

METAL-INSULATOR TRANSITIONS IN CuInGaO_4 AND $\text{CuIn}_2\text{Ga}_2\text{O}_7$ HOMOGENEOUS PHASES

Naratip Vittayakorn^{1,*} and David P. Cann²

¹Department of Chemistry, Faculty of Science, King Mongkut's Institute of Technology
Ladkrabang, Bangkok 10520 THAILAND

²Faculty of Materials Science, Department of Mechanical Engineering, Oregon State
University, Corvallis, OR 97331, USA

ABSTRACT

The compounds CuInGaO_4 and $\text{CuIn}_2\text{Ga}_2\text{O}_7$ crystallize in the $(\text{LnFeO}_3)_n\text{FeO}$ layer structure. In this paper, the electrical properties of CuInGaO_4 and $\text{CuIn}_2\text{Ga}_2\text{O}_7$ ceramics prepared by solid-state synthesis were examined. Both compounds exhibited a dramatic change in physical properties across a second-order phase transition at 226 K identified by calorimetry experiments. Above this temperature, the conductivity increased over four orders of magnitude and the relative permittivity increased and became strongly dispersive. These observations are explained on the basis of a hole-hopping mechanism in the Cu layers within the $(\text{LnFeO}_3)_n\text{FeO}$ crystal structure.

KEYWORDS: Ceramics, Electrical properties, Electroceramics, Semiconductors

1. INTRODUCTION

The $\text{CuO-In}_2\text{O}_3\text{-Ga}_2\text{O}_3$ ternary-phase diagram described by Kimizuka and Takayama [1] reveals two ternary compounds, CuInGaO_4 and $\text{CuIn}_2\text{Ga}_2\text{O}_7$. Both phases crystallize in the $(\text{LnFeO}_3)_n\text{FeO}$ structure with a hexagonal unit cell where $n = 1$ for CuInGaO_4 and $n = 2$ for $\text{CuIn}_2\text{Ga}_2\text{O}_7$ (Fig. 1) [2–4]. The structures can be derived from sequencing of layers composed of Ln_2O_3 and Fe_4O_5 for the $n = 1$ phase, and layers of Ln_2O_3 , Fe_4O_5 , and Fe_2O_3 for the $n = 2$ phase. The Ln site is in octahedral coordination with oxygen and the Fe sites are in fivefold coordination with oxygen via a trigonal bipyramidal configuration. In the $n = 1$ structure, both Fe sites are equivalent. In the $n = 2$ structure, one of the Fe sites is occupied solely by Fe^{3+} while the other Fe site has an average charge of $\text{Fe}^{2.5+}$ [3].

A series of compounds was synthesized by Kimizuka and Takayama [1] by substituting for Fe with a combination of divalent (M) and trivalent (Me) cations via $\text{LnM}^{2+}\text{Me}^{3+}\text{O}_4$ and $\text{Ln}_2\text{M}^{2+}\text{M}_2^{3+}\text{O}_7$. No evidence of ordering was observed in the X-ray diffraction (XRD) data for any of the $n = 1$ compounds. In the $n = 2$ compounds, it is assumed that the trivalent cation must substitute on the Fe^{3+} site, leaving a mixture of M^{2+} and Me^{3+} on the remaining $\text{Fe}^{2.5+}$ site. In the compounds CuInGaO_4 and $\text{CuIn}_2\text{Ga}_2\text{O}_7$, In^{3+} substitutes for the Ln ion, and Cu^{2+} and Ga^{3+} substitute for the Fe^{2+} and Fe^{3+} ions [1]. There are only a limited number of reports on the electrical properties of compounds with this crystal structure. Tanaka et al. [5] observed anomalous electrical properties in YFe_2O_4 polycrystals and single crystals. Most notably, they observed an abrupt change in the resistivity at approximately 250 K, which they attributed to a charge-ordering transition of the Verwey type. In this work, the electrical properties of CuInGaO_4 and $\text{CuIn}_2\text{Ga}_2\text{O}_7$ polycrystalline ceramics prepared via solid-state synthesis are presented.

