

# Investigating Bandgap Energies, Materials, and Design of Light-Emitting Diodes

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**S** Supporting Information

**ABSTRACT:** A student laboratory experiment to investigate the intrinsic and extrinsic bandgaps, dopant materials, and diode design in light-emitting diodes (LEDs) is presented. The LED intrinsic bandgap is determined by passing a small constant current through the diode and recording the junction voltage variation with temperature. A second visible wavelength emission method is used to determine the active bandgap for comparative purposes. The active bandgap data is used along with literature values to interpolate the ratio of elemental dopant atoms in the LED semiconductor. This work also discusses the fundamentals of bandgap theory, LEDs, and diode design and how these experimental measurements correlate to the diode structure and dopant material used to manipulate the bandgap energy and observed emission profile. Suggested questions are provided in the supplemental materials to help students further explore and understand the topic. While this laboratory experiment was created for upper level undergraduates, it can be revised and simplified for use in high school and introductory level undergraduate courses.

**KEYWORDS:** Upper-Division Undergraduate, High School/Introductory Chemistry, Laboratory Instruction, Physical Chemistry, Hands-On Learning/Manipulatives, Materials Science, Laboratory Equipment/Apparatus, Semiconductors, Spectroscopy

## INTRODUCTION

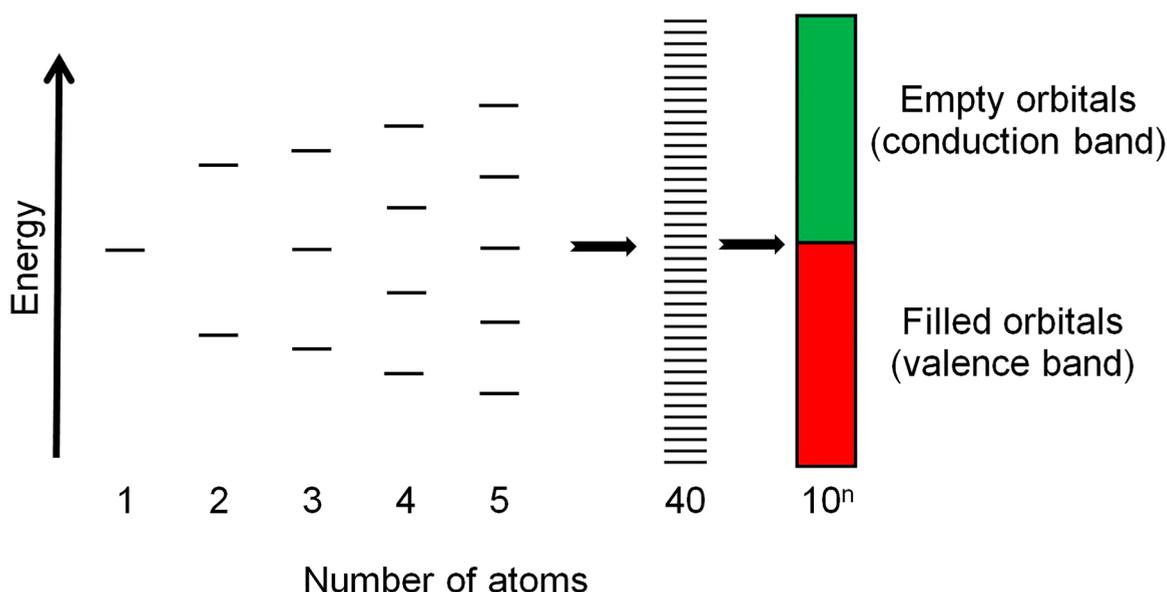
Light-emitting diodes (LEDs) are everywhere in technology. Vehicle lights, flashlights, general lighting in buildings, and color specific indicator lights for electronic devices are all examples where these low cost and energy efficient devices are being used. It is a technology that continues to be researched and developed for future applications. At the heart of the LED is a semiconductor p–n junction diode, which is one of the most important devices in electronic circuits. Understanding semiconductors, p–n junctions, electronic band theory, and how they are integral parts to LEDs allows one to develop a broader understanding of these topics and how diodes are used to control electron flow in circuits. The fields of engineering, material science, and chemistry continue to merge as technologies become increasingly more complex and based on fundamental chemical principles. Surface science, nanotechnology, bioengineering, and material design are disciplines in science that required collaboration between fundamental scientists and engineers in order to develop. The ACS journal, *Chemistry of Materials*, specifically covers research and development at the interface of chemistry, chemical engineering, and materials science. For example, research and development of LEDs,<sup>1–3</sup> LED phosphor coatings for attenuating wavelength emission,<sup>4,5</sup> and organic materials for LEDs<sup>6–8</sup> are topics frequently published through this journal and provide evidence to the ever increasing overlap of the science and engineering disciplines. Consequently, providing cross-discipline educational experiences, such as this laboratory experiment, is important and necessary to help students prepare for the nature of research and development in today's world.

The fundamentals of LEDs and diodes have been discussed for decades in education journals. The continuous change in LED design and materials requires updated reports and

