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# Studies on microstructure and density of sintered ZnO-based non-linear resistors

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Systematic studies have been made of the grain growth and density of sintered ZnO-based systems containing one or more additive oxides of the type $Nb_2O_5$, $Bi_2O_3$, $Sb_2O_3$, CoO, $Cr_2O_3$, $MnO_2$, NiO and $Al_2O_3$. These samples were characterized using such techniques as scanning electron microscopy, X-ray diffraction and electron probe microanalysis. The influence of the nature and amount of additive oxides and sintering temperature is discussed in relation to microstructure, density and the phases present.

## 1. Introduction

Sintered ZnO-based ceramic composites containing several additive oxides such as $Bi_2O_3$, $Sb_2O_3$, CoO, $Cr_2O_3$, are known to exhibit high non-ohmic behaviour and excellent surge withstanding capability [1–4]. In view of this, ZnO-based composites have found extensive applications over the past decade, as non-linear resistor (NLR) elements in gapless surge arresters. Considerable literature is available to date on the physical and electrical properties of several ZnO-based composites [5–7]. Despite this, the explicit role of the additive oxides on the microstructural features of ZnO is not clearly understood. It is therefore desirable to investigate the influence of the additives on microstructure and density of ZnO and to correlate it to electrical behaviour of these composites.

In the present work, attempts have been made to study the effect of one or more additive oxides on microstructure and density of ZnO with a view to understand the influence of individual oxides on the above properties. The studies on microstructure and density were therefore carried out for several binary systems, selected ternary and multicomponent systems which has led to the development of ZnO-based NLR having better electrical and physical properties [8]. In addition, results on densification and grain growth of ZnO in the presence of various additives have also been highlighted in this paper.

## 2. Experimental procedures

### 2.1. Sample preparation

High-purity ZnO (> 99.9%) was mixed with one or more additive oxides of the type $Nb_2O_5$, $Bi_2O_3$, $Sb_2O_3$, CoO, $Cr_2O_3$, $MnO_2$, NiO and $Al_2O_3$. The amount of additive added in the case of binary systems, $ZnO–M_xO_y$, was limited to 5 wt %. In the case of multicomponent systems, the total amount of the additives added was extended up to 15 wt %. The mixture was ball milled for 1 to 2 h using deionized water as the grinding medium. The mixture was then dried and mixed with 5% polyvinyl alcohol (PVA), as a binder. The powder was subsequently pressed into discs of 20 mm diameter and 3 mm thickness at a pressure of $300\,kg\,cm^{-2}$. The green compacts were sintered at different temperatures ranging from 900 to 1300° C for 2 h in air and furnace-cooled to room temperature. The density of the sintered samples was found to be in the range 4.9 to $5.5\,g\,cm^{-3}$ which is about 90 to 98% of the theoretical density of pure ZnO.

### 2.2. Characterization

### 2.2.1. Density and microstructure

The density of the sintered pellets was calculated from their weight and dimensions. In all cases, the density was calculated from the measurement made on four to six samples of the same type and an average value was taken. For a given batch, variation in the density from sample to sample was found to be within ± 2%.

Specimens for metallographic examinations were prepared as follows. The surface of the sintered specimen was lapped and polished to a mirror-like finish on microcloth polishing wheel using finer alumina (10, 5 and 2 $\mu$m particle size) powder followed by final polishing with diamond paste (2, 1 and 0.25 $\mu$m particle size). The polished specimens were degreased with tri-chloroethylene and cleaned thoroughly by ultrasonic stirring. The samples were mild-etched with 5% glacial acetic acid. The surface structure was examined by scanning electron microscopy (SEM). Since most of these metal oxides possess very high resistivity, the surface of the samples had to be metallized with a thin coating of gold to reduce charging effects and to improve the definition and resolution of the image. The grain size was calculated by counting the number of grain boundaries intercepted by a line of known length and taking the average of four such measurements randomly made across the micrographs.

