First-Principles Calculations of x-Dependent Ground Structures and Optical Properties of Ca\(_x\)La\(_{1-x}\)B\(_6\)

Satoshi Yoshio* and Kenji Adachi

**ABSTRACT:** High transparency in the visible region is desired to manufacture solar control films and glasses for various applications. To improve the visible light transparency of LaB\(_6\) nanoparticles which exhibit strong absorption in the near-infrared region, the substitution of La with Ca is investigated using first-principles calculations. Among the numerous atomic replacement configurations in Ca\(_x\)La\(_{1-x}\)B\(_6\), all 762 structures existing in the supercells that are up to 8 times the primitive cell are comprehensively evaluated, and the most stable ground structures in Ca\(_x\)La\(_{1-x}\)B\(_6\) are deduced. The optical properties of the ground structures are derived by performing high-precision calculations using the HSE06 functional, which reveal that Ca\(_x\)La\(_{1-x}\)B\(_6\) with 0 < x < 1/4 is preferred as a solar shielding material with improved visible transparency. This method is effective for the investigation of the effect of substitutional elements in composite compounds on their physical properties.

**INTRODUCTION**

Lanthanoid metal hexaboride, RB\(_6\), possesses unique physical properties such as high conductivity, high hardness, and superconductivity.\(^1\) In particular, LaB\(_6\) has been studied extensively as a thermionic emission material owing to its low work function and high melting temperature.\(^2\) Recently, it was found that the nanoparticles of LaB\(_6\) produce a strong absorption in the near-infrared region coupled with high transparency in the visible light region.\(^3\) This allowed its application in solar control films and glasses, including automotive monolithic, laminated, and polycarbonate glasses, and extended applications in laser welding and cancer therapies employing their efficient photothermal conversion capabilities.\(^4\)\(^–\)\(^13\)

The near-infrared absorption of LaB\(_6\) dispersed layers occurs with a strong dependence on the particle size and does not occur at a micron scale.\(^10\) Its absorption energy agrees with the plasmon energy (1.3 eV) measured using electron energy-loss spectroscopy.\(^8\) These observations confirm that the near-infrared absorption of LaB\(_6\) fine particles is caused by the localized surface plasmon resonance (LSPR) of free electrons, similar to Ag, Au, and ITO (In\(_2\)O\(_3\);Sn) fine particles.

However, the visible light transparency of LaB\(_6\) is not as high as the transparent conductive material of ITO and the nearly transparent plasmonic material of Cs\(_{0.33}\)WO\(_3\), owing to a strong green tint caused by an absorption in the visible region. If the visible light transparency of LaB\(_6\) is increased, the tint neutralization and adjustment using color pigments in glass processing can be made easier, and a high near-infrared absorption can be realized at a given visible light transmittance to save energy consumption.

One of the techniques for improving visible light transparency is elemental substitution. A few studies have been reported to control the plasma resonance wavelength of LaB\(_6\) by elemental substitution.\(^14\)\(^–\)\(^17\) Bao et al. synthesized the alloys of Sm\(_{1/4}\)La\(_{1/4}\)B\(_6\) and Eu\(_{1/4}\)La\(_{1/4}\)B\(_6\) in which La was replaced by Sm and Eu, respectively, in LaB\(_6\) and reported that the plasmon resonance wavelength shifted toward a longer wavelength.\(^15\)\(^,\)\(^16\) However, these results indicate that the absorption in the visible region also increases and is not suitable for solar shielding applications because both high visible transparency and strong near-infrared absorption are simultaneously required. Mattox et al. also reported the results for Eu-doped La\(_{1/4}\)Eu\(_{1/4}\)B\(_6\) containing B vacancies.\(^17\) The red shift of the plasma resonance wavelength and the decrease in the visible absorption were the same as those reported by Bao et al. and did not improve the solar control properties.