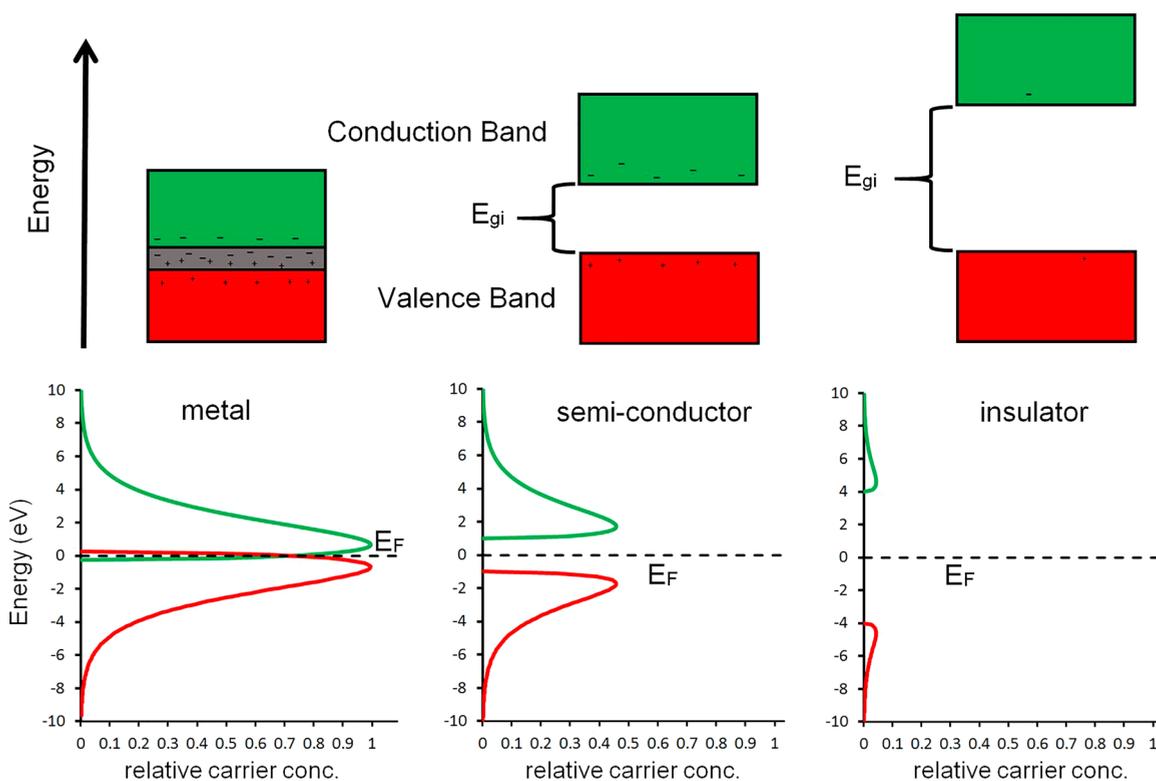
experiments to stay current. In this *Journal*, the earliest report on LEDs was by Gurnee back in 1969.<sup>9</sup> Since then, reports in this *Journal* have included demonstrations,<sup>10</sup> emission correlation to bandgap of the diode,<sup>11</sup> and general discussions of LED technology and how they are used in electronics.<sup>12</sup> Physics education literature has focused on experiments created and designed to measure the bandgap of diodes.<sup>13–18</sup> Precker has also reported on a method to relate bandgap energy of the LED to the wavelength of emission.<sup>19</sup> However, none of these reports specifically address the LED junction design and the details of how the intrinsic bandgap energy measured in these experiments is not necessarily the same as the active bandgap energy. Further, none of these previous educational publications discuss how to correlate the active bandgap energy to the relative doping composition of the semiconductor material. The active bandgap is the energy difference between the valence and conduction bands in the semiconductor material that creates the emission wavelength of the LED when an electron decays between these two bands. The reason for the difference between the intrinsic and active bandgaps is that nearly all modern LEDs use variations on the double heterojunction diode design rather than a basic homojunction discussed in the education literature cited above. The purpose of this work is to provide more details on modern double heterojunction, band theory, types of diode materials, p–n junction designs, and the difference between intrinsic and active bandgaps. In addition, a student laboratory experiment is provided to investigate these topics by measuring both the intrinsic and active bandgap energies of LEDs. The experiment provides a method to

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**Figure 1.** A sketch indicating how electron energy levels become compressed together as the number of atoms and formed orbitals increase. The difference in energy between orbitals decreases and, at a high number of atoms, eventually form a band.

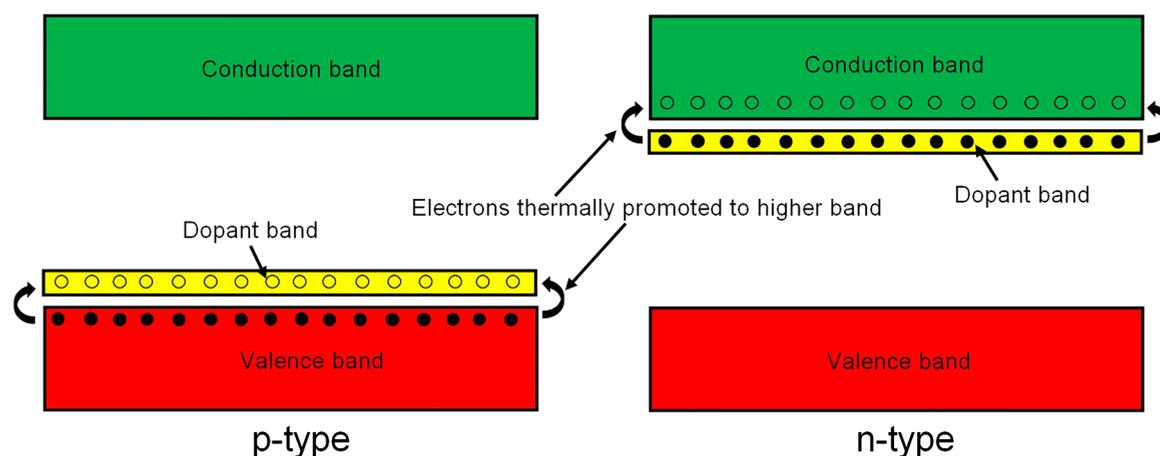


**Figure 2.** (Top) Relative comparison of band diagrams for an insulator, a semiconductor, and a metal. The intrinsic bandgap energy,  $E_{gi}$ , is the separation between the top of the valence band and the bottom of the conduction band. In metal systems, there is no effective bandgap and oftentimes the valence and conduction band overlap (gray area). (Bottom) Relative comparison of carrier concentration profile. As the energy gap increases, the number of electrons promoted from the valence to conduction band decreases significantly. As a result, conductivity of the material decreases. The carrier concentration profile is determined by the density of states (spacing of the energy levels in the band) and Boltzmann's distribution. The charge carriers in the bands are represented by the plus and minus symbols. The Fermi level ( $E_F$ ) is represented by the dashed line.

calculate the relative elemental dopant composition of each diode by using data from literature in combination with the experimental results.