### 2.2.2. Phase analysis

Phase analysis of the sintered samples was carried out using an X-ray diffractometer with high density $CuK_\alpha$ radiation ($\lambda = 0.15405$ nm). Specimens for X-ray examinations were prepared in the following way:

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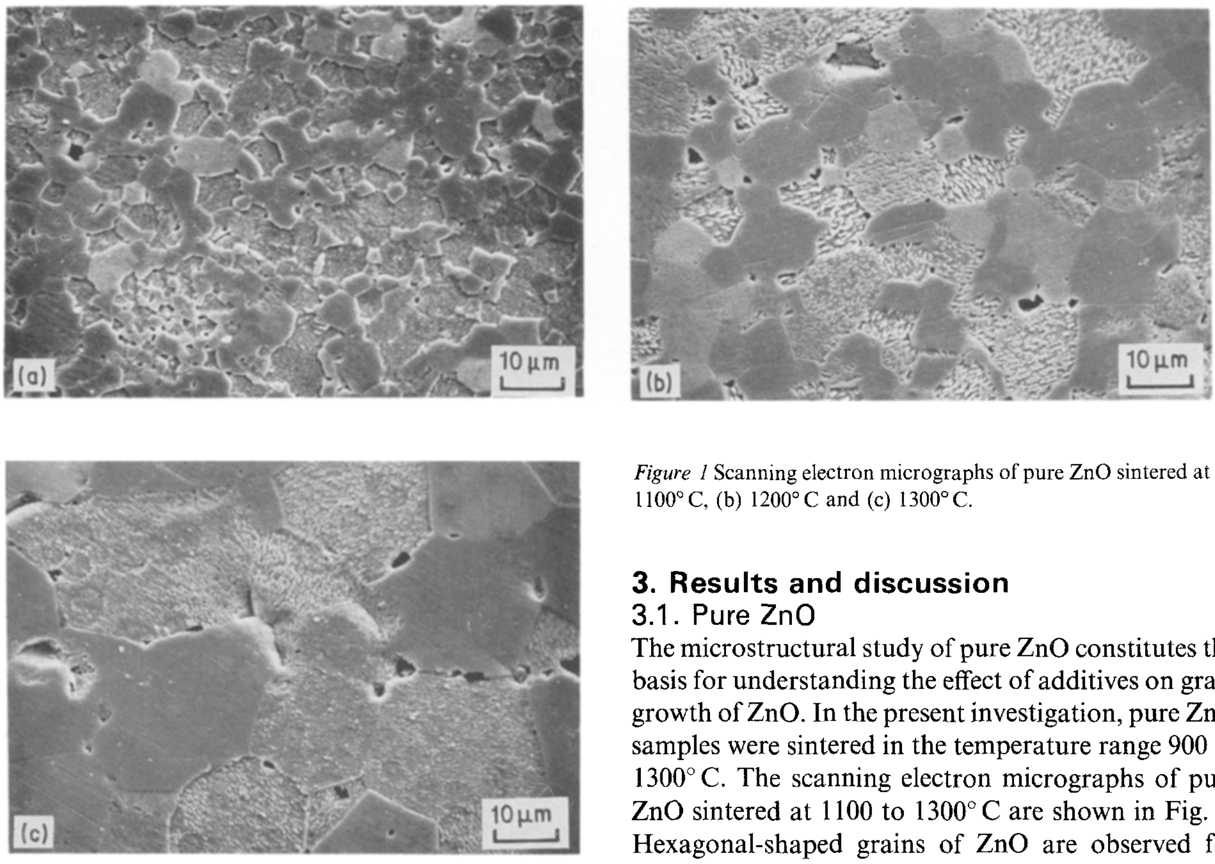


*Figure 1* Scanning electron micrographs of pure ZnO sintered at (a) 1100° C, (b) 1200° C and (c) 1300° C.

sintered samples were treated with 10% $HClO_4$ for 1 h at room temperature partially to leach out ZnO. The residue containing ZnO and other minor phases was filtered, dried and used for X-ray diffraction (XRD) study. This method permitted unambiguous identification of the phases present in the sample.

### 2.2.3. *EPMA studies*

The sintered samples polished to mirror-like finish were mild-etched using 5% glacial acetic acid. The etched surface of the sample was then coated with carbon to a thickness of 30 to 40 nm. These samples were used for the elemental distribution analysis employing a scanning electron probe microanalyser (SEPMA).

