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# The Inductive Effect of Neighboring Cations in Tuning Luminescence Properties of the Solid Solution Phosphors

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**Supporting Information** 

**ABSTRACT:** Forming solid solutions through cation substitution is an efficient way to improve the luminescence properties of  $Ce^{3+}$  or  $Eu^{2+}$  activated phosphors and even to develop new ones, which is badly needed for phosphor-converted white LEDs. Here, we report new color tunable solid solution phosphors based on  $Eu^{2+}$  activated  $K_2Al_2B_2O_7$  as a typical case to demonstrate that, besides crystal field splitting of 5*d* levels, centroid shift and Stokes shift can be dominant in tuning excitation and emission spectra as well as thermal stability of solid solution phosphors, both of which were previously considered to be negligible. Moreover, a general model involving the inductive effect of neighboring cations is proposed to explain the obvious variations in centroid shift and Stokes shift with cation substitution. Our work is propitious for the construction of more reasonable structure–property relations and thus offers theoretical guidance for designing solid solution phosphors.



#### 1. INTRODUCTION

As the most simple, efficient, and reliable way to generate white light for the time being, phosphor-converted white LEDs have been widely used and commercialized.<sup>1,2</sup> Nevertheless, because of the insufficient red component and the existence of a "valley" between the blue and green spectral regions, commercial white LEDs, dominantly made of a blue InGaN LED chip and a yellow phosphor (Y,Gd)<sub>3</sub>(Al,Ga)<sub>5</sub>O<sub>12</sub>:Ce<sup>3+</sup>, are not yet fully acceptable, especially for special lighting where superhigh color rendering is required. Thus, cyan as well as red phosphor is blended with the yellow one to address this issue.<sup>1,3-5</sup> In addition, another type of white LEDs with near UV LED chips has also been proposed.<sup>2,6</sup> However, satisfactory phosphors are not yet available for both cases.<sup>1,6</sup> Hence, new phosphors are badly needed and have attracted great attention. Though free of intellectual property conflict, now it is extremely difficult to find new suitable host crystals for phosphors from the conventional crystallographic databases, and it is ineffective to synthesize novel host crystals that do not exist in any databases even by a combinatorial chemistry approach.<sup>7-9</sup> Instead, forming solid solutions through chemical substitution is much more targeted and thus more efficient for the identification of new phosphors from the reported phosphors activated by Eu<sup>2+</sup> or Ce<sup>3+</sup> which are already superior in some respect(s).<sup>8,9</sup> The structure– property relations can be established along the way, which will in turn provide theoretical guidance for designing solid solution phosphors and even discovering novel phosphors. Therefore, plenty of recent research is focused on the ionic engineering to

design solid solution phosphors, from which there are many benefits other than the linearly tunable emission color, such as the improved moisture or thermal stability,  $^{10-12}$  the increased quantum efficiency,  $^{13-15}$  and the appearance of an additional emission band.  $^{16-18}$ 

The luminescence properties of the 4f-5d transition in Eu<sup>2+</sup> or Ce<sup>3+</sup> are strongly dependent on the structure and composition of the host crystal owing to the strong interaction of the 5d orbital with their surroundings. In brief, as illustrated in Figure 1, the excitation band is determined by the values of the centroid shift ( $\varepsilon_c$ ) and the crystal field splitting ( $\varepsilon_{cfs}$ ) of the 5d levels, while besides them the emission band is also influenced by its Stokes shift ( $\Delta S$ ). The centroid shift is usually associated with the covalency effect and the correlated motion between 5d electron and ligand electrons; the value of  $\varepsilon_c$  has been recently related well with the polarizability of the anion ligands.<sup>19,20</sup> In contrast, the crystal field splitting depends strongly on the shape and size of the anion coordination polyhedron, and it shows completely different behavior from the centroid shift in changing with the crystal environment.<sup>21-23</sup> Generally, as the host cations are replaced by smaller ones, the emission band will shift to a longer wavelength and vice versa, which is ascribed to the  $R^{-2}$ dependence of  $\varepsilon_{cfs}$  on the average distance R from the central ion to its coordinating anions, i.e.,  $\varepsilon_{cfs} = \beta R^{-2}$  summarized by

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**Figure 1.** Schematic illustration of the excitation and emission energy of *5d* levels for free Eu<sup>2+</sup> and Eu<sup>2+</sup> in a crystal including the effects of centroid shift ( $\varepsilon_c$ ), crystal field splitting ( $\varepsilon_{cfs}$ ), and Stokes shift ( $\Delta S$ ) (left), and two thermal quenching mechanisms including thermal ionization to the conduction band and thermal release through the crossing point in the configurational coordinate (right).

