Transparent conducting oxides (TCOs) are ceramic compounds that are commonly found in the form of thin films in applications such as flat panel displays, solar cells, and energy efficient windows. The electrical and optical properties of two such TCOs, scheelite gallium-indium-tin-oxide (GITO) and bixbyite zinc-indium-tin-oxide (ZITO), have been well-established, but the combination of the two materials presents opportunities to create materials with novel properties. GITO and ZITO are of great interest as alternatives to the industry standard indium tin oxide (ITO) because they both require less indium. This is desirable because the cost of indium is high and prone to fluctuation and ITO has some chemical shortcomings in solar cell applications. GITO and ZITO are potential solutions to these problems, and combining them is of particular interest.

TCOs take the form of a primary metal oxide (such as indium oxide, In$_2$O$_3$) with one or more other metals added called dopants. Doping a material refers to the optimization of its properties by adding small amounts of a different material. This research will focus on doping GITO with ZnO and ZITO with Ga$_2$O$_3$ to determine how the material properties change. TCOs are special materials because they exhibit two properties that are usually mutually exclusive: they have high electrical conductivity and are transparent in thin film form. This makes them idea for solar cells. The properties of interest in TCOs are their lattice parameter (the size of the crystalline unit cell), bandgap (the energy required for the onset of optical absorption), conductivity (how readily the material transmits electrons), and work function (the energy needed to remove an electron from the surface to the vacuum level).

The objective of this research will be to investigate the unknown composition tie line between the GITO and ZITO compounds by doping GITO with small amounts of ZnO and doping ZITO with small amounts of Ga$_2$O$_3$. The doped GITO and ZITO materials will be analyzed with respect to how their properties differ from either pure undoped material. The resultant materials will add to TCO knowledge and help to solve the economic and functionality issues faced by the current standard ITO.

The GITO crystal structure relevant to this research is known as scheelite and can be represented by the chemical formula Ga$_{3-x}$In$_{5+x}$Sn$_2$O$_{16}$ where x can range from 0.3 to 1.6. The crystal has the same structure across the values of x. The ZITO crystal structure relevant to this research is called bixbyite and can be represented by the chemical formula Zn$_x$In$_{2-2x}$Sn$_x$O$_3$ where x can range from 0 to 0.4 (see Appendix B Figures 1 and 2 for phase diagrams). Scheelite GITO and bixbyite ZITO are very similar in structure. For many compositions of x the chemical formulae are similar, often with the number of oxygen atoms being close or equal. For example, multiplying by a factor of 5 the ZITO formula at x=0.4 yields Zn$_2$In$_6$Sn$_2$O$_{15}$, whereas the GITO formula at x=1 gives Ga$_2$In$_6$Sn$_2$O$_{16}$; these formulae differ only in oxygen content.

It has been documented that the metal ions in GITO have 4, 6, 7, and 8-fold coordination with all of the 4-fold coordination sites occupied by Ga in the scheelite crystal structure (see Appendix B Figure 3). At the indium-rich end of the scheelite GITO line compound the proportion of Ga on the 4-fold coordination sites over Ga in other sites is maximized. Since it has been well-documented in the literature that Zn is more stable in 4-fold coordination, I expect
that when GITO is doped with Zn that the Zn will replace the Ga on the 4-fold coordination sites. My expectation is that Zn-doped scheelite GITO will have a lower conductivity than pure scheelite GITO because Zn\(^{2+}\) ions are replacing Ga\(^{3+}\) ions, i.e. they are acceptors. This effectively removes an electron for each substitution, which reduces conductivity. I expect that Ga-doped bixbyite ZITO will have a higher conductivity than pure bixbyite ZITO for the opposite reason, i.e. Ga\(^{3+}\) on Zn\(^{2+}\) sites should be donors. In addition to this I will answer the following questions in this research: (1) What is the solubility limit (if any) of Zn in GITO and Ga in ZITO? (2) How do the lattice parameter, bandgap, conductivity, work function change as the amount of dopant increases? (3) Will the conductivity in GITO decrease as it is doped with Zn, and conversely will the conductivity in ZITO increase as it is doped with Ga as expected?

The following procedure will be followed to make the doped samples and analyze the results. All samples will be synthesized with conventional solid state synthesis techniques, which include making ceramic pellets of GITO and ZITO from powder precursors with varying amounts of dopant and firing them in a furnace. To find the solubility limit of the dopant in the host material, I will use X-ray diffraction and Reitveld refinement software to find the lattice parameters of the samples. Then the lattice parameters will be plotted versus the amount of dopant added and by Vegard’s law should exhibit a linear relationship. When the lattice parameter no longer changes with doping, but remains constant, then the solubility limit has been reached. The conductivity of each sample will be found with a 4-point conductivity probe test (see Appendix B Figure 4 for schematic). The thermopower will also be measured by placing the pellets between a heating element and heat sink, with probes on either side to measure the voltage potential as temperature difference changes; changes in carrier content can then be inferred from the thermopower data. The work function of each pellet will be measured by Kelvin Probe under ambient conditions. The bandgap will be calculated by analyzing optical diffuse reflectance data with the Kubelka-Munk method. The data from the tests of the doped samples will be compared to that of the pure GITO and ZITO to determine how the properties of the materials vary as they are doped.

This research will break new ground and provide critical knowledge on how the properties of GITO and ZITO can be further manipulated to offer a more diverse array of TCO properties. The basics of ceramic structure that I have learned in Materials Science 301 combined with the knowledge of phase diagrams and diffusion that I am learning in Materials Science 315 are directly relevant to my project, and in turn my project has allowed me to apply concepts I have learned in class. I have already begun synthesizing pure and doped GITO and ZITO in the Mason Group Lab, and continuing this research over the summer will allow me to investigate these materials more rigorously as well as add to my rapidly-growing understanding of materials science. I have been trained to use all of the equipment that I will use to conduct my tests and so far have three months’ experience in the laboratory. This research endeavor will expose me to novel research in my field that will hopefully lead to a publication of the results. The combined laboratory and publication experience will also prepare me to apply for graduate school in the future and propel me into a career as a materials science researcher.
Appendix 1: References


Appendix 2: Figures

Figure 1: GITO phase diagram\textsuperscript{6}. The scheelite crystal structure is indicated by the arrow. $x=0.3$ corresponds to the left side of the line and $x=1.6$ corresponds to the right side of the line.

Figure 2: ZITO Phase diagram\textsuperscript{4}. The bixbyite crystal structure is represented by the vertical line extending from the top at the InO$_{1.5}$ tip of the diagram. The top of the line corresponds to $x=0$ and the bottom corresponds to $x=0.4$. 
Figure 3: The GITO unit cell showing the 4, 6, 7, and 8-fold coordination sites. The areas of 4-fold coordination are represented in orange. In the 4-fold coordinated sites a gallium (Ga) atom is surrounded by 4 oxygen atoms. I expect that the Zn added to GITO will occupy these sites.

Figure 4: Schematic of the 4-point conductivity testing apparatus. A current is applied across the outer probes and the voltage is measured across the inner two probes. Source: http://fabweb.ece.uiuc.edu:1999/Equipment/4PointProbes/Instructions.html