Density functional study for optical properties of blue silicate phosphor: BaCa$_2$MgSi$_2$O$_8$

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Abstract. A density functional calculation is performed to investigate optical properties of blue silicate phosphor, BaCa$_2$MgSi$_2$O$_8$:Eu (BCMS:Eu). The optical absorption and emission processes are discussed based on electronic band structures and density of states. Our calculation indicates that hybridization of the wave function plays an important role for nonradiative migration of electrons and holes. Our results also explain adequately the luminescence feature of BCMS which exhibits two components of blue emission from Eu ion substituted for Ba and Ca site. In addition, it is shown that the structural relaxation around Eu ion does work effectively to describe appropriately the difference of crystal field strength between Ba and Ca sites in BCMS host.

1. Introduction
Inorganic phosphors are widely used in daily life such as fluorescent lamps for lighting and components of plasma display panels (PDPs) and are usually activated by doping with rare-earth elements (the activators). It is generally accepted that, in the optical absorption and emission processes, the absorption of vacuum ultraviolet (VUV: $\lambda=147, 172$nm) excitation energy by the host crystal is followed by energy transfer to the activators and then the activators can emit visible light [1]. However, the general interpretation is often based on conventional band scheme and, thus, a detailed description would necessitate further theoretical consideration.

From the viewpoint of industrial application, blue phosphors particularly play an important role for the development of PDPs to realize a full and clear color display. At present, Barium magnesium aluminon BaMgAl$_{10}$O$_{17}$(BAM), which is activated by Eu$^{2+}$ doping, is widely used as the blue-light-emitting phosphor for the PDPs because of its high quantum efficiency, good chromaticity and strong absorption for VUV excitation [2, 3]. On the other hand, a new silicate phosphor, Calcium magnesium...
silicate CaMgSi$_2$O$_6$ (CMS), has been recently reported [4] with blue luminescence by Eu$^{2+}$ doping under VUV excitation. The degradation of luminous efficiency of CMS from the VUV irradiation and the baking process compared with BAM was decreased [5,6].

In our previous report [7], we discussed the optical and emission properties of CMS in detail based on electronic band calculation and proposed an excitation mechanism in which hybridization of wave function plays an important role for nonradiative migration of electrons and holes. In addition, by means of computational materials screening to investigate the optical band gap of various silicate hosts, we also revealed that BaCa$_2$MgSi$_2$O$_8$ (BCMS) has an optical band gap similar to that of BAM and, therefore, BCMS has potential of light response to 172nm excitation. Our discussion on BCMS in the previous study, however, was restricted to the optical band gap only and did not make specific mention of other optical properties and its excitation mechanism.

In this work, density functional band calculation has been carried out to investigate the optical properties of BCMS and BCMS:Eu. The optical excitation process is discussed based on the electronic band structures and the density of states (DOS). In our previous study, the calculations on BCMS were carried out with reference to crystal structure data determined by XRD measurements and Rietveld refinements made by Yonesaki et al. [8]. They, however, recently reinvestigated the crystal structure using combined powder X-ray and neutron Rietveld techniques and, as a result, determined that BCMS crystallizes in the trigonal space group P3$_2$ instead of the previously believed space group P3$_1$[9]. Thus, we have also recalculated the electronic band structures and DOS of BCMS and BCMS:Eu based on their reinvestigated crystallographic data and discuss the optical properties and its excitation mechanisms.

2. Details of computation

Crystallographic data including atomic positions of BCMS is taken from the report made by Park et al. [9]. The host has a trigonal space group with the P3$_2$ (S.G. No.147, $a_0=5.427$, $c_0=6.7946\text{Å}$) as shown in Figure 1. The primitive cell used in band calculation for BCMS contains 14 atoms, composed by one Ba, two Ca, one Mg, two Si and eight O. On the other hand, to construct a model of BCMS including Eu ion (BCMS:Eu), a $1\times1\times2$ super-cell containing 28 atoms extended to c-axis is used; this super-cell has two Ba and four Ca sites, and then two kinds of models, BCMS:Eu$_{Ba}$ and BCMS:Eu$_{Ca}$, are constructed by which one of two Ba and two of four Ca are substituted by Eu ion, respectively. The same space group of the primitive cell, P3$_2$ (S.G. No.147), are imposed on these substituted models.