2. EXPERIMENTAL

The CuInGaO_4 and $\text{CuIn}_2\text{Ga}_2\text{O}_7$ compounds were prepared via solid-state reaction from powders of CuO (Alfa Aesar 99%), In_2O_3 (Indium 99.99%), and Ga_2O_3 (All-Chemie 99.999%). After vibratory milling in ethanol with zirconia media, a precursor-phase InGaO_3 was prepared first by reacting In_2O_3 and Ga_2O_3 in air at 1100 °C for 4 h.

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Corresponding author.

E-mail address: naratipcmu@yahoo.com

After remilling, the InGaO_3 powders were reacted in air in the appropriate stoichiometric ratios with CuO to form CuInGaO_4 at 1100°C for 4 h or $\text{CuIn}_2\text{Ga}_2\text{O}_7$ at 1200°C for 4 h. The powders were then mixed with approximately 5 wt.% organic binder and 12.5-mm-diameter pellets were prepared by cold uniaxial pressing. Finally, the pellets were sintered in air at temperatures ranging from 1100 to 1200°C . XRD was utilized to verify the phase purity of the powders and sintered pellets. Gold electrodes were applied via sputtering.

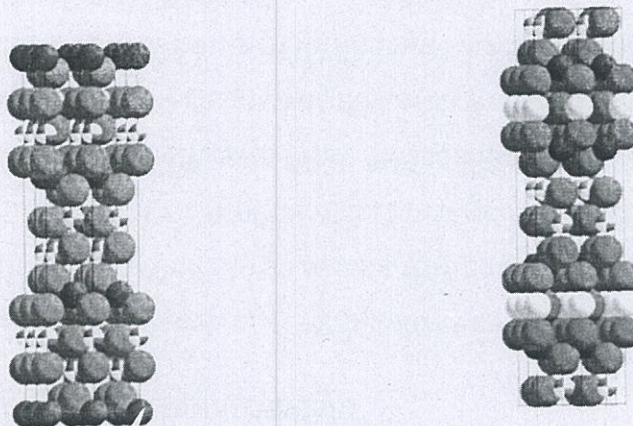


Fig. 1. Crystal structure of CuInGaO_4 (left) and $\text{CuIn}_2\text{Ga}_2\text{O}_7$ (right). The darkest atoms are In, gray atoms are Ga, white atoms are oxygen, and the two-tone atoms are Ga/Cu. A cluster of four unit cells is shown.

The dielectric properties as a function of temperature were measured via an HP 4274A LCR meter. Resistivity as a function of temperature was measured using a Keithley 6517A electrometer. Both measurements were performed upon cooling at a rate of $2^\circ\text{C}/\text{min}$. Room temperature impedance spectroscopy measurements utilized an HP 4194A impedance analyzer. All electrical measurements were carried out using gold electrodes; however, impedance spectroscopy measurements were conducted using both gold and In–Ga electrodes to verify that the contact resistance was negligible [7].

3. RESULTS

The XRD data for the sintered ceramics are presented in Figs. 2 and 3. The data show that the CuInGaO_4 compound is nearly phase-pure with one small unidentifiable parasitic peak. In contrast, the XRD data show that the $\text{CuIn}_2\text{Ga}_2\text{O}_7$ compound is phase-pure. For both compounds, the measured lattice parameters are in close agreement with those reported by Kimizuka and Takayama [1]. Because of the variable valance of Cu, deviations from the exact stoichiometry are possible.

