Effect of Sintering Temperature and Heat Treatment on Electrical Properties of Indium Oxide Based Ceramics

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Abstract.

Indium oxide based ceramics with bismuth oxide addition were sintered in air in the temperature range 800-1300 ºC. Current-voltage characteristics of In_2O_3-Bi_2O_3 ceramics sintered at different temperatures are weakly nonlinear. After an additional heat treatment in air at about 200 ºC samples sintered at a temperature within the narrow range of about 1050-1100 ºC exhibit a current-limiting effect accompanied by low-frequency current oscillations. It is shown that the observed electrical properties are controlled by the grain-boundary barriers and the heat treatment in air at 200 ºC leads to the decrease in the barrier height. Electrical measurements, scanning electron microscopy and X-ray photoelectron spectroscopy results suggest that the current-limiting effect observed in In_2O_3-Bi_2O_3 can be explained in terms of the modified barrier model proposed earlier for the explanation of similar effect in In_2O_3-SrO ceramics.

1 Introduction

At low electric fields the current-voltage characteristic of a sample is generally linear and Ohm's law is obeyed. An increase in the electric field can cause some deviations from Ohm's law. Two cases are possible: superlinear, exploited in varistors, where the current rises more strongly than voltage, or sublinear where current rises more weakly than voltage. The nonlinear current-voltage characteristic can be approximated by the empirical equation

$$I = BU^{\beta}, \qquad (1)$$

where I is the current, U is the voltage, β is the nonlinearity coefficient $\beta = (U/I)(dI/dU)$ and B is some constant. In the case of superlinear current-voltage characteristic $\beta > 1$ and in the case of sublinear current-voltage characteristic $\beta < 1$.

At the present time, sublinear current-voltage characteristics have been found in some polycrystalline materials [1-7] and several explanations of this effect were suggested [1,3,8-11]. In particular, such behaviour has been observed in In_2O_3-SrO ceramics [5,6]. In this material the addition of strontium leads to an increase in resistivity at low electric fields and the appearance of non-Ohmic behaviour (saturation and even decrease in current density) at higher fields. The mechanism of such current limiting effect in In_2O_3-SrO ceramics can be related to the increase in the grain-boundary barrier height with applied electric field due to the additional oxygen adsorption as a result of electron capture at the grain-boundary states [12,13].

From a materials science view-point it would be interesting to study indium oxide based non-Ohmic ceramics with other additives. Indium oxide exhibits n-type conduction and is widely used for the preparation of transparent electrodes for optoelectronic devices [14-16] and gas-sensors [17-19]. However, it is well known that the addition of bismuth oxide (Bi_2O_3) improves the sintering and promotes an increase in the nonlinearity coefficient in zinc oxide based and tin dioxide based varistor ceramics [20-25]. This suggests that bismuth oxide addition may also induce non-ohmic behavior in indium oxide ceramics. Moreover, some bismuth oxide phases in such ceramics can have ionic conduction with oxygen ion as a carrier [26-28] this can be favorable for the manifestation of the current limiting mechanism proposed by Bondarchuk *et al.* [12,13].

To investigate this idea, we present a study of the electrical properties and microstructure of indium oxide based In_2O_3-Bi_2O_3 ceramics sintered at different temperatures and with different post-production heat-treatment processes.

2 Experimental Method

Indium oxide based ceramics (mol.%) $95In_2O_3$-$5Bi_2O_3$ were prepared by the conventional mixed oxides method. Distilled water was used to prepare a mixture, tablets were pressed at axial pressure 45 MPa and sintered in air at 800, 900, 1050, 1100, 1200 or 1300 ^oC (1 hour) with slow heating and cooling (5^oC/min).

Secondary electron images and spectra of energy dispersive X-ray microanalysis (EDX) were obtained utilising a Zeiss Supra 35VP field emission scanning electron microscope (FE-SEM). For X-ray photoelectron spectrometery (XPS) samples were mounted on polished copper to provide a known background and examined within VG EscaLab 210, utilising an aluminium anode. Survey spectra were collected over a wide energy range to provide general composition information; resolution was increased for expansions conducted over various peak positions, for elemental identification and intensity quantification, utilising empirically derived atomic sensitivity factors [29]. X-ray diffraction measurements were conducted within a Bruker D8 AXS spectrometer.

