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## Tunable Light Emission through the Range 1.8–3.2 eV and p-Type Conductivity at Room Temperature for Nitride Semiconductors, $Ca(Mg_{1-x}Zn_x)_2N_2$ (x = 0–1)

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#### **S** Supporting Information

ABSTRACT: The ternary nitride CaZn<sub>2</sub>N<sub>2</sub>, composed only of earth-abundant elements, is a novel semiconductor with a band gap of ~1.8 eV. First-principles calculations predict that continuous Mg substitution at the Zn site will change the optical band gap in a wide range from  $\sim 3.3-1.9$  eV for  $Ca(Mg_{1-x}Zn_x)_2N_2$  (x = 0-1). In this study, we demonstrate that a solid-state reaction at ambient pressure and a highpressure synthesis at 5 GPa produce x = 0 and 0.12 and 0.12 <  $x \leq 1$  polycrystalline samples, respectively. It is experimentally confirmed that the optical band gap can be continuously tuned from  $\sim$ 3.2 to  $\sim$ 1.8 eV, a range very close to that predicted by



theory. Band to band photoluminescence is observed at room temperature in the ultraviolet-red region depending on x. A 2% Na doping at the Ca site of  $Ca(Mg_{1-x}Zn_x)_2N_2$  converts its highly resistive state to a p-type conducting state. Particularly, the x =0.50 sample exhibits intense green emission with a peak at 2.45 eV (506 nm) without any other emission from deep-level defects. These features meet the demands of III-V group nitride and arsenide/phosphide light-emitting semiconductors.

#### INTRODUCTION

Rapid exploration of novel functional materials, composed only of earth-abundant elements, has been urgently required for the future realization of a sustainable society. Furthermore, such functional materials will lead to highly efficient energy conversion, storage, and optoelectronic functionalities, such as electron transport and light emission, and will be able to replace those materials currently being used, such as heavy, rare, and toxic elements. To fulfill such a role, nitrides are promising candidates because they are environmentally benign and remain unexplored in comparison with other materials systems, such as oxides, chalcogenides, and pnictides (e.g., arsenides and phosphides). The primary reason for such exploration results from the very high stability of a nitrogen molecule with a triple bond in comparison with an oxygen molecule, chalcogen, or pnictogen. N2 is therefore inactive even at high temperatures and under high pressures without appropriate catalysts, which has led to the historical reluctance for the wider exploration of nitrides in comparison with other compounds, in addition to very successful research on III-V group nitrides, because one may easily use solid reagent sources in cases of oxides, chalcogenides, and pnictides. This is the reason associated with the requirements of more active nitrogen sources, such as ammonia and discharged plasma, for novel nitride research. Thus, the currently commercialized nitride semiconductors have mostly been limited to III-V group nitrides, GaN, and its solid solutions, with appropriate band gaps intentionally tuned by solid-solution alloying techniques.

A light-emitting semiconductor with electron current injection is one of the key components in practical optoelectronic devices. Although such components have been commercially used, especially the III-V group semiconductors, such as (Ga,Al,In)N- and (Ga,Al,In)(As,P)-based materials, there remains a strong demand for next-generation materials to exhibit higher performance in terms of light brightness, quantum efficiency, and color accuracy (i.e., emission bandwidth).<sup>1</sup> However, irrespective of the rapid growth in science and technology, light-emitting semiconductors have a serious issue, the so-called green gap problem, where the emission quantum efficiency drastically decreases to ca. 20% in the particular wavelength region around green light, even for the practical III-V group based light-emitting diodes.<sup>2</sup> This is mainly because of the large in-plane lattice mismatch between In-based III-V nitrides and single-crystal substrates and the thermal instability of In-based III-V nitrides. Thus, no highly efficient green-light-emitting semiconductor material has yet



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been realized for next-generation optoelectronic devices. Therefore, it is necessary to explore and discover novel semiconductor materials, which possibly have higher thermal stability and more compatible in-plane lattice mismatches with III–V group nitrides, with a high quantum efficiency of light emission in the green wavelength region (band gap 2.3–2.5 eV, wavelength  $\lambda = 500-550$  nm).