Dorenbos.<sup>22</sup> This empirical rule is used to explain the observed tunable emission color in solid solution phosphors by cation substitution. However, it does not always hold, and the opposite has happened in many cases, which is called an abnormal shift. In order to explain it, two mechanisms have been proposed given that the type of coordinating anions is unchanged; one is distortion of the coordination polyhedron,<sup>24,25</sup> and the other is the compression effect of neighboring cations on activator sites,<sup>18,26,27</sup> Obviously, both of them are still related to the change in crystal field splitting from the views of the shape and size of the coordination polyhedron, respectively. It is worth noting that most of them come to their conclusions only by analyzing the emission spectra, which may lead to confusing results. It is most likely that the values of  $\varepsilon_{c}$  and  $\Delta S$  are considered to be nearly constant in solid solution phosphors and thus play a negligible role in shifting the excitation and emission bands. Yet this is not always true, especially where the abnormal shift has been observed. On the contrary, the variation of  $\varepsilon_c$  may be dominant over that of  $\varepsilon_{cfs}$  in shifting the lowest 5*d* level,<sup>21,28,29</sup> which can be only reflected in excitation spectra, and a sizable change in Stokes shift may also result in tunable emission accompanied by the variation of emission band width  $\Gamma^{em}$ .<sup>29–31</sup> Furthermore, combined with the energy distance  $E_{dC}$  from the relaxed lowest 5*d* level to the bottom of the conduction band, the value of  $\Delta S$ determines the thermal stability of 5d emission, which is of particular importance for a high-power white LED.<sup>32-34</sup>

Herein, we first report the tunable luminescence properties of the solid solution phosphors based on Eu<sup>2+</sup> activated  $K_2Al_2B_2O_7$  (KAB:Eu<sup>2+</sup>) as a representative case where the variations of  $\varepsilon_c$  and  $\Delta S$  play key roles in regulating the luminescence properties. Moreover, a general model is proposed to explain the unique luminescence properties by introducing the inductive effect of neighboring cations on the centroid shift and Stokes shift simultaneously. Finally, two factors influencing the strength of the inductive effect are given, as we attempt to understand why there is a so-called abnormal shift and thus offer some guidelines for designing solid solution phosphors.

#### 2. EXPERIMENTAL SECTION

2.1. Materials. All the powder samples doped with a fixed Eu<sup>2+</sup> or  $Eu^{3+}$  concentration of 0.5 mol % were prepared by a modified hightemperature solid-state reaction. Typically, Eu<sub>2</sub>O<sub>3</sub> (4 N) and Ga<sub>2</sub>O<sub>3</sub> (G.R.) were dissolved into  $HNO_3$  (G.R.) to obtain  $Eu(NO_3)_3$  and  $Ga(NO_3)_3$ , respectively. Then, for the sample series  $K_{2(0.995-x)}Na_{2x}$ -Al<sub>2</sub>B<sub>2</sub>O<sub>7</sub>:Eu the stoichiometric amounts of K<sub>2</sub>CO<sub>3</sub> (A.R.), Na<sub>2</sub>CO<sub>3</sub> (G.R.), Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O (A.R.), H<sub>3</sub>BO<sub>3</sub> (A.R.), and Eu(NO<sub>3</sub>)<sub>3</sub> were weighed and continuously stirred for 1 h, and subsequently heated in an oven at 85 °C until the solvent dried up completely. The material was then heated at 150 °C to remove the crystalliferous water. Finally, the mixtures were preheated at 500 °C for 5 h and then sintered at 900–1000 °C (depending upon x or y) for 10 h in the air to obtain Eu<sup>3+</sup> doped samples or in a CO reducing atmosphere to obtain Eu<sup>2+</sup> doped samples. The synthesized product was reground into fine powder for characterizations. In addition, the preparation of other sample series is almost the same as that mentioned above.