This experiment is part of a series of material sciences experiments in development for our physical chemistry laboratory II curriculum. The reason for its development is to

keep current with the educational needs of our students and the recommendations of the American Chemical Society, which is to provide in-depth and concentrated coursework in a specific discipline of chemistry.<sup>20</sup> While the experiment was developed for our physical chemistry II undergraduate lab course, it is adaptable for high school and college general chemistry courses



**Figure 3.** (Left) N-type semiconductors have dopant atoms with one “extra” electron mixed into the material. This forms a dopant band just below the conduction band allowing ionization of electrons to the conduction band with room temperature thermal energy. The extra electrons that are charge carriers in the circuit are represented by dots. The cations, or holes, are also charge carriers in the circuit and are represented by circles. (Right) P-type semiconductors have dopant atoms with one “less” electron mixed into the material. This forms an empty dopant band just above the valence band. In this case, the dopant band is now effectively the conduction band.

and can also be designed to emphasize either the engineering aspects or fundamental theory behind electrical conduction in semiconductors.

## ■ BACKGROUND

Light-emitting diodes are made from semiconductor materials. At the heart of these devices are the electronic energy levels, which comprise energy bands that allow electrical conduction or insulation based on the material. Electronic bands are created when many atoms of an element are bonded together allowing orbital overlap. For example, when sodium atoms are metallically bonded together, the valence 3s orbitals are added together to create the valence delocalized orbital and the unoccupied antibonding conduction orbital that is also delocalized. The number of valence and conduction orbitals increases as the number of atoms increases. As this occurs, the levels become more closely spaced and their energy differences are quite small to the point where room temperature thermal energy allows electrons to move easily between energy levels (Figure 1). Essentially, all the energy levels are “banded” together because the probability of finding electrons in many levels in the band is significant at room temperature.

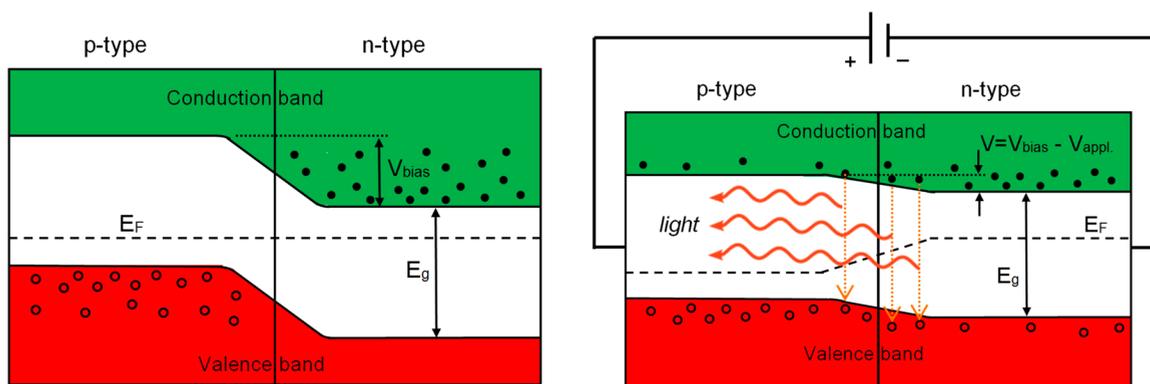
In sodium, like all metals, the valence and conduction band overlap when there are a large number of atoms bonded together. Consequently, the electrons from the valence band move easily into the conduction band creating a partially filled valence and conduction band. This imbalance creates positive charge carriers, often referred to as holes, in the valence band and negative charge carriers, or electrons, in the conduction band. The charge is able to flow through the bands by moving from one atom to the next. Figure 2 depicts the positive and negative charge carriers for the two bands as the bandgap ( $E_{gi}$ ) increases. The carriers in the conduction band are the electrons and they are free to move throughout the atoms in the material because of metallic bonding orbital overlap. If the conduction band was completely empty of electrons, then clearly no current flow would exist. The valence band can also participate in current flow, but in an opposing direction due to the holes created by promotion of electrons to the conduction band.

The principles used to describe metal conductors can be applied to semiconductors and insulators. However, with

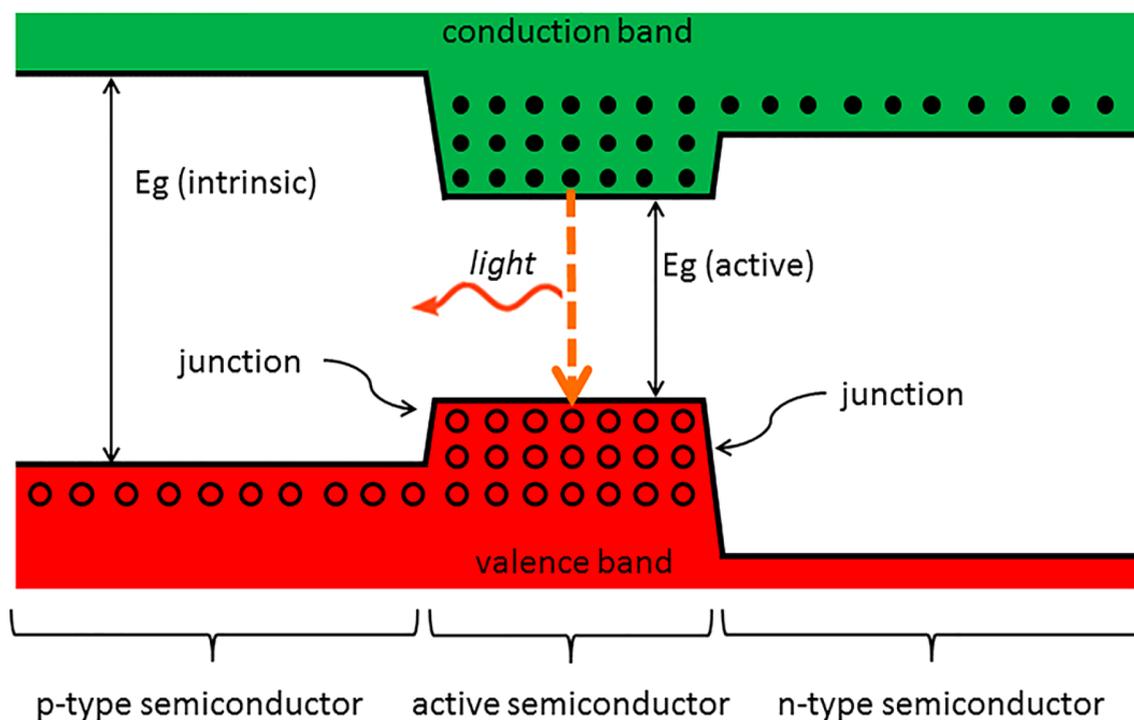
semiconductors the elemental matrix is covalently bonded together. As a covalent orbital is formed between two atomic orbitals, it creates bonding and antibonding molecular orbitals (MOs). However, the two MOs are separated in energy and create two distinctly different levels. As more atoms are added, the valence and conduction bands form. Since there is an energy separation between these two bands, promotion of electrons from the valence to conduction band is not easily achieved at room temperature. Consequently, the carrier concentration decreases as the separation in band energy increases (Figure 2). This separation is referred to as the bandgap energy. The bandgap for insulators is typically above 4 eV. On the basis of Boltzmann’s distribution of electron density with respect to energy level, thermal energy at 300 K is insufficient to allow few, if any, electrons from the valence band to be promoted to the conduction band in an insulator. In this case, the valence band is fully occupied, the conduction band is empty, and there is no significant conduction.