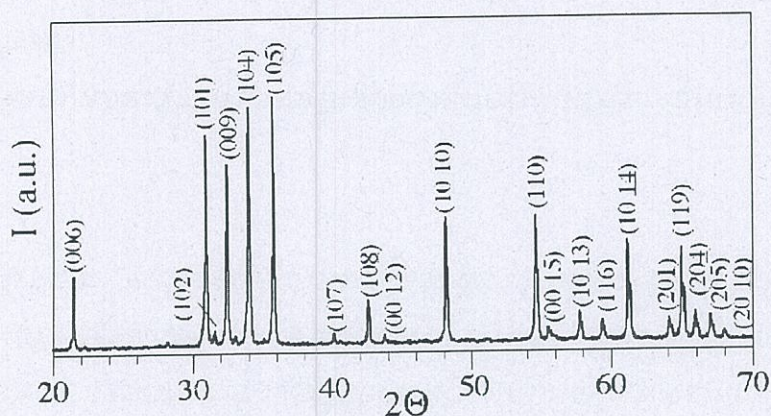


Fig. 2. XRD pattern of polycrystalline CuInGaO_4 ceramic.

Therefore, the CuInGaO_4 and $\text{CuIn}_2\text{Ga}_2\text{O}_7$ compounds referred to in this paper are the nominal batch compositions. The conductivity versus inverse temperature data for the CuInGaO_4 and

$\text{CuIn}_2\text{Ga}_2\text{O}_7$ ceramics are shown in Fig. 4. Both phases exhibit a temperature-independent conductivity below approximately 220 K, possibly due to the presence of impurities. Above this temperature, both exhibit a dramatic increase in conductivity of nearly five orders of magnitude up to 420 K. The slope $d(\ln \sigma)/d(1/T)$ in both curves corresponds to an Arrhenius activation energy of 0.52 eV.

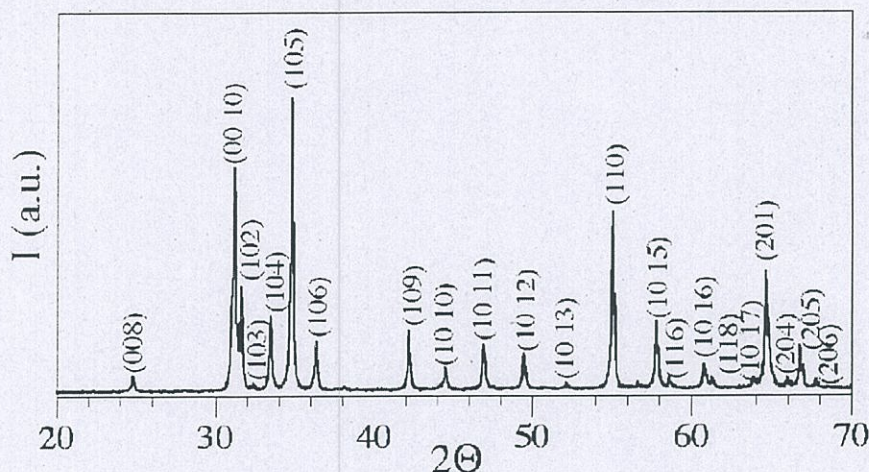


Fig. 3. XRD pattern of polycrystalline $\text{CuIn}_2\text{Ga}_2\text{O}_7$ ceramic.