Recent progress of materials informatics, which combines comprehensive first-principles calculations with experimental validations, has led to an acceleration in the discoveries and/or predictions of novel ternary nitride semiconductors, such as  $Cu(Nb,Ta)N_{2,3}^{3}$  LaWN<sub>3,4</sub> and CaZn<sub>2</sub>N<sub>2,5</sub> which were all previously unknown. Therefore, materials informatics provides the possibility to overcome the aforementioned historical lack of exploration research of novel functional nitride compounds. CaZn<sub>2</sub>N<sub>2</sub> was predicted through such an approach and was proposed with experimental validation as a novel promising optoelectronic functional nitride semiconductor with a band gap of  $\sim 1.8$  eV because of its small electron and hole effective masses and direct transition-type energy band structure with a wide tunability of its optical band gap of isomorphism nitrides by an alloying technique similar to III-V group semiconductors. In ref 5, it was predicted that the band gaps could be widely tuned from  $\sim 3.3$  eV (for CaMg<sub>2</sub>N<sub>2</sub>, i.e., ultraviolet region) to ~1.6 eV (for  $SrZn_2N_2$ ) and ~0.4 eV (for  $CaCd_2N_2$ ) (i.e., red-infrared region) by solid-solution alloying at both the Ca and Zn sites. This prediction indicates that this nitride is a promising host candidate as a light-emitting semiconductor with high electron and hole transport properties in the widely tunable ultraviolet-infrared wavelength region.

In this study, we focused on an earth-abundant Ca- $(Mg_{1-x}Zn_x)_2N_2$  (x = 0-1) complete solid-solution nitride system because its band gap is controllable in the range of ~1.9 to ~3.3 eV, following the computational prediction. Here we experimentally report the validity of the prediction; that is, its band gap is tunable, the x = 0.50 sample exhibits an intense green emission without deep defect emission even at room temperature, and it can be doped to a p-type semiconductor by 2% Na doping at the Ca site.

#### STRUCTURE AND PHASE PURITY OF Ca $(Mg_{1-x}Zn_x)_2N_2$ (x = 0-1)

Figure 1a shows XRD patterns of polycrystalline Ca- $(Mg_{1-x}Zn_x)_2N_2$  (x = 0-1). The results of Rietveld analysis are summarized in Figure S1. We confirmed that the main crystalline phase of all the samples had the same crystal structure as that of both end members, CaMg<sub>2</sub>N<sub>2</sub><sup>6</sup> and  $CaZn_2N_{22}$  which consisted of a hexagonal structure of a trigonal system with  $P\overline{3}m1$  (No. 164): that is, the successful fabrication of complete solid-solution samples between x = 0and 1. With an increase in *x*, the three diffraction peaks of  $10\overline{1}1$ and  $01\overline{11}$ ,  $10\overline{12}$  and  $01\overline{12}$ , and 0003 of the Ca(Mg<sub>1-x</sub>Zn<sub>x</sub>)<sub>2</sub>N<sub>2</sub> main phase, which are surrounded by dotted squares in Figure 1a, were continuously shifted to higher  $2\theta$  positions. Corresponding to this peak shift, both the a and c axis lattice parameters shrank with increasing x [(see Figure 1b). In comparison with the calculated results by first-principles structure relaxation,<sup>5</sup> the absolute values of both end members (x = 0 and 1) and their variation trend with a change in x agreed well with each other, although the calculated values were slightly smaller than the observed values. Because the ionic radii of  $Mg^{2+}$  and  $Zn^{2+}$  are almost the same, that is, 57 pm



