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Novel blue-emitting K_{Ba}GdSi₂O₇:Eu²⁺ phosphor used for near-UV white-light LED

--Manuscript Draft--

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Abstract:	<p>Novel blue-emitting K_{Ba}GdSi₂O₇:Eu²⁺ phosphors were designed and synthesized through solid-state reaction method. The structural properties, concentration and temperature-dependent luminescence behaviors of this phosphors were investigated in detail in this paper. Studies revealed that K_{Ba}GdSi₂O₇:Eu²⁺ phosphors have an intense absorption in the broad wavelength ranging from 250 nm to 400 nm that is suitable for the commercial near-UV LED, and give out intense blue light peaked at 475 nm with a full-width half-maximum (FWHM) of 75 nm. The crystallographic information of K_{Ba}GdSi₂O₇ phase is revealed from XRD pattern by Rietveld refinement. Band gap is derived to be 3.93 eV through diffuse reflection spectra (DRS) through Kubelka Munk function. The concentration quenching mechanism is identified as the dipole–dipole interaction. Moreover, the thermal quenching experiment was also conducted and the activation energy is calculated as 0.3069 eV, which indicates this novel K_{Ba}GdSi₂O₇:Eu²⁺ phosphor has good thermal stability. These properties exhibit its potential commercial application for near-UV white-light LEDs (w-LEDs).</p>	
Additional Information:		
Question	Response	

<p>Journal of Materials Science considers only outstanding papers that make a distinct contribution to the field of experimental electronic materials. This includes optoelectronic and photonic materials as well.</p> <p>Please explain in point form why your work is outstanding and what distinguishes this work from past work. What are the outstanding and exceptional contributions of this paper? How does it contribute to the state-of-the art?</p>	<ol style="list-style-type: none"> 1. This study designed and synthesized a novel luminescence host $\text{KBaGdSi}_2\text{O}_7$, and its crystallographic information was revealed from XRD pattern by Rietveld refinement; 2. Eu^{2+} ions in $\text{KBaGdSi}_2\text{O}_7$ host show an intense absorption in the broad wavelength in 250-400 nm range which is suitable for the commercial near-UV LED chip, and emit strong blue light peaked at 475 nm; 3. The thermal quenching result showed the novel $\text{KBaGdSi}_2\text{O}_7:\text{Eu}^{2+}$ phosphor possesses good thermal stability.
<p>Does this manuscript belong to a special issue?</p>	<p>No</p>
<p>Was your manuscript previously rejected by this journal because of textual overlap with previous or other papers?</p>	<p>No</p>

Dear Editor,

Thank you very much for your letter and the issues about our paper submitted to “*Journal of Materials Science: Materials in Electronics*” (No.: JMSE-D-19-04416).

We have paid attention to the issues and checked the manuscript and revised it accordingly. We have highlighted the changes that we have done with our original submission in blue in the revised manuscript. We submit here the revised manuscript as well as the list of changes. If you have any questions about our paper, please don't hesitate to let us know.

We hope that the revised version of the manuscript is now acceptable for publication in your journal. The following summarizes how we solve the issues.

We look forward to hearing from you soon.

Yours sincerely,

Renli Fu

A point-by-point response to reviewers' comments

Manuscript Number: JMSE-D-19-04416

Manuscript Title: Novel blue-emitting $\text{KBaGdSi}_2\text{O}_7:\text{Eu}^{2+}$ phosphor used for near-UV white-light LED

Authors: Qinjiang He, Renli Fu, Weijun Gao, Haitao Zhu, Xiufeng Song, Xinqing Su

Dear reviewers:

Thank you for your valuable comments and good suggestions for our manuscript. This manuscript has been carefully revised according to your comments. We have marked the changes in blue color that we have done with our original submission in the revised manuscript.

Responses to the reviewer's comments as follows:

Reviewer #1:

This paper reported the blue-emitting $\text{KBaGdSi}_2\text{O}_7:\text{Eu}^{2+}$ phosphors. The structural properties, concentration and temperature-dependent luminescence behaviors of this phosphors were investigated. $\text{KBaGdSi}_2\text{O}_7:\text{Eu}^{2+}$ phosphors have an intense absorption in the broad wavelength ranging from 250 nm to 400 nm, and $\text{KBaGdSi}_2\text{O}_7:\text{Eu}^{2+}$ phosphor also has good thermal stability. The concentration quenching mechanism is identified as the dipole-dipole interaction. This paper contains enough experimental and analysis for the publication in *Journal of Materials Science: Materials in Electronics*. As I think, minor revision as listed below should be considered before its final publication.

1. Your comment: The authors proposed that $\text{KBaGdSi}_2\text{O}_7$ belongs to a newcomer of $\text{KMReSi}_2\text{O}_7$. What is the advantage of this kind of $\text{KMReSi}_2\text{O}_7$ host? Possibly, the initial structural model and the design principle can be studied, as reported previously. As a kind of mixed cations phosphor host, such related reference on this topic should be cited.

Our responses: Thank you for your kind suggestion. As suggested by the Reviewer, we have made careful revision in the introduction part and some new references were added (as highlighted in blue in the References part). I hope the revision can give readers a better understanding about this host.

2. Your comment: The authors discussed the Eu^{2+} sites, and they compared the corresponding coordination number (CN) and the radii of Eu^{2+} , and then they proposed Eu^{2+} ions are preferable to substitute Ba^{2+} sites. Possibly, this is not reasonable. Please check the Ref. 18, the previous studies don't find Eu^{2+} will substitute such a site. The authors can check the XRD diffraction shift in Figure 1b and find more solid evidence on this occupation.

Our responses: Thank you for your careful comments. We have made a mistake that $\text{NaBaScSi}_2\text{O}_7$ indeed should not be included in $\text{KMReSi}_2\text{O}_7$ family, which has been revised in the new submission. $\text{NaBaScSi}_2\text{O}_7$ is much different from $\text{KMReSi}_2\text{O}_7$, especially for structure parameters (as shown in Table R1). So, the occupation of Eu^{2+} in other $\text{KMReSi}_2\text{O}_7$ -based phosphors can serve as more convincing references. Ref. 19, Ref. 21, Ref. 22, and Ref. 33 pointed out that Eu^{2+} will occupy M sites in $\text{KMReSi}_2\text{O}_7$ host. And by Van Uitert calculation, the theoretical wavelengths of Eu^{2+} are estimated to be ~ 495 nm, ~ 478 nm and ~ 647 nm successively when Eu^{2+} occupy K^+ , Ba^{2+} , and Gd^{3+} respectively. Our experimental result is ~ 475 nm, confirming that Eu^{2+} ions will substitute Ba^{2+} sites. Therefore, we have not paid more attention to the occupation of Eu^{2+} in this paper. With respect to XRD diffraction shift, we once checked the Fig. 1b and found the shift of main peaks is not obvious (as shown in Fig. R1), which may be ascribed to the low doping content, small difference between Ba^{2+} and Eu^{2+} ions and other factors.

Table R1 Structure parameters of $\text{KBaGdSi}_2\text{O}_7$ and $\text{NaBaScSi}_2\text{O}_7$ compound.

Formula	$\text{KBaGdSi}_2\text{O}_7$	$\text{NaBaScSi}_2\text{O}_7$	
Units, N	4	Units, N	2
a (Å)	9.842	a (Å)	6.845
b (Å)	5.738	b (Å)	5.626
c (Å)	13.189	c (Å)	8.819
V (Å ³)	720.8	V (Å ³)	320.47
α (°)	90	α (°)	90
β (°)	104.603	β (°)	109.33
γ (°)	90	γ (°)	90

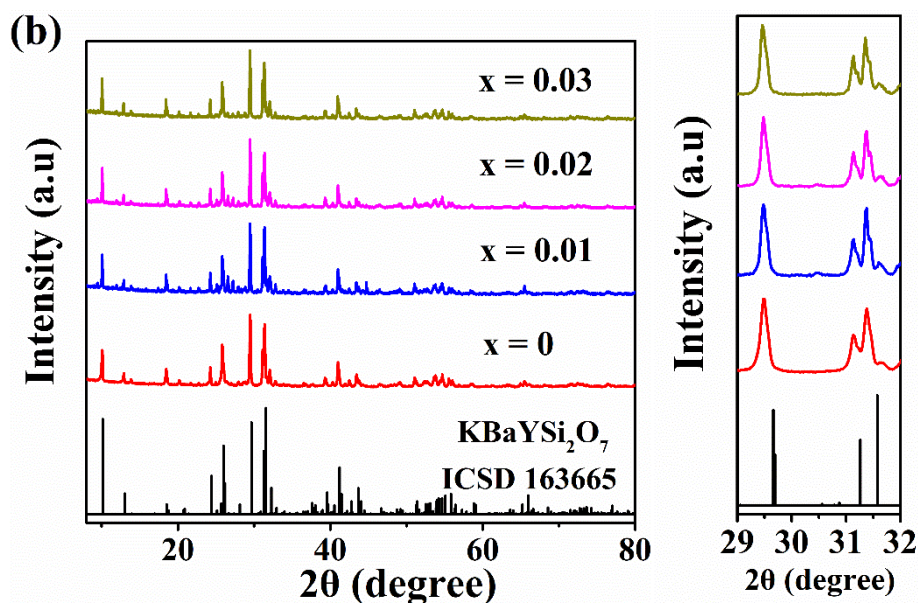


Fig. R1 XRD patterns of $\text{KBa}_{1-x}\text{GdSi}_2\text{O}_7: x\text{Eu}^{2+}$ ($0.005 \leq x \leq 0.03$) samples. The right is the magnification XRD patterns between 29.0° and 32.0° .