## 3. Results and discussion

### 3.1. Pure ZnO

The microstructural study of pure ZnO constitutes the basis for understanding the effect of additives on grain growth of ZnO. In the present investigation, pure ZnO samples were sintered in the temperature range 900 to 1300° C. The scanning electron micrographs of pure ZnO sintered at 1100 to 1300° C are shown in Fig. 1. Hexagonal-shaped grains of ZnO are observed for specimens sintered at these temperatures. The dependence of grain size and density on sintering temperature is shown in Fig. 2. The sample sintered at 1300° C is found to possess maximum grain size of about 20 $\mu$m and also maximum bulk density of 5.34 $g\,cm^{-3}$, which is about 95% of the theoretical density of ZnO. Similar results have also been reported by Gupta and Coble [9].

### 3.2. Binary systems

The densification and microstructural studies of binary systems of ZnO containing one of the additive oxides $Nb_2O_5$, $Bi_2O_3$, $Sb_2O_3$, CoO or $Cr_2O_3$, have been carried out. Because the ZnO composites were generally sintered at 1300° C, this temperature is taken as the basis to classify the additive oxides into low- and high-melting point oxides, depending upon whether

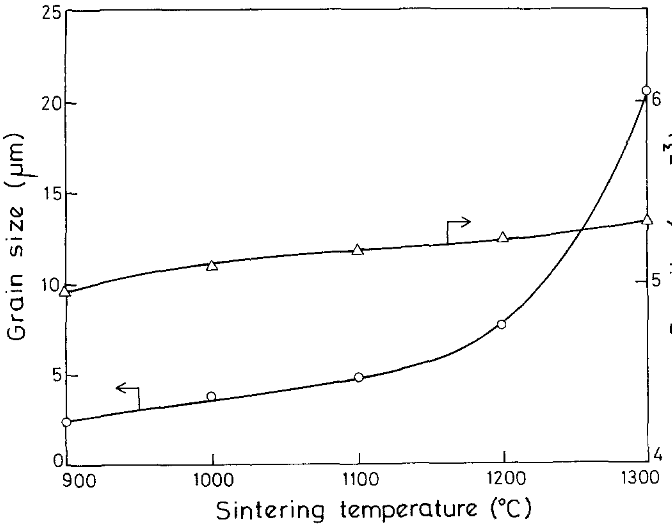


*Figure 2* Influence of sintering temperature on bulk density and grain size of pure ZnO.

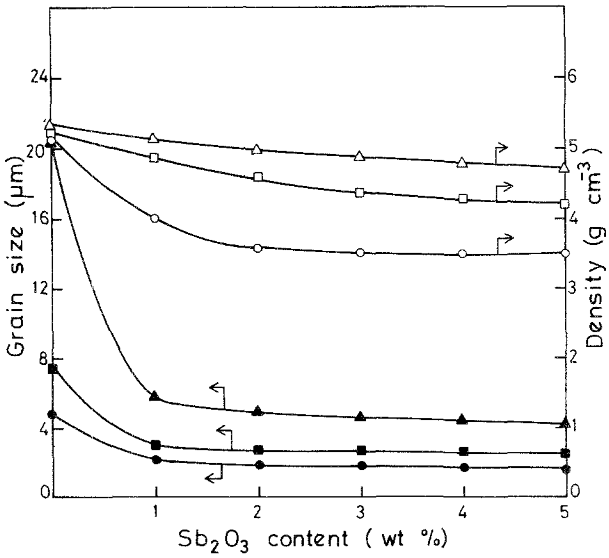


*Figure 3* Variation of bulk density and grain size in the ZnO–Sb$_2$O$_3$ binary system with Sb$_2$O$_3$ content at different sintering temperatures. (○, ●) 1100° C, (□, ■) 1200° C, (△, ▲) 1300° C.

the melting point of the added oxide is lower or higher relative to 1300° C.

