for light-emitting diodes, *Chem. Mater.* 23 (2011) 3698–3705.
- [16] S. Mahlik, A. Lazarowska, M. Grinberg, T.C. Liu, R.S. Liu, Luminescence Spectra of β -SiAlON/ Pr^{3+} Under High Hydrostatic Pressure, *J. Phys. Chem. C* 117 (2013) 13181–13186.
- [17] H. Ryu, B.K. Singh, K.S. Bartwal, M.G. Brik, I.V. Kityk, Novel efficient phosphors on the base of Mg and Zn co-doped SrTiO_3 : Pr^{3+} , *Acta Mater.* 56 (2008) 358–363.
- [18] N. Chanthima, K. Boonin, P. Limsuwan, J. Kaewkhao, Visible Luminescence of Pr^{3+} in Bismuth Borate Glasses, *Adv. Mater. Res.* 770 (2013) 59–63.
- [19] F.B. Xiong, D.S. Guo, H.F. Lin, L.J. Wang, H.X. Shen, W.Z. Zhu, High-color-purity red-emitting phosphors RE_2WO_6 : Pr^{3+} (RE=Y, Gd) for blue LED, *J. Alloys Compd.* 647 (2015) 1121–1127.
- [20] U. Fawad, M. Oh, H. Park, H.J. Kim, S. Kim, Synthesis and characterization of Ce^{3+} -, Pr^{3+} -, Tm^{3+} -doped $\text{Li}_6\text{Lu}(\text{BO}_3)_3$ phosphors for X-ray and neutron imaging, *J. Kor. Phys. Soc.* 62 (2013) 1102–1107.
- [21] A.B. Gawande, R.P. Sonekar, S.K. Omanwar, Combustion synthesis and energy transfer mechanism of $\text{Bi}^{3+} \rightarrow \text{Gd}^{3+}$ and $\text{Pr}^{3+} \rightarrow \text{Gd}^{3+}$ in YBO_3 , *Combust. Sci. Tech.* 186 (2014) 785–791.
- [22] P.P. Pawar, S.R. Munishwar, R.S. Gedam, Physical and optical properties of $\text{Dy}^{3+}/\text{Pr}^{3+}$ co-doped lithium borate glasses for W-LED, *J. Alloys Compd.* 660 (2016) 347–355.
- [23] N.S. Bajaj, S.K. Omanwar, Combustion synthesis and characterization of phosphor $\text{KSr}_4(\text{BO}_3)_3$: Dy^{3+} , *Opt. Mater.* 35 (2013) 1222–1225.
- [24] Y. Zhang, M. Ji, B. Wang, Y. Kong, and J. Xu, Structure and photoluminescence