Reviewer #2:

1. Your comment: The manuscript by He et al. reports the synthesis and characterizations of a series of blue-emitting $\text{KBaGdSi}_2\text{O}_7:\text{Eu}^{2+}$ phosphor used for near-UV white-light LED. They investigated the structure, luminescence and thermal stability. They also suggest that the $\text{KBaGdSi}_2\text{O}_7:\text{Eu}^{2+}$ phosphor could be applied potentially in w-LEDs excited by near-UV light. The paper reports routine results on the investigation of a seemed new silicate phosphor, which is a derivative of known $\text{KBaYSi}_2\text{O}_7:\text{Eu}^{2+}$. The scientific content is OK and ranks average level. In my opinion this paper is publishable on the condition that they must fabricate a WLED using $\text{KBaGdSi}_2\text{O}_7:\text{Eu}^{2+}$ and a UVLED chip with appropriate wavelength to demonstrate that they are potentially useful, as the authors claimed.

Our responses: Thank you for your positive comment and suggestion. As suggested by the reviewer, we have fabricated several WLEDs using as-prepared $\text{KBaGdSi}_2\text{O}_7:\text{Eu}^{2+}$, commercial green (525 nm) and red phosphors (615 nm) with a UVLED chip (365 nm). When the mass ratio among them is 12:4:1,

the luminescence spectra is shown in Fig. R2 and detailed parameters are listed in Table R2.

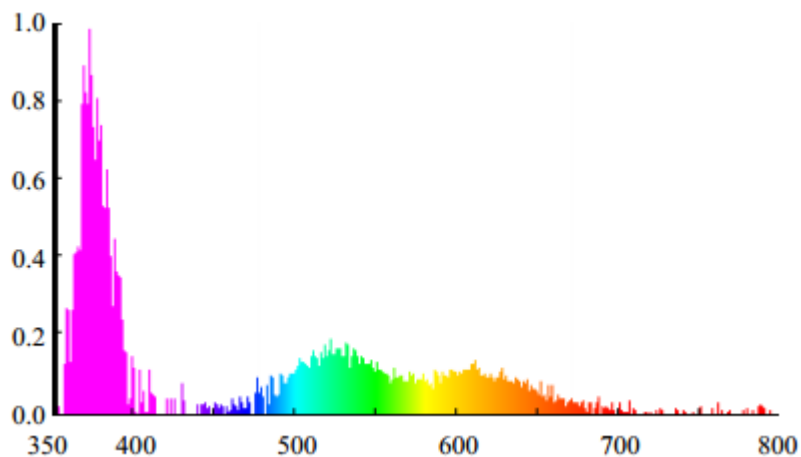
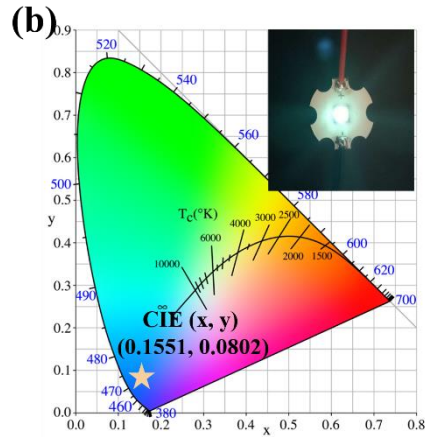


Fig. R2 The luminescence spectra of as-fabricated w-LED

Table R2 The detailed parameters of as-fabricated w-LEDs

Drive voltage	3.27 V	Drive current	25 mA
CIE coordinate	(0.3760, 0.4793)	CRI	78.1
Color Temperature	4605 K	Luminescence Efficiency	9.17 lm/W

The optical performance is OK. As you can also see, the intensity of blue phosphor is not comparable to commercial green and red phosphors, but it is normal because the luminescence efficiency of phosphors will be improved efficiently by optimizing synthesis condition and post-treatment process such as particle selecting, acid treatment, coating, etc before commercial application. Increasing the amount of blue phosphors can result in better optical performance, but the higher ratio of blue phosphors can not reflect the actual package condition. Our paper aimed to explore the new member of $\text{KMReSi}_2\text{O}_7$ family used for Eu^{2+} doping and investigated its structural and luminescent properties and we have not improved its intensity intentionally. So we think it may be better to retain the original statement outside of adding an inset in Fig. 4b and related description as following:



“as shown in Fig. 4b, which is located at blue region in the CIE diagram. Accordingly, the $\text{KBaGdSi}_2\text{O}_7:0.015\text{Eu}^{2+}$ phosphor is combined with a 365 nm UV LED and appreciable blue emission could be observed under a driving current of 30 mA from the inset of Fig. 4b, which indicates its promising usage as a blue-emitting phosphor for w-LEDs”.

We tried our best to improve the manuscript and made some changes in the manuscript. These changes will not influence the content and framework of the paper. We feel grateful for Editors/Reviewers’ warm work earnestly, and hope that the correction will meet with approval.

Once again, thank you very much for your comments and suggestions.

Sincerely!

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3 **Novel blue-emitting KBaGdSi₂O₇:Eu²⁺ phosphor used for near-UV**
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Abstract

Novel blue-emitting $\text{KBaGdSi}_2\text{O}_7:\text{Eu}^{2+}$ phosphors were designed and synthesized through solid-state reaction method. The structural properties, concentration and temperature-dependent luminescence behaviors of this phosphors were investigated in detail in this paper. Studies revealed that $\text{KBaGdSi}_2\text{O}_7:\text{Eu}^{2+}$ phosphors have an intense absorption in the broad wavelength ranging from 250 nm to 400 nm that is suitable for the commercial near-UV LED, and give out intense blue light peaked at 475 nm with a full-width half-maximum (FWHM) of 75 nm. The crystallographic information of $\text{KBaGdSi}_2\text{O}_7$ phase is revealed from XRD pattern by Rietveld refinement. Band gap is derived to be 3.93 eV through diffuse reflection spectra (DRS) through Kubelka Munk function. The concentration quenching mechanism is identified as the dipole–dipole interaction. Moreover, the thermal quenching experiment was also conducted and the activation energy is calculated as 0.3069 eV, which indicates this novel $\text{KBaGdSi}_2\text{O}_7:\text{Eu}^{2+}$ phosphor has good thermal stability. These properties exhibit its potential commercial application for near-UV white-light LEDs (w-LEDs).

Keywords: $\text{KBaGdSi}_2\text{O}_7$; Blue phosphor; Silicate; White-light LEDs; Thermal stability; Rietveld refinement.

1 Introduction

Recently, white light-emitting diode (w-LED) has received increasing attention in the display and illumination industry by virtue of the high efficiency, duration service, and environmental protection, etc [1-3]. Nowadays, a typical strategy to obtain white light is by coupling blue LED chip with yellow phosphor (YAG: Ce³⁺). Nevertheless, on the grounds of the deficiency of red light in the spectra, the w-LED devices suffer high color temperature (CCT) (≥ 7000 K) and poor color rendering index (CRI) ($R_a \leq 80$), which restricts its application in more vivid usages [4]. Therefore, many researchers propose to adopt another method by combining near-UV chip and blue/green/red tricolor phosphors, which exhibits higher CRI and relatively uniform spectral distribution in the visible range [5]. Therein the quality of phosphors is the key factor to the illumination quality of w-LED devices [6].

At present, BaMgAl₁₀O₁₇:Eu²⁺ (BAM: Eu²⁺) is the most commercially used blue phosphor, which has a blue emission peaking at 452 nm with the FWHM of 55 nm [7]. Regretfully, the absorption of this phosphor in near-UV spectral region is not so ideal [8]. So, it is highly desirable to design and prepare novel blue phosphors effectively pumped by near-UV light. Up to now, much attention has been paid to explore blue-emitting phosphors, such as Li₂Sr₂Al(PO₄)₃ [9], RbBaPO₄:Eu²⁺ [10], Gd_{4.67}Si₃O₁₃:Bi³⁺ [11], Al_{1-x}Si_xC_xN_{1-x}:Eu²⁺ [12], etc. However, it still leaves much to be desired in some aspects including matched absorption region with commercial near-UV LED chip, facile synthesis condition and especially robust thermal stability [13-14]. Therefore, it is meaningful and urgent to explore novel luminescence matrices to satisfy the above requirements. Among many alternative matrices, silicates are regarded as good candidates of luminescence matrix due to their excellent physical and chemical stability, relatively facile synthesis as well as the diversity of composition [15].