Figure 1. Structure, crystalline phase, and composition of Ca- $(Mg_{1-x}Zn_x)_2N_2$  (x = 0-1) polycrystalline samples obtained. (a) XRD patterns. The three dashed rectangles denote areas of the diffraction peak positions, which are assigned as  $10\overline{1}1$  and  $01\overline{1}1$  ( $2\theta = 32.6-$ 33.3°), 1012 and 0112 (41.7-42.5°), and 0003 (44.6-45.1°) diffractions from the  $Ca(Mg_{1-x}Zn_x)_2N_2$  main phase with a hexagonal structure of a trigonal system with P3m1. Diffraction peak positions of Zn, Mg<sub>3</sub>N<sub>2</sub>, CaO, and MgO impurities are indicated at the bottom by vertical bars. A small amount of BN, which is the material of the capsules in the high-pressure cells, was observed at the vertical arrow positiona (~26.8°). (b) Lattice parameters a and c as a function of x. Closed circles and triangles are a and c obtained in this study, respectively. Open circles and triangles are the calculated results with their structure relaxation reported in ref 5. Straight lines are shown on the assumption of Vegard's law between both end members. (c) Volume fraction of the main phase and impurities as a function of *x*. All of the data are taken from the results of the Rietveld analysis. The fitted raw results are provided in Figure S1.

for  $Mg^{2+}$  and 60 pm for  $Zn^{2+}$  in the case where the coordination number is 4,<sup>7</sup> this variation trend with changing x implied that the chemical bond between (Mg,Zn) and N was more covalent than ionic because the covalent bond radius of Zn is slightly smaller than that of Mg. Note that a small amount of BN was observed at  $2\theta \approx 26.8^{\circ}$ , which is indicated by vertical arrows in Figure 1a. It was very difficult to completely remove this BN impurity in some samples because a high pressure and a high temperature of 5.0 GPa and 1300 °C were applied to the mixed-powder disks tightly contacted with capsules made of BN in the high-pressure cells. However, this thin BN impurity located only around the outside wall of the resulting disk samples, that is, the BN impurity, did not diffuse inside the bulk region of the samples. It should be noted that we observed the phase stability in air at room temperature became strong with increasing *x*, that is, the x = 0sample was unstable in air because it decomposed into the amorphous-like hydroxide  $Ae(OH)_2$  (Ae = Mg, Ca) just after air exposure, which is similar to the result reported on the binary nitride precursors  $Mg_3N_2$  and  $Ca_3N_2$ .<sup>8</sup> In contrast, the x  $\geq$  0.50 samples were stable at room temperature in air. In

addition, the sample purity strongly depended on the x content. The volume fraction of the main phase and impurity concentration for each x sample are summarized in Figure 1c. The phase purity of the x = 0 sample was the best (~90%) among all the x contents. Addition of Zn decreased the volume fraction of the main phase to 50–60% for the x = 0.29-1 samples. Accordingly, the Mg<sub>3</sub>N<sub>2</sub> impurity slightly increased up to ~20% at x = 0.29, and the metal Zn impurity drastically increased at  $x \ge 0.69$ .

# • OPTICAL PROPERTIES OF $Ca(Mg_{1-x}Zn_x)_2N_2$ (x = 0-1)

Figure 2 shows the optical properties of polycrystalline  $Ca(Mg_{1-x}Zn_x)_2N_2$  (x = 0-1) at room temperature. With an increase in x, the absorption edge (nearly equal to the optical band gap energy in this case) continuously shifted to the lower energy side from ~3.2 to ~1.8 eV (see black slope lines for  $(\alpha h\nu/s)^2$  versus  $h\nu$  plots (data plotted by solid lines) in Figure 2a). This continuously controllable band gap agreed well with



**Figure 2.** Optical properties of  $Ca(Mg_{1-x}Zn_x)_2N_2$  (x = 0-1) polycrystalline samples at room temperature. (a) PL (open circles) and R (= $\alpha/s$ , solid lines) spectra. The dashed lines are the results of the deconvolution of PL spectra. The PL peak positions arising from band to band transitions are shown by vertical bars. The black slope lines for  $(\alpha h\nu/s)^2$  versus  $h\nu$  plots are used to estimate the absorption edges. A vertical arrow in the x = 0.29 spectrum indicates an emission band from a BN impurity. (b) Optical band gaps determined on the basis of the plots of  $(\alpha h\nu/s)^2$  versus  $h\nu$  in (a) as a function of x. The calculated values (open circles) by the HSE06 hybrid functional, reported in ref 5, are shown for comparison.

