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Thermal Properties and Electrical Conductivity of Pure In_2O_3 and Doped with ZrO_2

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The thermal properties (TGA, DTA) and AC electrical conductivity of pure In_2O_3 and ZrO_2 doped In_2O_3 have been studied. The dopants ratio were 1, 3, 5, 8 and 10 mol % of ZrO_2. The AC conductivity as a function of temperature was measured in the temperature range 298-753 K at a frequency 20 KHz. The plots of log $\sigma(\Omega^{-1}\ cm^{-1})$ *vs.* 1/T (K^{-1}) showed that all curves have three parts and the activation energies for conduction were calculated.

Key Words: TGA, DTA, ZrO_2, Doped In_2O_2, Electrical properties.

INTRODUCTION

Hanafi *et al.*[1] measured the electrical conductivity of In_2O_3 prepared from $In(OH)_3$ and $In(NO_3)_3$ at 450, 650 and 850 ºC. The results indicated that the sample which prepared from $In(OH)_3$ at 850 ºC for 3 h is the most stoichiometric one.

The effect of doping of Ti, Nb, Ta, W, or Ge on the electrical conductivity of In_2O_3 single crystal is negligible while Zr and Hf have a strong effect, these results were reported by Kani[2]. Qadri *et al.*[3] studied In_2O_3 doped transparent conducting oxides of ZrO_2 and studied the the electrical conductivity of ZrO_2 doped In_2O_3, the ratio of ZrO_2 ranges from 0-15 mol %[4].

TGA and DTA analyses of standard In_2O_3 were studied by different authors[5-9]. Comparatively less work concerning the thermal properties and AC electrical conductivity of In_2O_3 and ZrO_2 doped In_2O_3 was found in the literature. Thus, it is worthwhile to study the effect of ZrO_2 on In_2O_3.

EXPERIMENTAL

Pure In_2O_3 was prepared by the method stated by Hanafi *et al.*[1] and those doped with different concentrations of ZrO_2 additives (1, 3, 5, 8 and 10 mol %) were prepared according to the method described by Kiyoyoshi and Kenji[10]. Table-1 shows the different samples of ZrO_2 doped In_2O_3 respectively, with the standard In_2O_3 sample (undoped).

All samples were sieved through 0.2 mesh and subjected to XRD, IR, TGA and DTA analyses. The discs required to AC electrical conductivity measurements were agglomerated by compressing 2 g of powder under a pressure of 10 ton/cm^2. It may

TABLE-1
UNDOPED In_2O_3 AND ZrO_2 DOPED In_2O_3

Samples	Samples
$(In_2O_3)_{1-x}(ZrO_2)_x$	x = 5 mol % ZrO_2
standard In_2O_3	x = 8 mol % ZrO_2
x = 1 mol % ZrO_2	x = 10 mol % ZrO_2
x = 3 mol % ZrO_2	–

be noted that the thickness, surface area of the disc and pressure for all samples were constant. The measurements were taken at a frequency 20 KHz and temperature ranging from 25-480 ºC using the circuit as described[11].

RESULTS AND DISCUSSION

Fig. 1a shows the thermogravimetric analysis (TGA) of pure In_2O_3 and ZrO_2 doped In_2O_3. A minute loss in weight over range 25-100 ºC was detected. This may be due to water elimination. These results in comfirmity with Lehmann *et al.*[12]. Generally, all prepared samples did not show any change in weight up to *ca.* 600 ºC. Fig. 1b represents the differential thermal analyses DTA curves of the prepared samples. An endothermic peak or plateau in the temperature less than 100 ºC are observed in the samples. This may correspond to the water elimination observed in TGA measurements.

It must be mentioned here that a small exothermic peak at *ca.* 303 ºC was observed in sample contains 10 mol %. This sample may contains excess ZrO_2 in the tetragonal form which changes to monoclinic modification at *ca.* 303 ºC. This assumption is in agreement with that obtained by Komissarova *et al.*[13].

Weiher[14,15] found that In_2O_3 has an extrinsic conductivity in the temperature range from room temperature up to 800 ºC. For this reason, the conductivity measurements were carried out over the temperature range from 25 ºC up to 480 ºC to detect only the role of imperfections on the electrical measurements.

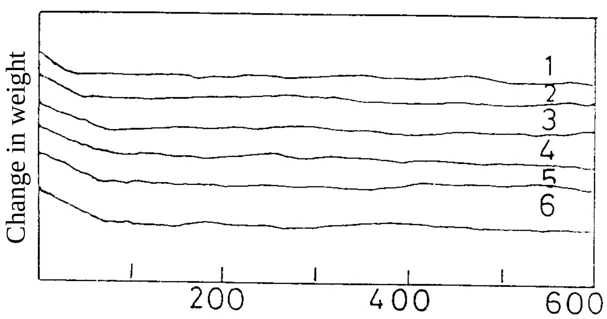

Fig. 1a. Thermogravimetric analysis of ZrO_2-doped In_2O_3 samples: (1) Undoped In_2O_3 (standard) (2) 1 mol % ZrO_2 (3) 3 mol % ZrO_2 (4) 5 mol % ZrO_2 (5) 8 mol % ZrO_2 (6) 10 mol % ZrO_2