1 A novel silicate compound, $\text{KBaYSi}_2\text{O}_7$ with space group of P21/n was discovered by U. Kolitsch
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3 in 2009 [16]. In this paper, the author mentioned two superiorities of this compound. The first one is
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5 the rigid structural network, which results in the remarkable thermal stability. The second one is the
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7 flexible common topology that allows more silicate derivatives isotypic with $\text{KBaYSi}_2\text{O}_7$. The
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9 framework of $\text{KBaYSi}_2\text{O}_7$ is based on a YO_6 octahedron that shares each of its apices with an oxygen
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11 atom of the Si_2O_7 group. The asymmetric unit contains one Ba, one K, one Y, two Si and seven O
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13 atoms, where Ba^{2+} or Y^{3+} sites can be effectively substituted by rare-earth or alkali-earth metal element
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15 to form new compounds with $\text{KBaYSi}_2\text{O}_7$ type structure, viz, $\text{KMReSi}_2\text{O}_7$ (M = alkali-earth metal, Re
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17 = rare earth) compound family [17-18]. The blue emission of Eu^{2+} and Ce^{3+} doped $\text{KBaYSi}_2\text{O}_7$ have
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19 been reported by Feng et al. [19] and Zhang et al. [20] respectively. Moreover, other members of
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21 $\text{KMReSi}_2\text{O}_7$ family, $\text{KSrScSi}_2\text{O}_7$ and $\text{KBaScSi}_2\text{O}_7$ have been reported as the host for Eu^{2+} doping and
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23 exhibited a blue emission peaked at ~ 436 nm and cyan emission peaked at ~ 488 nm [21-22].
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25 Especially, it was observed that the emission intensity of them can generally retain above 90% at
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27 150 °C with respect to that measured at room temperature. The compound family greatly expands the
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29 choices of blue-emitting phosphors and deserves to be further explored.
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42 In the present work, we designed and synthesized a novel compound $\text{KBaGdSi}_2\text{O}_7$ as a newcomer
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44 of $\text{KMReSi}_2\text{O}_7$ family by chemical composition substitution. Accordingly, a series of blue-emitting
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46 $\text{KBa}_{1-x}\text{GdSi}_2\text{O}_7:\text{xEu}^{2+}$ phosphors ($0 \leq x \leq 0.03$) were prepared, and the structure, luminescence
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48 properties and thermal stability were also studied in detail. Our investigation suggests that the blue-
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50 emitting $\text{KBaGdSi}_2\text{O}_7:\text{Eu}^{2+}$ phosphor could be applied potentially in w-LEDs excited by near-UV light.
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58 2 Experimental procedure

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2.1 $\text{KBa}_{1-x}\text{GdSi}_2\text{O}_7:x\text{Eu}^{2+}$ phosphor synthesis

A series of $\text{KBa}_{1-x}\text{GdSi}_2\text{O}_7:x\text{Eu}^{2+}$ ($0 \leq x \leq 0.03$) phosphors were synthesized via traditional solid-state reaction. K_2CO_3 (4N), BaCO_3 (4N), Gd_2O_3 (4N), SiO_2 (4N) and Eu_2O_3 (4N) were directly utilized as starting materials. Firstly, all the ingredients were weighed stoichiometrically. Then, the above powder reactants were mixed uniformly by ball-milling technique for 1 h, and then dried at 60°C for 6h in an oven. Afterwards, the resultant powder was sintered at 1200°C for 5 h under reducing atmosphere (20% H_2 -80% N_2). Lastly, the products were cooled naturally inside the furnace and ground into powder for later analysis.

2.2 Characterization

X-ray diffraction (XRD) patterns of as-prepared phosphors were obtained on a diffractometer (Smartlab 9kw, Japan) with $\text{Cu K}\alpha$ radiation ($\lambda = 0.15405$ nm) at step size of 0.02° , measured at 40 kV and 30 mA. Rietveld refinement of XRD profile was made by GSAS program. The diffuse reflectance spectra (DRS) from the phosphors with fine grain size were collected by an UV-Vis-NIR spectrophotometer (UV-3600, Shimadzu, Japan) using BaSO_4 as the reference at a step of 0.5 nm. Photoluminescence excitation (PLE) and emission (PLE) spectra were measured with a fluorescence spectrophotometer (Cary Eclipse, Agilent, USA) equipped with a Xe lamp (450 W). Thermal quenching property was performed on a fluorescence spectrophotometer (F-4600, Hitachi, Japan) attached with a temperature-controlled apparatus (TAP-02).

3 Results and discussions

In order to understand its crystal structure, Rietveld refinement of $\text{KBaGdSi}_2\text{O}_7$ host was conducted and the result is shown in Fig. 1a. Therein, the initial structure model was established with

1 the reported crystallographic data of $\text{KBaYSi}_2\text{O}_7$ with space group of P21/n [16]. The refinement
2 converged with the residual factors $R_p = 5.54\%$, $R_{wp} = 7.14\%$, which confirms the reliability of initial
3 structure model and the purity of the sample. On the basis of structural refinements result, the
4 $\text{KBaGdSi}_2\text{O}_7$ compound are well crystallized in a monoclinic structure of P21/n space group. More
5 detailed structural information are presented in Table 1. The cell parameters of $\text{KBaGdSi}_2\text{O}_7$ host are
6 larger compared to $\text{KBaYSi}_2\text{O}_7$, which is fairly normal because the radius of Gd^{3+} (0.94 Å, CN = 6) is
7 bigger than Y^{3+} (1.01 Å, CN = 6). Moreover, Fig. 1b shows the XRD patterns of series of
8 $\text{KBaGdSi}_2\text{O}_7:x\text{Eu}^{2+}$ ($0 \leq x \leq 0.03$) phosphors. By comparison, all the diffraction peaks are well
9 consistent with $\text{KBaYSi}_2\text{O}_7$ (ICSD 163665), indicating that the introduction of Eu^{2+} will not bring out
10 significant changes to host lattice.

11 Fig. 2a depicts the double cell sketch of $\text{KBaGdSi}_2\text{O}_7$ viewed along $[0\bar{1}0]$ direction by Diamond
12 software. It shows that the framework of $\text{KBaGdSi}_2\text{O}_7$ compound consists of Si_2O_7 groups and GdO_6
13 octahedra. Adjacent GdO_6 octahedra in (001) plane layered arrangement are linked to each other by
14 neighboring Si_2O_7 groups oriented parallel to the c axis. Moreover, 9-coordinated Ba^{2+} and 8-
15 coordinated K^+ cations are stacked in voids and arranged with an alternate -K-Ba-K-Ba- sequence,
16 which forms a quite rigid lattice possessing condensed network. Fig. 2b extracts three type of cationic
17 sites suitable for the occupation of luminescent center, viz, one Gd, one K, and one Ba. According to
18 the report by Shannon [23], the effective ionic radii (Å) of them are 0.94 Å, 1.51 Å, and 1.47 Å
19 successively for the corresponding coordination number (CN) and the radii of Eu^{2+} with the same CN
20 are 1.17, 1.25 and 1.30 Å, respectively. It is widely accepted that effective substitution will be difficult
21 if the radii difference between two ions is above 30% [24]. To keep electroneutral and effective
22 substitution, it is reasonably inferred Eu^{2+} ions are preferable to substitute Ba^{2+} sites.

23 The DRS of $\text{KBaGdSi}_2\text{O}_7$ host and $\text{KBaGdSi}_2\text{O}_7:0.02\text{Eu}$ phosphors are presented in Fig. 3.
24 $\text{KBaGdSi}_2\text{O}_7$ host has a strong absorption band from 200 to 300 nm, which originates from the

1 electronic transition from the valence band composed of O2p to conduction band mainly formed by
 2 metal orbitals [20]. However, once Eu²⁺ ions are doped, a broad absorption band from 200 nm to 500
 3 nm is observed clearly, which stems from the 4f-5d transition of Eu²⁺ ion. The Kubelka Munk function
 4 is generally employed to obtain relation between absorption and scattering from the DRS of host [25]:
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$$10 \quad F(R_{\infty}) = \frac{(1 - R_{\infty})^2}{2R_{\infty}} = \frac{K}{S} \quad (1)$$

11 Here, R_∞ stands for the reflectivity, K and S represent absorption and scattering coefficient,
 12 respectively. Moreover, Tauc relation constructs one model to determinate band gap, E_g, by photon
 13 energy hv, molar absorption coefficient α, and proportion constant B1 [26].
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$$22 \quad \alpha hv = B1(hv - E_g)^{\frac{n}{2}} \quad (2)$$

23 General analysis considers K to be proportionate to α [27]. Since scattering coefficient is the
 24 constant at certain temperature and concerning the above two equation, it can be derived that:
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$$31 \quad (F(R_{\infty})hv)^{\frac{2}{n}} = B2(hv - E_g) \quad (3)$$

