

Growth and Physical Properties of Metallic In_2O_3 Single Crystals

ZERI S. TEWELDEMEDHIN, K. V. RAMANUJACHARY,
AND M. GREENBLATT¹

*Department of Chemistry, Rutgers, The State University of New Jersey,
Piscataway, New Jersey 08855*

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Single crystals of metallic indium oxide were grown for the first time by molten salt electrolysis and their electrical and magnetic properties were investigated. The crystals are the cubic form of indium oxide with a C-type rare earth oxide structure as inferred by X-ray powder diffraction. The crystals are highly reflective and have colors ranging from dark green to green–yellow depending on the crucible used for preparation and on the location of the crystals at the cathode surface. The resistivity as a function of temperature, on all the crystals, showed metallic behavior up to about 100 K and almost temperature-independent behavior down to ~ 2 K. The room temperature resistivity of the dark green sample is in the range of 10^{-4} Ω -cm. Qualitative Seebeck measurements indicate that electrons are the primary charge carriers. The temperature variation of the magnetic susceptibility is Pauli paramagnetic, consistent with the observed metallic property. The crystals were found to be stable up to ~ 1200 K upon exposure to oxidizing atmospheres. The measured physical properties are supportive of the presence of a small concentration of charge carriers with high mobilities. © 1990 Academic Press, Inc.

I. Introduction

Elements of group IIIA form oxides that exist in more than one structural form and their electrical conducting behavior varies from insulator to metallic down the group. Thallium oxide, the end member of group IIIA oxides, has room temperature resistivity in the order of 10^{-5} Ω -cm and is an *n*-type degenerate semiconductor (1–3). Earlier studies on the electrical resistivity of the cubic form of indium oxide indicated that the room temperature resistivity values and their temperature variation depended both on the crystallinity of the sample and the chemical effects induced by impurities. Single crystals of indium oxide prepared

from the vapor phase of indium metal and oxygen showed room temperature resistivity in the range of 0.10 Ω -cm (4). Thermoelectric power measurement on these crystals revealed that electrons are the primary charge carriers. Optical properties (5) and magnetoresistance (6) of indium oxide crystals prepared by this method have also been reported.

Relatively large single crystals of indium oxide were grown by Remeika and Spencer by the ΔT flux technique in which a mixture of indium oxide, boron oxide, and lead monoxide was melted at a temperature of 1473 K and then cooled to about 773 K at a controlled rate before allowing it to cool to room temperature (7). Indium oxide crystals grown by this method are conducting at room temperature (~ 2 Ω -cm); however, the

¹ To whom correspondence should be addressed.

temperature dependence of electrical resistivity showed semiconducting behavior. A sharp break in the conductivity plot at about 40 K was also observed on these crystals, which has been attributed to change in the conduction mechanism. Another study on pressed samples of polycrystalline indium oxide, in the temperature range 453 K to 733 K, showed that the samples are semiconducting, with relatively high room temperature resistivities (8).

De Wit has compared the electrical properties of indium oxide from the literature (4, 7–10) with his data on both single crystals and polycrystalline indium oxide pellets (11). The crystals, prepared by flux and vapor techniques, were black and green, respectively. These samples have room temperature resistivity greater than $\sim 0.1 \Omega\text{-cm}$ and showed an irreversible decrease of resistivity with temperature between 298 K and 1073 K in nitrogen atmosphere, presumably, due to the loss of oxygen in inert atmospheres. The same irreversible behavior was observed upon repeated heating and cooling. Electrical property of indium oxide single crystals has also been studied at temperatures in excess of 1073 K (4, 12).

The electrical conductivity of oxygen-deficient polycrystalline indium oxide films has been extensively investigated (13–17). High electrical conductivity of indium oxide films prepared by thermal evaporation of a mixture of indium and indium oxide has been reported by Pan and Ma (17). Heat-treated samples of indium oxide films have shown resistivity behavior dependent on the conditions during heat treatment and have been used to study metal-insulator transitions (14, 15).

The hexagonal form of indium oxide (the high pressure form, with the corundum structure) has electrical resistivity in the order of $10^{-3} \Omega\text{-cm}$ at room temperature (18). This form of indium oxide has a lower resistivity than its cubic analog. Semiconducting behavior was speculated in the hexagonal

form of In_2O_3 ; however, the temperature dependence of its electrical conductivity was not reported.