There are also elements on the periodic table, such as silicon and germanium, referred to as semimetals. These elements form a band structure with a bandgap that is much smaller than an insulator. For example, silicon has a bandgap energy of 1.12 eV at room temperature. At absolute zero, the probability of an electron being promoted up to the conduction band in silicon is zero, so it is an insulator. As the temperature increases, thermal energy creates vibrations in crystal lattice and a few electrons break their covalent bonds and move to the conduction band. These systems are referred to as semiconductors because, depending on the temperature, they can act as an insulator or conductor. In silicon crystal at room temperature, it is roughly only one atom in  $10^{10}$  that exists with a broken bond. Such a semiconductor is known as intrinsic semiconductor and the resistivity of such a semiconductor is quite high. As the temperature increases, conduction increases rapidly and resistivity falls. However, the conductivity is still quite poor compared to a metal conductor.

Since intrinsic semiconductors, such as pure silicon, are not very good conductors, they are mixed with other elements to improve conductivity. Adding impurity atoms from the 3A or 5A group of elements on the periodic table can increase conduction. This process of adding atoms different from the



**Figure 4.** Schematic of a diode with no applied circuit potential (left) and with a forward applied voltage ( $V_{\text{appl}}$ ) (right). The bias potential ( $V_{\text{bias}}$ ) is large in a diode and does not allow flow of electrons, represented as dots, and holes, represented as circles. As  $V_{\text{appl}}$  increases, the energy difference between the p-type and n-type bands is reduced allowing conduction as well as electron–hole recombination to produce light.



**Figure 5.** Schematic of a double heterojunction diode under forward bias. The positive hole charge carriers are represented by the circles, and the electron charge carriers are represented by the dots. Carrier density is increased in the active semiconductor due to the differences in the energy levels and the smaller bandgap. This increases the recombination current pathway and increases the light output.

parent material known as doping and the doped semiconductor becomes an extrinsic semiconductor. Addition of dopant atoms from group 5A on the periodic table results in n-type doped semiconductor and addition of dopant atoms from group 3A results in p-type doped semiconductor. Dopant levels are typically quite small, usually in the range of  $10^{-8}$  to  $10^{-5}$  dopant atoms to parent material atoms. The dopant element energy levels lie in the bandgap of the intrinsic material. For n-type dopants, the energy band is very close to the bottom of the intrinsic conduction band, and room temperature provides enough energy to promote electrons from the dopant to conduction band and improves conductivity (Figure 3) by flowing through the partially filled bands. The same is true for p-type dopant materials except that the dopant energy level is empty and very close to the top of the intrinsic valence band allowing the valence electrons to be promoted to the dopant

band and improve conductivity. It is important to note that electron flow requires a partially filled or partially empty orbital. In this situation, the electrons can move to empty orbitals of other atoms in the material. When a voltage potential is applied to the material, the electrons will flow in a direction to offset the applied potential.

This lab experiment is focused on investigating the bandgap of the semiconductor because electrons that decay from the conduction band to the valence band can release energy in the visible region of the spectrum. However, if only an n-type semiconductor is present, the electrons can decay from the conduction to dopant band. If only a p-type semiconductor is present, decay can occur from the dopant band to the valence band. Neither of these transitions has an energy difference large enough to create emission in the visible spectrum. If these two types of extrinsic semiconductors are put together, they form a

diode that will allow a significant number of electrons to decay from the dopant band of the n-type to the p-type dopant band (Figure 4). This current pathway is referred to as recombination and is a much bigger energy transition that will produce visible spectrum emission. Very often in physics and electrical engineering textbooks, the dopant bands are assumed to be part of the conduction and valence bands rather than as separate bands. Figure 4 is drawn with this assumption and as a result, the conduction band of the n-type semiconductor is lower in energy than the p-type. Likewise, the valence band of the p-type semiconductor is higher in energy than the n-type valence band. Under an open circuit, the energy difference between the two conduction bands, as well as between the two valence bands, is significantly large and electron flow through the junction between the two extrinsic semiconductors is not likely at room temperature. When the diode is connected to a circuit and driven by a forward bias voltage, the energy difference is lowered and electron flow will occur. The forward direction is defined by electron flow from the negative terminal (anode) of the power source into the n-type semiconductor and back out the p-type semiconductor to the positive terminal of the power source (cathode). The maximum forward voltage, referred to as the bias voltage ( $V_{\text{bias}}$ ), is the difference in energy of the bands.