32 Here, n is equal to 4 for indirect allowed transition. As a result, the band gap of KBaGdSi₂O₇ host
 33 is ascertained as 3.93 eV by extrapolating the tangent line to [F(R_∞)hv]^{1/2} = 0, according to the plot of
 34 [F(R_∞) hv]^{1/2} versus hv, as shown in the inset of Fig. 3.
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42 Fig. 4a displays the emission (λ_{ex} = 285 nm/323 nm/340 nm) and excitation (λ_{em} = 475 nm) spectra
 43 of KBaGdSi₂O₇:0.15Eu phosphor. By monitoring at 475 nm, a broad excitation band with three peaks
 44 around 285, 323, and 340 nm emerges, which covers the whole n-UV region. It indicates this phosphor
 45 is compatible well with the commercial near-UV LED [28]. Upon excitation at 285, 323 or 340 nm,
 46 KBaGdSi₂O₇:0.015Eu²⁺ phosphor exhibits a broad blue emission peaked at 475 nm with the FWHM
 47 of 75 nm, which originates from the typical 4f⁶5d¹-4f⁷ transition of Eu²⁺ ion. The emission peak does
 48 not shift and the band possess high symmetry even at various excitation wavelength, indicating that
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1 Eu²⁺ only occupy Ba²⁺ sites. Moreover, the CIE coordinates of KBaGdSi₂O₇:0.015Eu²⁺ excited by 340
2 nm are calculated to be (0.1551, 0.0802), as shown in Fig. 4b, which is located at blue region in the
3 CIE diagram. Accordingly, the KBaGdSi₂O₇:0.015Eu²⁺ phosphor is combined with a 365 nm UV LED
4 and appreciable blue emission could be observed under a driving current of 30 mA from the inset of
5 Fig. 4b, which indicates its promising usage as a blue-emitting phosphor for w-LEDs.
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14 Since near-UV LED is one of the most commercially used light source for w-LEDs application,
15 special attention is focused on the photoluminescence properties of KBaGdSi₂O₇ phosphors excited
16 by near-UV light. Fig. 5 exhibits the PL ($\lambda_{ex} = 340$ nm) spectra of KBaGdSi₂O₇:Eu²⁺ phosphors with
17 increasing Eu²⁺ content. It shows that there was no obvious change in the peak wavelength and spectra
18 shape for all the samples. However, the emission intensities vary with increasing content of Eu²⁺. The
19 emission intensity increases continually until x reaches the value of 1.5 or 2 mol. % (shown in the inset
20 of Fig. 5), and subsequently decreases with further increase of Eu²⁺ content as a result of “concentration
21 quenching”.
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36 Concentration quenching effect is always related to the non-radiative energy transfer between
37 activators. Increasing the doping content can result in shorter distance between activators, the
38 probability of non-radiative energy also increases. So, the critical distance R_c, is put forward to
39 represent the shortest average distance between the activators. On the basis of Blases’s viewpoint, the
40 critical distance (R_c) can be estimated according to the formula as below [29-30]:
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$$50 \quad R_c = 2[3V/(4\pi X_c N)]^{1/3} \quad (4)$$

51 V is the volume of crystal lattice, X_c represents the critical content of dopant, N means the number
52 of available cation sites per unit cell. The values of V = 720.8 Å³ and N = 4 are decided through the
53 refinement results of KBaGdSi₂O₇ host, and the X_c value is presumably 1.5 mol. % ~ 2 mol. %.
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1 Ultimately, the R_c value is calculated as $25.82 \text{ \AA} \sim 28.42 \text{ \AA}$ for $\text{KBaGdSi}_2\text{O}_7:\text{Eu}^{2+}$ phosphors. It is
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3 widely accepted that the exchange interaction takes effect if the critical distance (R_c) between Eu^{2+}
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5 ions is shorter than 5 \AA . The R_c value ($25.82 \text{ \AA} \sim 28.42 \text{ \AA}$) manifests that the type of energy transfer
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7 is dominated by the multipolar–multipolar interaction.
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11 From the Dexter’s research, the type of the multi-polar interaction can be determined using the
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13 equation as follows [31]:
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$$16 \quad \lg \frac{I}{x} = c - \frac{\theta}{3} \lg(\beta x) \quad (5)$$

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18 Here, I denotes the emission intensity at activator content x , c and β are the constants. θ can have
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20 the values of 6, 8, 10, representing dipole–dipole (d–d), dipole–quadrupole (d–q) and quadrupole–
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22 quadrupole (q–q) interactions, successively. Fig. 6 depicts the fitting of $\lg(I/x)$ to $\lg(x)$ of
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24 $\text{KBaGdSi}_2\text{O}_7:\text{Eu}^{2+}$ phosphors. The fitting result shows the slope of $-\theta/3$ is -1.555 , thus the θ value is
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26 4.665 , which is near to 6. So, it is concluded that d–d interaction should take charge of the concentration
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28 quenching phenomenon.
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36 Thermal stability is one of the critical properties for application. Normally, the photoluminescence
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38 intensity of phosphors will decrease with increasing temperature since high temperature can raise the
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40 probability of non-radiative transition [32]. The temperature-dependent luminescence spectra of
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42 $\text{KBaGdSi}_2\text{O}_7:0.015\text{Eu}^{2+}$ under excitation of 340 nm are depicted in Fig. 7a. It is obviously aware that
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44 the emission intensity decreases continually upon increasing temperature because of thermal
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46 quenching effect. Inset is the normalized intensity of $\text{KBaGdSi}_2\text{O}_7:0.015\text{Eu}$ phosphor at increasing
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48 temperatures. The PL intensity at 423 K is around 44.9% of the original intensity at 298 K, which
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50 indicates that the $\text{KBaGdSi}_2\text{O}_7:\text{Eu}^{2+}$ phosphor has good thermal stability for practical LED application.
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1 Increasing activation energy causes the higher barrier for the non-radiative transition, which
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3 always leads to the better thermal stability. For purpose of further exploration towards thermal
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5 quenching effect, the activation energy could be determined via a Arrhenius-type function [4]:
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$$I_T = I_0 [1 + C \exp\left(-\frac{Ea}{kT}\right)]^{-1} \quad (6)$$

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9 Here, I_0 and I_T represent the emission intensities of $\text{KBaGdSi}_2\text{O}_7:\text{Eu}$ phosphors at 298 K and
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11 different testing temperature T respectively, k is the Boltzmann constant ($8.629 \times 10^{-5} \text{ eV/K}^{-1}$), C is a
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13 constant and Ea represents the activation energy. After simple arrangement, Eq. (6) can be expressed
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15 as below:
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$$\ln\left[\frac{I_0}{I_T} - 1\right] = -\frac{Ea}{kT} + \ln C \quad (7)$$

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22 Based on the Eq. (7), the relation of $\ln[(I_0/I_T-1)]$ and $1/kT$ for $\text{KBaGdSi}_2\text{O}_7:0.015\text{Eu}$ phosphor is
23
24 illustrated in Fig. 7b. All of the coordinates can be well fitted to a straight line whose slope is -0.3069.
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26 So, it is deduced that the activation energy, Ea is 0.3069 eV, which is higher than or comparable to
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28 other $\text{KMReSi}_2\text{O}_7$ -type phosphors [19-20, 22, 33]. Higher activation energy indicates lower probability
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30 of non-radiative process involving better thermal stability. So, other $\text{KBaGdSi}_2\text{O}_7$ -based phosphor with
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32 high thermal stability deserved to be further investigated.
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44 Conclusion

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46 In summary, a novel blue phosphor $\text{KBaGdSi}_2\text{O}_7:\text{Eu}^{2+}$ was discovered and prepared via solid-
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48 state reaction method. Its structural information, concentration and temperature-dependent
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50 luminescence behaviors of as-prepared phosphors were studied in detail. Rietveld refinement results
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52 show this compound presents a monoclinic structure of $P21/n$ space group and cell parameter values
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54 are obtained. Band gap is calculated to be 3.93 eV from DRS through Kubelka Munk function. This
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1 novel phosphor exhibits a broadband blue emission peaked at 475 nm with the FWHM of 75 nm. It
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3 also exhibits a broad excitation band in 250-400 nm range composed of three major peaks at 285 nm,
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6 323 nm and 340 nm, which is suitable for the commercial near-UV LED chips. It is concluded that the
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9 critical distance is $25.82 \text{ \AA} \sim 28.42 \text{ \AA}$ and dipole–dipole interaction dominates the quenching of
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12 luminescence. Moreover, the thermal quenching result shows this type of phosphor possesses good
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15 thermal stability: 44.9% at 150 °C of that measured at 298 K and the activation energy is identified as
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18 0.3069 eV. The results of our study exhibit its potential commercial application in near-UV light
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21 excitable w-LEDs.
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27
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37 Education Institutions (PAPD), Nanjing, China.
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Tables and figure captions:

Fig. 1 (a) Rietveld refinement result from XRD profile of $\text{KBaGdSi}_2\text{O}_7$ host; (b) XRD patterns of $\text{KBa}_{1-x}\text{GdSi}_2\text{O}_7: x\text{Eu}^{2+}$ ($0 \leq x \leq 0.03$) phosphors with various Eu^{2+} content as well as the referential diffraction peaks of $\text{KBaYSi}_2\text{O}_7$ host.

Fig. 2 (a) Double cell representation of $\text{KBaGdSi}_2\text{O}_7$ host viewed along $[0\bar{1}0]$ direction and (b) coordinate environments of Ba^{2+} , Gd^{3+} and K^+ sites.

Fig. 3 The DRS of $\text{KBaGdSi}_2\text{O}_7$ host and $\text{KBaGdSi}_2\text{O}_7:0.02\text{Eu}^{2+}$ phosphors, inset depicts the plot of $[F(R_\infty)hv]^{1/2}$ versus photon energy hv for $\text{KBaGdSi}_2\text{O}_7$ host.