In both models, the substitution ratio corresponds to 50% concentration of Eu and there could be a concern if such high concentration of Eu ion affects the electronic structures of BCMS:Eu as discussed in our previous study on CMS:Eu [7]. We, hence, have also checked the Eu concentration dependency by taking into account a model with 25% substitution of Eu ion for BCMS:Eu$_{Ca}$. The cell with 25% substitution model of BCMS:Eu$_{Ca}$ has lower symmetry of P3$_1$ (S.G. No. 143) including 28 atoms and one fourth Ca sites is substituted by a Eu ion. Table 1 shows the results for the band energies and the bandwidths using the different Eu concentration models. As clearly shown, those band energies and the bandwidths are independent of Eu concentration. Thus we will further use in this paper the results of the $1\times1\times2$ super-cell (50% concentration model) to discuss the electronic structures and the optical properties of BCMS:Eu.

Figure 1. Crystal structure of non-doped BCMS. The white tetrahedron and the gray octahedron stand for SiO$_4$ and MgO$_6$ unit, respectively; the black and gray spheres stand for Ba and Ca, respectively; the small black spheres stand for O. The crystal structure is visualized by using VESTA [10].
Table 1. Band energies $\varepsilon$ of BCMS:Eu$_{\text{Ba}x}$ for valence band top (VBT), 4f-band and conduction band bottom (CBB); band widths for O2p, Eu 4f, Ba 5d, Ca 3d and Eu 5d bands for the different Eu concentrations using the full-potential linearized augmented plane-wave (FLAPW) method.

| Eu concentration (%) | $\varepsilon$(VBT) (eV) | $\varepsilon$(4f) (eV) | $\varepsilon$(CBB) (eV) | Band Width (eV) | O 2p (occ.) | Eu 4f (occ.) | Ba 5d (unocc.) | Ca 3d (unocc.) | Eu 5d (unocc.) |
|----------------------|-------------------------|------------------------|------------------------|----------------|------------|------------|--------------|--------------|--------------|
| 25                   | -3.9                    | -0.88                  | 0.9                    | 6.80           | 0.24       | > 7.1      | > 7.1        | > 7.1        | > 7.1        |
| 50                   | -3.9                    | -0.90                  | 0.9                    | 6.78           | 0.26       | > 7.1      | > 7.1        | > 7.1        | > 7.1        |

The band calculation of BCMS and BCMS:Eu has been performed by means of the full-potential linearized augmented plane-wave (FLAPW) method [11-14] within the local density approximation (LDA) and the LDA with the on-site Coulomb repulsion (LDA+U) [15,16]. The linearization for the APW method is done by the scheme of Takeda and Kübler. The muffin-tin (MT) radii are 2.5 a.u. for Eu, 2.7 for Ba, 2.6 a.u. for Ca, 2.2 a.u. for Mg, 1.55 a.u. for Si and 1.4 a.u. for O. The energy cutoff parameters are 12 Ry for the wave function and 48 Ry for charge density and the potential. The angular momentum expansion is truncated at $l_{\text{max}}=7$ for the wave function, and at $l_{\text{max}}=6$ for the charge density and the potential. We take 30 $k$ points in the irreducible Brillouin zone, which corresponds to 144 $k$ points in the whole Brillouin zone.

In the LDA+U calculation of BCMS:Eu, ferromagnetic state of Eu (4f$^7; S=7/2$) is assumed and $U_{\text{eff}}=5.99$ eV for Eu 4f state is used in line with our previous study on CMS:Eu [7]. Here, we have mentioned only about U parameter dependency in the range of 4.35 to 7.62eV for band energy difference between Eu 4f band and VBT of BCMS:Eu; we have obtained a result that the dependence is almost linear as is the case with the report by Hölsä et al. [17]. In addition, we can see that BCMS:Eu$_{\text{Ba}x}$ and BCMS:Eu$_{\text{Ca}x}$ exhibit the different values of the band energy difference which is decreased with an increase in U parameters such as $ca.$ 2.8 to 1.5 eV and $ca.$ 3.7 to 2.6 eV, respectively. The band energy differences of BCMS:Eu$_{\text{Ba}x}$ and BCMS:Eu$_{\text{Ca}x}$ for $U_{\text{eff}}=5.99$ eV are 2.0 and 3.0 eV respectively and those values are slightly small compared with that of CMS obtained in our previous study [7].