The basic p–n structure in Figure 4 is referred to as a homojunction, which means the intrinsic material for both the n- and p-type semiconductors is the same. The two differ only in the dopants used to make it a p- or n-type semiconductor. For example, gallium (group 3A) can be used as a dopant to create a dopant band approximately 0.072 eV above the valence band in silicon. Phosphorus (group 5A) can be used to make a dopant band approximately 0.045 eV below the conduction band in silicon. Diode current flows through the partially filled conduction and partially empty valence bands without needing to go through recombination decay at the junction. This current flow process is referred to as diffusion or drift. When looking at the diode design in Figure 4, there is no method or engineered design to make recombination the more dominant pathway in the diode. Consequently, the efficiency of the LED is diminished in this basic design. Further, reabsorption of the photons is likely because the bandgap energy of the entire diode is consistent throughout the device. Again, this decreases the LED efficiency. LEDs in use today have been developed past this basic homojunction design and are far more efficient. The key to increasing efficiency is to limit diffusion current and reabsorption of the photons. To accomplish this, the basic homojunction is not used. Instead, modern LEDs use double heterojunctions. In a double heterojunction diode, there are three parts to the diode that create two junctions (Figure 5). The p- and n-type semiconductor are on either side of the active semiconductor region that has a bandgap smaller than the n- or p-type semiconductor. This forces the carriers to collect in the active semiconductor region rather than continue through the diode as diffusion current. The carriers collected in the active region decay through recombination and produce light. The photons created have energy less than the bandgap of the n and p semiconductors. Consequently, the photons are not reabsorbed by these materials.

There are many varieties of extrinsic semiconductor materials available for LEDs to create a specific color of light. In the experiment presented here, silicon, InGaN, and AlGaInP diodes are used for the investigation. The silicon diode, which does not produce light, is included in the investigation as an internal

standard because the intrinsic bandgap value is well documented in literature. The silicon diode is a simple homojunction design that uses boron or gallium dopant for the p-type section of the diode and phosphorus or arsenic for the n-type section.

InGaN is used as the material for the green and blue LEDs in this experiment. GaN is the intrinsic material used for the n and p sections of the diode. It is referred to as a group III–V semiconductor and the ratio of gallium to nitrogen can be adjusted to make it an n-type or p-type semiconductor. This is referred to as compensation doping. Indium is added to the GaN material to create the active region material and bandgap of the LED. As more indium dopant is added, the optical bandgap decreases and the color of light produced changes accordingly. LEDs made with these materials can have optical bandgaps from 3.4 eV (pure GaN) to 0.7 eV (pure InN).<sup>21–24</sup> A more precise correlation between the ratio of gallium to indium is given by

$$E_g = 3.42 \text{ eV} + 2.65 \text{ eV}(x) - x(1 - x)2.4 \text{ eV} \quad (1)$$

where  $x$  = ratio of indium.<sup>25</sup> The formula for the diode is written as  $\text{In}_x\text{Ga}_{1-x}\text{N}$  to represent the variations in relative concentration of indium to gallium.

AlGaInP diodes are used for the red, orange, and yellow LEDs in this experiment. The alloy formulation written as  $(\text{Al}_x\text{Ga}_{1-x})_y\text{In}_{1-y}\text{P}$  typically has  $y = 0.5$  and the ratio of gallium to aluminum ( $x$  variable) is adjusted to change the optical bandgap.<sup>26,27</sup> Consequently, the ratio of Al to Ga used to attenuate the active bandgap is determined. For example, Sugawara reported a wavelength of 620 nm when  $x = 0.2$  and 563 nm when  $x = 0.5$ .<sup>28</sup> A more precise correlation between the ratio of aluminum and gallium is given by

$$E_g = 0.61 \text{ eV}(x) + 1.91 \text{ eV} \quad (2)$$

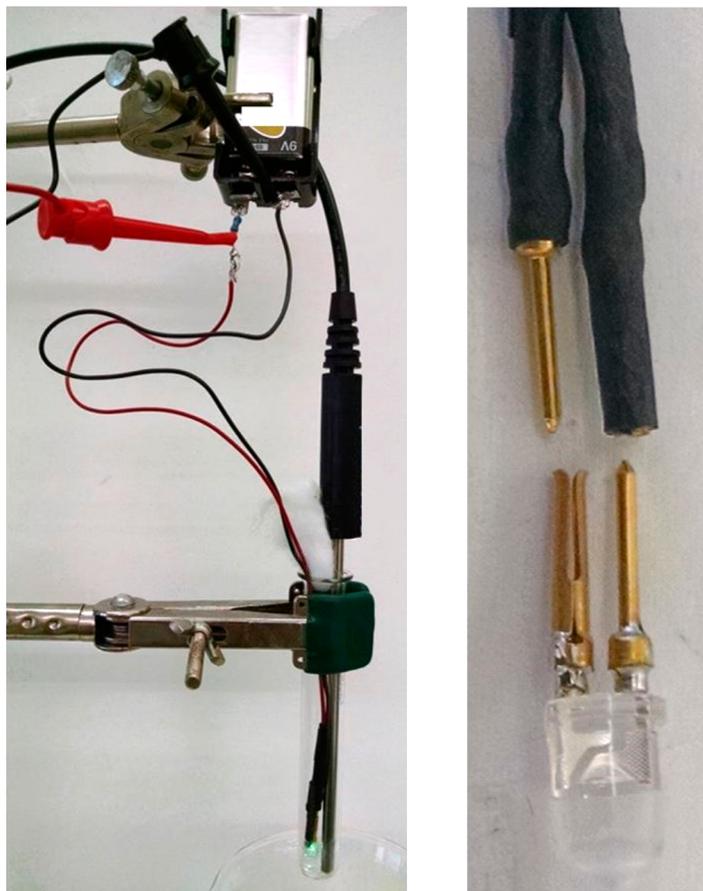
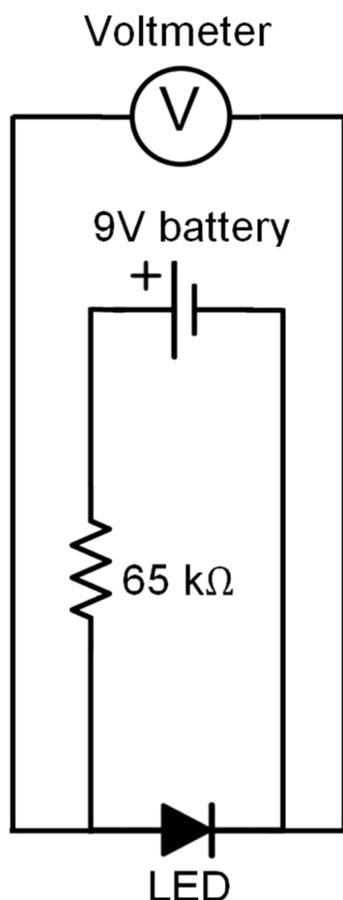
where  $x$  = ratio of Al.<sup>25</sup>

Determination of the optical bandgap is easily performed by measurement of the LED emission wavelength. The peak emission wavelength can then be used along with literature data of elemental ratios provided above to determine the ratio of aluminum to gallium in the red, yellow, and orange LEDs through linear interpolation. The same process can be used to determine the indium to gallium ratio for the green and blue LEDs.