Fig. 4 (a) Emission ($\lambda_{\text{ex}} = 285 \text{ nm}/323 \text{ nm}/340 \text{ nm}$) and excitation ($\lambda_{\text{em}} = 475 \text{ nm}$) spectra of $\text{KBaGdSi}_2\text{O}_7:0.015\text{Eu}^{2+}$ phosphor; (b) CIE chromaticity diagram of this phosphor excited at 340 nm, and the inset shows a photograph of this phosphor excited by 365 nm UV LED.

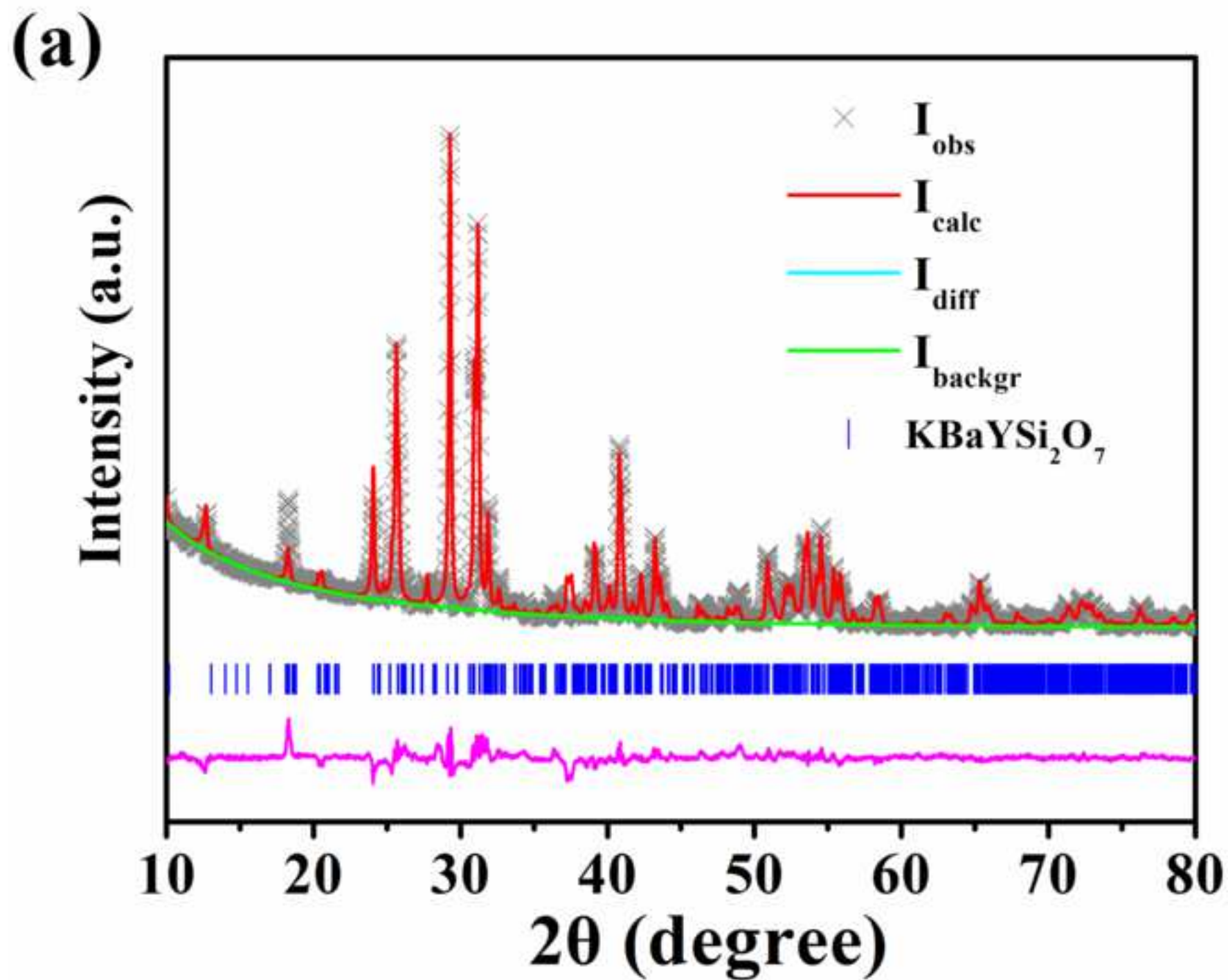
Fig. 5 The emission ($\lambda_{\text{ex}} = 340 \text{ nm}$) spectra of samples doping various Eu^{2+} content ($x = 0.05-0.30$), inset describes the corresponding dependence of PL intensity.

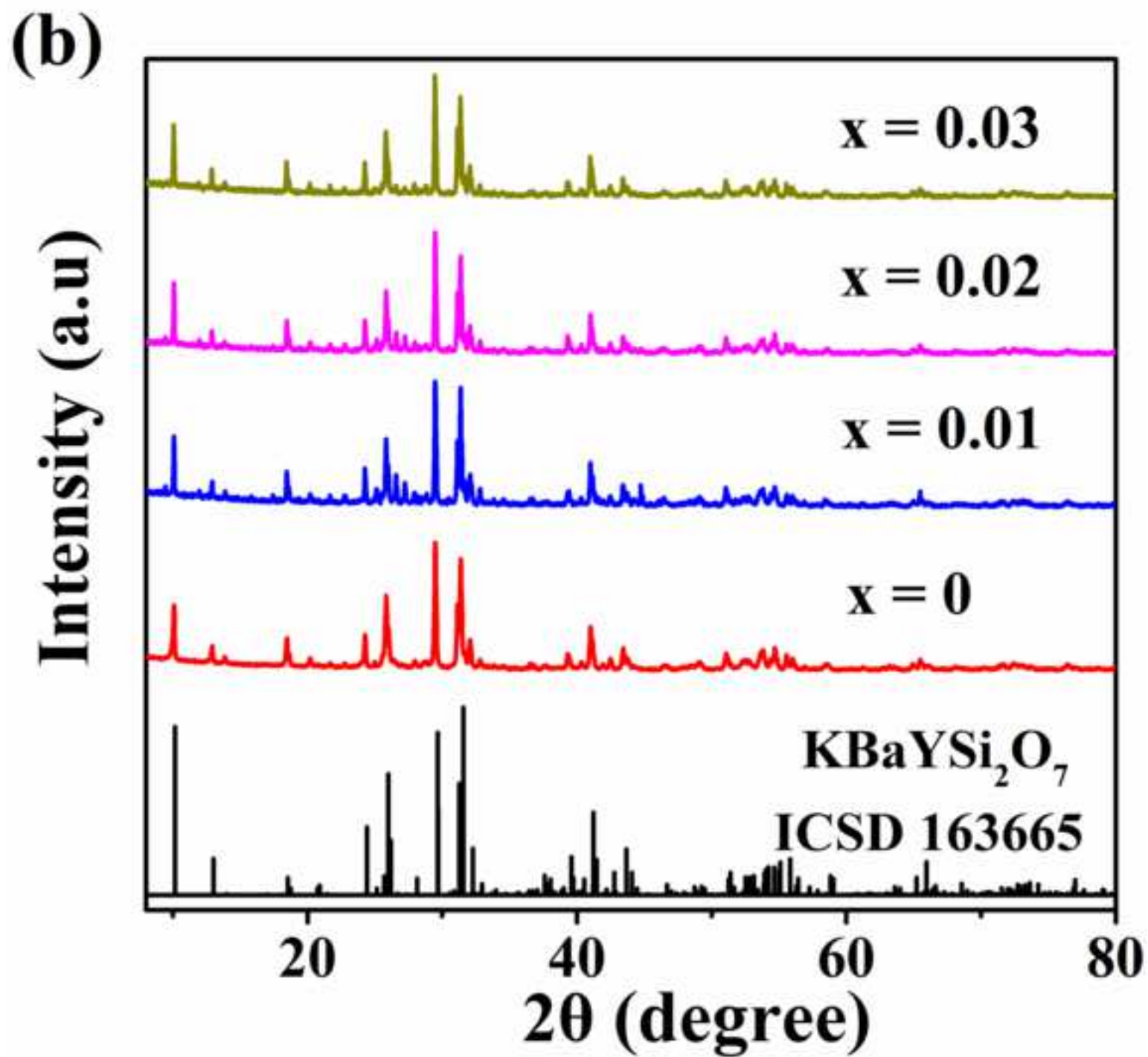
Fig. 6 Curve of $\lg(I/x)$ versus $\lg(x)$ in $\text{KBaGdSi}_2\text{O}_7:\text{Eu}^{2+}$ samples.