Thus, the previously reported studies were limited to LaB\(_6\) with the replacement of La by other lanthanoid elements, where the wavelength control of the plasmon resonance was only toward the long wavelength and the transparency in the visible region was impaired. However, developments that lead to a true improvement in the optical characteristics, that is, a...
RESULTS AND DISCUSSION

The crystal structure of LaB₆ is shown in Figure 1. LaB₆ has a CsCl-type simple cubic crystal structure, where \( a = b = c \) and \( \alpha = \beta = \gamma = 90^\circ \). The space group belongs to \( Pm\bar{3}m \), consisting of La at the Cs position and B₆ at the Cl position. Similarly, CaB₆ has a CsCl-type simple cubic crystal structure in which La is replaced by Ca.

A previous study reported by our research group shows that the optical characteristics of LaB₆ can be reproduced quantitatively by considering the Drude term, which includes the effect of free electrons, and by calculating the effect of interband transitions using a hybrid calculation method that accurately reproduces the band gap. Details are described in the Methods section.

The structures of CaB₆, SrB₆, and BaB₆ are represented in Figure 1, where La is replaced by Ca, Sr, and Ba. Figure 2 shows the results of the calculation of the dielectric functions of LaB₆, CaB₆, SrB₆, and BaB₆. Focusing on the imaginary part of the dielectric function, LaB₆ shows a small absorption in the visible region and a large absorption in the low-energy region below 1.8 eV, which makes it suitable for application as a solar radiation shielding material.

Considering the \( \varepsilon_2 \) values for CaB₆, SrB₆, and BaB₆, the substitution of trivalent La with a divalent alkaline earth metal reduces the free electrons and significantly decreases the absorption in the low-energy side derived from the Drude term. Considering the energy at which \( \varepsilon_1(\omega) = 0 \), which determines the screened plasma resonance frequency (\( \Omega_p \)), the \( \Omega_p \) values of BaB₆, SrB₆, and CaB₆ are all significantly lower than that of LaB₆. That is, BaB₆, SrB₆, and CaB₆ are not expected to absorb near infrared light. In contrast, \( \varepsilon_2 \) value in the visible energy is high for BaB₆ and decreases for SrB₆ and CaB₆ in this order. Therefore, CaB₆ was selected as a substitution material for LaB₆.

Next, the effect of Ca substitution of La in CaₓLa₁₋ₓB₆ was examined in detail. Figure 3 shows the convex hull and the mixing energy of each structure of CaₓLa₁₋ₓB₆ obtained by the first-principles calculations, where the energies of LaB₆ and CaB₆ are set at 0 eV. For each \( x \) of CaₓLa₁₋ₓB₆, the energies of the possible configurations vary significantly depending on the difference in the substitution sites, that is, the difference in the microscopic crystal structure. The convex hull that traces the envelope of the lowest energies includes all energies of the most stable states of CaₓLa₁₋ₓB₆.

In addition to LaB₆ and CaB₆, six compositions are found as the ground states that constitute the most stable state of concurrent increase in the visible transparency and near-infrared absorption, has not yet been reported. Therefore, in this study, a detailed investigation of the visible light transparency of LaB₆ is conducted using first-principles calculations.

It has been previously reported by our research group that the dielectric functions that determine the optical properties of LaB₆ can be predicted with high accuracy by first-principles calculations. The optical properties of nanoparticle dispersions are analyzed by the dielectric functions and Mie scattering theory, but when the particle shape and dielectric functions are modulated during the nanoparticle formation, as in the case of LaB₆, a new analysis method such as the Mie scattering integration (MSI) method is used to describe the optical response. The MSI method integrates the individual Mie scattering waves from particles with inhomogeneous physical properties and/or shapes in an ensemble.

The visible transparency of LaB₆ was also analyzed recently, and it was found to be essentially derived from the wide-gap band structure and reduced transition probability because of the selection rule that prohibits transitions from the B-p orbital in the valence band to the B-p and La-p orbitals in the conduction band. The spectral blue-side transmission is restricted by the band-edge absorption and the red-side transmission is strongly affected by the LSPR wavelength. Therefore, a wide-gap band structure and low plasma frequency are the requisites for a replacement material for LaB₆. In this study, the substitution of La with divalent ions, specifically, alkaline earth metals, is investigated. Alkaline earth metal hexaborides such as CaB₆, SrB₆, and BaB₆ are wide-gap semiconductors/insulators and are isomorphic with LaB₆. The electronic structures of CaB₆, SrB₆, and BaB₆ are reported in prior literature reports, but no detailed studies including the dielectric functions have been published. Therefore, high-accuracy calculations of the optical properties of CaB₆, SrB₆, and BaB₆ were performed to determine the candidate substitution element, and the effects of the elemental substitution in LaB₆ at various proportions were examined.