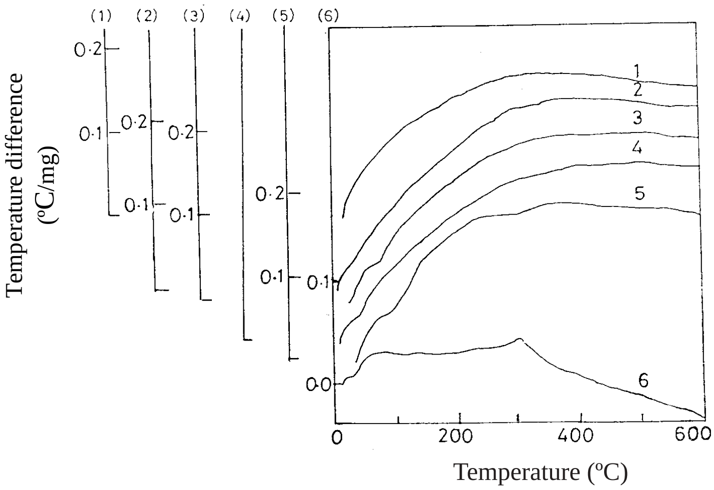

Fig. 1b. Differential thermal analysis of ZrO_2-doped In_2O_3 samples.
(1) Undoped In_2O_3 (standard) (2) 1 mol % ZrO_2 (3) 3 mol % ZrO_2
(4) 5 mol %ZrO_2 (5) 8 mol % ZrO_2 (6) 10 mol % ZrO_2

Fig. 2 can be divided into three regions I, II and III. In region I, In_2O_3 (undoped) behaves as a semiconductor whereas the electrical conductivity values increased continuously with temperature. In region II exhibits minimum in the curve *i.e.* a negative temperature coefficient of conductivity was observed. After the previous behaviour In_2O_3 exhibits the semi conducting properties region III.

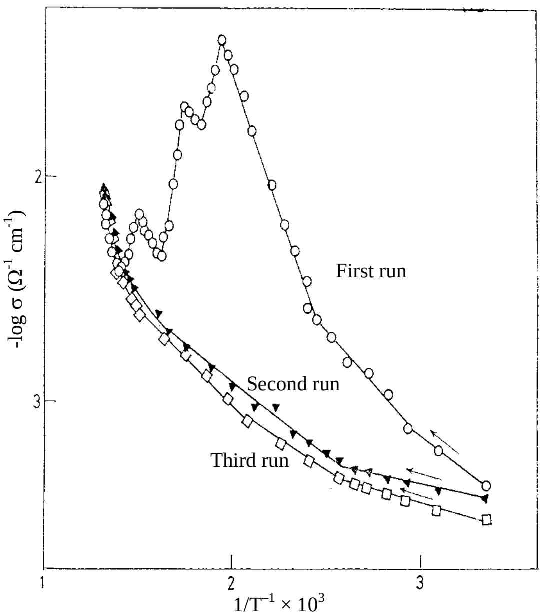

Fig. 2. Electrical conductivity of undoped In_2O_3 as a function of temperature

It is of great interest to state that the negative temperature behaviour disappeared when pure In_2O_3 cooled after heating and immediately subjected to a second and third run[8].

In general, by comparison the general feature of all samples Fig. 3 it can be seen that the curves can be divided also into three regions I, II and III.

In the region I the curves consists of two or three distinct linear parts separated by Knee. It is clear from Table-2 which represents the variation of Knee temperature with concentration of the dopant.

TABLE-2
KNEE TEMPERATURE VALUES FOR PURE In_2O_3 AND ZrO_2 DOPED In_2O_3

Sample		Knee temperature	
Pure In_2O_3	69	51	-
1 mol % ZrO_2	187	135	-
3 mol % ZrO_2	110	76	-
5 mol % ZrO_2	215	108	57
8 mol % ZrO_2	218	115	55
10 mol % ZrO_2	174	135	78

It is clear from Table-2 that the Knee temperature of pure In_2O_3 and 3 mol % dopant have the lowest Knee temperature value which indicate that these samples contains a minimum lattice defect[16]. From the slope of these parts, the activation energies ΔE_1, ΔE_2 and ΔE_3 for all samples were calculated and listed in Table-3.

TABLE-3
ACTIVATION ENERGY VALUES OF PURE In_2O_3 AND ZrO_2 DOPED In_2O_3

Sample		ΔE ev	
		Region I	
Pure In_2O_3	0.24	0.40	0.89
1 mol % ZrO_2	0.37	1.23	-
3 mol % ZrO_2	0.09	0.57	1.09
5 mol % ZrO_2	0.16	0.55	1.31
8 mol % ZrO_2	0.12	0.35	1.39
10 mol % ZrO_2	0.30	0.82	1.60

The discrepancy between the values of the activation energy obtained in this work and those given by different authors[1,5,14,17-21]. This is due to the purity, nature and thermal history of the specimens used by different investigators. It was assumed that In_2O_3 has an extrinsic behaviour in this region I thus, the deviation may be either due to: (i) Possible movement of impurities in the same relatively disorder region of grain boundaries. (ii) The existence of phase transition which affects the conductivity in this temperature range. (iii) Different concentration of imperfections present.