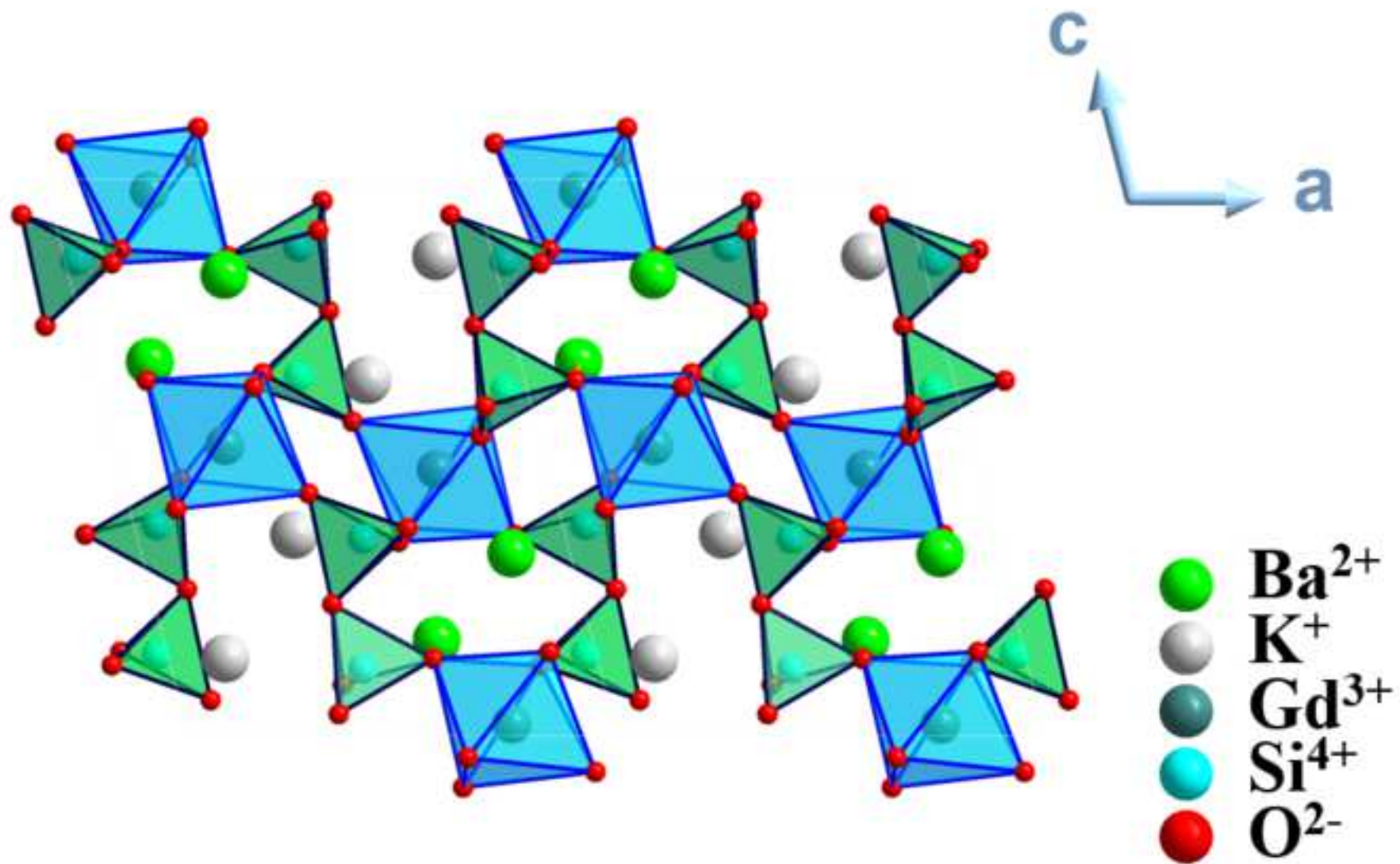
Fig. 7 (a) Temperature-dependent emission spectra of $\text{KBaGdSi}_2\text{O}_7:0.015\text{Eu}^{2+}$ ($\lambda_{\text{ex}} = 340 \text{ nm}$), inset shows normalized intensity of $\text{KBaGdSi}_2\text{O}_7:0.015\text{Eu}^{2+}$ phosphors at increasing temperature; (b) the calculated activation energy, E_g by plotting $\ln[(I_0/I_T)-1]$ vs. $1/kT$.

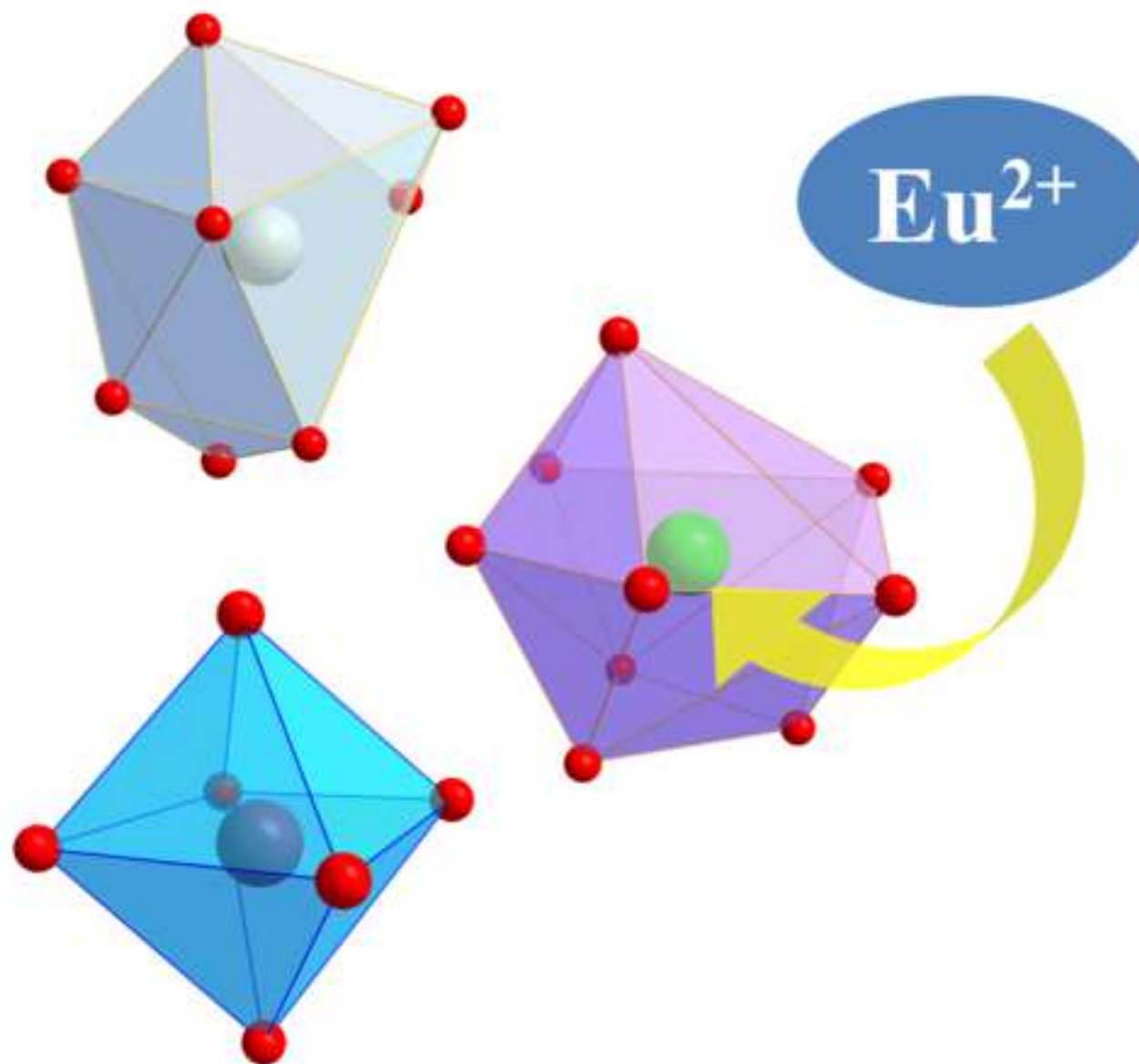
Table 1 Structure parameters of $\text{KBaGdSi}_2\text{O}_7$ compound by Rietveld refinement.