In the present study single crystals of cubic indium oxide were grown by electrolysis of a molten mixture of indium oxide, lithium molybdate, and molybdenum trioxide. These crystals have colors that depend on the type of crucible used and on the relative location of the crystals grown at the cathode surface. Single crystals of indium oxide grown by this method have relatively high electrical conductivities and show metallic behavior. The observed electrical and magnetic properties of these crystals are discussed in terms of small degree of oxygen vacancy in the structure similar to that reported in the literature for crystals of thallium oxide, Tl_2O_3 .

II. Experimental

Crystals were grown by molten salt electrolysis of a mixture of $\text{In}_2\text{O}_3\text{-Li}_2\text{MoO}_4\text{-MoO}_3$ in the mole ratio of 0.4 : 1.0 : 1.0. The lithium molybdate (98.5%, Alfa products) was dried at 433 K for 5 hr, the molybdenum trioxide (99.5%, J. T. Baker) was fired at 748 K before use, and the indium oxide (99.99%, AESAR) was used as supplied. Appropriate amount of each of the component oxides were mixed to give a total weight of about 39.0 g. The mixture was then ground to a fine powder and introduced into a porcelain or alumina crucible. Electrolysis was carried out at a temperature of 1113 K by passing a constant current of 35 mA for about 6 days. The crystals were grown on a platinum cathode of $0.50 \times 2.0 \text{ cm}$ size. The anode used was platinum foil of the size $1.0 \times 1.0 \text{ cm}$.

Phases were identified by X-ray powder diffraction, recorded on a Scintag PAD V X-ray diffractometer using $\text{CuK}\alpha$ radiation. Silicon was used as an internal standard. Elemental analysis of crystalline samples was carried out by DC plasma emission

spectrometer (Spectrametrics, Inc.), thermogravimetric analysis (TGA), and electron microprobe analysis. Solution of sample for plasma emission spectrometry was prepared by weighing the powdered crystals to the nearest tenth of a milligram and dissolving them in aqua regia while warming and stirring before diluting it to the desired volume with deionized water. A DuPont 9900 Thermal Analyser system was used in the thermogravimetric study. Elemental analysis by TGA was achieved by reducing powdered In_2O_3 single crystals in 15% H_2 - N_2 gas mixture (supplied by J. W. S. Technologies Inc.). The heat ramp was 4 K/min up to 1223 K and equilibrated at about the same temperature for 3 hr.

The resistivity measurement was done by a standard four-probe technique using a Displex cryostat for the temperature range 10 to 298 K. Liquid helium cryostat was also used in the low temperature range down to about 2 K. Typically four copper wire leads, two for the current and two for the voltage, were attached to the faces of a crystal under a microscope using Silver Paint (GC Electronics).

Magnetic susceptibility on selected single crystals was recorded in a Quantum Design SQUID magnetometer in the temperature range of 1.8 to 300 K at an applied magnetic field of 1000G.

III. Results

Typically, the crystals grown in porcelain crucibles were dark green in color whereas those grown in alumina crucibles were green-yellow. The powdered sample from the crystals grown in porcelain crucible were gray, while those from the alumina crucible were yellow. The crystals were recovered from the cathode by dissolving the molten flux surrounding the cathode assembly in dilute nitric acid solution. Crystals of indium oxide were also obtained from melt compositions in which the mole ratio of in-

dium oxide was less than the amount indicated above (i.e., <0.4). However, such compositions required higher temperature (about 1173 K) for the growth of very small indium oxide crystals. Further, it has been observed that for mixtures containing low indium oxide mole ratio, low electrolysis temperature and higher amount of current resulted in the growth of MoO_2 crystals on the cathode surface. We note that both the size and the amount of the indium oxide crystals obtained increased with increasing mole ratio of indium oxide in the flux. The temperature at which these crystals are grown is also relatively lower at higher indium oxide mole ratio. In compositions, where mixtures of In_2O_3 crystals and MoO_2 grew together on the cathode, the indium oxide crystals were always seen at the upper part of the cathode while MoO_2 crystals were formed at the lower part of the electrode. In most of the experiments the upper part of the platinum cathode, where the In_2O_3 crystals grew, was not completely immersed in the melt. This may indicate that the melt may not be homogeneous and that the crystals are formed from the less viscous and indium oxide-rich top part of this melt. Crystals up to $\sim 1.6 \times 1.0 \times 1.1$ mm in size could be grown in this way.