To precisely determine the absorption of the substituted material in the visible region, it is necessary to quantitatively evaluate the effect of interband transitions. However, in a ternary compound in which a portion of La atoms is replaced by another element, the energy and electronic state of the compound strongly depend on the positional relationship between the substituted and matrix elements, and correspondingly different optical characteristics are observed. In the literature, first-principles calculations of several substituted hexaborides have been reported, such as La₉₋ₓSmₓCaₓB₆ and Ca₉₋ₓLaₓSmₓB₆, but these do not incorporate the various substitutional configurations and calculate only a single type of replacement arrangement. The calculations with only a limited type of arrangement do not afford a satisfactory prediction for the experiments. In the present study, a comprehensive and exhaustive approach is used for the arrangement of elements, and the lowest-energy ground structures of LaB₆ with the substitution of La by an alkali earth element at various proportions are identified. Furthermore, the changes in the optical properties with variations in the ground structures are analyzed in detail, and the optical properties of the actual nanoparticle ensembles are inspected.
Ca$_{x}$La$_{1-x}$B$_6$. These include Ca$_{7}$La$_{1}$B$_{48}$ ($x = 1/8$), Ca$_{5}$La$_{1}$B$_{36}$ ($x = 1/6$), Ca$_{6}$La$_{1}$B$_{48}$ ($x = 1/4$), Ca$_{3}$La$_{1}$B$_{36}$ ($x = 1/2$), Ca$_{3}$La$_{1}$B$_{24}$ ($x = 3/4$), and Ca$_{7}$La$_{1}$B$_{36}$ ($x = 7/8$). The integer corresponds to
the number of atoms contained in the calculated unit cell. The
most stable state of Ca$_{x}$La$_{1-x}$B$_6$ is composed of these eight
types of structures.

In other words, LaB$_6$ and Ca$_{7}$La$_{1}$B$_{48}$ coexist when the Ca
substitutional fraction $x$ is in the range of $0 < x < 1/8$, and
Ca$_{5}$La$_{1}$B$_{36}$ and Ca$_{7}$La$_{1}$B$_{36}$ coexist in the range of $1/8 < x < 1/6$.
In the range of $1/6 < x < 1/4$, Ca$_{6}$La$_{1}$B$_{48}$ and Ca$_{3}$La$_{1}$B$_{36}$ coexist,
whereas in the range of $1/2 < x < 3/4$, Ca$_{3}$La$_{1}$B$_{36}$ and
Ca$_{3}$La$_{1}$B$_{24}$ coexist. Furthermore, Ca$_{3}$La$_{1}$B$_{24}$ and Ca$_{3}$La$_{1}$B$_{36}$
coexist in the range of $3/4 < x < 7/8$, and in the range of $7/8 < x < 1$,
a mixed state including Ca$_{7}$La$_{1}$B$_{48}$ and Ca$_{7}$B$_6$ can be realized.

At finite temperatures, structures other than the ground-state
structures can be realized considering the mixing energies
being on the order of room temperature, but it is still
important to examine the ground-state structures in detail. The
six ground structures excluding the terminal structures are
shown in Figure 4. For simplification, only the atoms for the La
site are shown, and the B$_6$ cluster is not drawn. Figure 4a shows a structure in which 1/8 La atoms are replaced by Ca in
a supercell that is 8 times as that of LaB$_6$ and Ca is arranged
continuously in the c-axis direction. A structure in which 1/6
La atoms are replaced by Ca is shown in Figure 4b. Ca is not
present at the nearest La site. In the structure in Figure 4c, 1/4
La atoms are replaced by Ca. Two Ca atoms are connected in
the c-axis direction in a manner similar to that shown in Figure 4a.
Figure 4d shows a structure in which a half of La atoms are
replaced by Ca, where La and Ca are clustered in the separated
regions. Figure 4e,f shows structures in which 3/4 and 7/8 La
atoms, respectively, are replaced by Ca atoms. These atomic
configurations are opposite to those in Figure 4a,c, where La is
placed apart instead of Ca. Thus, the Ca substitution site in
the most stable structure varies considerably depending on the
fraction of Ca substitution. Figure 4 shows that Ca atoms tend
to locate close to each other. This could cause a local bias in
charge, but because the large anion of the B$_6$ cluster forms a
strong network of sublattice and shields the influence of charge
bias, the structure stays stable. The tendency of Ca to cluster is
thought to be because of the different electronic behaviors of
La and Ca in the B$_6$ sublattice. The shielding of the local
charge is confirmed in the small absolute values of mixing
energies, as shown in Figure 3.