Ag-electrodes were used in electrical measurements. After grinding of a sintered sample, a suitable silver paste was overlapped at the flat surfaces and the sample was heat treated in air up to a maximum temperature of 800^oC with slow heating, maintaining this temperature for 10 mins followed by slow cooling. An additional heat treatment in air atmosphere at 800^oC was conducted in a similar way but the sample was kept at 800^oC for 1 hour. An additional heat treatment in air atmosphere at 200^oC was performed by slowly heating a sample with Ag-electrodes up to 200^oC, maintaining this temperature for 1 hour and subsequently quenching to room temperature.

Current-voltage characteristics were studied in the “voltage source” regime utilizing a Keithley-237 unit. DC voltage was applied, current was measured and voltage was dropped to zero to avoid overheating the sample. The process was repeated with a higher voltage applied, thus producing voltage in the form of rectangular pulses with increasing amplitude. An automatic recording voltage was applied during 10 ms (current was measured at the end of this interval) and the voltage was reduced to zero for a period of 100 ms. In the sublinear region at dc voltages above about 60 V current oscillations always took place and current scattering was observed. In some cases to avoid such a scattering in the figures the average current values were plotted. Electric field E_{-5} was calculated at the current density $j = 1 \cdot 10^{-5}$ A cm^{-2}.

Temperature dependence of dc electrical conductivity $\sigma(T)$ was obtained in the range of 290-370 K in air at heating and cooling of a sample with a rate of about 1.5 K/min. The activation energy of electrical conduction E_σ was found from the equation:

$$\sigma(T) = \sigma_0 \exp(-E_\sigma / kT) \qquad (2)$$

where σ is the electrical conductivity, σ_0 is a constant, k is the Boltzmann´s constant, T is the absolute temperature.

3 Experimental Results and Discussion

3.1 Sintering Temperature. SEM micrographs of the as-sintered surface of the samples obtained at different sintering temperature are shown in figure 1. The grain size increases with sintering temperature; for example, in the sample sintered at 1100 ^{o}C grains in the range 0.5-2 μm are observed, in contrast to the sample sintered at 800^{o}C where the grain size is 200 – 500 nm. All samples are quite porous, though they are sufficiently solid due to Bi_2O_3 addition responsible for liquid-phase sintering.