Determination of the intrinsic bandgap, the material on either side of the active region, cannot be performed through spectroscopy. Instead the LED intrinsic bandgap is investigated by measuring the voltage or current of a diode circuit with temperature change. To fully understand the relationship of voltage, current, and the effect of temperature on these parameters, the fundamentals of current flow through a semiconductor must be examined and are discussed below.

## INTRINSIC BANDGAP THEORY

Current in the forward direction of a semiconductor is affected primarily by diffusion and recombination. Diffusion is the electrical flow through the partially filled bands. It is the ideal electrical current expected when the semiconductor is connected to a power source with a potential high enough to overcome the diode bias. Diffusion will flow in the opposite direction of the applied forward bias voltage bias ( $V_{\text{bias}}$ ); hence, it is often referred to as the reverse saturation current and is defined by



**Figure 6.** (Left) Schematic of LED circuit and (center) corresponding picture of circuit setup with temperature probe in a test tube. The 65 kΩ series resistor is between the battery and the voltage probe. A Vernier voltage probe (VP-BTA) and temperature probe (TMP-BTA) are used in conjunction with the LabQuest Mini interface to collect the voltage and temperature data on a computer. (Right) Close up view of the pin and socket connectors used for the LED and circuit.

$$I_{\text{rev}} = B_{\text{rev}} T^3 e^{(-E_{\text{gi}}/kT)} [e^{(qV/kT)} - 1] \quad (3)$$

where  $B_{\text{rev}}$  is reverse saturation current constant,  $I_{\text{rev}}$  is the reverse current or reverse saturation current,  $E_{\text{gi}}$  is the intrinsic bandgap of diode,  $V$  is the diode junction voltage,  $q$  is electron charge in Coulombs,  $k$  is Boltzmann's constant, and  $T$  is temperature in Kelvin.<sup>21,29</sup> The constant  $B_{\text{rev}}$  is slightly temperature dependent.<sup>30</sup> However, over small temperature changes, as in this experiment, it can be assumed to be constant. Recombination is the current attributed to when the electrons recombine with the holes across the p-n junction. This is the current associated with the light emission of the LED, although recombination can occur at other wavelengths outside of the visible spectrum. The recombination current is defined by

$$I_{\text{rec}} = B_{\text{rec}} T^{3/2} e^{(-E_{\text{gi}}/2kT)} [e^{(qV/2kT)} - 1] \quad (4)$$

where  $I_{\text{rec}}$  is the recombination current and  $B_{\text{rec}}$  is the recombination current constant.<sup>21,29</sup> For both  $I_{\text{rev}}$  and  $I_{\text{rec}}$ , the “- 1” term can be ignored at room temperature because it is much smaller than the exponential term. The total forward current is the sum of  $I_{\text{rev}}$  and  $I_{\text{rec}}$ .

$$I = B_{\text{rec}} T^{3/2} e^{(-E_{\text{gi}}/2kT)} [e^{(qV/2kT)}] + B_{\text{rev}} T^3 e^{(-E_{\text{gi}}/kT)} [e^{(qV/kT)}] \quad (5)$$

To simplify this equation and arrange it into a useable form for this experiment, the exponential terms are combined by using a new constant,  $\eta$ , referred to as the ideality factor with a value typically between 1 and 2.

$$I = (B_{\text{rec}} T^{3/2} + B_{\text{rev}} T^3) e^{(qV - E_{\text{gi}}/\eta kT)} \quad (6)$$

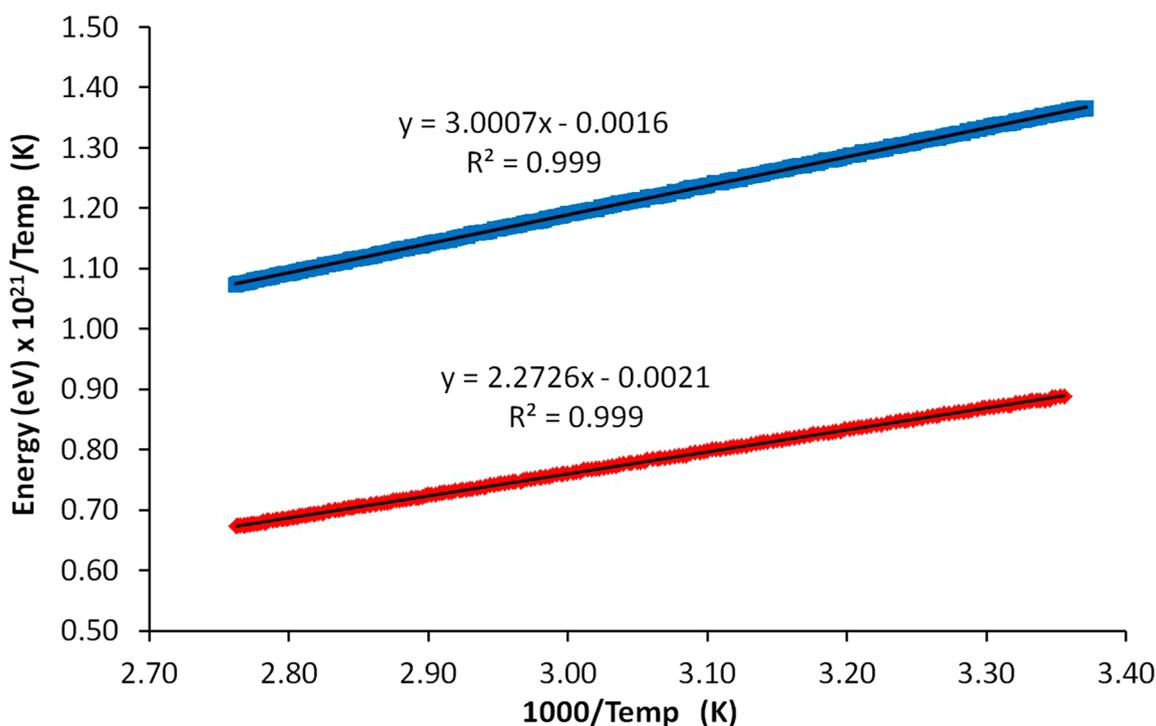
Rearranging and taking natural logarithm of both the sides, we obtain the slope intercept form of the equation that represents a straight-line graph created by holding the current constant and measuring the diode voltage values with respect to temperature.