The changes in the plasma frequencies and dielectric
functions of CaB$_6$, LaB$_6$, and the six structures constituting
the most stable state were also examined in detail. Table 1
shows the changes in plasma frequencies of these structures.
The plasma frequency was found anisotropic; thus, the values
in the $x$, $y$, and $z$ directions as well as the averages are listed.
Because trivalent La is substituted by divalent Ca in
Ca$_{7}$La$_{1}$B$_{48}$, it is expected that the number of free electrons
and plasma frequency decrease with increasing Ca content in
a simple random substitution model. Thus, the plasma frequency

Figure 2. Dielectric functions of LaB$_6$ and XB$_6$ (X = Ca, Sr, Ba) derived from first-principles calculations using VASP with a HSE06 hybrid functional.

Figure 3. Results of energy calculations of 762 substitutional configurations showing convex hull in Ca$_{x}$La$_{1-x}$B$_6$.

Figure 4. Ground structure in Ca$_{x}$La$_{1-x}$B$_6$: (a) Ca$_{7}$La$_{1}$B$_{48}$, (b) Ca$_{5}$La$_{1}$B$_{36}$, (c) Ca$_{6}$La$_{1}$B$_{48}$, (d) Ca$_{3}$La$_{1}$B$_{36}$, (e) Ca$_{3}$La$_{1}$B$_{24}$, and (f) Ca$_{7}$La$_{1}$B$_{36}$. The boron sublattice is not drawn for clarity.
LaB$_6$ and the six ground structures. Here, the averaged values \(\varepsilon_z\) respectively, that is, the free electrons can move in the \(z\) direction but not in the \(\varepsilon_x\) and \(\varepsilon_y\) represented by blue and gray lines, respectively. In terms of frequency, considering substitution, similar to the trend observed for plasma shielding materials are CaLa$_7$B$_{48}$, CaLa$_5$B$_{36}$, and Ca$_2$La$_6$B$_{48}$. The range of \(0 < x < 1/4\) for Ca$_x$La$_{1-x}$B$_6$ is preferable because the \(\varepsilon_1\) values of these compositions are small in the visible region, which is an indication of high transparency in the visible region. This study shows that even when La in LaB$_6$ is substituted with a typical element such as Ca, the change in optical properties is not uniform and varies significantly depending on the substitution fraction and structure.

Next, to determine the characteristics of actual nanoparticle dispersions, the absorption efficiency was calculated using the Mie scattering theory. The optical properties of the nanoparticle dispersions depend on various factors, in particular, the particle shape, dielectric function, and their ensemble inhomogeneities, which are known to have a considerable influence on the optical response.$^{12,19,20}$ For LaB$_6$ nanoparticles, the absorption band width has been shown to become 7 times as that of a single spherical particle because of the effect of disk-shaped ensemble inhomogeneity. Lattice defects$^{19}$ introduced during the preparation of nanoparticles are analyzed to reduce the relaxation time and increase the base level of \(\varepsilon_2\), both of which cause their ensemble effects. However, the ensemble inhomogeneity of nanoparticles was ignored in this study as it is outside the scope of this report. An ideal uniform ensemble of spherical particles with an average diameter of 20 nm was assumed, and the absorption efficiency was calculated based on the dielectric function of each structure. For cases where modifications are introduced in the particle shape and/or dielectric function, the corresponding experimental profiles can be predicted by the methods described in refs.$^{12,20,21}$