The X-ray powder diffraction patterns of the indium oxide crystals, regardless of their color, compares well with that of the cubic form indium oxide (pale yellow, JCPDS file No. 6-416) space group $I2_13$ (199) with $a = 10.118 \text{ \AA}$, $Z = 16$. The cubic indium oxide form has a C -type rare earth oxide structure. Although the X-ray powder diffraction pattern of indium oxide crystals prepared by electrolysis suggest that the sample is the cubic indium oxide form, the color and other physical properties of these crystals are different from those previously reported for cubic In_2O_3 .

The amount of indium in the dark green and green-yellow samples based on electron microprobe and plasma emission anal-

yses was consistent with the theoretically expected value within the error associated with the measurement. Chemical analysis, using plasma emission, for certain other elements in crystals grown in porcelain crucible indicated <0.09 wt % molybdenum, <0.04 wt % lithium, ~0.13 wt % aluminum, and ~0.2 wt % silicon. The amounts of these impurities are more than twice the amount found in the crystals grown in alumina crucible, by similar analysis. Electron microprobe analysis (EMPA) study has also shown the presence of these impurities within the range found by plasma analysis for the two samples. In addition, EMPA showed the presence of tin at a concentration of less than 0.06 wt % in both samples.

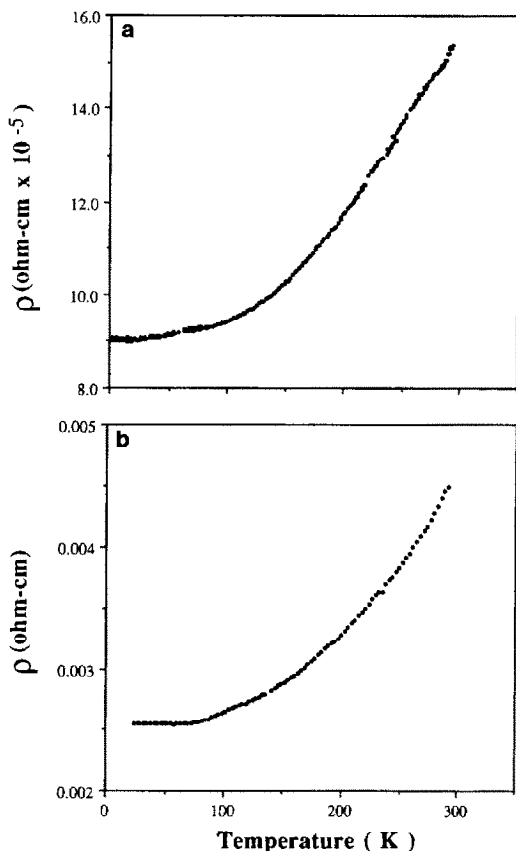


FIG. 1. Resistivity as a function of temperature for two different dark green crystals (a and b).

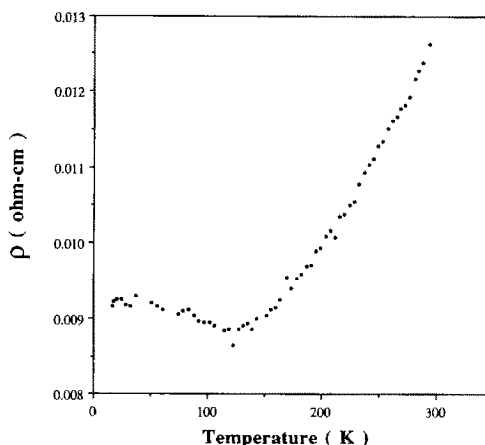


FIG. 2. Resistivity as a function of temperature for green-yellow crystal.

Results from TGA study on powdered samples of both the dark green and green-yellow crystals in 15% H₂-N₂ gas mixture were in agreement with the plasma emission data within experimental error, thus implying that the nonstoichiometry of oxygen in these crystals, if any, is immeasurably small. Both the dark green and green-yellow colored crystals or powdered samples of these crystals grown in the present study retained their color when heated in air or oxygen, and inert atmosphere up to a temperature of 1223 K.