**2.2. Characterization.** The powder X-ray diffraction (XRD) patterns of all samples were collected on a Bruker D8 Focus diffractometer, in the  $2\theta$  range from 10° to 100° with Cu K $\alpha$  radiation  $(\lambda = 1.54056 \text{ Å})$  operated at 40 kV and 40 mA. Also, the step scanning rate was 2 s per step with a step size of 0.02°. Structure refinement was carried out by the Rietveld method using the FullProf program. The emission and excitation spectrum measurements were performed on a Hitachi F-7000 spectrometer equipped with a 150 W xenon lamp as the excitation source spectra, and all the spectra were corrected according to the spectral instrumental response and the spectral output of the light source. The temperature-dependent luminescence properties were also carried out on an F-7000 spectrometer with an external heater. A process controller (OMEGA CN76000) equipped with a thermocouple was assembled to control the temperature. All of the measurements were conducted at room temperature except the temperature-dependent emission spectrum measurement.

#### 3. RESULTS AND DISCUSSION

The aluminum borate KAB crystal, space group P321, a wellknown deep UV nonlinear optical crystal, was found to be an efficient blue-emitting phosphor with good thermal stability when doped with  $Eu^{2+}$ .<sup>35</sup> In the KAB crystal, the nearly planar  $(Al_3B_3O_6)$  networks are stacked perpendicular to the *c* axis and bridged to each other by oxygen atoms, between which the potassium cations are located (Figure S1a in Supporting Information). Along the view of the *c* axis, one can find that the potassium cations are in such channels that are embraced by six-membered rings consisting of  $[AlO_4]^{5-}$  tetrahedra and [BO<sub>3</sub>]<sup>3-</sup> triangles, and form -K1-K2-K1-K2- cationic chains where K1 is coordinated by 10 oxygen atoms and K2 by 9 oxygen atoms (Figure S1b). Accordingly, two Eu<sup>2+</sup> emission centers exist when occupying two K<sup>+</sup> sites, and the resulting charge mismatch can be easily compensated by some defects like K<sup>+</sup> vacancy when the Eu<sup>2+</sup> concentration is relatively low (0.5 mol %). Since two K<sup>+</sup> ions are alternately arranged in the interstices formed by the adjacent  $(Al_3B_3O_6)$ layers, it is reasonable to assume the luminescence properties of both Eu<sup>2+</sup> emission centers will vary in a similar way with a change in the composition of the host. Such surroundings of K<sup>+</sup> ions render the emission of Eu2+ to be somewhat anomalous with very large  $\Delta S$  (larger than 4000 cm<sup>-1</sup>, see Table 1 below) as compared with that of the normal Eu<sup>2+</sup> (around 1350 cm<sup>-1</sup>). It has been attributed to the  $Eu^{2+}$  5d orbital preferential orientation due to the positive charges of cation neighbors in the chain direction.<sup>36</sup> The sample series of  $K_{2(0.995-x)}$ -N a  $_{2x}$  A l  $_{2}$  B  $_{2}$  O  $_{7}$ : 0.01 E u  $^{2+}$  (K A B : 2 x N a) and  $K_{1.99}Al_{2(1-y)}Ga_{2y}B_2O_7:0.01Eu^{2+}$  (KAB:2yGa) doped with a constant concentration (0.5 mol %) of Eu<sup>2+</sup> were synthesized and characterized. As shown in Figure 2, the satisfactory XRD

Table 1. Lower-Energy  $(E^{\text{low}})$  and Higher-Energy  $(E^{\text{high}})$ Excitation Peaks, Emission Peaks, Emission Band Width  $(\Gamma^{\text{em}})$ , and Stokes Shift  $(\Delta S)$  of KAB:2xNa and KAB:2yGa  $(\text{cm}^{-1})$ 

compound	$E^{\rm low}$	$E^{high}$	$E^{\mathrm{em}}$	$\Gamma^{\rm em}$	$\Delta S$
KAB	25 598	31 148	22 222 (450 nm)	2713 (56 nm)	4343
<i>x</i> = 0.2	25 547	32 322	21 505 (465 nm)	3256 (70 nm)	4734
<i>x</i> = 0.4	24 976	32 519	21 052 (475 nm)	3485 (80 nm)	5090
<i>x</i> = 0.6	24 963	33 893	20 534 (487 nm)	3472 (89 nm)	5634
y = 0.1	25 610	31 009	21 978 (455 nm)	2937 (57 nm)	4437
y = 0.2	25 432	30 435	21 786 (459 nm)	2951 (58 nm)	4519
y = 0.3	25 077	30 157	21 598 (463 nm)	2995 (61 nm)	4534
y = 0.4	24 976	29 740	21 367 (468 nm)	3025 (62 nm)	4616