### *3.2.1. ZnO with low melting point oxides ($Bi_2O_3$, $Sb_2O_3$)*

Microstructural studies were made on ZnO containing Bi$_2$O$_3$ or Sb$_2$O$_3$. Since the melting points of these oxides are very low compared to the sintering temperatures used in the present work, densification in these two systems occurs in the presence of a liquid phase. However the influence of Sb$_2$O$_3$ on the densification and grain growth of ZnO is found to be different from that of Bi$_2$O$_3$ as substantiated in Figs 3 and 4. Addition of Sb$_2$O$_3$ to ZnO decreases the bulk density and grain size at all temperatures thereby indicating that Sb$_2$O$_3$ inhibits the grain growth of ZnO. Scanning electron micrographs shown in Fig. 5 support this view. This effect can be attributed to the formation of spinel phase which becomes anchored within the ZnO grains, thereby impeding material transport. The formation of spinel phase in the ZnO–Sb$_2$O$_3$ system was confirmed by X-ray diffraction study. Fig. 6 shows the X-ray diffractogram of ZnO + 3% Sb$_2$O$_3$ sample sintered at 1100° C. Evidence for presence of Zn$_7$Sb$_2$O$_{12}$ spinel particle at the grain boundaries is given by electron probe microanalysis. Fig. 7 shows the X-ray image of elemental zinc and antimony. It can be seen from the figure that the concentration of antimony at grain boundaries is very high. In contrast to these observations, addition of Bi$_2$O$_3$ enhances the grain growth as seen in Fig. 4. This can be attributed to the formation of liquid phase which solidifies on cooling along the grain boundary, thus isolating the ZnO grains. A typical scanning electron micrograph of the ZnO–Bi$_2$O$_3$ binary system is shown in Fig. 8. It was also observed that the density increases with Bi$_2$O$_3$ content up to the sintering temperature, 1100° C, whereas the density decreases with Bi$_2$O$_3$ content beyond this temperature. This could be due to the

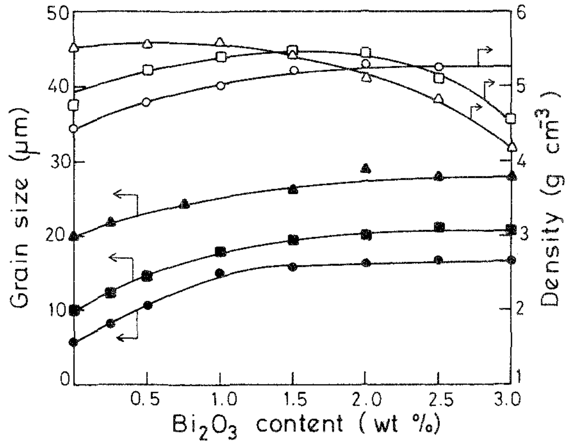


*Figure 4* Variation of bulk density and grain size in the ZnO–Bi$_2$O$_3$ binary system with Bi$_2$O$_3$ content at different sintering temperatures. (○, ●) 1100° C, (□, ■) 1200° C, (△, ▲) 1300° C.

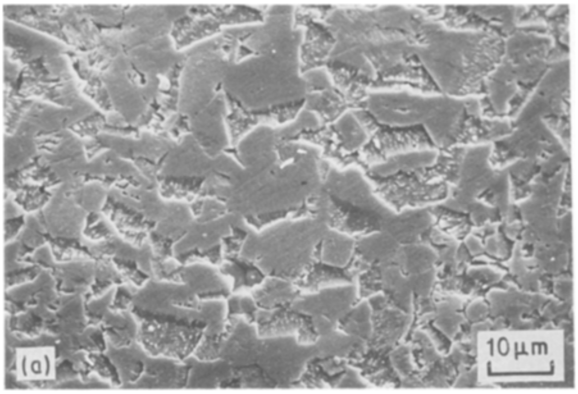
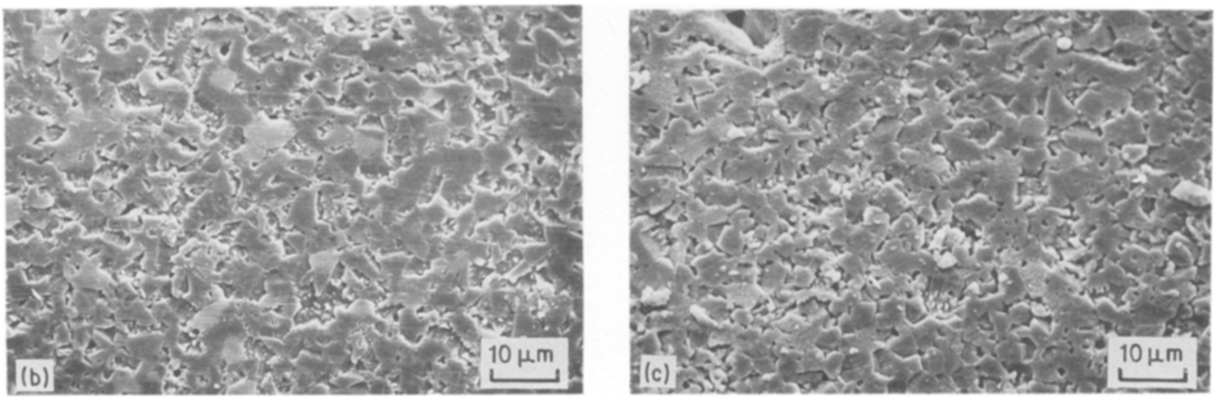