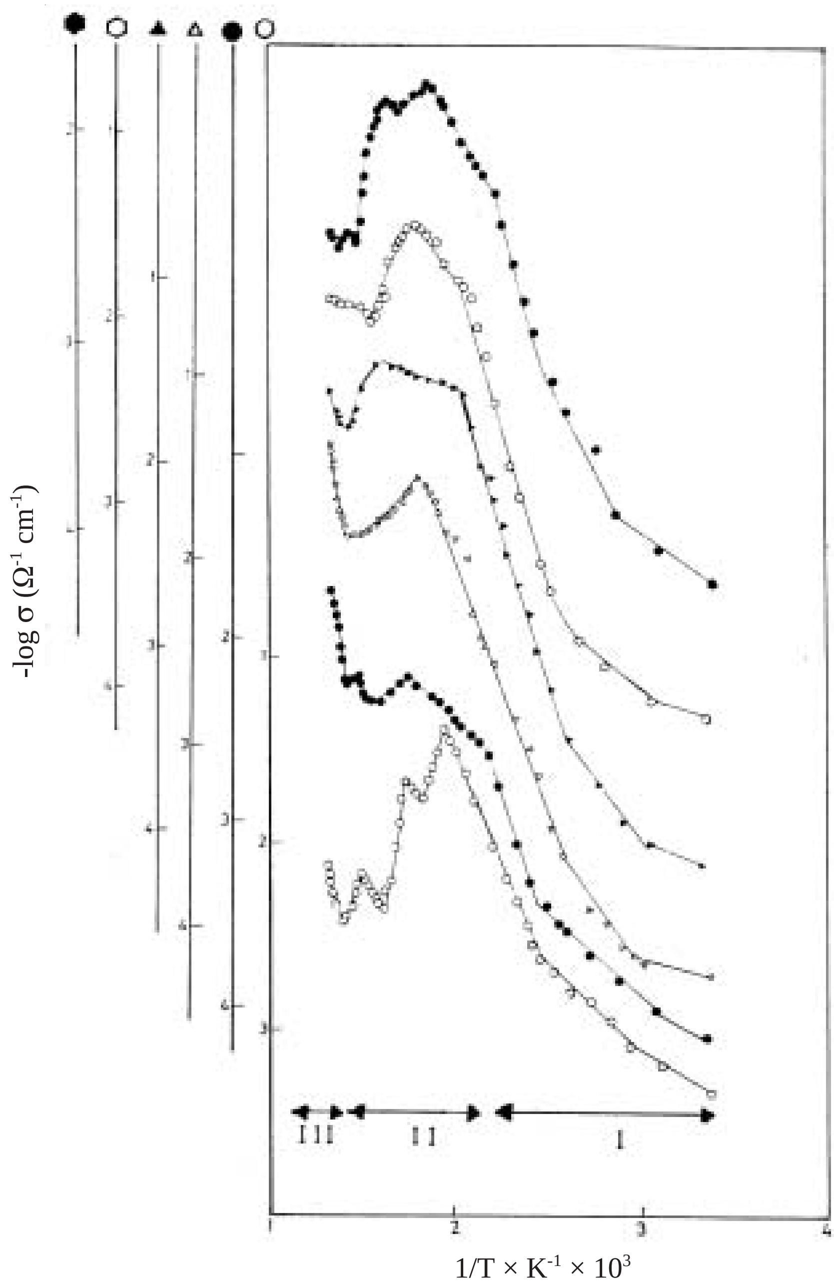

Fig. 3: Electrical conductivity of undoped and ZrO_2-doped In_2O_3 samples as a function of temperature

(○) Undoped In_2O_3 (standard) (●) 1 mol % ZrO_2

(△) 3 mol % ZrO_2 (▲) 5 mol % ZrO_2

(⬡) 8 mol % ZrO_2 (⬢) 10 mol % ZrO_2

It is of great interest to state that the first process is less dominant due to the frequency dispersion method chosen for the conductivity measurements. Further all samples have been subjected to the same conditions.

The decrease of conductivity with increase in temperature was observed in all samples. This phenominum was detected by previous authors which represented by region II it may be attributed to decrease in carrier mobility and/or carrier concentration[1,13]. This decrease in carrier mobility can arises from: (i) A change in the scattering mechanism. (ii) An increase in the carrier effect mass or a combination of both. Qadri *et al.*[4] had found that as the ZrO_2 content increases from 0-15 mol % the electrical resistivities increased, the carrier densities and hall mobilities decreased.

According to previous authors[22,23] this behaviour may be easily explained on the basis of thermal scattering of electron in the lattice. After the anomalous behaviour the conductivity of some samples increases again with temperature region III.

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