Rietveld refinements of these samples as well as the linear variations of the obtained lattice parameters demonstrate that solid solutions are formed. Since the structure of Na<sub>2</sub>Al<sub>2</sub>B<sub>2</sub>O<sub>7</sub> belongs to space group  $P\overline{3}1c$  although it displays some structural features similar to those of KAB, only limited solid solutions with  $x \leq 0.6$  were obtained.<sup>37</sup>

Figure 3 shows the normalized excitation and emission spectra of the sample series KAB:2*x*Na (the corresponding spectra on the energy scale are shown in Figure S2). As *x* increases, new color tunable solid solution phosphors KAB:2*x*Na are developed. The emission color (see Figure S3) can be tuned from blue (peaking at 450 nm) to cyan (peaking at 487 nm) with *x* increasing from 0 to 0.6, and correspondingly, the emission band is broadened from 56 nm ( $\Gamma^{em} = 2713 \text{ cm}^{-1}$ ) to 89 nm ( $\Gamma^{em} = 3472 \text{ cm}^{-1}$ ), as listed in Table 1. The redshift as well as the broadening of the solid solution phosphors is beneficial to improving the color quality of white LEDs for general lighting, which is different from that for display.<sup>8,9,38</sup> The emission intensity increases first with the Na<sup>+</sup> content and then decreases (Figure S4) when x = 1.2,



Figure 2. Rietveld refinements of XRD data for four representative samples:  $K_2Al_2B_2O_7$  (a),  $K_{12}Na_{0.8}Al_2B_2O_7$  (b),  $K_2Al_{1.2}Ga_{0.8}B_2O_7$  (c), and  $K_2Ga_2B_2O_7$  (d). Variations in the lattice parameters and volumes with the 2x values or 2y values in KAB:2xNa (e) and KAB:2yGa (f), respectively.



**Figure 3.** Normalized emission (a) and excitation (b) spectra of solid solution phosphors KAB:2xNa, and schematic inductive effect of Na<sup>+</sup> (occupying K1 site) on Eu<sup>2+</sup> (occupying K2 site) (c) where the red arrow denotes the redistribution of the electrons.

which is probably due to higher crystallinity since more Na<sup>+</sup> results in a lower sintering temperature needed. Usually, such a redshift in emission is attributed to the increased crystal field splitting owing to the shrinkage of the coordination polyhedron because K<sup>+</sup> ions are replaced by smaller Na<sup>+</sup> ions (Figure 2e). Moreover, one can find that the excitation band shows a small redshift at the low-energy side ( $E^{low}$ ) and expands in both directions (Figure 3b), indicating that the lowest Eu<sup>2+</sup> 5*d* level is lowered (approximately by 625 cm<sup>-1</sup>) which now can be definitely attributed to a larger crystal field splitting. As we

know, the crystal field splitting is largely controlled by the shape and size of the coordination polyhedron.<sup>21,22</sup> In order to determine if there is any distortion of the polyhedron, we used Eu<sup>3+</sup> luminescence as the spectral probe to investigate the local structure of K<sup>+</sup> sites, which is frequently employed due to its simple electronic energy level scheme and hypersensitive  ${}^{5}D_{0}-{}^{7}F_{2}$  transition of Eu<sup>3+</sup>.<sup>39,40</sup> As shown in Table S1 and the corresponding discussion, the shape of the polyhedron is basically maintained in these solid solutions. Therefore, the contraction of the polyhedron is responsible for the larger value of  $\varepsilon_{cfs}$ .