*Figure 5* Scanning electron micrographs of the ZnO–Sb$_2$O$_3$ binary system sintered at 1300° C for 2 h. (a) ZnO + 1% Sb$_2$O$_3$, (b) ZnO + 3% Sb$_2$O$_3$, and (c) ZnO + 5% Sb$_2$O$_3$.



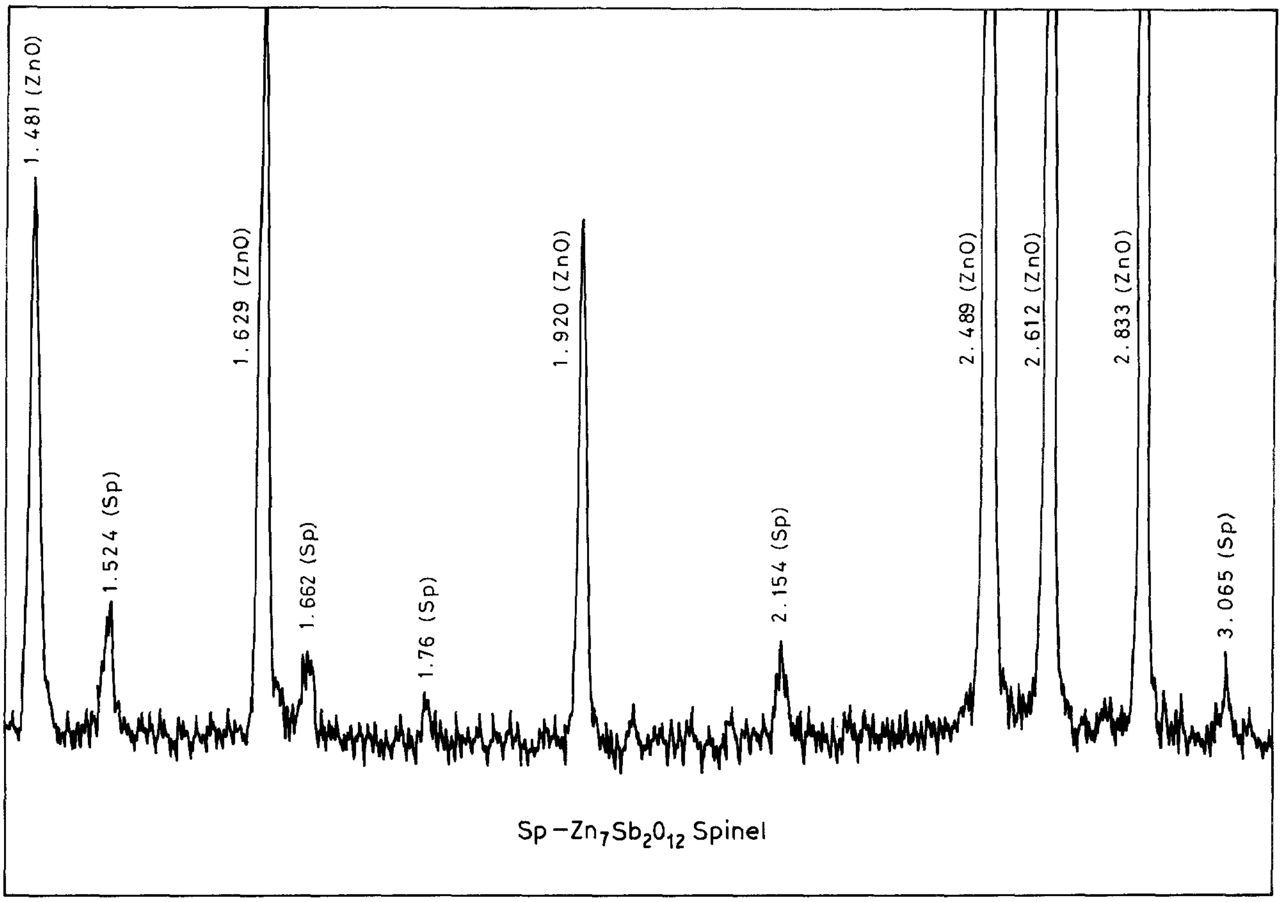


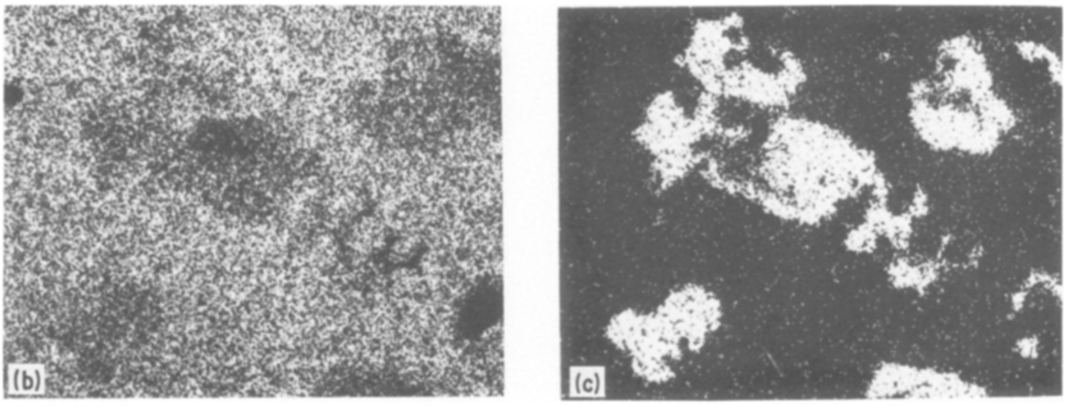
*Figure 6* X-ray diffractogram of ZnO + 3% $Sb_2O_3$ sample sintered at 1100° C.

significant evaporation of $Bi_2O_3$ at higher sintering temperature in view of its high vapour pressure.

### 3.2.2. ZnO with high melting point oxides ($Nb_2O_5$, CoO, $Cr_2O_3$)

A detailed study of the density and microstructure of ZnO–$Nb_2O_5$ binary systems is discussed elsewhere [10]. Because the melting point of $Nb_2O_5$ is higher than the sintering temperature (i.e. 1300° C), it is believed that densification in the ZnO–$Nb_2O_5$ system occurs by solid-state sintering. Similarly, in the sintering of ZnO in the presence of other high-melting point additives such as CoO and $Cr_2O_3$, it is presumed that the densification in these systems takes place by solid-state sintering. It was observed that addition of CoO and $Cr_2O_3$ above 0.5 wt% reduces the sintering efficiency of ZnO considerably as evidenced by negligible shrinkage, low density and small grain size. The scanning electron micrographs of ZnO containing 1 wt% CoO and 1 wt% $Cr_2O_3$ sintered at 1200° C are included in Fig. 8. The densities of these systems are 4.5 and 4.1 $g\,cm^{-3}$ which are about 80% and 73% of the theoretical value of pure ZnO.

*Figure 7* SEM (a) and (b, c) EPMA (X-ray image) photographs of ZnO + 3% $Sb_2O_3$ sample sintered at 1100° C. (b) Zn, (c) Sb.