Structural optimization for BCMS:Eu has been performed by using the VASP code [18] within the GGA-PBEsol scheme [19]. The energy cutoff of 400eV and 5x5x5 $k$-point grid are used. We set the convergence criteria of $1 \times 10^{-5}$ eV for SCF iterations and $1 \times 10^{-2}$ eV for the net forces acting on the atoms. During the optimization calculations, the positions of all atoms are relaxed within the fixed lattice parameters of the super cell.

3. Results and discussions
3.1. Band structure and density of states (DOS)

Figure 2 shows the LDA band structure and partial DOS for non-doped BCMS in the nonmagnetic state. The origin of the band energy is taken at the Fermi level. The valence band (VB) is mostly composed of the occupied O 2p bands between -9.1 and -2.4eV, whereas the unoccupied bands, which are located at +2.4eV or above, mostly consist of Ca 3d and Ba 5d bands mixing with O 2p bands. The lowest dispersive unoccupied band possesses mostly s-band character composed of Ba 6s, Ca 4s, O 2s, Mg and Si 3s bands, in which Ba 5d and Ca 3d components are slightly mixed.
Figure 2. The band structure (a) and DOS (b) for non-doped BCMS in the nonmagnetic state obtained from FLAPW method within the LDA scheme. The Brillouin zone (BZ) is depicted in (c) with the special k-points.

On the other hand, Figure 3 and 4 show the LDA+U band structures and partial DOS in the ferromagnetic up spin state for BCMS:Eu, respectively; the left and right illustration in each figure represent BCMS:Eu_{(Ba)} and BCMS:Eu_{(Ca)}, respectively. Those of the down spin state are not presented here because those are almost the same as that of non-doped BCMS. In Figure 3, the localized flat bands are Eu 4f bands, which are located at -1.3 eV in BCMS:Eu_{(Ba)} and -0.9 eV in BCMS:Eu_{(Ca)} below the Fermi level, respectively. The magnetization in both Eu substitution models is $7 \mu_B$, which corresponds to the ground state of Eu (4f$^7$; S=7/2). For both models, the DOS shown in Figure 4 are very similar; the VB between -10.0 and ca.-4.0 eV are mostly composed of the O 2p bands and the unoccupied bands located at ca. +2.0 eV or above are mostly composed of the Ca 3d, Ba 5d and Eu 5d bands mixing with O 2p bands. Furthermore, it is noteworthy that the component from the Eu 5d states is mixing slightly with the lowest dispersive unoccupied band possessing s-band character.
These results shown in Figure 3 and 4 exhibit that there are two possible optical absorptions of BCMS:Eu; one is the direct transition from Eu 4f bands and the other is the host interband transition which occurs from O 2p bands. In the direct transition, electrons could be excited into the unoccupied bands mainly consisting of the Ba 5d, Ca 3d and Eu 5d bands. However, the occupied Eu 4f wave function is strongly localized on Eu atom and the overlap of the wave functions between Eu 4f and Ba 5d and/or Ca 3d orbital might be small. Therefore, by symmetry, the optical transition of Eu direct excitation should be almost restricted to the Eu 4f → 5d transition. On the other hand, the host interband transition is attributed to charge transfer from O 2p bands to cation d bands and the optical transition induces electron-hole pair on the host lattice; electrons are excited into the unoccupied bands mainly consisting of the Ba 5d, Ca 3d and Eu 5d bands and holes are generated into the O 2p bands.