$$\frac{qV}{T} = E_{\text{gi}} \left( \frac{1}{T} \right) + \left[ \eta k \ln \left( \frac{1}{(B_{\text{rec}} T^{3/2} + B_{\text{rev}} T^3)} \right) \right] \quad \text{or}$$

$$\frac{qV}{T} = E_{\text{gi}} \left( \frac{1}{T} \right) + C \quad (7)$$

When we plot  $(qV/T)$  versus  $(1/T)$ , the intrinsic bandgap value ( $E_{\text{gi}}$ ) can be found from the slope. While the intercept does have temperature as a variable, its effect on the calculated bandgap value is insignificant. It is possible to multiply eq 7 by temperature and use the intercept to determine the bandgap energy.

To experimentally determine  $E_{\text{gi}}$ , a small forward constant current of 100  $\mu\text{A}$  is passed through the diode at various temperatures. The voltage developed at the LED junction with



**Figure 7.** Intrinsic bandgap determination for the red and blue LEDs. The slope of the line represents the intrinsic bandgap energy in electron volts.

respect to the temperature is recorded and the data is used to determine the intrinsic bandgap energy.

## MATERIALS

An Ocean Optics USB4000 spectrometer fitted with an optic cable and connected to a computer for data collection was used for the LED emission measurement and active bandgap determination. A constant current circuit for the intrinsic bandgap measurement was constructed using a 9 V battery and a 65 K ohm resistor in series to limit the current to approximately 100  $\mu\text{A}$  (Figure 6). While this is not a true constant current circuit, we found less than a 3% change in current over a 70  $^{\circ}\text{C}$  temperature range. TE crimp snap in contact pins (66506) and sockets (66504) for wire size 20–24 are used as connectors on the LEDs and circuit to simplify changing out LEDs in the system and ensure that the LEDs were connected with the correct polarity (Figure 6). We used Kingbright T-1 LEDs in blue (WP7113QBC/D), green (WP7113ZGC), yellow (WP7113SYC/J3), red (WP7113SEC/J3), and orange (WP7113SEC). Datasheets are available for these LEDs and show that the green and blue LEDs are made from GaInN semiconductor material and the other colors are made from AlGaInP semiconductors.<sup>31</sup> The n and p sections are also made from AlGaInP for the red and yellow diodes, but doped with another element to make it an n- or p-type semiconductor. The orange diode uses GaAs with compensation doping for the n- and p-type sections of the diode. A standard silicon diode 1N4007 was also included in our experiment for use as an internal standard. The connectors, LEDs and 1N4007 diode can be purchased from electronic equipment suppliers. Voltage and temperature data were collected using the Vernier voltage probe (VP-BTA) and temperature probe (TMP-BTA) connected to the Vernier LabQuest Mini computer interface. A temperature controlled water bath was created using a 250 mL beaker on a stirring hot

plate. A small diameter test tube, lowered into the water bath and supported by a clamp, was used to hold the LED and temperature probe in the bath.

## GENERAL PROCEDURE

The entire experiment can easily be completed in a 3 h laboratory period. The procedure for determining the intrinsic bandgap consists of connecting the LED to the constant current circuit and putting the LED and thermocouple into the test tube and filling the opening with cotton to limit air circulation. Ideally, the voltage probe leads should be placed as close as possible to both LED leads. However, the voltage drop in such a small circuit is insignificant. Therefore, it is easiest to attach the voltage probe leads to the circuit in a location outside of the temperature bath, but between the LED and resistor (Figure 6). The test tube is lowered into the temperature controlled water bath and the hot plate is turned on to a high setting. Data collection on the computer begins once there is an increase in temperature. The heating rate is monitored and should not exceed 4–5  $^{\circ}\text{C}$  per min. Temperature and voltage data are collected on the computer through the Vernier LoggerPro software at a rate of 10 points/min. Once the temperature of the circuit and LED reaches 90  $^{\circ}\text{C}$ , data collection stops and the test tube is removed from the bath to cool the LED and circuit in preparation for the next experiment.

Measuring the LED emission for determination of the active bandgap is a straightforward process using the Ocean Optics spectrometer fitted with a fiber optic cable and the LoggerPro software. The LED is plugged into the intrinsic bandgap circuit making sure to match the orientation specific connectors. The LED will be dimly lit, but well enough for measurement. With the use of ring stand clamps to hold both the fiber optic cable end and the LED, the two are arranged so that enough light from the LED goes into the optic cable to produce an