Table 1. Plasma Frequency of Ca$_x$La$_{1-x}$B$_6$

| composition | \(x\) (eV) | \(y\) (eV) | \(z\) (eV) | average (eV) |
|------------|-------------|-------------|-------------|--------------|
| LaB$_6$    | 3.64        | 3.64        | 3.64        | 3.64         |
| Ca$_2$La$_4$B$_{48}$ | 0.00 | 0.00 | 4.31 | 1.44 |
| Ca$_2$La$_3$B$_{36}$ | 2.63 | 2.63 | 0.00 | 1.75 |
| Ca$_3$La$_2$B$_{36}$ | 3.76 | 3.57 | 4.70 | 4.01 |
| Ca$_2$La$_5$B$_{36}$ | 1.49 | 1.49 | 1.71 | 1.56 |
| Ca$_3$La$_4$B$_{36}$ | 2.44 | 2.44 | 2.44 | 2.44 |
| Ca$_2$La$_6$B$_{48}$ | 2.19 | 2.58 | 1.96 | 2.24 |
| CaB$_6$ | 0.36 | 0.36 | 0.36 | 0.36 |

of CaB$_6$ is close to 0 eV. However, the data included in Table 1 show that the changes in plasma frequencies upon the variation of \(x\) are not uniform. For example, the largest plasma frequency is 4.01 eV for Ca$_2$La$_6$B$_{48}$. Furthermore, anisotropy is particularly prominent in CaLa$_7$B$_{48}$ and CaLa$_5$B$_{36}$. CaLa$_5$B$_{36}$ includes the substitution of 1/8 La atoms, and the plasma frequencies in the \(x\), \(y\), and \(z\) directions are 0.0, 0.0, and 4.3 eV, respectively, that is, the free electrons can move in the \(z\) direction but not in the \(x\) and \(y\) directions.

Figure 5 shows the dielectric functions obtained for CaB$_6$, LaB$_6$, and the six ground structures. Here, the averaged values in the \(x\), \(y\), and \(z\) directions are shown. LaB$_6$ and CaB$_6$ are represented by blue and gray lines, respectively. In terms of \(\varepsilon_z\), LaB$_6$ absorbs weakly in the visible light region, and a high absorption is observed in the low-energy side including \(\omega_{sp}\) of CaLa$_5$B$_{36}$ and Ca$_2$La$_6$B$_{48}$. This study shows that \(\Omega_{sp}\) of the Ca substitution configuration shifts toward lower energy in comparison to that of LaB$_6$. However, the change in \(\Omega_{sp}\) is not uniform with respect to the variation in Ca content, for example, the \(\Omega_{sp}\) values of CaLa$_5$B$_{36}$ and Ca$_2$La$_6$B$_{48}$ are located on the lower side than that of Ca$_2$La$_6$B$_{48}$. To obtain sufficient absorption in the near-infrared region, the \(\Omega_{sp}\) value should be approximately 1.3 eV of CaLa$_5$B$_{36}$ or greater among those corresponding to the ground-state compositions. That is, the compositions that can be employed as solar radiation shielding materials are Ca$_2$La$_4$B$_{48}$, Ca$_2$La$_3$B$_{36}$, and Ca$_3$La$_2$B$_{36}$. The range of \(0 < x < 1/4\) for Ca$_x$La$_{1-x}$B$_6$ is preferable because the \(\varepsilon_1\) values of these compositions are small in the visible region, which is an indication of high transparency in the visible region. This study shows that even when La in LaB$_6$ is substituted with a typical element such as Ca, the change in optical properties is not uniform and varies significantly depending on the substitution fraction and structure.

The dielectric function of Ca$_x$La$_{1-x}$B$_6$ does not show a uniform change with variation in the amount of Ca substitution, similar to the trend observed for plasma frequency. Considering \(\varepsilon_z\), the absorption in the visible region generally decreases with an increase in the amount of Ca substitution, and the transparency in the visible region tends to improve. However, the Ca$_3$La$_2$B$_{36}$ and Ca$_2$La$_6$B$_{48}$ compositions with 25 and 50% Ca substitution, respectively, show higher absorptions in the visible region than LaB$_6$, whereas Ca$_4$La$_3$B$_{14}$ shows a weaker absorption than Ca$_2$La$_6$B$_{48}$. These phenomena originate from the high anisotropy because of the Ca substitution configurations.