Selected crystals of dimensions of about $0.9 \times 0.5 \times 0.6$ mm show resistivities of the order of 10^{-3} – 10^{-4} and 10^{-2} Ω -cm at room temperature for the dark green and green-yellow crystals, respectively. In both types of crystals the resistivity as a function of temperature shows a decrease till about 100 K which then remains almost temperature independent down to the low temperature region. The lowest resistivity observed was about 9.0×10^{-5} Ω -cm at 2.2 K for the dark green and about 9.0×10^{-3} Ω -cm at 100 K for the green-yellow crystals. Figures 1 and 2 present the resistivity variation as a function of temperature for dark green and

green–yellow crystals, respectively. It is evident from these plots that the green–yellow crystals showed slight increase in the resistivity below 100 K, while the dark green crystals showed nearly temperature-independent behavior below this temperature. These measurements were made on several different crystals from different batches of growth and each exhibit similar behavior in the temperature variation of the resistivity. Qualitative Seebeck measurements on these crystals indicated *n*-type conductivity, regardless of their color.

Figure 3a and 3b present the magnetic susceptibility as a function of temperature for randomly oriented dark green and green–yellow crystals, respectively. The susceptibility remains nearly temperature independent in the range 40–300 K, reminiscent of a Pauli paramagnetic-type behavior. The low temperature upturns seen in the magnetic susceptibility plots have been attributed to the presence of small amounts of magnetic impurities in the crystals. However, when corrections for the Curie tails were made, the susceptibility remained nearly temperature independent down to low temperatures.

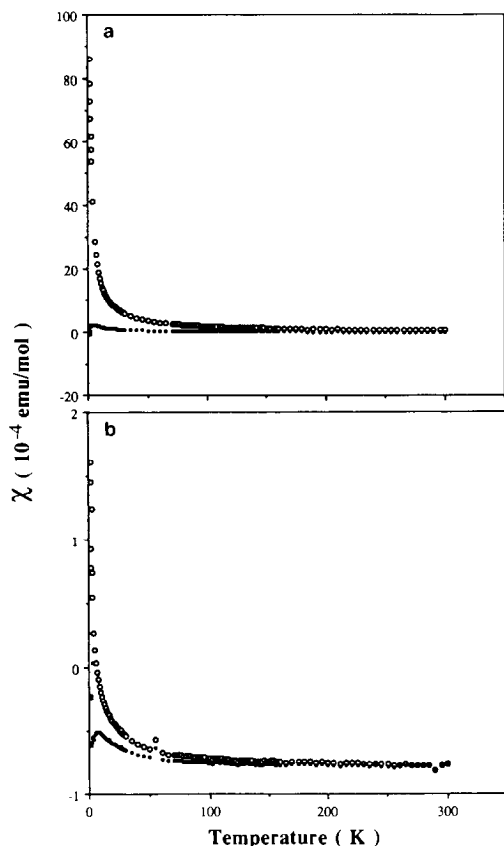


FIG. 3. Magnetic susceptibility as a function of temperature for (a) dark green crystals of (b) green–yellow crystals. (○, before; ●, after Curie correction was made.)

IV. Discussion

The Indium oxide single crystals grown in the present study are nearly stoichiometric, as revealed by Plasma emission analysis and TGA techniques. However, since the crystals were grown on cathodic surfaces, it is possible that there might exist a small range of oxygen deficiency, although not detectable by usual analytical techniques. The fact that the crystals grown in the same batch exhibited a range of colors can be mainly attributed to the different degrees of oxygen deficiency. However, the presence of trace amounts of impurities, to a different extent, in both the dark green and green–yellow crystals of different batches could also account for the observed difference in their color. The hexagonal form of In_2O_3 prepared by high-pressure synthetic techniques often developed blue color due to oxygen deficiency, which could be bleached by annealing them in O_2 stream at 773 K for several hours (18). However, we did not observe any change in the color of the crystals grown by electrolysis when heated in O_2 or air, and in inert atmosphere up to 1223 K for several hours. This might imply that the anion vacancies in the crystals are ordered and hence are resistant to significant uptake of oxygen.