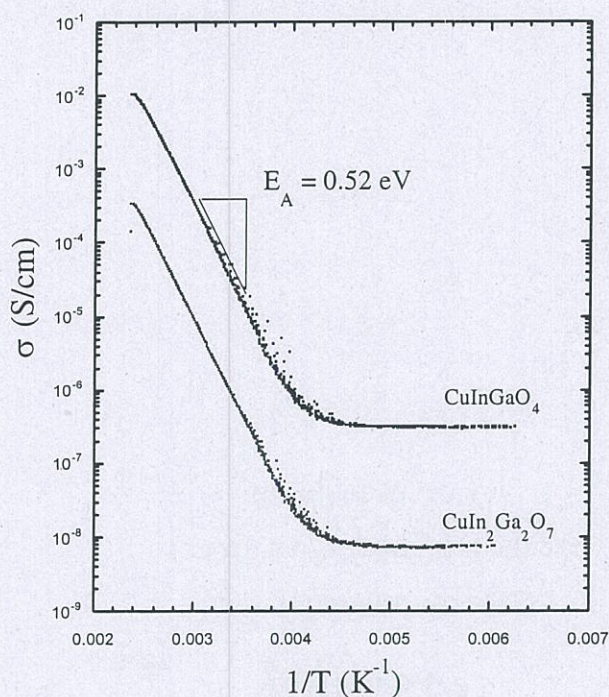


Fig. 4. Conductivity versus inverse temperature of CuInGaO_4 and $\text{CuIn}_2\text{Ga}_2\text{O}_7$.

This result is nearly double the value observed in the resistivity transition observed in polycrystalline YFe_2O_4 [5]. The overall conductivity of the CuInGaO_4 was larger than $\text{CuIn}_2\text{Ga}_2\text{O}_7$ by a factor of 30. Since it is likely that the conductivity in this structure is most strongly associated with the Cu layers, the higher conductivity observed in the CuInGaO_4 is due to the higher fraction of Cu layers as compared to $\text{CuIn}_2\text{Ga}_2\text{O}_7$. The dielectric spectra of the CuInGaO_4 sample are shown in Fig. 5. At low temperatures, the relative permittivity is relatively temperature-independent at a value of 16 at 10 kHz. The dielectric spectra of $\text{CuIn}_2\text{Ga}_2\text{O}_7$ are nearly identical, with a low-temperature permittivity of

18 at 10 kHz. The calculated value of the permittivity using the ionic polarizabilities of Shannon [7] and the Clausius–Mosotti equation is 10 for both compounds. This deviation is most likely related to the remanent conductivity at these temperatures. Above the critical temperature of 220 K, the permittivity increases dramatically and becomes strongly frequency dependent.