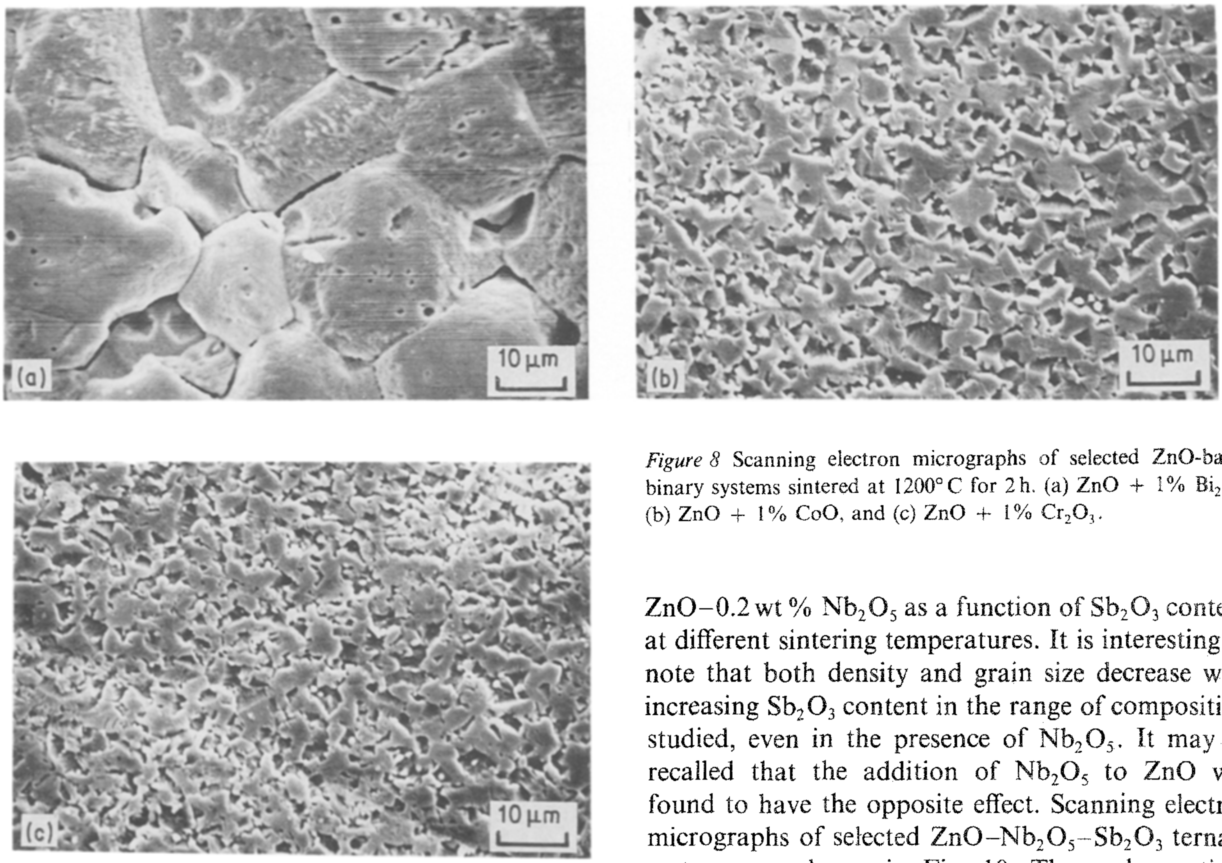


*Figure 8* Scanning electron micrographs of selected ZnO-based binary systems sintered at 1200° C for 2 h. (a) ZnO + 1% $Bi_2O_3$, (b) ZnO + 1% CoO, and (c) ZnO + 1% $Cr_2O_3$.

### 3.3. Ternary and multicomponent systems

The above studies were also extended to ternary and multicomponent systems for the reasons mentioned in Section 1. In all these cases $Nb_2O_5$ was taken as a common constituent in view of its benign effects on the grain growth and bulk density of ZnO. The amount of $Nb_2O_5$ added in all these cases was 0.2 wt %, because ZnO containing 0.2 wt % $Nb_2O_5$ was found to possess a large grain size [10]. Fig. 9 depicts the variation of grain size and density of ZnO–0.2 wt % $Nb_2O_5$ as a function of $Sb_2O_3$ content at different sintering temperatures. It is interesting to note that both density and grain size decrease with increasing $Sb_2O_3$ content in the range of composition studied, even in the presence of $Nb_2O_5$. It may be recalled that the addition of $Nb_2O_5$ to ZnO was found to have the opposite effect. Scanning electron micrographs of selected ZnO–$Nb_2O_5$–$Sb_2O_3$ ternary systems are shown in Fig. 10. These observations suggest that it is possible to control the grain size of ZnO to the desired range by careful control of composition and the sintering temperature.