Another subtle but important change in excitation spectra is that, with increasing Na<sup>+</sup> content, the higher-energy side  $(E^{high})$ of the excitation band is markedly blueshifted, the amount  $(2745 \text{ cm}^{-1})$  of which is about 4 times larger than that of the redshift of  $E^{\text{low}}$  (Figure 3b and Table 1). In general, the Eu<sup>2+</sup> 5d levels will split into two groups, the triplet  $t_{2g}$  ( $\vec{E}^{low}$ ) and the doublet  $e_g$  ( $E^{high}$ ), by crystal field splitting at the octahedral site, or further splitting into more sub-bands (at most five) at lowersymmetry sites.<sup>22,23</sup> The lower- and higher-energy bands in excitation spectra should have similar magnitudes of shift despite being in opposite directions if they are caused by variations in crystal field splitting.<sup>21,22</sup> Hence, such a big difference in our case demonstrates that the variation in the centroid shift of the 5d levels should be taken into consideration, which has mostly been neglected in previous works. Unlike crystal field splitting, the variation in the centroid shift will cause the lower- and higher-energy excitation bands to shift in the same direction as well as with the same magnitude.<sup>19-21</sup> Consequently, crystal field splitting and centroid shift have a synergistic effect on shifting the lowerenergy excitation band,  $E^{\text{low}}$ , but have an antagonistic effect on shifting the higher one,  $E^{high}$ . With rare exceptions, the complicated energy level scheme of the  $Eu^{2+} 4f^{6}5d$  electronic configuration prevents the determination of the exact value of the centroid shift as well as the crystal field splitting; however, in practice it is viable to qualitatively determine their changing trends through analyzing the position variations of the lower and higher 5d excitation bands due to their different sensitivities to  $\varepsilon_{c}$  and  $\varepsilon_{cfs}$  as discussed above (illustrated more vividly in Figure S5). Note that the wavelength where the excitation intensity has dropped to 20% on the lower-energy side is regarded as the position of the lowest 5d level, i.e., the aforementioned  $E^{\text{low}}$ , as Dorenbos suggested.<sup>23</sup> In solid solution phosphors KAB:2xNa, the crystal field splitting becomes larger while the centroid shift is smaller with increasing  $x_i$ , the combined effect of which makes the lower-energy excitation band go down slightly and the higher one, however, go up notably, as it appears in Figure 3b.

Moreover, we notice that the redshift D(A) of the lowest 5d level, namely, the shift of  $E^{\text{low}}$  mentioned above, is only about one-third of that (1688 cm<sup>-1</sup>) of the emission band (Table 1); therefore, the tunable emission does not mainly result from the lowered position of the lowest 5d level, but a sizable increase in the Stokes shift of 5d emission. The value of the Stokes shift is estimated on the basis of the mirror-image relationship between at room temperature (see the details in Figure S6).<sup>31,41</sup> As tabulated in Table 1, the Stokes shift increases by 1291 cm<sup>-1</sup> with increasing Na<sup>+</sup> content, which is thus predominant in tuning the emission color. The increased Stokes shift is also confirmed indirectly by the broadened emission band (see Table 1) since Stokes shift  $\Delta S$  and emission band width  $\Gamma^{\text{em}}$  are

positive correlated with each other in terms of the Huang–Rhys parameter S and the effective phonon energy  $\hbar\omega$ .<sup>29,31</sup>

It has been demonstrated that centroid shift as well as Stokes shift depend strongly on the covalency of the bonds between the central cation M and the anions X.<sup>19,20,30,42</sup> To better understand the above peculiar changes in  $\varepsilon_c$  and  $\Delta S$  with cation substitution, we introduce the well-known inductive effect in solid-state chemistry to highlight the key role of neighboring cations in controlling centroid shift and Stokes shift simultaneously.<sup>20,43-45</sup> Since the anions X should be bonded with a second cation T other than M, the property of the M-X bond will be modified by the T-X bond. If T is more electronegative than M, the anions X will tend to share more electrons with T, and thus, fewer electrons will be available for the M-X bond, resulting in a less covalent M-X bond. This is the so-called inductive effect on the M-X bond of the countercation T, which is also the neighboring cation for M. As shown in Figure 3c, in the KAB crystal each K<sup>+</sup> ion is connected with two neighboring  $K^+$  ions by three  $O^{2-}$  ions, respectively, along the K<sup>+</sup> ion chain; therefore, an obvious inductive effect is expected. Given that Eu<sup>2+</sup> occupies the K2 site and its neighboring cation K1 is increasingly replaced by Na<sup>+</sup>, the covalency of the three Eu-O bonds will be attenuated by the replacement of K<sup>+</sup> by Na<sup>+</sup> because Na<sup>+</sup> is more electronegative than K<sup>+</sup>. Such a reduction in the covalency of Eu–O bonds, on one hand, leads to a smaller centroid shift of the 5d levels; on the other hand, it also enlarges the Stokes shift of 5d emission.