- properties of $\text{KSr}_4(\text{BO}_3)_3: \text{Eu}^{3+}$ red-emitting phosphor, *Opt. Mater. Exp.* 2 (2012) 92–102.
- [25] L.H. Jiang, Y.L. Zhang, C.Y. Li, J.Q. Hao, Q. Su, *Synthesis, photoluminescence, thermoluminescence and dosimetry properties of novel phosphor $\text{KSr}_4(\text{BO}_3)_3: \text{Ce}$* , *J. Alloys Compd.* 482 (2009) 313–316.
- [26] L. Wu, X. L. Chen, Y. P. Xu, Y. P. Sun, Y. P. Xu, and X. Z. Li, *Structure determination and relative properties of novel noncentrosymmetric borates $\text{MM}'_4(\text{BO}_3)_3$ ($\text{M} = \text{Na}$, $\text{M}' = \text{Ca}$ and $\text{M} = \text{K}$, $\text{M}' = \text{Ca}$, Sr)*, *Inorg. Chem.* 45 (2006) 3042–3047.
- [27] R.H. Petit, P. Evesque, and J. Duran, *Dimers and clusters in $\text{CaF}_2: \text{Pr}^{3+}$. Laser selective excitation and time-resolved spectroscopy*, *J. Phys. C* 14 (1981) 5081–5090.
- [28] X. Feng, W. Feng, M. Xia, K. Wang, H. Liu, D. Deng, X. Qin, W. Yao, and W. Zhu, *Co-precipitation synthesis, photoluminescence properties and theoretical calculations of $\text{MgWO}_4: \text{Eu}^{3+}$ phosphors*, *RSC Adv.* 6 (2016) 14826–14831.
- [29] J.P. Kim, P.E. Jeon, J.C. Choi, and G.C. Kim, *Warm-white-light emitting diode utilizing a single-phase full-color $\text{Ba}_3\text{MgSi}_2\text{O}_8: \text{Eu}^{2+}, \text{Mn}^{2+}$ phosphor*, *Appl. Phys. Lett.* 84 (2004) 2931–2933.
- [30] G. Blasse, *Energy transfer in oxidic phosphors*, *Philips Res. Rep.* 24 (1969) 131–44.
- [31] D.L. Dexter and J. H. Schulman, *Theory of concentration quenching in inorganic phosphors*, *J. Chem. Phys.* 22 (1954) 1063–1070.
- [32] L.G. Van Uitert, *Characterization of energy transfer interactions between rare earth ions*, *J. Electrochem. Soc.* 114 (1967) 1048–1053.
- [33] A. Brenier, I.V. Kityk, *Spectroscopic properties of Pr^{3+} -doped $\text{Ca}_4\text{GdO}(\text{BO}_3)_3$ (GdCOB)*, *J. Appl. Phys.* 90 (2001) 232–236.
- [34] X. Feng, W. Feng, K. Wang, *Experimental and theoretical spectroscopic study of praseodymium(III) doped strontium aluminate phosphors*, *J. Alloys Compd.* 628 (2015) 343–346.
- [35] D.R. James and W.R. Ware, *Recovery of underlying distributions of lifetimes*

from fluorescence decay data, Chem. Phys. Lett. 126 (1986) 7–11.

- [36] J.R. Knutson, J.M. Beechem, L. Brand, Simultaneous analysis of multiple fluorescence decay curves: a global approach, Chem. Phys. Lett. 102 (1983) 501–507.

Figures and Captions.

Fig. 1 X-ray diffraction patterns and crystal structure of $\text{KSr}_4(\text{BO}_3)_3:\text{Pr}^{3+}$ and $\text{KSr}_4(\text{BO}_3)_3:\text{Pr}^{3+},\text{Li}^+$ phosphors. All main peaks can be indexed by an orthorhombic structure with space group of *Ama2*.

Fig. 2 Scanning electron microscopy images of (a) $\text{KSr}_{3.985}(\text{BO}_3)_3:0.015\text{Pr}^{3+}$ and (b) $\text{KSr}_{3.97}(\text{BO}_3)_3:0.015\text{Pr}^{3+},0.015\text{Li}^+$ phosphors.

Fig. 3 PL and PLE spectra of $\text{K Sr}_{4-x}(\text{BO}_3)_3: x\text{Pr}^{3+}$ ($x=0, 0.005, 0.01, 0.015, 0.02$) and $\text{K Sr}_{3.97}(\text{BO}_3)_3:0.015\text{Pr}^{3+}, 0.015\text{Li}^+$.

Fig. 4 PL intensity vs. Pr^{3+} concentration (x) of $\text{K Sr}_{4-x}(\text{BO}_3)_3: x\text{Pr}^{3+}$ phosphors. The inset shows the dependence of $\lg(I/x)$ on $\lg x$.

Fig. 5 CIE chromaticity coordinates of $\text{KSr}_{3.985}(\text{BO}_3)_3: 0.015\text{Pr}^{3+}$ and $\text{KSr}_{3.97}(\text{BO}_3)_3: 0.015\text{Pr}^{3+}$, 0.015Li^+ phosphors.

Fig. 6 The decay curves of typical (a) $\text{KSr}_{3.985}(\text{BO}_3)_3: 0.015\text{Pr}^{3+}$ and (b) $\text{KSr}_{3.97}(\text{BO}_3)_3: 0.015\text{Pr}^{3+}$, 0.015Li^+ samples.