the calculated results by the Hevd-Scuseria-Ernzerhof (HSE06) hybrid functional,<sup>5</sup> although all of them were slightly lower than the calculated values (see Figure 2b). Accordingly, band to band PL originating from each band gap was clearly observed even at room temperature (see open circles and vertical bars in Figure 2a). For the x = 0 sample, an additional large and broad emission band that peaked at  $\sim 2.6$  eV was observed. The decay curve of this emission band was decomposed into two components, which were a relatively short component of <~30 ns and a longer component of ~670 ns (see Figure S2). Although the exact origins of these two lifetimes were unclear, we propose possible origins. The former could be related to a small amount (7 mol %) of the  $Mg_3N_2$ impurity because the energy position is close to the band gap of  $Mg_3N_2$  (~2.5 eV)<sup>9</sup> or PL originating from recombination of holes and electrons at in-gap state defects in Mg<sub>3</sub>N<sub>2</sub>.<sup>10</sup> The latter could originate from defects such as donor-acceptor pairs in CaMg<sub>2</sub>N<sub>2</sub> because the sample has a defective polycrystalline nature and the lifetime of  $\sim$ 670 ns is close to those of donor-acceptor pairs with a short donor-acceptor distance  $\ll 10$  nm of conventional semiconductors.<sup>11</sup> For the *x* = 0.29 sample, we confirmed that the emission lifetime of an emitting band that peaked at  $\sim 2.8$  eV was  $\sim 7$  ns (see Figure \$3), which is comparable to the pulse width of the excitation laser we used: that is, the exact lifetime could not be estimated by this experiment. However, the information on a short lifetime was sufficient to assign it to a band to band transition. Therefore, we concluded that the  $\sim$ 2.8 eV PL band originates from a band to band emission for x = 0.29. In addition, an emission band that peaked at a  $\sim$ 3.1 eV was observed. This PL originated from the BN impurity,<sup>12</sup> because we also observed the same emission band from the x = 0.50 and 0.69 samples when we set the observation wavelength region of the spectrometer around this region (data not shown) and a small amount of BN impurity was commonly observed in these three samples in their XRD patterns (see vertical arrows at  $2\theta$ =  $\sim 26.8^{\circ}$  in Figure 1a). Consequently, on the basis of the above experimental optical properties at room temperature, we continuously and widely tuned the optical band gaps and emission bands from ~3.2 eV ( $\lambda$  = ca. 390 nm, ultraviolet region) to ~1.8 eV (ca. 670 nm, red region) in complete solidsolution samples of  $Ca(Mg_{1-x}Zn_x)_2N_2$  (x = 0-1). In particular, it should be noted that the x = 0.50 sample exhibited intense green light emission that peaked at  $\sim$ 506 nm ( $\sim$ 2.45 eV) even at room temperature.

In this study, we focused on light-emitting semiconductors in the green color region (i.e., band gap 2.3–2.5 eV,  $\lambda = 500-$ 550 nm). Thus, we examined the PL properties of the x = 0.50sample in more detail because the PL band was located in the appropriate wavelength region for green emission. Figure 3a shows the temperature dependence of the PL spectra. We observed three emission bands, A-C. Band A originated from a small amount of a BN impurity,<sup>12</sup> as discussed in the last section. Band B was assigned to a band to band transition because the emission peak position at 300 K was almost the same as that of the absorption edge observed in Figure 2a. Band C arose from deep-level defects and/or impurity phases because the energy difference between B and C was ~200 meV at 20 K, although the origin was unclear because the emission peak energy of band C did not depend on the measurement temperature and almost disappeared at ≥150 K. Because a similar temperature dependence has been reported for a Mg acceptor in GaN:Mg,<sup>13</sup> band C could have similar origins: that