In order to verify the existence of the inductive effect of neighboring cations in tuning the luminescence properties of KAB:Eu<sup>2+</sup>, we also replaced another neighboring cation Al<sup>3+</sup> by Ga<sup>3+</sup> to obtain the solid solution phosphors KAB:2yGa. The excitation as well as emission spectra show an obvious redshift, as shown in Figure 4, where a blueshift is expected due to the lattice expansion (Figure 2f) since Ga<sup>3+</sup> is larger than Al<sup>3+</sup>. Indeed, the decreased crystal field splitting is indicated by the narrowing excitation band. Besides, the redshift in excitation spectra appears not only at the lower-energy side but also at the higher-energy side, and the latter is of greater magnitude. This suggests that the centroid shift becomes larger and outweighs the crystal field splitting in changing the position of the lowest 5d level, thus leading to the abnormal redshift in excitation spectra. This can be explained well by the inductive effect of neighboring cation Ga<sup>3+</sup> on the Eu-O bond. As the Al-O bond is replaced by the more ionic Ga–O bond (Figure 4c), more electrons of  $O^{2+}$  will be shared with  $Eu^{2+}$ , and thus, the covalency of the Eu-O bond will be enhanced, resulting in the larger centroid shift. It is believed that if the surrounding cations are those ions with small radius and high charge, the quenching temperature will be relatively high due to a small Stokes shift which is recently related to the structural rigidity of the host crystal by using Debye temperature as a proxy.<sup>34,46</sup> Apparently, Ga<sup>3+</sup> replacing Al<sup>3+</sup> will reduce the rigidity, and thus, a larger Stokes shift is expected, but the estimated Stokes shift remains unchanged within errors accompanied by the constant emission band width (Table 1). It is possible that the effect of having less rigidity of the host crystal on the Stokes shift of 5d emission is counteracted by the enhanced covalency of Eu–O, both of which result from Ga<sup>3+</sup> replacing Al<sup>3+</sup>.

Hence, these results definitely reveal the existence of the inductive effect of neighboring cations in controlling the centroid shift of 5d levels and Stokes shift of 5d emission of  $Eu^{2+}$  in blue phosphor KAB: $Eu^{2+}$ , as a typical case. In addition, the inductive effect can be applied to explain those reported



**Figure 4.** Normalized emission (a) and excitation (b) spectra of solid solution phosphors KAB:2*y*Ga, and schematic inductive effect of Ga<sup>3+</sup> (replacing Al<sup>3+</sup>) on Eu<sup>2+</sup> (replacing K<sup>+</sup>) (c) where the red arrow denotes the redistribution of the electrons.

abnormal shift as well as improve the luminescence properties of other phosphors for white LEDs. Below we give general discussions about where the inductive effect of neighboring cations may obviously take effect and play a key role in shifting the lowest 5d level. Since it is involved in the electron redistribution of the coordinated anions, an influencing factor is the number of anions X shared by the central cation M and the counter (neighboring) cation T to be replaced by the doping cation.<sup>42</sup> The more shared anions X there are, the stronger the inductive effect, which is supported by the fact that an anomalous shift is observed in those oxides with a large ratio between the cation to be replaced and the other cations, such as

 $(Sr_{3-x}Ba_x)SiO_5:Eu^{2+} (3/1)$ ,<sup>24</sup>  $Ca_{3-x}Sr_x(PO_4)_2:Eu^{2+} (3/2)$ ,<sup>26</sup> and  $Sr_{3-m}Ca_mB_2O_6:Eu^{2+} (3/2)$ .<sup>27</sup> Another is the sensitivity of the covalency of the M-X bond to the countercation T. While this is difficult to quantify, it can be gauged by the type of anion X on this point. The spectroscopic polarizability of anions related to the centroid shift of  $Ce^{3+} 5d$  levels scales linearly with the inverse square power of the average cation electronegativity, and the susceptibility b of anions in changing its polarizability to the average cation electronegativity varies greatly for different kinds of compounds.<sup>20</sup> For fluorides, oxides, and nitrides, the value of b was determined to be  $1.2^{20}_{,2}$  4.7,<sup>20</sup> and 18.76,<sup>28</sup> respectively, which implies that the stronger influence of the cations on the polarizability of the anions is expected in nitrides than oxides, and this is weakest in fluorides. Likewise, the inductive effect of neighboring cation is obvious for those bonds with large covalency like in nitrides.<sup>12,44,45,47</sup> In addition, as the polyhedral size depends on the size of the substituted cation as well as the other cations, but more strongly on the size of the anions, the larger the anions are, the less sensitive the polyhedral size is to the size of the cations.<sup>21</sup> Accordingly, the crystal field splitting will change more smoothly with the cations in nitrides than in oxides and fluorides, contrasting significantly with the situation for the centroid shift. It should also be noted that the value of  $\beta$  in  $\varepsilon_{cfs} = \beta R^{-2}$  and the sensitivity of crystal field splitting to the polyhedral distortion vary for different types of polyhedra; for example, crystal field splitting appears to be quite sensitive to polyhedral distortion when the coordination is a tricapped trigonal prism or cuboctahedron while deviation from the regular dodecahedron does not influence  $\varepsilon_{cfs}$  much.<sup>21,22</sup> Considering that only 1/r(A) (r(A) is usually between 1.7 and 2.4) of the crystal field splitting contributes to the redshift D(A) of the lowest 5d level,<sup>22</sup> the inductive effect associated with the centroid shift and Stokes shift can be dominant in tuning the emission color as well as shifting the lowest 5d level (excitation band), especially in the relatively covalent compounds such as (oxy)nitrides or those oxides with a high proportion of large cations.