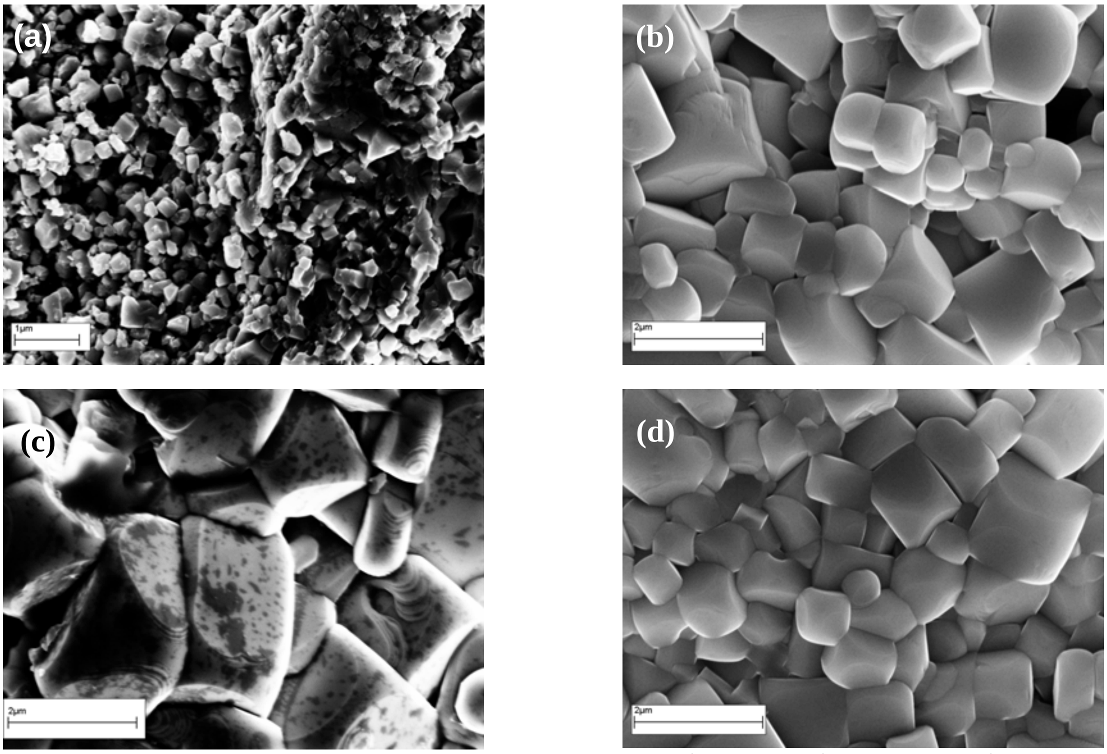

Fig.1. SEM micrographs of In_2O_3-Bi_2O_3 ceramics sintered at (a) 800^{o}C, (b) 1100^{o}C and (c) 1300^{o}C. The sample sintered at 1100^{o}C and heat treated at 200^{o}C is shown in (d)

The analysis volume of the EDX technique is comparable with the grain size in these samples; however, spectra taken from a grain centre (fig.2,a) show intense indium signal and small lines from bismuth and oxygen, and the bismuth signal increases at the edge of grain

(Fig.2,b). This analysis suggests samples contain In_2O_3 grains and small amount of Bi_2O_3 phase, predominantly at the boundaries. XRD measurements are consistent with bismuth oxide as a boundary phase, rather than incorporated into In_2O_3 lattice.

Current-voltage characteristics of In_2O_3-Bi_2O_3 ceramics sintered at different temperatures (fig.3) are weakly superlinear ($\beta > 1$). The increase in sintering temperature causes a decrease in the low-field conductivity (at 800-1050°C) followed by an increase at 1050-1300°C. This means that electric field, E_{-5} , at fixed current density ($j = 1 \cdot 10^{-5}$ A cm^{-2}) passes through a maximum (fig.4, curve 1).

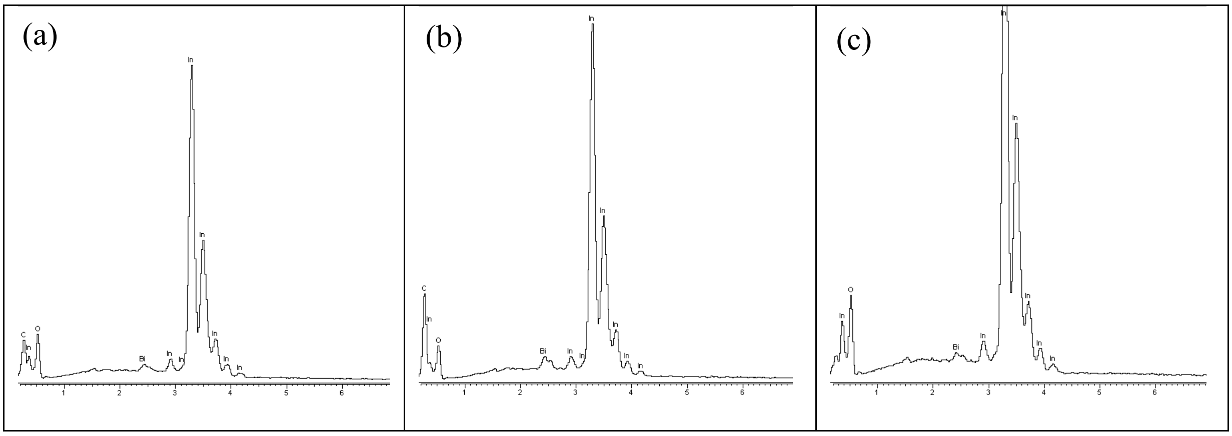

Fig.2. EDX spectra of In_2O_3-Bi_2O_3 ceramics sintered at 1100 C. (a) central part of In_2O_3 grain; (b) edge of In_2O_3 grain; (c) sintered at 1100 C and heat treated at 200 C.