**Figure 3.** (a) Temperature dependence of PL spectra of the  $Ca(Mg_{1-x}Zn_x)_2N_2$  (x = 0.50) polycrystalline sample. The dashed lines are deconvolution results of each PL spectrum. Note that the spectrum at 300 K is the same as that for x = 0.50 in Figure 2a. (b) PL peak energy (squares, left axis) and normalized PL intensity (circles, right axis) of band B originating from band to band transition as a function of measurement temperature. The vertical arrow indicates the position of an anomalous blue shift between 75 and 100 K.

is, point defects trapped at doped-impurity sites (e.g., band to impurity transitions). Owing to the band to band recombination, the energy of band B shifted to the lower energy side with increasing temperature from 2.49 eV at 20 K to 2.45 eV at 300 K (see Figure 3b). At 75–100 K, an anomalous PL peak shift from 2.48 to 2.49 eV (i.e., a blue shift with increasing temperature) was observed. The possible origin of this anomalous shift was a result of a transition from bound excitons to free excitons, as observed in room-temperatureexciton (i.e., electron-hole pairs stable at room temperature) materials, such as ZnO<sup>14</sup> and LaCuOS;<sup>15</sup> whereas details of its origin should be discussed using more high resolution and continuous wave excited PL measurements on higher quality samples, such as single crystals and epitaxial films. The PL intensity was decreased by approximately 1 order of magnitude from 20 to 300 K, owing to temperature deactivation (see Figure 3b). The origin of this temperature quenching would be defects originating from the polycrystalline nature of the sample. However, the emission observed in the x = 0.50sample shown in Figure 2a was also clearly observed at room temperature. Next, we examined the emission lifetime of bands B and C. The estimated lifetimes at 20 K were ~2 ns for band B and ~250 ns for band C (see Figure S4). Because the pulse width of the excitation Nd:YAG we used was ~7 ns, the lifetime of band B could not be exactly estimated. This result suggested that the emission band B originated from bound/ free excitons because the lifetime was sufficiently shorter than several nanoseconds. The relatively fast lifetime of  $\sim$ 250 ns for band C was roughly consistent with the origin proposed above, that is, point defects trapped at doped-impurity sites, because the lifetime of the Mg acceptor in GaN:Mg has been reported

to be on the sub-nanosecond order.<sup>16</sup> However, these above assignments are tentative and speculative possibilities.

### ELECTRONIC TRANSPORT PROPERTIES OF Na 2% Doped $(Ca_{1-y}Na_y)(Mg_{1-x}Zn_x)_2N_2$ (x = 0.67 and y = 0.02)

Although Na-undoped  $(Ca_{1-y}Na_y)(Mg_{1-x}Zn_x)_2N_2$  (x = 0-1and y = 0) samples were all too highly resistive to allow measurement of the electrical conductivity (much higher than  $10^6 \Omega$  cm), 2% Na doping exhibited measurable conductivity. Figure 4a shows an enlargement of the strongest  $10\overline{11}$  and



**Figure 4.** Structure and electronic transport properties of the  $(Ca_{1-y}Na_y)(Mg_{1-x}Zn_x)_2N_2$  (x = 0.67 and y = 0.02) polycrystalline sample. (a) XRD diffraction pattern around  $10\overline{1}1$  and  $01\overline{1}1$  (red pattern), which is the strongest peak of the main phase. The peak of the undoped sample (black pattern) is plotted for comparison. (b) Temperature dependence of electrical resistivity ( $\rho$ ). The inset shows thermoelectric power ( $\Delta V$ ) as a function of difference in temperature ( $\Delta T$ ) at room temperature (RT), revealing successful carrier doping and its p-type electrical conductivity at room temperature.