In the real part of the dielectric function, LaB$_6$ has \(\varepsilon_1(\omega) = 0\) on the highest energy side among the other compositions. This shows that \(\Omega_{sp}\) of Ca$_x$La$_{1-x}$B$_6$ shifts toward lower energy in comparison to that of LaB$_6$. However, the change in \(\Omega_{sp}\) is not uniform with respect to the variation in Ca content, for example, the \(\Omega_{sp}\) values of CaLa$_5$B$_{36}$ and Ca$_2$La$_6$B$_{48}$ are located on the lower side than that of Ca$_2$La$_6$B$_{48}$. To obtain sufficient absorption in the near-infrared region, the \(\Omega_{sp}\) value should be approximately 1.3 eV of CaLa$_5$B$_{36}$ or greater among those corresponding to the ground-state compositions. That is, the compositions that can be employed as solar radiation shielding materials are Ca$_2$La$_4$B$_{48}$, Ca$_2$La$_3$B$_{36}$, and Ca$_3$La$_2$B$_{36}$. The range of \(0 < x < 1/4\) for Ca$_x$La$_{1-x}$B$_6$ is preferable because the \(\varepsilon_1\) values of these compositions are small in the visible region, which is an indication of high transparency in the visible region. This study shows that even when La in LaB$_6$ is substituted with a typical element such as Ca, the change in optical properties is not uniform and varies significantly depending on the substitution fraction and structure.

Next, to determine the characteristics of actual nanoparticle dispersions, the absorption efficiency was calculated using the Mie scattering theory. The optical properties of the nanoparticle dispersions depend on various factors, in particular, the particle shape, dielectric function, and their ensemble inhomogeneities, which are known to have a considerable influence on the optical response.$^{12,19,20}$ For LaB$_6$ nanoparticles, the absorption band width has been shown to become 7 times as that of a single spherical particle because of the effect of disk-shaped ensemble inhomogeneity.$^{12}$ Lattice defects$^{19}$ introduced during the preparation of nanoparticles are analyzed to reduce the relaxation time and increase the base level of \(\varepsilon_2\), both of which cause their ensemble effects. However, the ensemble inhomogeneity of nanoparticles was ignored in this study as it is outside the scope of this report. An ideal uniform ensemble of spherical particles with an average diameter of 20 nm was assumed, and the absorption efficiency was calculated based on the dielectric function of each structure. For cases where modifications are introduced in the particle shape and/or dielectric function, the corresponding experimental profiles can be predicted by the methods described in refs.$^{12,20,21}$

Figure 5. (a) Real and (b) imaginary parts of the calculated dielectric functions of the ground structures in Ca$_x$La$_{1-x}$B$_6$. Crystal anisotropy is ignored, and only the averaged profiles are shown.
relative transmission in the visible region did not improve.

whereas for preserving the plasmon absorption in the near-infrared region, transmittance in the visible light region improved while an appropriate synthesis method. For deviations in the non-spherical shape and high relaxation time accompanying ensemble inhomogeneity that are likely introduced in the mechanical production process, the plasmon absorption band should be peaked at the longer-wavelength side with a broader full width at half-maximum, where the composition, CaLa7B48 and CaLa5B36, could be an attractive choice. For calculations, including the effects of nonspherical particle shape, lattice defects, surface modifications, internal stress, and their ensemble inhomogeneity effects, methods are detailed in the previous researches.12,19–21

Figure 6a shows the absorption efficiencies of LaB6, CaLa7B48, CaLa5B36, and Ca2La6B48 nanoparticles of size 20 nm. Therefore, the compositions with 0 < x < 1/4 in CaLa1−xB6 were preferred as solar shielding materials. In general, the physical properties of the substituted composite compounds are effectively analyzed by using this approach, that is, the ground structures are extracted by creating a convex hull through an exhaustive and comprehensive evaluation of low-energy substitution configurations.