If conduction is controlled by the grain-boundary barriers, then the barrier height in this case should also pass through a maximum. If we additionally assume that the Fermi level in the bulk of indium oxide grains is situated not more than several tenths of eV below the conduction band edge and, therefore, the barrier height φ in the studied In_2O_3-Bi_2O_3 ceramics is only slightly less than the activation energy E_σ of electrical conduction, $\varphi \cong E_\sigma$, then one can expect that the activation energy also should pass through the maximum. Experimental data confirm such assumption: the activation energy for different sintering temperatures indeed goes through a maximum at 1100°C (Fig.4, curve 2).

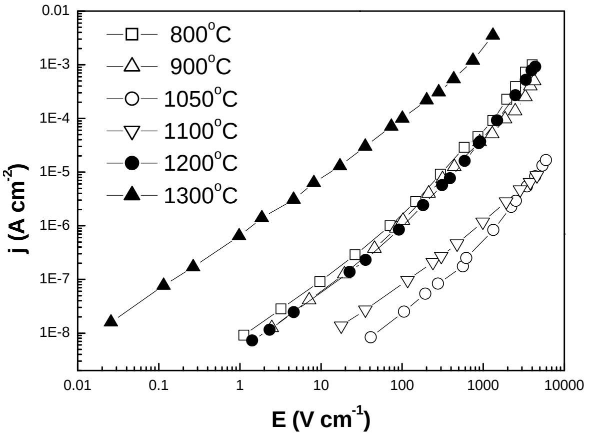

Fig.3. Current-voltage characteristics of In_2O_3-Bi_2O_3 ceramics sintered at different temperatures.

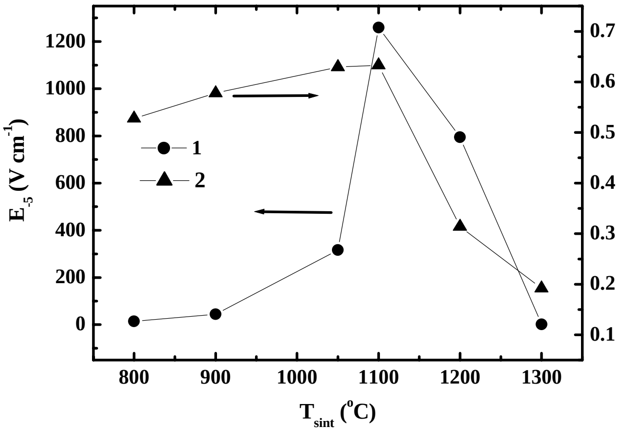

Fig.4. (1) electric field at fixed current density and (2) activation energy of conduction versus sintering temperature.

Probably, due to n-type conduction in indium oxide, the increase in sintering temperature up to 1100°C leads to some growth in oxygen content at the grain boundaries related to the presence of liquid Bi_2O_3 though at higher temperatures the evaporation of bismuth oxide becomes significant and oxygen content at the grain boundaries is decreased. In any case, observed correlation supports the assumed barrier conduction mechanism: the higher the barrier height, the lower the conductivity (Fig.3) and, therefore, the higher the electric field at fixed current density (Fig.4, curve 1).

3.2 Additional Heat Treatments. In the samples sintered at different temperatures, sublinear I(U) and current oscillations were not initially manifested. It has been shown previously [30] that in In_2O_3-Bi_2O_3 ceramics obtained at 1100 °C, current limiting and low-frequency current oscillations effects appeared after a heat treatment in air at about 200 °C with sharp cooling. Therefore, samples sintered at different temperatures were subjected to the additional heat treatment at 200 °C. It was observed that samples sintered at 1050 and 1100°C exhibit sublinear current-voltage characteristics, relatively weak in the sample sintered at 1050°C and quite strong for the sample sintered at 1100°C (Fig.5) samples sintered at other temperatures retain the slight superlinearity of current-voltage characteristic, even after the additional heat treatment. Low-frequency current oscillations accompany the observed sublinearity but to avoid some complexity, current-voltage characteristics in the sublinear region are presented using average current values. The current limiting effect and low-frequency current oscillations are reproducible and symmetric. Some degradation of the current-voltage characteristics after numerous measurements is observed in these In_2O_3-Bi_2O_3 ceramics, although such a degradation is less than was found in In_2O_3-SrO ceramics [12].