0111 peak region  $(2\theta \approx 33^\circ)$  in the XRD pattern of the Na 2% doped polycrystalline sample. The Rietveld analysis result is shown in Figure S5. The main phase purity was low, 25%, while those of Zn and Mg<sub>3</sub>N<sub>2</sub> impurities that might possibly exhibit electrical conduction were also small, 8% and 15%, respectively. Thus, it was considered that such small amounts of possibly electrical conductive impurities should not dominate the electrical conduction of the sample. Irrespective of almost the same ionic radii of Ca<sup>2+</sup> and Na<sup>+</sup>, the XRD peak slightly shifted to the higher  $2\theta$  side by Na doping, which indicated its lattice shrinkage. Although the undoped sample with  $x \ge 0.5$  was chemically stable, the Na-doped sample with  $x \ge 0.5$  was quite sensitive to air exposure. As observed in Figure S5, Na substitution at the Ca site would be the assertive doping process for the main crystalline phase because phase separation of CaMg<sub>2</sub>N<sub>2</sub> is observed only in this Na-doped sample and higher concentration doping did not work effectively. The temperature dependence of  $\rho$  exhibited a thermally activated type behavior, which implied that metallic zinc did not contribute to the electronic conduction. The inset of Figure 4b is the result of a thermoelectric power

measurement at room temperature. These data indicate p-type electrical conduction with a positive Seebeck coefficient of +2.3  $\mu$ V/K. The absolute value of this Seebeck coefficient seems to be too low for semiconductors; however, as discussed above, the amounts of impurity phases observed are too small to contribute electrical conduction of this sample by considering percolation threshold ( $\sim$ 30% in three-dimensional volume). Therefore, we concluded that this positive sign of Seebeck coefficient comes from the Na-doped main crystalline phase. However, the activation energy estimated using an Arrhenius plot (see Figure S6) was ~330 meV, which suggested that relatively deep acceptor levels formed within the energy band gap upon Na doping. We also tried n-type carrier doping by adding La or Y to the Ca site, but no enhancement of electrical conduction was observed. Finally we tried to measure PL spectra of this Na-doped sample, but no PL could be observed. This is due to easy degradation of the surface arising from very high sensitivity to the ambient atmosphere. These results indicated that we could successfully obtain a p-type semiconducting sample with an appropriate band gap near green emission by selecting proper x and Na doping amounts.

#### CONCLUSION

In summary, we synthesized  $Ca(Mg_{1-x}Zn_x)_2N_2$  (x = 0-1) by a conventional solid-state reaction for x = 0 and 0.12 and highpressure synthesis at 5 GPa for 0.12 <  $x \le 1$  in  $Ca(Mg_{1-x}Zn_x)_2N_2$ .<sup>17</sup> It was experimentally validated that the optical band gaps can be tuned continuously from  $\sim$ 3.2 to ~1.8 eV. Owing to the direct transition type band structure, ultraviolet-red photoluminescence was clearly observed in the entire x = 0-1 region even at room temperature. p-type electrical conduction was also demonstrated by 2% Na doping at the Ca site. Especially, the sample with x = 0.50 exhibited an intense green emission, which is strongly demanded in III-V group light-emitting semiconductors. On the basis of this achievement, the important issues of this new material series for future application as light-emitting or photovoltaic devices are growth of high-quality single-crystalline films by conventional vapor phase epitaxy methods such as molecular beam epitaxy and chemical vapor deposition and fabrication of a p-n heterojunction using them.