Figure 6b shows the absorption efficiency normalized by the near-infrared LSPR absorption. The CaLa7B48 and CaLa5B36 nanoparticles show significantly enhanced transparencies at high wavelengths in the visible region and intensified broadband absorptions in the near-infrared region. In comparison to LaB6, the color tint and transparency significantly improve in addition to an enhanced NIR absorption. The uniform ensemble of the spherical nanoparticles assumed in the present analysis can be produced experimentally by selecting an appropriate synthesis method. For deviations in the non-spherical shape and high relaxation time accompanying ensemble inhomogeneity that are likely introduced in the mechanical production process, the plasmon absorption band should be peaked at the longer-wavelength side with a broader full width at half-maximum, where the composition, CaLa7B48 and CaLa5B36, could be an attractive choice. For calculations, including the effects of nonspherical particle shape, lattice defects, surface modifications, internal stress, and their ensemble inhomogeneity effects, methods are detailed in the previous researches.12,19–21

Figure 6. (a) Absorption efficiencies and (b) absorption efficiencies normalized by LSPR absorption peak calculated using the Mie scattering theory for LaB6, CaLa7B48, CaLa5B36, and Ca2La6B48 spherical nanoparticles of size 20 nm.

METHODS

Vienna ab initio simulation package (VASP)26–29 was used for the first-principles calculations. As the exchange–correlation functional, a hybrid HSE06 functional30 that reproduced the band gap with high accuracy was used.

The dielectric function ε(ω) that determines the optical characteristics is composed of the real part ε1(ω) and imaginary part ε2(ω), as shown in eq 1, which are interrelated through the Kramers–Krönig equation (eq 2).

\[ \varepsilon_2(\omega) = \varepsilon_1(\omega) + \omega^2 \frac{d\varepsilon_2(\omega)}{d\omega} \]  

\[ \varepsilon_1(\omega) = 1 + \frac{2}{\pi} \int_0^\infty \frac{\varepsilon_2(\omega')\omega'}{\omega^2 - \omega'^2} d\omega' \]  

ε2(ω) of the dielectric function corresponds to the absorption of photons by electrons and is composed of the Lorentz term, which is the contribution of the interband transition shown in eq 3, and the Drude term, which is the contribution of free electrons.

\[ \varepsilon_2^{\text{Lorentz}}(\omega) = \frac{4\pi^2 \hbar^2}{V} \lim_{\omega \to 0} \sum_{\varepsilon_k} \frac{1}{\omega^2} \int_{-\infty}^{\infty} \frac{2\omega_k \delta(E_{\varepsilon_kq} - E_{\varepsilon_{k+q}} - \omega)}{\left< \hat{u}_{\varepsilon_{k+q}} \hat{u}_{\varepsilon_k} \right>^2 \left< \hat{u}_{\varepsilon_{k+q}} \hat{u}_{\hat{u}_{\varepsilon_k}} \right>} \]  

where V is the unit cell volume; c and v are subscripts indicating the valence band and conduction band, respectively; E is the energy level; \( \varepsilon \) is the unit vector; \( \mu \) is the periodic part of the orbit; and \( \omega_k \) is the weight of the k points.31

LaB6 is a conductor whose Fermi energy crosses the conduction band. Therefore, in addition to the Lorentz term, \( \varepsilon_2^{\text{Lorentz}}(\omega) \), the Drude term is also required. Especially at low energies, the Drude term becomes dominant over the Lorentz term, thereby dictating the low-energy behaviors with the analytical expression of the Drude term.

\[ \varepsilon_2(\omega) = \varepsilon_2^{\text{Lorentz}}(\omega) + \varepsilon_2^{\text{Drude}}(\omega) \]  

\[ \varepsilon_2^{\text{Drude}}(\omega) = \frac{n_e^2}{\hbar^2} \frac{2\pi}{V} \sum_{\varepsilon_k} \frac{1}{\omega^2} \int_{-\infty}^{\infty} \frac{2\omega_k \delta(E_{\varepsilon_kq} - E_{\varepsilon_{k+q}} - \omega)}{\left< \hat{u}_{\varepsilon_{k+q}} \hat{u}_{\varepsilon_k} \right>^2 \left< \hat{u}_{\varepsilon_{k+q}} \hat{u}_{\hat{u}_{\varepsilon_k}} \right>} \]  