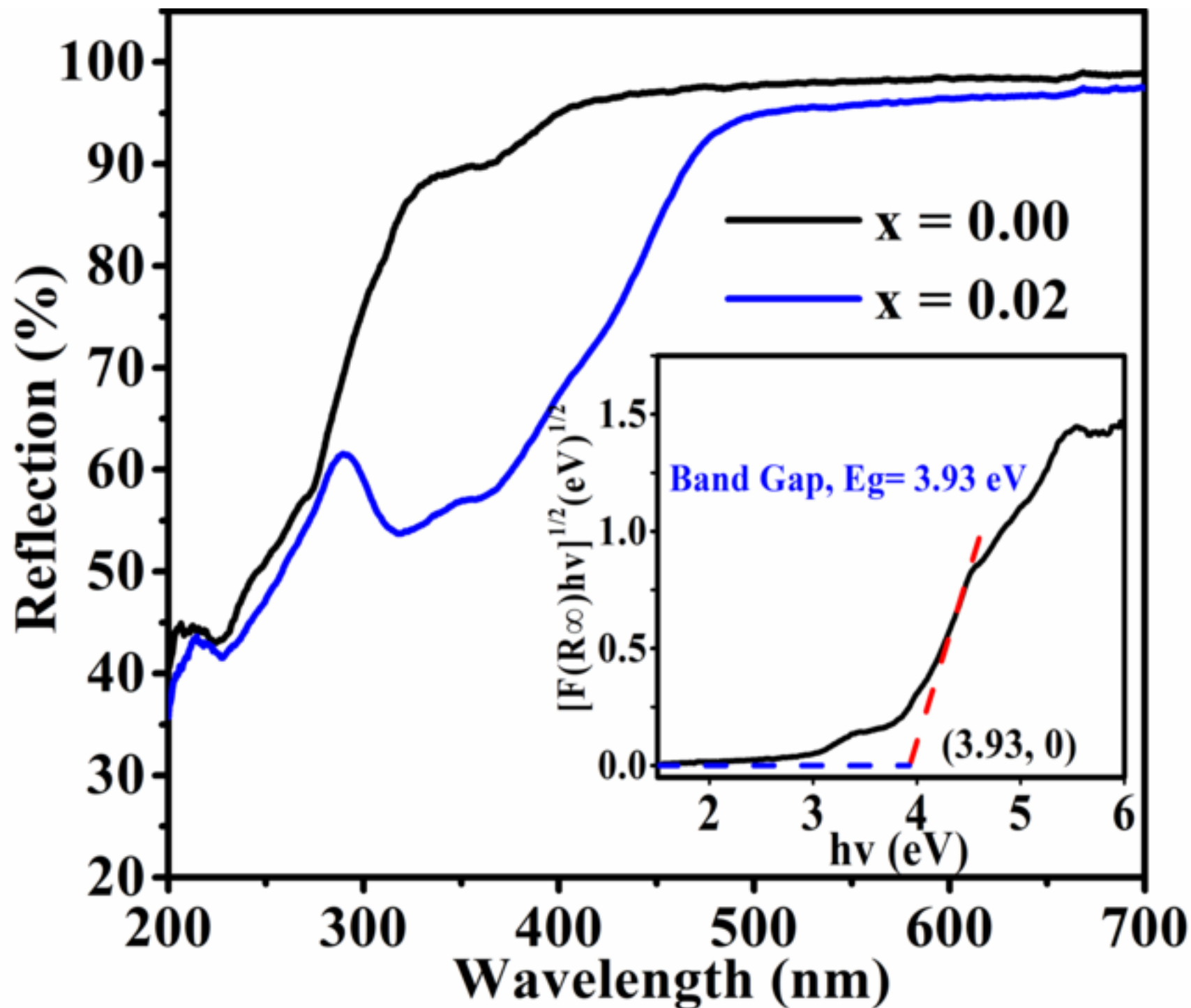
Formula	$\text{KBaGdSi}_2\text{O}_7$		
Units, N	4	$V (\text{\AA}^3)$	720.8
a (\AA)	9.842	α ($^\circ$)	90
b (\AA)	5.738	β ($^\circ$)	104.603
c (\AA)	13.189	γ ($^\circ$)	90
R_p	5.54%	R_{wp}	7.14%