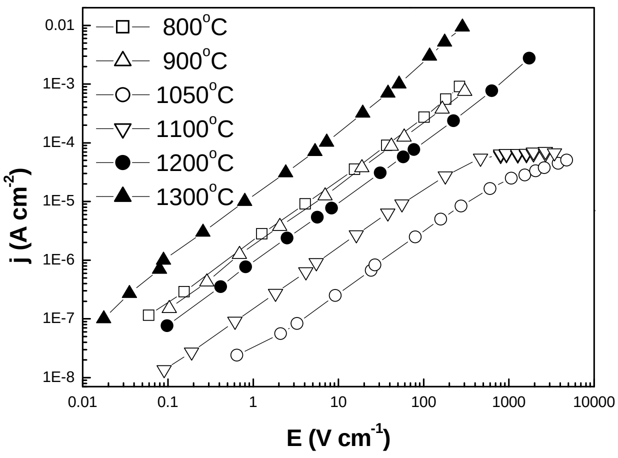

Fig.5. Effect of the heat treatment in air at 200°C on current-voltage characteristics of In_2O_3-Bi_2O_3 ceramics sintered at different temperatures

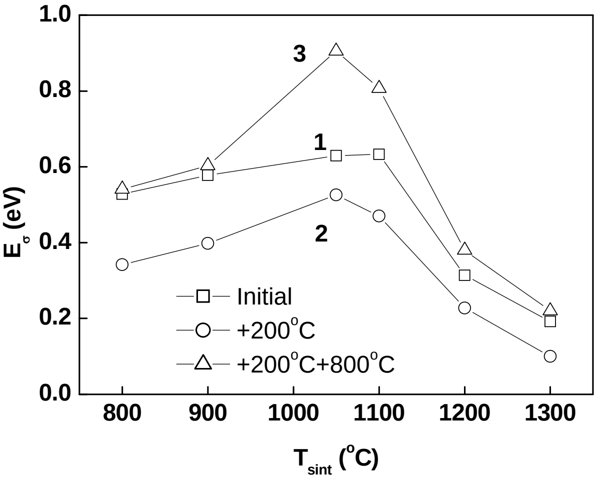

Fig.6. Activation energy of electrical conduction versus T_{SINT} measured after the additional heat treatment in air (1) at 800 °C (during formation of electrodes) then (2) at 200 °C and then (3) at 800 °C again.

So far we relate both the current limiting effect and current oscillation to the grain-boundary barriers, which appear in these ceramics as a result of sintering in the oxidizing atmosphere. The additional heat treatment at 200 °C affects electrical properties of the samples sintered at 1100°C; it would therefore be interesting to study the effect of this heat treatment on the barrier height. As shown in figure 6, the heat treatment in air at 200°C with rapid quenching causes the barrier height to decrease for all sintering temperatures. An additional heat treatment in air at 800 °C causes barrier height to increase, equally or exceeding initial values. The barrier height as a function of sintering temperature has a maximum at about 1050-1100°C regardless of the subsequent heat-treatment process.

The system with decreased barrier height after the heat treatment in air at 200°C appears to be quite stable. Similar time-stability of electrical properties was observed in SnO_2-ZnO-Bi_2O_3 varistor ceramics after the heat treatment in air at 200-400 °C [22]. Only an application of electric field causes subsequent electron capture, resulting in an increase of barrier height as electric field increases due to additional oxygen absorption, thus causing the observed current-limiting effect.