#### EXPERIMENTAL METHODS

Three polycrystalline binary nitrides, calcium nitride  $(Ca_3N_2)$ , magnesium nitride  $(Mg_3N_2)$ , and zinc nitride  $(Zn_3N_2)$ , were used as starting precursors for undoped  $(Ca_{1-y}Na_y)(Mg_{1-x}Zn_x)_2N_2$  (x = 0-1, y = 0; i.e., not hole carrier doped) polycrystalline samples. Ca<sub>3</sub>N<sub>2</sub> powder was synthesized by heating Ca metal (purity 99.99%), which was put on a rolled Fe foil in a silica-glass tube, at 900 °C for 10 h under a N<sub>2</sub> gas flow atmosphere (G1 grade, flow rate of N<sub>2</sub> gas 100 mL/min). For Mg<sub>3</sub>N<sub>2</sub> powder, Mg metal (purity 99.5%) was reacted with  $N_2$  gas in almost the same manner as that of the  $\mbox{Ca}_3N_2$ precursor. All of these processes, including heating, were performed in an Ar-filled glovebox (oxygen concentration  $\leq 0.0$  ppm, dew point <-100 °C) without exposure to air because both the binary nitrides are sensitive to air; that is, the silica-glass tube furnace was directly connected to the glovebox. Such a direct nitridization process of alkali-earth metals under an N2 atmosphere is similar to previous reports.<sup>18,19</sup> The Zn<sub>3</sub>N<sub>2</sub> powder we used was a commercially available product (purity 99%). Colors of the precursor powders were rubric black for  $Ca_3N_2$ , dark chrome yellow for  $Mg_3N_2$ , and gray for  $Zn_3N_2$ , which were roughly consistent with their reported optical band gaps of ~1.5 eV for  $Ca_3N_2$ ,  $^{20}$  ~2.5 eV for  $Mg_3N_2$ ,  $^9$  and ~0.85 eV for Zn<sub>3</sub>N<sub>2</sub>.<sup>21</sup> Ca<sub>3</sub>N<sub>2</sub> and Mg<sub>3</sub>N<sub>2</sub> powders were synthesized just before

mixing and heating experiments for syntheses of  $Ca(Mg_{1-x}Zn_x)_2N_2$  (x = 0-1) and were completely used within 2 days, as it was difficult to store them without degradation even in the glovebox for a long time, such as ~1 week.

To synthesize polycrystalline Ca(Mg<sub>1-x</sub>Zn<sub>x</sub>)<sub>2</sub>N<sub>2</sub> (x = 0 and 0.12), a conventional solid-state reaction was employed. Stoichiometric mixtures of Ca<sub>3</sub>N<sub>2</sub>, Mg<sub>3</sub>N<sub>2</sub>, and Zn<sub>3</sub>N<sub>2</sub> precursor powders with molar ratios of Ca<sub>3</sub>N<sub>2</sub>:Mg<sub>3</sub>N<sub>2</sub>:Zn<sub>3</sub>N<sub>2</sub> = 1:2(1-x):2x were pressed into disks (size: diameter of ~6 mm and height of ~7 mm) in the glovebox, which were sealed in Ar-filled stainless tubes, followed by a heating process at 1050 °C for 24 h, as has previously been reported for CaMg<sub>2</sub>N<sub>3</sub>.<sup>6</sup>

In contrast, to synthesize Zn-substituted nitrides with higher x $Ca(Mg_{1-x}Zn_x)_2N_2$  (0.12 <  $x \le 1$ ) solid solutions, we used a belt-type high-pressure apparatus<sup>22</sup> to realize a high nitrogen chemical potential during the chemical reaction between precursors in the high-pressure cells. Stoichiometric mixtures of each binary precursor were pressed into disks, which were put into BN capsules, followed by setting up in high-pressure cells made of NaCl (+10 wt % ZrO<sub>2</sub>) with a graphite heater. We also examined Na doping at the Ca site for hole-carrier doping because the ionic radius of Na is close to that of Ca (100 pm for Ca<sup>2+</sup> and 102 pm for Na<sup>+</sup> for the case where their coordination numbers are 6),<sup>7</sup> whereas the atomic/covalent bond radius of Na is slightly smaller than that of Ca. A commercially available NaN3 reagent powder (99.5%) was used as a sodium source. As-received NaN<sub>3</sub> was thermally annealed under a vacuum of  $\sim 10^{-2}$  Pa at 250 °C for 6 h to purify before mixing. We mixed the precursor powders so as to obtain  $(Ca_{1-y}Na_y)(Mg_{1-x}Zn_x)_2N_2$  (x = 0.67 and y = 0.02).

The pressure and heating temperature of the high-pressure cells, including BN capsules and pressed disks in the glovebox for the synthesis of undoped and Na-doped  $Ca(Mg_{1-x}Zn_x)_2N_2$  (0.12 <  $x \le 1$ ), were commonly increased to 5.0 GPa and 1300 °C, respectively, and they were then kept for 30 min. The final size of the high-pressure-synthesized samples was a diameter of ~5.5 mm and thickness of ~2 mm (after polishing). More details of the experimental procedure and apparatus of the high-pressure synthesis are reported in ref 5.