In order to produce the effective emission followed by the VUV excitation, it is necessary that excited electrons and holes on the host lattice transfer efficiently to Eu ions. In the partial DOS of Figure 4, it should be noted that the unoccupied Ba 5d and Ca 3d bands are mutually well hybridized with the Eu 5d bands; the hybridization could assist the efficient electron transfer from the host lattice to the Eu ion. Furthermore, interestingly, hybridization between the occupied Eu 4f and O 2p bands can also be seen in the partial DOS; it could also help for transferring the hole generated on the host lattice to the Eu ion. Consequently, it can be concluded that, even in BCMS:Eu, the hybridization of the wave functions plays an important role for the nonradiative migration of excited electrons and holes from the host lattice to the luminescence centre.

Figure 3. Band structures for ferromagnetic up-spin state of BCMS:Eu obtained from FLAPW method within LDA+U scheme; (a) BCMS:Eu_{(Ba)} (left) and (b) BCMS:Eu_{(Ca)} (right). The Coulomb U parameter of 5.99eV is used for Eu 4f state.

Figure 4. Partial density of states for BCMS:Eu using FLAPW method within LDA+U scheme; (a) up-spin: BaCa\textsubscript{2}Mg\textsubscript{2}Si\textsubscript{2}O\textsubscript{8}:Eu(Ba) and (b) down-spin: BaCa\textsubscript{2}Mg\textsubscript{2}Si\textsubscript{2}O\textsubscript{8}:Eu(Ca). The Coulomb U parameter of 5.99eV is used for Eu 4f state.
The emission process of Eu$^{2+}$ is usually explained in terms of $4f^65d^g\gamma$ transition [4,9]. The present calculation supports that the assignment is reasonable from the viewpoint of the band structure, that is, the intra-atomic transition corresponds to the transition between band edges of Eu 4f band and the lowest dispersive unoccupied band. As was pointed out previously, the lowest unoccupied band possesses some Eu 5d component mixing with the main s-band characters. Thus, from the viewpoint of the symmetry, the dipole transition between Eu 4f and 5d states should be allowed in the emission process. Indeed, our FLAPW method takes account of symmetry of crystal and we have confirmed that the optical dipole transition at $\Gamma$ point is allowed by selection rule based on the symmetry. This is a qualitative discussion and, in fact, it might be necessary to take into account many-body effect such as excitonic effect for further accurate description of the emission process. Here, however, it is important for us to grasp that the lowest unoccupied band of BCMS:Eu is available to participate in the emission process due to possessing non-zero Eu 5d component. This interpretation is essentially in common with that of CMS discussed in our previous study [7] and we can, therefore, conclude that the optical absorption and emission process in both CMS and BCMS are attributed to the same mechanism.

3.2. Luminescence feature of BCMS:Eu

We, here, discuss the luminescence feature of BCMS:Eu in more detail because basic understanding of such a luminescence feature is important to materials design and development in industry. BCMS has two different substitution sites, Ba and Ca sites, for Eu ion and it is therefore suggested that BCMS:Eu exhibits two components of luminescence; as shown in the band structures and the DOS in Figures 3. The emission process of Eu$^{2+}$ is usually explained in terms of $4f^65d^g\gamma$ transition [4,9]. The present calculation supports that the assignment is reasonable from the viewpoint of the band structure, that is, the intra-atomic transition corresponds to the transition between band edges of Eu 4f band and the lowest dispersive unoccupied band. As was pointed out previously, the lowest unoccupied band possesses some Eu 5d component mixing with the main s-band characters. Thus, from the viewpoint of the symmetry, the dipole transition between Eu 4f and 5d states should be allowed in the emission process. Indeed, our FLAPW method takes account of symmetry of crystal and we have confirmed that the optical dipole transition at $\Gamma$ point is allowed by selection rule based on the symmetry. This is a qualitative discussion and, in fact, it might be necessary to take into account many-body effect such as excitonic effect for further accurate description of the emission process. Here, however, it is important for us to grasp that the lowest unoccupied band of BCMS:Eu is available to participate in the emission process due to possessing non-zero Eu 5d component. This interpretation is essentially in common with that of CMS discussed in our previous study [7] and we can, therefore, conclude that the optical absorption and emission process in both CMS and BCMS are attributed to the same mechanism.