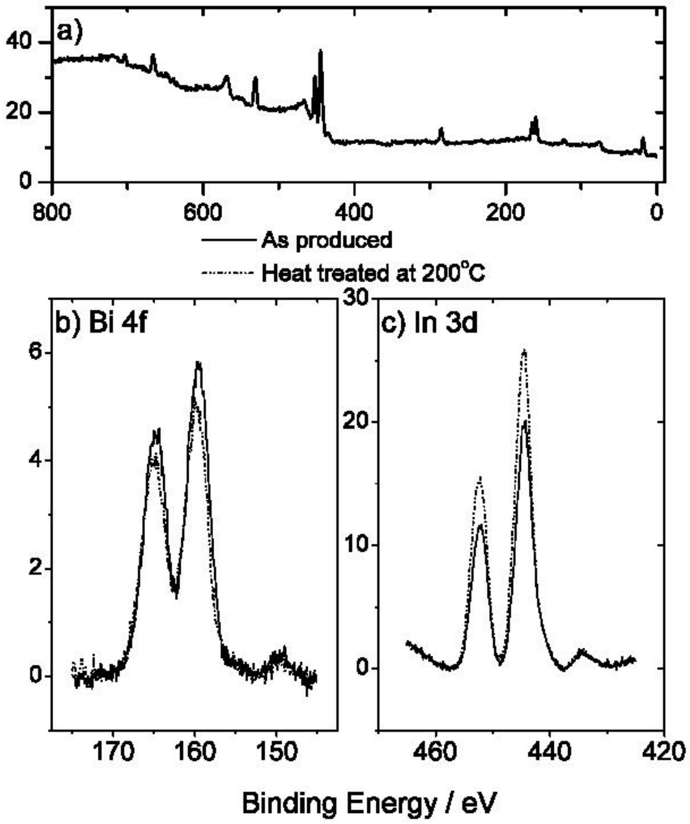

Fig. 7. XPS spectra of In_2O_3-Bi_2O_3 ceramics sintered at 1100°C before and after the heat treatment at 200°C. (a) survey spectrum, and dominant peaks for (b) bismuth and (c) indium

The observed decrease in the barrier height after the heat treatment in air at 200°C could be explained by a decrease in oxygen content at the grain boundaries. Therefore, to further explore the oxygen content in the sample we studied XPS spectra of the samples sintered at 1100 °C, with and without additional heat treatment in air at 200°C. Figure 7 a) shows typical XPS spectra of In_2O_3-Bi_2O_3 ceramic. Expansions for the sample sintered at 1100 C, before and after heat treatment at 200°C, are shown in Figure 7 b) and c) for bismuth 4f and indium 3d peaks, respectively. There is a slight increase in the relative oxygen content of the sample surface following heat-treatment; however, this can most likely be related to the decrease in hydrocarbon contamination on the sample surface, as there is no significant change in the ratio of oxygen content to the sum of the indium and bismuth contents. More noticeably, the XPS data show a change in the indium:bismuth ratio at the sample surface; this ratio increases by a factor of approximately 1.4 following heat treatment at 200°C. There is no concurrent shift in the photoelectron peak position, indicating at most only a negligible change in the oxidation state. This alteration in the surface chemistry is not accompanied by a change in the morphology, or by a change in the bulk In:Bi ratio as detected by EDX – a technique with a penetration depth in the order of micrometres, rather than the 1 - 10nm analysis depth of XPS. However, the EDX spectra do suggest some change in the oxygen content within the grains (fig 2), suggesting the heat treatment and rapid quench do cause some redistribution of the oxygen within the ceramic. Although the difference in oxygen content is not entirely clear, we believe that the change in chemistry of the grain boundaries with additional heat treatment processes results in the observed current-limiting effect caused by additional oxygen absorption as an applied electric field is increased [12,13].

Conclusions

In_2O_3-Bi_2O_3 ceramics with current-limiting effect (sublinear I(U) dependence, nonlinearity coefficient < 1) are investigated. The materials were sintered in air in the temperature range 800-1300 ºC. The grain size increases with increase in sintering temperature. It is found that sublinear I(U) characteristics are observed only in In_2O_3-Bi_2O_3 ceramics sintered at a temperature within the narrow range of about 1050-1100 ºC, and with subsequent heat treatment in air at 200 ºC with rapid quenching. It is shown that the observed electrical properties are controlled by the grain-boundary barriers and the heat treatment leads to the decrease in the barrier height. Electrical measurements, scanning electron microscopy and X-ray photoelectron spectroscopy results suggest that the current-limiting effect observed in In_2O_3-Bi_2O_3 can be explained in terms of the modified barrier model proposed earlier for the explanation of similar effect in In_2O_3-SrO ceramics.

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