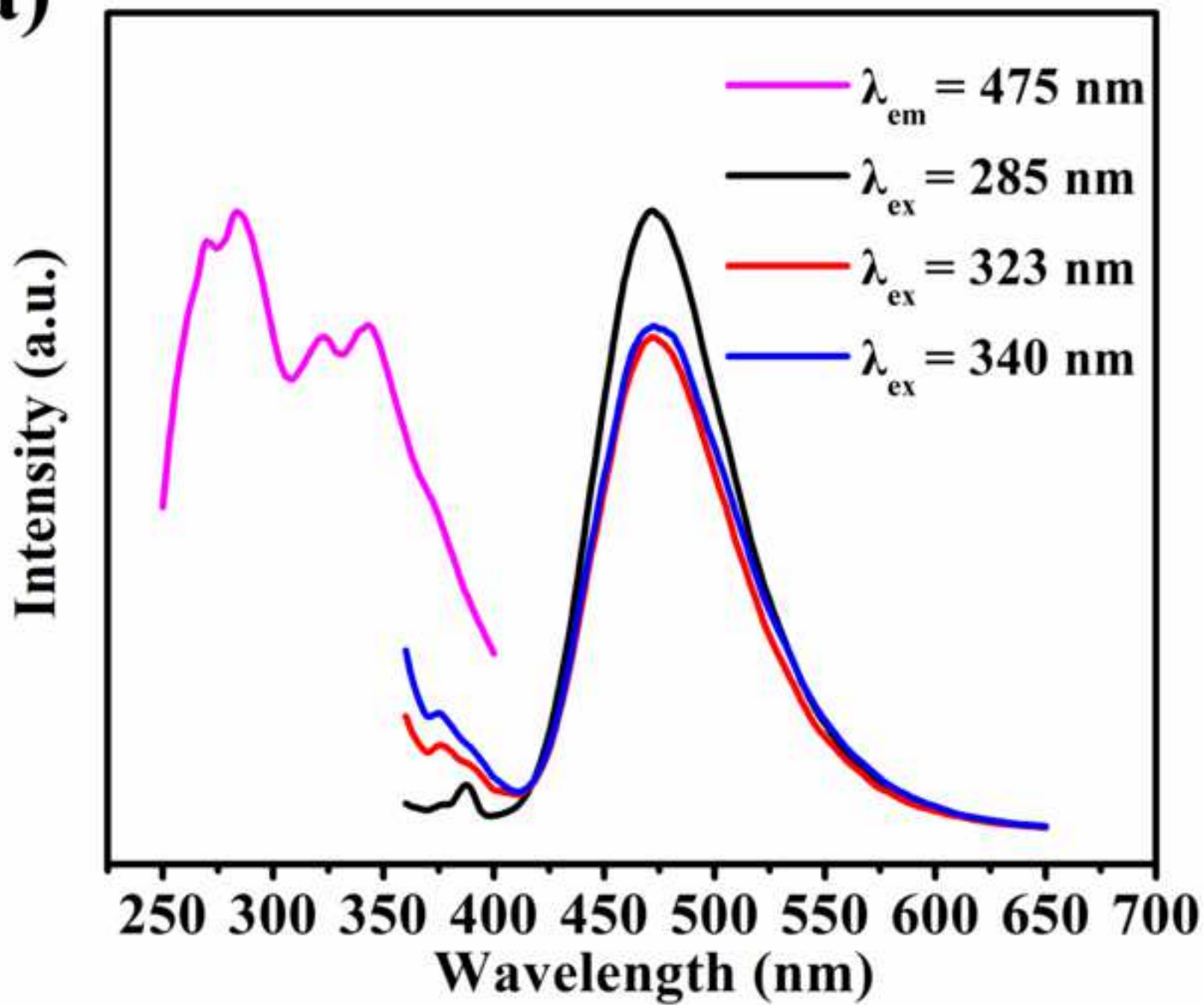


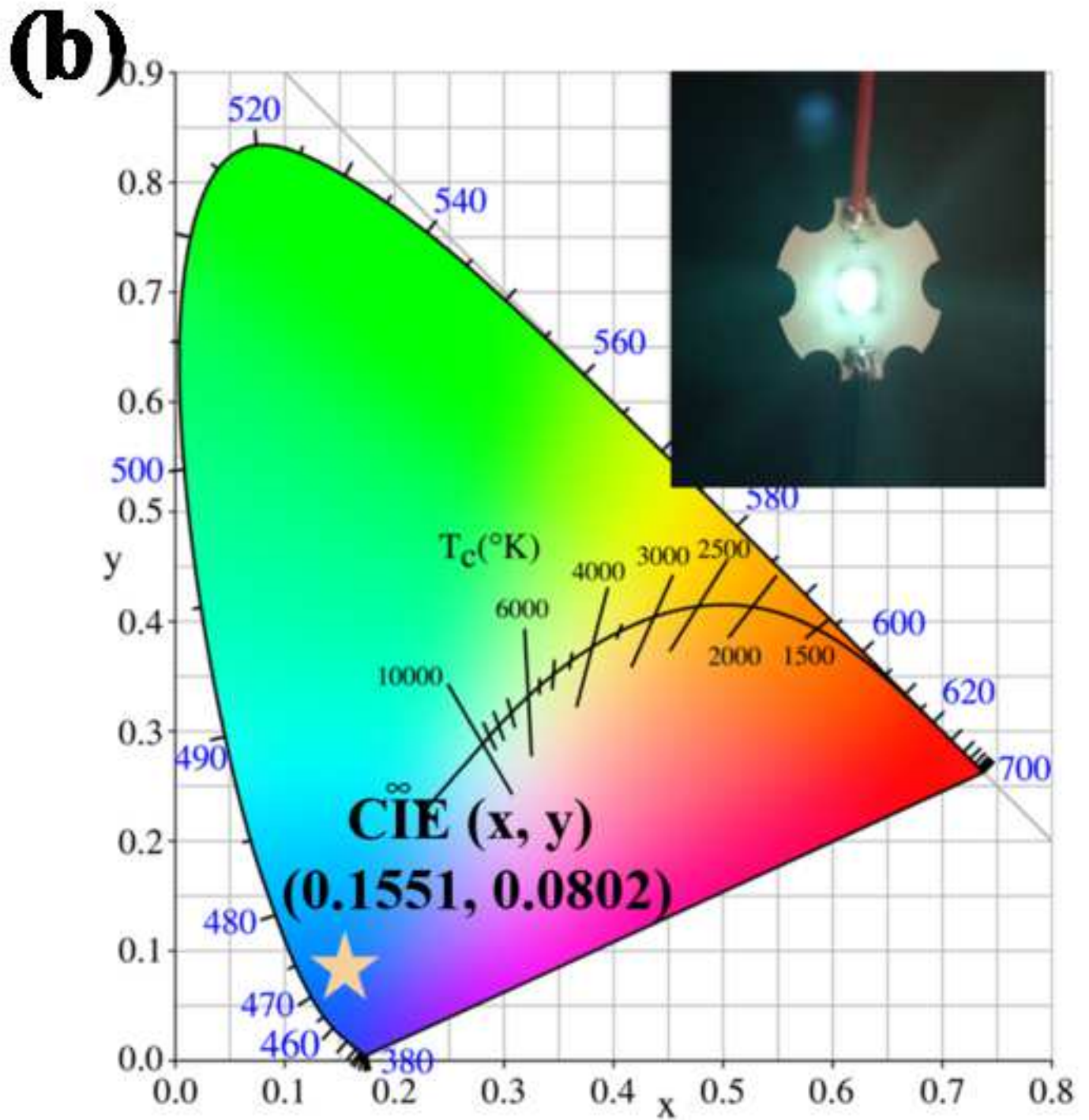


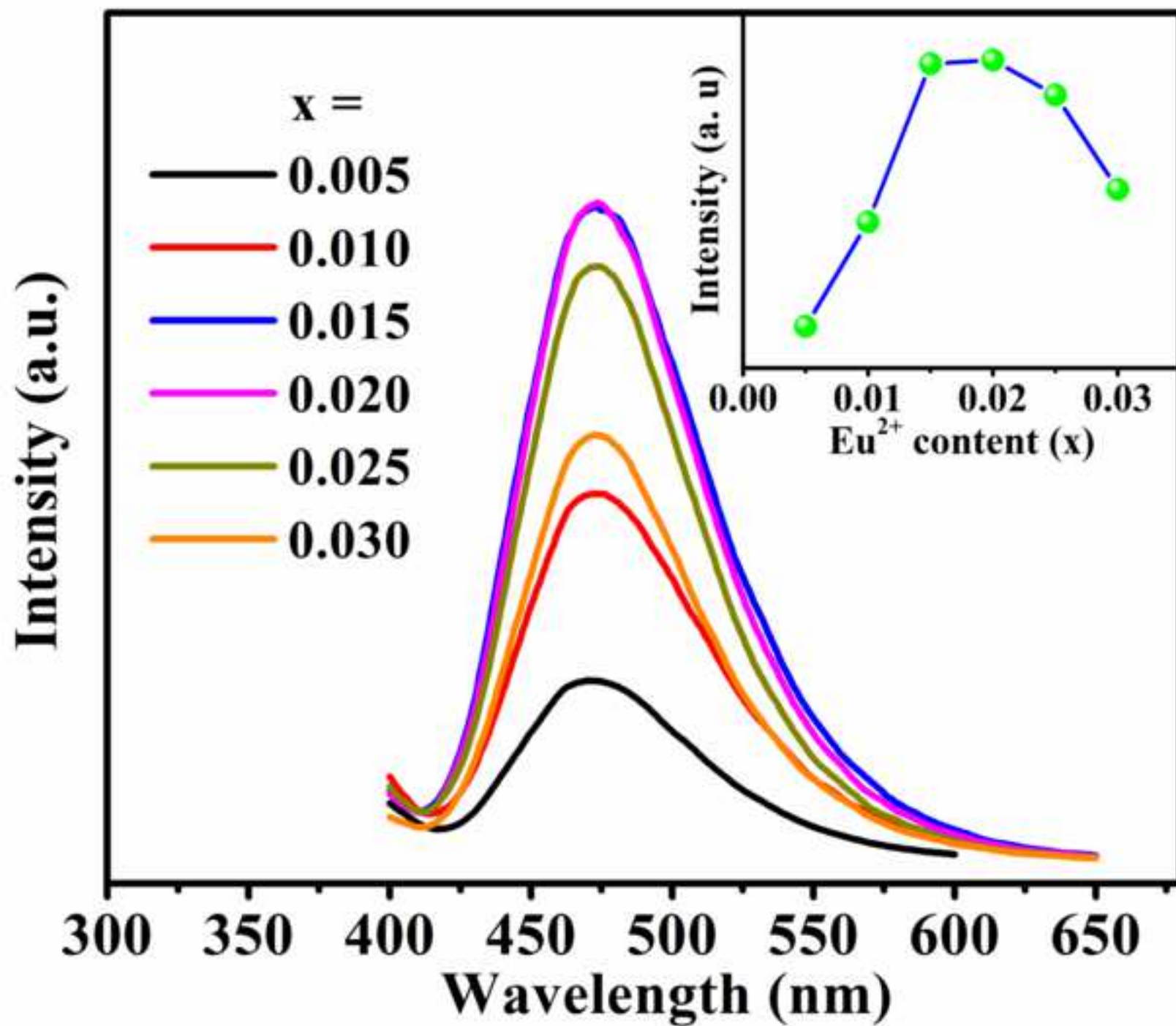
(a)

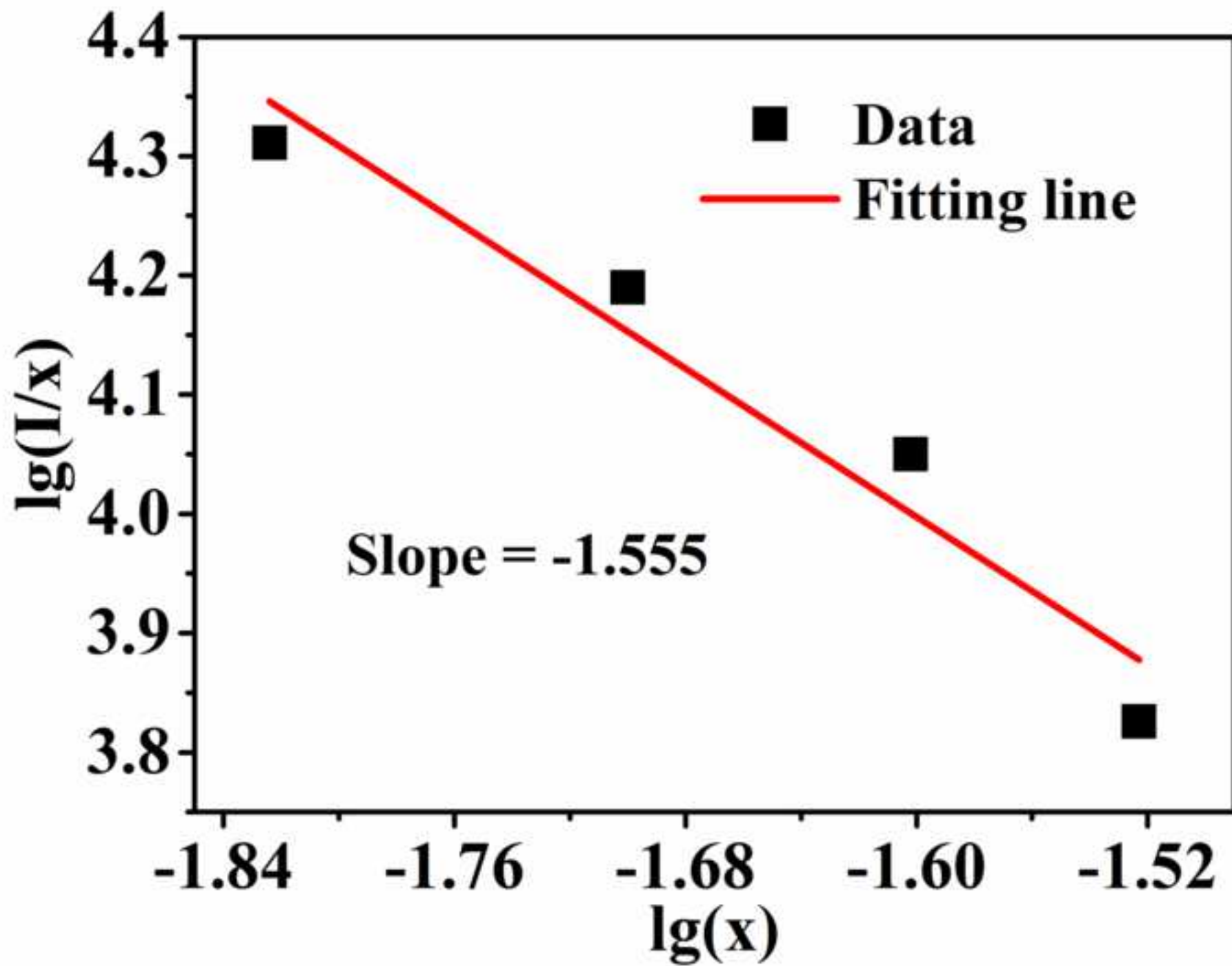
(b)



(a)







(a)