CONCLUSIONS

An alkaline-earth hexaboride was studied as a replacement material to improve the transparency of LaB6 by first-principles calculations, and CaB6 was selected. The most stable structures of CaLa1−xB6 among 762 substitutional configurations with different compositions were comprehensively searched, and eight basic ground structures were found. Examinations of the optical characteristics of the ground structures using high-precision calculations revealed that the influence of Ca substitution varied significantly, depending on the substitutional positions and fractions, and the changes in the optical characteristics were not uniform. It was determined that in the range of 0 < x < 1/4 in CaLa1−xB6, the transmittance in the visible region improved while preserving the plasmon absorption in the near-infrared region, whereas for x > 1/4, the plasmon absorption weakened and the relative transmission in the visible region did not improve.
the measured dielectric functions in LaB$_6$ including the low-energy region.\textsuperscript{18} The Drude term can be written as eq 5 and 6 using the plasma frequency $\omega_p$, shown in eq 4, and relaxation time $\tau = 1/\gamma$.

$$\omega_p = \frac{ne^2}{\varepsilon_0 m^*} \frac{4\pi^2}{V} \sum f_{\text{loc}} \frac{\partial^2 E}{\partial k \partial k}$$  \hspace{1cm} (4)

$$\varepsilon_1^{\text{Drude}}(\omega) = 1 - \frac{\omega_p^2}{\omega^2 + \gamma^2}$$  \hspace{1cm} (5)

$$\varepsilon_2^{\text{Drude}}(\omega) = \frac{\omega_p^2 \gamma}{\omega^2(\omega^2 + \gamma^2)}$$  \hspace{1cm} (6)

where $f$ is the Fermi–Dirac distribution function, $n$ is the free electron density, $e$ is the charge of the electron, $\varepsilon_0$ is the permittivity of the vacuum, and $m^*$ is the effective mass of the electron.\textsuperscript{19}

The plasma frequency can be obtained from the band structure using eq 4. The relaxation time $\tau = 1/\gamma$ represents the scattering effect because of the electron–phonon, electron–electron, and electron–lattice defect interactions; however, the influence on the dielectric function because of the fluctuation of $\gamma$ is not very large,\textsuperscript{18} such that we set $\hbar \tau = 0.1$ eV in this study.

An infinite number of Ca-substituted configurations exist in the Ca$_{x}$La$_{1-x}$B$_6$ structure. The possible substitutional configurations depend on the size of the supercell. Therefore, in this study, the supercell size was increased stepwise; the LaB$_6$ primitive cell was doubled, tripled, and eventually expanded up to 8 times the primitive cell. First-principles calculations were performed for all 762 structures of Ca$_{x}$La$_{1-x}$B$_6$, which covered all the possible substitutional configurations assumed in all supercells that were up to 8 times the primitive cell and containing 56 atoms. In this step, the generalized gradient approximation-Perdew–Burke–Ernzerhof functional was used as the exchange–correlation functional. The crystal size, shape, and atomic position were fully relaxed. The $x$-dependence of the most stable energy state of Ca$_{x}$La$_{1-x}$B$_6$ that is, the convex hull, was obtained, and the most stable structure at each substitutional fraction $x$ was identified. Thereafter, for each of the most stable structures obtained, high-precision band structure calculation using the HSE06 functional was performed to derive the optical characteristics. For executing the automatic expansion and replacement operations of the primitive cells, the cluster expansion program ICET\textsuperscript{13} was used.

**AUTHOR INFORMATION**

**Corresponding Author**

Satoshi Yoshio – Department of Computer-Aided Engineering and Development, Sumitomo Metal Mining Co., Ltd., Nishima 792-0001, Japan; orcid.org/0000-0002-7820-878X; Email: satoshi.yoshio.w5@smm-g.com

**Author**

Kenji Adachi – Ichikawa Research Center, Sumitomo Metal Mining Co., Ltd., Ichikawa 272-8588, Japan; orcid.org/0000-0003-0487-3442

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.9b03323

**Notes**

The authors declare no competing financial interest.

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