Crystal structures of the samples, such as crystalline phases and lattice parameters, were determined by powder X-ray diffraction (XRD) with the Bragg–Brentano geometry with a Cu K $\alpha$  radiation source at room temperature, where an Ar-filled O-ring-sealed sample holder was used because the Mg-rich samples (x < 0.5) were sensitive to air. The lattice parameters of the main phase were determined by the Pawley method using the TOPAS ver. 4.2 program (Karlsruhe, Germany: Bruker AXS GmbH). Rietveld analysis, where the fundamental parameter (FP) method is employed, was performed to estimate the volume fraction of each crystalline phase observed and x in  $Ca(Mg_{1-x}Zn_x)_2N_2$  (i.e., crystallographic site occupancy of the (Mg,Zn) site) using the TOPAS program after initially determining the lattice parameters by the Pawley method because it was difficult to exactly distinguish the main phase of  $Ca(Mg_{1-x}Zn_x)_2N_2$  from some impurity phases, such as Zn and Mg<sub>3</sub>N<sub>2</sub>, by conventional spectroscopic quantitative techniques, such as X-ray fluorescence spectroscopy and electron probe microanalysis.

Diffuse reflectance (*R*) spectra were measured at room temperature with a spectrophotometer in the wavelength ( $\lambda$ ) region of 200–2400 nm. The obtained *R* spectra were converted using the Kubelka–Munk function  $(1 - R)^2/(2R) = \alpha/s_i^{23}$  where  $\alpha$  and *s* denote the optical absorption coefficient and scattering factor, respectively, to obtain the quasi-optical absorption spectra. The optical band gap of each sample was estimated from plots of  $(\alpha h \nu / s)^2$  versus  $h\nu$ , where *h* and  $\nu$  are the Planck constant and frequency, respectively, because the band structures of both end members (i.e., x = 0 and 1) have been reported to be of the direct transition type.<sup>5</sup> Photoluminescence (PL) spectra and emission lifetimes at 20–300 K were attained with a CCD camera and a spectrometer under excitation by  $3\omega$  of a Nd:YAG laser ( $\lambda = 355$  nm, pulse width ~7 ns, excitation density ~30 mJ/cm<sup>2</sup>); whereas only for the CaMg<sub>2</sub>N<sub>2</sub> (i.e., x = 0) sample,  $4\omega$  of the Nd:YAG ( $\lambda = 266$  nm, excitation density ~10 mJ/cm<sup>2</sup>) was used because of the widest band gap in Ca(Mg<sub>1-x</sub>Zn<sub>x</sub>)<sub>2</sub>N<sub>2</sub> (x = 0-1). Note that the sequence of performing experiments both of syntheses and measurements was step by step; it took 2 years from x = 1 finally to x = 0. If we obtained all the samples at the same time, we could employ the shortest wavelength.

Electronic transport properties were measured only for the  $(Ca_{1-y}Na_y)(Mg_{1-x}Zn_x)_2N_2$  (x = 0.67 and y = 0.02) sample because the electrical resistivity of the other undoped samples (i.e., x = 0-1 and y = 0) was too high to allow measurement of their transport properties. We initially confirmed the electrical conduction with a conventional electric tester in the glovebox because the Na-doped sample was air sensitive. The temperature dependence of the electrical resistivity and thermoelectric power ( $\Delta V$ ) as a function of difference in temperature ( $\Delta T$ ) at room temperature (i.e., the Seebeck effect) were measured with a physical property measurement system. For these electrical measurements, we transferred the Na-doped sample from the glovebox to the measuring system within ~1 min together with surface protection using commercially available Apiezon grease to disturb the degradation.

#### ASSOCIATED CONTENT

#### **S** Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.9b01811.

XRD patterns and their Rietveld analysis results and emission decay curves (PDF)

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#### Notes

The authors declare no competing financial interest.

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