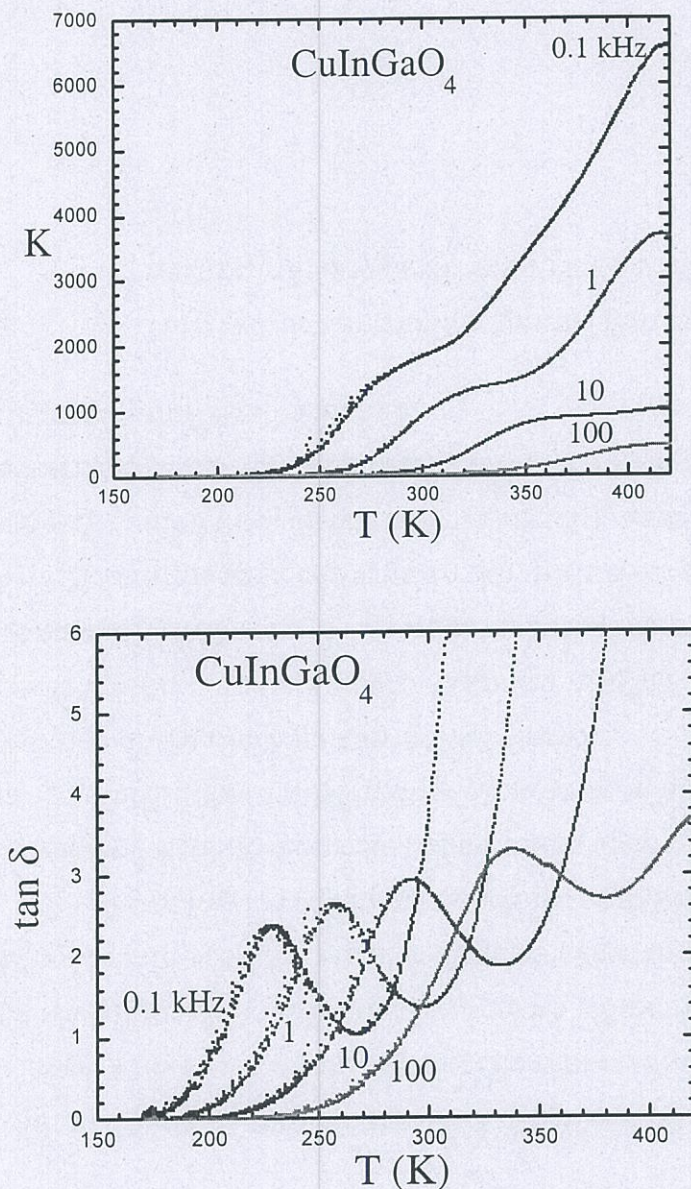


Fig. 5. Dielectric data on CuInGaO_4 at 0.1, 1, 10, and 100 kHz.

The precession of dielectric loss peaks is Debye in nature and follows an Arrhenius relationship with activation energies of 0.42 and 0.50 eV for CuInGaO_4 and $\text{CuIn}_2\text{Ga}_2\text{O}_7$, respectively. For both compounds, the pre-exponential derived from the Arrhenius fit is on the order of 1011 Hz. This is indicative of the presence of a mobile charges species (e.g., hole hopping) and is consistent with the observed conductivity transition in these materials. As the samples were polycrystalline, the observed polarization is likely due to grain boundary barriers. Lastly, shown in Fig. 6 are differential scanning calorimetry (DSC) data under a cooling rate of 10 K/min. Above the transition, both CuInGaO_4 and $\text{CuIn}_2\text{Ga}_2\text{O}_7$ exhibit an identical slope. However, upon reaching the transition temperature, clearly identified in the data as 226 K, there is a change in slope but virtually no peak. This is indicative of a second-order phase transition, possibly related to a change in magnetic ordering

within the Cu layer. In general, the electrical properties observed in CuInGaO_4 and $\text{CuIn}_2\text{Ga}_2\text{O}_7$ share many similarities with the properties of CuO with the tenorite structure. From Zheng et al. [8,9], the conduction mechanism in CuO can be described by hole hopping between Cu^{3+} and Cu^{2+} sites. The strong temperature dependence of the conductivity in CuO , which mirrors that observed in CuInGaO_4 and $\text{CuIn}_2\text{Ga}_2\text{O}_7$, is attributed to charge ordering. A dramatic increase in the conductivity occurs above 200 K, coinciding with two magnetic transitions at 213 and 230 K. Zheng et al. [8] also presented dielectric data that closely match those in Fig. 5. Arrhenius fits to the dielectric relaxation data produce a similar activation energy of 0.32 eV and a preexponential factor of 1013 Hz. The Cu^{2+} ion in CuO and in many other Cu-containing oxides exhibits a square planar configuration. In contrast, in both CuInGaO_4 and $\text{CuIn}_2\text{Ga}_2\text{O}_7$, the Cu^{2+} ion exists in five-fold coordination within a double layer of corner-shared trigonal bipyramids, as shown schematically in Fig. 7. It is important to note that in both structures, Ga^{3+} coexists with Cu^{2+} within the five-fold coordinated sites with no evidence of ordering. There are a number of materials which have layers with Cu-containing trigonal bipyramids including variants of the hexagonal rare earth type structure (i.e., YAlO_3) [10]. Elements of this structure occur in materials such as $\text{La}_4\text{Cu}_3\text{MoO}_{12}$ and $\text{La}_3\text{Cu}_2\text{VO}_9$, for example [11,12].