Earlier studies on the electrical conductivity of polycrystalline or single crystals of indium oxide, prepared by different methods, have established that nonstoichiometric indium oxide is an *n*-type semiconductor with interstitial indium ions as predominant defects (4, 11). The poor reproducibility of the electrical properties observed in all of these experimental data has been attributed to the nonstoichiometry due to the conditions of preparation or presence of impurities (7, 8, 11). Further, it is possible that the presence of impurities could also play an important role in imparting the observed color differences on these samples, as also is observed in the present study.

Previous studies (13–15, 17) on the electrical conductivity of crystalline indium oxide thin films, prepared by different methods in reduced oxygen partial pressures, have exhibited room temperature resistivities in the range of 10^{-2} to 10^{-4} Ω -cm. The difference in the room temperature resistivity among different samples has been attributed mainly to changes in the effective density of free carriers caused by differences in the oxygen stoichiometry. The room temperature resistivity of a given sample was also reported to be sensitive to the heat treatment, due to the changes in the carrier mobility induced by vacancy ordering effects. In view of these observations, the differences in the room temperature conductivities of dark green and green–yellow crystals may be hard to explain, in the absence of Hall measurements. However, in the case of $\text{In}_2\text{O}_{3-x}$ crystalline films, the temperature variation of electrical resistivity was observed to be dependent on the room temperature resistivity values (ρ_{RT}). For example, films having $\rho_{\text{RT}} < 3 \times 10^{-3}$ Ω -cm displayed positive temperature coefficient of resistance down to ~ 100 K, while a semiconducting behavior was observed when ρ_{RT} exceeds this critical value. In contrast, the crystals grown in the present

investigation always showed metallic behavior, although the ρ_{RT} values for the green–yellow crystals are in excess of this critical value. These results suggest that both the concentration and mobility of free carriers play a dominant role in the observed metallic property.

Our results on the electrical property of indium oxide crystals compares well with the previous study on thallium oxide crystals reported in the literature (1–3). Thallium oxide (Tl_2O_3) has the *C*-type rare earth oxide structure similar to that of indium oxide. It is established in the case of Tl_2O_3 , that electrons are the primary charge carriers and the electrical resistivity varies from 6.0×10^{-5} to 1.5×10^{-4} Ω -cm when the temperature is increased from 4 to 900 K (1–3). It is also reported that the charge carrier concentration remains temperature independent, while a saturation behavior was observed in the Hall mobility below ~ 80 K. Thus, the metal-like temperature variation in the resistivity of Tl_2O_3 seen above 80 K has been correlated with the changes in the carrier mobility. A degenerate *n*-type semiconductor, with the donor states in the conduction band due to native defects arising mainly from oxygen vacancies, has been proposed for thallium oxide. On the basis of similarities in the structure and electrical resistivity variations, for both Tl_2O_3 and In_2O_3 , we propose that the conduction mechanism is likely the same for both these oxides. Thus the primary source of charge carriers in the In_2O_3 crystals grown in the present study could well be from oxygen vacancies; however, the effect of impurities cannot be ignored. More detailed studies are necessary to characterize the nature and confirm the origin of the charge carriers in these crystals. Hall voltage measurement was not possible due to the small size and irregular morphology of the crystals; however, attempts to grow crystals suitable for such study are in progress.

V. Conclusion

We report here for the first time the growth of highly conducting ($\rho_{\text{RT}} \sim 10^{-4}$ $\Omega\text{-cm}$) In_2O_3 single crystals by electrolytic techniques. The crystals exhibit different colors ranging from dark green to green-yellow depending on the crucible used for preparation and the relative location of the crystals grown over the surface of the cathode. The plasma emission, TGA, and EMPA studies indicate that the crystals are nearly stoichiometric. The electrical property of the dark green and green-yellow crystals is different from that reported in the literature for single crystals of cubic indium oxide. Both types show a metallic behavior down to a low temperature and Pauli paramagnetism. The electrical behavior observed in our study is similar and the values are comparable to certain disordered or oxygen-deficient indium oxide films, $\text{In}_2\text{O}_{3-x}$, and that of Tl_2O_3 single crystals.

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