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and 4, the relative position of Eu 4f bands and CBB measured from Fermi level are slightly different between BCMS:Eu\(_{\text{(Ba)}}\) and BCMS:Eu\(_{\text{(Ca)}}\). Hence this subsection is devoted to a discussion of such a luminescence feature of BCMS:Eu from the viewpoint of band energy.

It is well known that the LDA calculation tends to underestimate the optical band gap. For a qualitative discussion about optical emission energy, a uniform shift of unoccupied band energy, so-called “scissors operator”, is often applied; that is, all of the energy levels of the unoccupied bands are uniformly shifted to adjust the energy difference between band edges associated with the luminescence under consideration to the observed emission energy. Validity of the approach using the scissors operator for unoccupied band of silicate phosphors was already discussed in our previous report in detail [7]. We, here, intend to investigate the relationship between the energies of the two emission components and the local structure environment around Eu substitution sites.

Table 2 shows the band edge energies and its energy differences of BCMS:Eu derived from LDA+U calculation. The uncorrected band energy differences of BCMS:Eu\(_{\text{(Ba)}}\) and BCMS:Eu\(_{\text{(Ca)}}\) are 2.51 and 1.81 eV, respectively, and those energies are smaller than those of experimental values due to the underestimation problem of band gap in LDA. Then, by means of the scissors operator, those energy differences are corrected; a value of 0.9 eV is applied to adjust the energy difference of BCMS:Eu\(_{\text{(Ca)}}\) to the experimental emission energy, 2.69 eV (460 nm). As a result, the other energy difference of BCMS:Eu\(_{\text{(Ba)}}\) is estimated at ca. 3.4 eV (365 nm) and the estimated energy is, however, too large (too short in wavelength) compared with the experimental emission energy, 2.88 eV (430 nm).

| System   | Band edge energy (eV) | Band energy difference (eV) | Exp. [9] |
|----------|-----------------------|-----------------------------|---------|
|          | uncorrected \(\varepsilon\text{(CBB)}\) | corrected \(\varepsilon\text{(CBB)}\) \(\varepsilon\text{(4f)}\) | uncorrected \(\varepsilon\text{(CBB)}-\varepsilon\text{(4f)}\) | corrected \(\varepsilon\text{(CBB)}-\varepsilon\text{(4f)}\) |
| BCMS:Eu\(_{\text{(Ba)}}\) | +1.25 | +2.15 | -1.25 | 2.51 (494) | 3.41 (364) | 2.88 (430) |
| BCMS:Eu\(_{\text{(Ca)}}\) | +0.90 | +1.80 | -0.90 | 1.81 (685) | 2.71 (458) | 2.69 (460) |

The discrepancy may arise from the difference of crystal field strength between Ba and Ca cations for Eu substitution; indeed, we can see that the Eu 4f bandwidth of BCMS:Eu\(_{\text{(Ca)}}\) is slightly wider than that of BCMS:Eu\(_{\text{(Ba)}}\) due to stronger crystal field. In general, Ba cation has a larger ionic radius compared with that of Ca cation. Coordination number of Ba and Ca site in BCMS host are twelve and seven, respectively [9] and, thus, the corresponding ionic radii by Shannon [20] are 1.61 and 1.06 Å, respectively. On the other hand, the ionic radii of Eu ion are 1.35 and 1.2 Å for ten and seven coordination number, respectively. Thus the coordination environment of Ba (Ca) site is looser (tighter) than that of Ca (Ba) site for Eu substitution.

Hence we should take into account structure relaxation effect on Eu substitution and have carried out the structure optimization using VASP code based on GGA+U calculation [18,19]. The optimized bond distances of Ba-O, Eu-O and Ca-O are summarized in Table 3. As would be expected, Eu substitution for Ba site shorten Eu-O bond compared with the original Ba-O bond distance and the substitution for Ca site makes Eu-O bond longer compared with the original Ca-O bond. Then, by means of adjusting the uncorrected band energy difference of BCMS:Eu\(_{\text{(Ca)}}\) to the experimental emission energy using the correction value of 0.7 eV, the other band energy difference of BCMS:Eu\(_{\text{(Ba)}}\) are estimated at ca. 2.94 eV (422 nm) as shown in Table 3. This result describes adequately the relative energy difference in the experimental luminescence of Eu ion for Ba and Ca site. In addition, we can see that spectrum width of the experimental luminescence profile of Eu for Ca site is slightly wider than that of Eu for Ba site. The fact might reflect that BCMS:Eu\(_{\text{(Ca)}}\) possesses a slightly wider bandwidth of Eu 4f bands compared with that of BCMS:Eu\(_{\text{(Ba)}}\) as shown in Figures 3 and 4.
Consequently, we conclude that the structural relaxation around Eu ion does work effectively to describe appropriately the difference of crystal field strength between Ba and Ca sites in BCMS host.