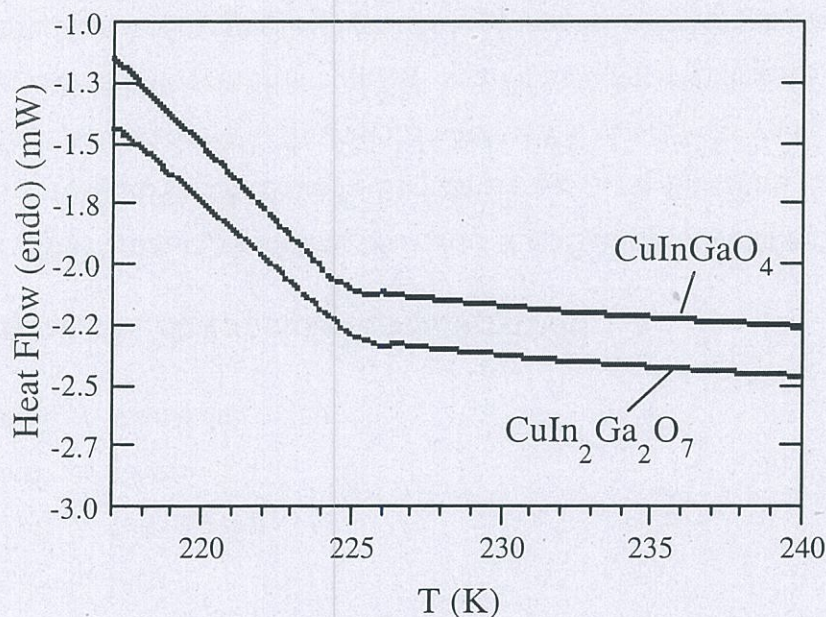


Fig. 6. DSC data for of CuInGaO_4 and $\text{CuIn}_2\text{Ga}_2\text{O}_7$ at a cooling rate of 10 K/min.

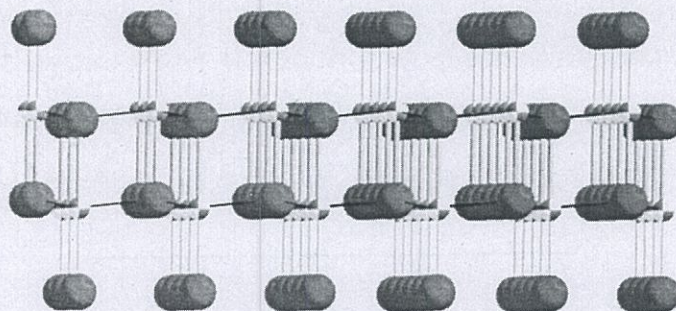


Fig. 7. Structure of the double layer of trigonal bipyramids. The cations are composed of disordered Cu^{2+} and Ga^{3+} ions in a 1:1 ratio.

Detailed electrical properties have not been reported, but recent work by Vander Griend et al. [11] showed that $\text{La}_4\text{Cu}_3\text{MoO}_{12}$ exhibited a number of magnetic transitions. Future work will confirm whether magnetic transitions indeed occur in CuInGaO_4 and $\text{CuIn}_2\text{Ga}_2\text{O}_7$. However, the sum of the conductivity, DSC, and dielectric data suggests that the observed phenomenon is the result of a hole-hopping mechanism within the Cu layers.

4. CONCLUSIONS

Polycrystalline ceramics of CuInGaO_4 and $\text{CuIn}_2\text{Ga}_2\text{O}_7$ prepared by solid-state synthesis exhibited a significant increase in conductivity above 226 K with an activation energy of 0.52 eV. This was accompanied by a frequency dependent increase in the relative permittivity. Arrhenius plots of the dielectric relaxation data yield activation energies of 0.42 and 0.50 eV for CuInGaO_4 and $\text{CuIn}_2\text{Ga}_2\text{O}_7$, respectively, and a preexponential coefficient for both compounds on the order of 10^{11} Hz. In addition, a second-order phase transition was observed at 226 K in the DSC data, suggesting a magnetic transition. The most likely explanation for the observed experimental data is a hole-hopping mechanism within the Cu-containing layers within the CuInGaO_4 and $\text{CuIn}_2\text{Ga}_2\text{O}_7$ crystal structure.

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