Although the estimated Stokes shift is as high as 4343 cm<sup>-1</sup>, KAB:Eu<sup>2+</sup> has such good intrinsic thermal stability that the emission intensity at 150 °C is still 87% of that at room temperature. Thermal ionization of the excited 5d levels to the conduction band can be excluded because if the 5d electrons thermally delocalize to conduction band states, they will be strongly bonded by the two effective positive charges on Eu<sup>3+</sup> left behind since Eu<sup>2+</sup> replacing K<sup>+</sup> has already caused an effective positive charge at the Eu<sup>2+</sup> site, resulting in a radiative transition to the Eu<sup>2+</sup> ground state from the impurity-trapped exciton state around Eu<sup>3+</sup>.<sup>32,48</sup> Instead, the energy loss is mainly caused by thermal release through the crossing point in the configuration coordinate diagram due to the large Stokes shift. As x increases, the thermal stability of solid solution phosphors KAB:2xNa deteriorates rapidly (Figure 5); however, because the optical bandgap is enlarged (Figure S7 and Table S2) while the charge transfer band of Eu<sup>3+</sup> has no detectable change (Figure S8), the energy distance  $E_{dC}$  becomes larger (Figure \$9), indicating weaker thermal ionization.<sup>32</sup> Therefore, the excited 5d electron will more easily go over the crossing point in configurational coordinate due to the increased Stokes shift (Figure S10), resulting in worse thermal stability. As for KAB:2yGa, the thermal stability degrades significantly as well, although the Stokes shift remains unchanged. Accordingly, this enhanced quenching is attributed to the intensified thermal

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**Figure 5.** Temperature-dependent emission intensity of KAB:Eu<sup>2+</sup>, KAB:2xNa (x = 0.2 and 0.4), and KAB:2yGa (y = 0.2 and 0.4).

ionization due to a much narrower bandgap when replacing  $Al^{3+}$  ions that have noble gas configurations with  $d^{10}$  ions  $(Ga^{3+})$  (Figure S9), and thus, a metal-metal charge transfer between Eu<sup>2+</sup> and Ga<sup>3+</sup> happens,<sup>36,49,50</sup> which is corroborated by the appearance of host excitation shorter than 250 nm and the red emission originating from the unreduced Eu<sup>3+</sup> in Figure 4b. For a better understanding of the temperature dependence of the photoluminescence, the activation energy was calculated by the Arrhenius equation (Figure S11), which coincides with the above discussion.<sup>51</sup> It follows that the thermal stability can be largely regulated by the variation not only of the energy distance  $E_{dC}$  but also that of the Stokes shift in solid solution phosphors designed by cation substitution, and the improved thermal stability has been reported as well elsewhere.<sup>11,12,52</sup>

## 4. CONCLUSION

In summary, we have shown an illustrative example of color tunable solid solution phosphors based on  $Eu^{2+}$  activated  $K_2Al_2B_2O_7$ , where the variations in centroid shift and Stokes shift play dominant roles in tuning the luminescence properties of  $Ce^{3+}$  or  $Eu^{2+}$  activated solid solution phosphors. A general model involving the inductive effect of the neighboring cation is proposed, which can well explain the tunable luminescence properties as well as the observed so-called abnormal emission shift. Our results not only reveal the correlations between local structure and luminescence properties of 5d levels but also shed light on the exploration of novel phosphors with particular performance for practical applications.

#### ASSOCIATED CONTENT

#### **Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.7b01457.

Figures S1–S11, Tables S1 and S2, and the related discussion (PDF)

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