Table 3. Optimized bond distances of Ba-O, Eu-O and Ca-O bond, and band energy differences derived from VASP/GGA+U calculation. U=5.99 eV is used. Values in parenthesis stand for wavelength of band energy difference. The original bond distances in BCMS are 2.772 and 3.134 Å for Ba-O, and 2.246, 2.421 and 2.733 Å for Ca-O, respectively [9]. A correction value of the scissors operator, 0.7 eV, is used here.

| System          | Optimized bond distance (Å) | Band energy difference (eV) |
|-----------------|-----------------------------|-----------------------------|
|                 | Ba-O(12)                      | Eu-O                        | Ca-O(7)                      |
|                 | uncorrected                  | corrected                   | uncorrected                  | corrected                   |
| BCMS:Eu_{Ba}    | 2.799                        | 2.719                       | 2.180-2.261                  | 2.24 (554)                  | 2.94 (422)                  |
|                 | 3.134                        | 3.135                       | 2.368-2.402                  | 2.730-2.783                |
| BCMS:Eu_{Ca}    | 2.738-2.782                  | 2.335                       | 2.195                        | 2.00 (620)                  | 2.71 (458)                  |
|                 | 3.133-3.136                  | 2.554                       | 2.402                        |                             |
   |                 | 2.731                        | 2.699                       |                             |

3.3. Revised result of computational materials screening for silicate phosphors

Finally, we intend to add a short comment on our previous result of computational materials screening for silicate phosphors; we presented a result of host excitation energy of various silicate hosts using computational materials screening in our previous study [7].

However as the calculation of BCMS was carried out by using the crystallographic data reported by Yonesaki et al. in ref. 8, the host excitation energy of BCMS should be checked with the revised crystallographic data. We, thus, have recalculated the host excitation energy of BCMS based on the revised crystallographic data using the same calculation procedure described in ref. 7. As a result, we have obtained ca. 6.05 eV as the host excitation energy of BCMS and it is almost same as the previous calculated value, 6.1 eV. We, therefore, can see that the relative position of the host excitation energy of BCMS among that of various silicate phosphors does not change.

Although our approach presented in this study might not be totally based on first-principles, we have demonstrated that such a practical manner using empirical manipulation combined with first-principles calculation is effective in basic understanding of luminescence feature of phosphors and in developing industrial phosphors. Probably, it would be one of great theoretical challenge to be able to predict the optical absorption and emission features of materials beyond current density functional theory.

4. Conclusion

The LDA and LDA+U band calculation have been performed for blue silicate phosphor, BCMS:Eu. From the electronic band structure and the partial DOS, we conclude that the optical absorption arises from the host interband transition and the Eu 4f \( \rightarrow \) 5d transition and, on the other hand, the optical emission attributes to the Eu 5d \( \rightarrow \) 4f transition which mainly contributes to band edge luminescence by symmetry. In particular, the results indicate that the hybridization of wave functions plays an important role for nonradiative migration of electrons and holes from the host to the luminescence centre. Thus, our results have revealed that the optical absorption and emission process in both CMS and BCMS are attributed to the same mechanism.

BCMS, however, exhibits two components of blue luminescence attributed to Eu 5d \( \rightarrow \) 4f transition for Ba and Ca substitution sites. Our results explained adequately such a luminescence feature of BCMS based on the band structures and the DOS analysis. In addition, it is shown that the structural optimization does work effectively to describe appropriately the difference of crystal field strength between Ba and Ca sites in BCMS host.
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