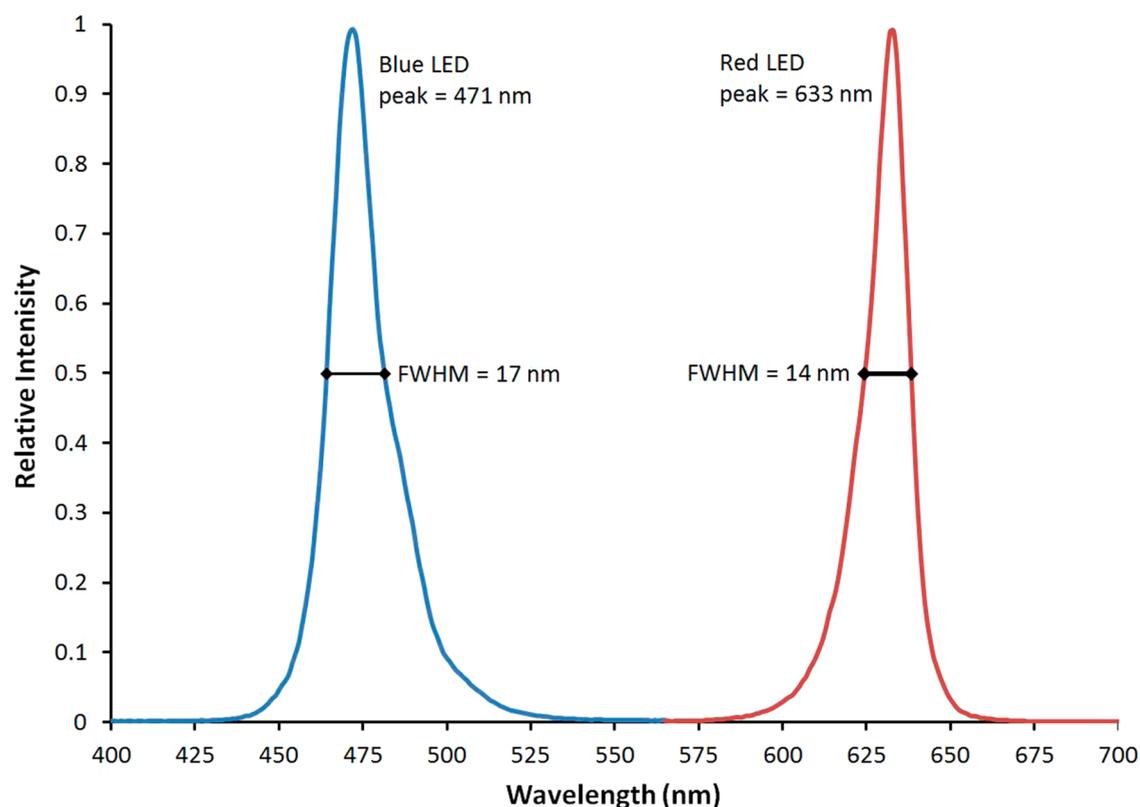


Figure 8. Emission spectra for the red and blue LEDs.

observable peak in the software. Once the peak wavelength is determined, linear interpolation is used with the data provided in literature to estimate the elemental ratio of aluminum to gallium in the red, yellow, and orange LEDs and the indium to gallium ratio for the green and blue LEDs. Detailed experimental procedures are available in the [Supporting Information](#).

## HAZARDS

There are no significant hazards associated with this experiment. Care should be taken to avoid burns from the heating system used to vary the temperature.

## RESULTS AND DISCUSSION

Example data and results for the red and blue LEDs are presented here. The intrinsic bandgap for the red LED was determined to be 2.27 and 3.00 eV for the blue LED (Figure 7). The emission spectra of the red and blue LEDs are shown in Figure 8. The peak emission value for the red LED was 633 nm or 1.95 eV and 471 nm or 2.63 eV for the blue LED. With eq 1, the ratio of indium to gallium in the blue LED was found to be 0.15:0.85. With eq 2, the ratio of aluminum to gallium in the red LED was found to be 0.12:0.78. Comparison of the intrinsic bandgap to the active bandgap showed a 0.32 eV difference for the red LED and a 0.37 eV difference for the blue LED. The accuracy of the intrinsic bandgap values was addressed by measuring the intrinsic bandgap of the 4007 silicon diode. It was found to be 1.17 eV, which is very close to the literature value of 1.12 eV, and provides evidence for the accuracy of this experimental method.<sup>25,29</sup>

This experiment has been a part of our curriculum for three semesters. Since it is not a required laboratory for most of our

chemistry majors, approximately 10% of the majors take this course. A limited number of chemical engineering majors have also taken this course. Students typically worked in pairs, but individuals have also conducted the experiment. Regardless of group size, completing the entire lab procedure for six samples in less than 3 h is common. The time to complete the experiment is most dependent on the rate of heating and cooling of the samples. Over the past year, we have observed groups obtaining very similar results with limited issues.

The impetus in developing this experiment came from discussions with students about general LED lighting technology and current flow in electronics. Through these conversations, it became clear that the vast majority of senior level chemistry students as well as chemical engineering students had a very limited understanding of these topics. When going deeper into the conversation, it also became evident that most did not understand electron flow as it relates to band theory and what a diode is or how it operates. Band theory and semiconductors are not part of our formal physical chemistry lecture curriculum, but may be discussed in a limited fashion as an example application for a bigger overarching topic. This appears to be typical for physical chemistry courses across the nation.<sup>32</sup> The chemical engineering coursework at our university also does not formally include diodes and band theory in the curriculum. Consequently, this experiment is the first in-depth experience on semiconductors, band theory, diode devices, and LEDs for these groups of students.

To address the efficacy of this experiment in educating students about semiconductors, LEDs, and band theory, an online survey was administered 1 week after completing the experiment. The primary purpose of the survey was to determine if students felt that the experiment helped them gain a better understanding of the topics covered. However, since

this is a low enrollment course, the total number of surveys collected was seven, which does not allow the possibility of statistical analysis. The survey and collected data are available in the [Supporting Information](#).

The experiment can be adapted for use in high school or introductory level undergraduate courses by eliminating the details of junction design and investigating only the active bandgap with spectroscopy. This still allows the determination of dopant material ratios and provides a good experience for understanding the basics of LEDs. The lab could also be made more complex for higher level students by looking more closely at the Fermi levels, Boltzmann's distribution, and estimating carrier concentration in the bands. While this experiment uses LEDs for the investigation, it could also include investigation of homojunction diodes used for circuitry rather than for producing light. This may be a more interesting and relevant approach for engineering students. Regardless of when or in what discipline the topic is introduced into the curriculum, its relevancy is important in the education of today's science and engineering students who need cross-disciplinary learning experiences.

## ■ ASSOCIATED CONTENT

### ● Supporting Information

The Supporting Information is available on the [ACS Publications website](#) at DOI: [10.1021/acs.jchemed.6b00165](https://doi.org/10.1021/acs.jchemed.6b00165).

Detailed student laboratory experiment instructions, suggested questions, student opinion survey on experiment efficacy ([PDF](#), [DOCX](#))

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### Notes

The authors declare no competing financial interest.

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