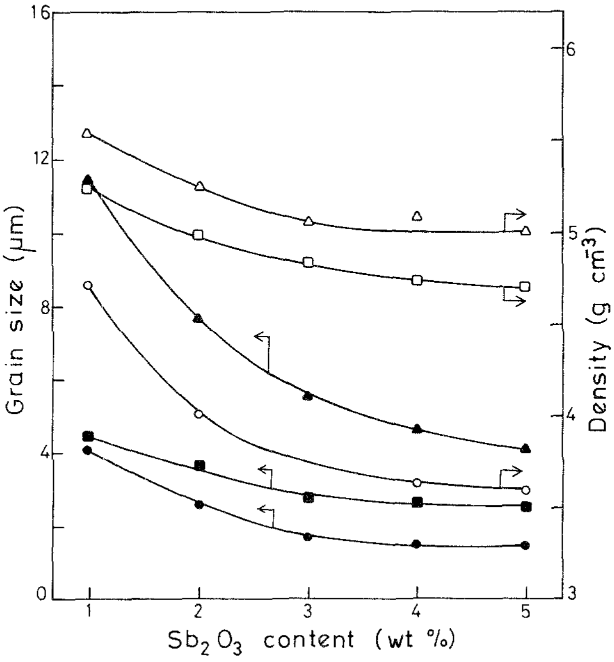
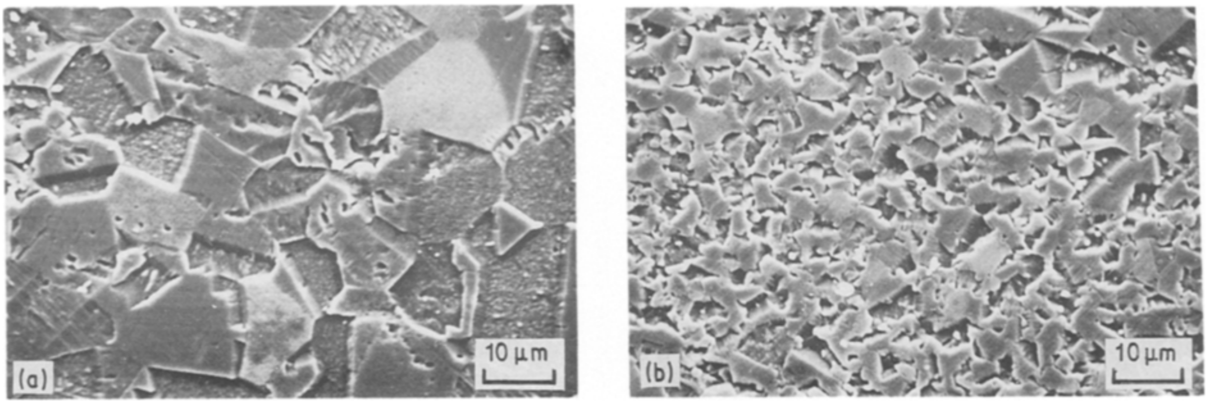


*Figure 9* Variation of bulk density and grain size in ZnO + 0.2% $Nb_2O_5$ + $Sb_2O_3$ ternary systems with $Sb_2O_3$ content at different sintering temperatures. (○, ●) 1100° C, (□, ■) 1200° C, (△, ▲) 1300° C.

Fig. 11 reveals the effect of $Bi_2O_3$ addition on the densification and grain growth of ZnO containing $Nb_2O_5$ and $Sb_2O_3$. In this case too the amount of $Nb_2O_5$ was kept constant (i.e. 0.2 wt %) and that of $Sb_2O_3$ and $Bi_2O_3$ was varied. It was found that the density increases with increasing $Bi_2O_3$ content and sintering temperature up to 1000° C. Above 1000° C it was observed that the density decreased drastically on increasing the $Bi_2O_3$ content. This is because of the evaporation of $Bi_2O_3$ at temperatures above 1000° C. It was also found that the weight loss of the sample sintered at 1300° C was nearly equal to the amount of $Bi_2O_3$ added. This indicates that almost complete evaporation of $Bi_2O_3$ takes place around 1300° C. Fig. 12 shows the X-ray diffractogram of the sample containing $Nb_2O_5$, $Sb_2O_3$ and $Bi_2O_3$ to ZnO sintered at 1300° C for 2 h. It can be inferred from Fig. 12 that there is no peak corresponding to $Bi_2O_3$. Further, it is interesting to note that the addition of $Bi_2O_3$ enhances the grain growth of ZnO composite even in the presence of $Sb_2O_3$ which is found to retard grain growth. Scanning electron micrographs of selected ZnO–0.2 wt % $Nb_2O_5$–$Sb_2O_3$–$Bi_2O_3$ systems sintered at 1300° C are shown in Fig. 13. From the above results it may be concluded that $Nb_2O_5$ and $Sb_2O_3$ do not prevent the evaporation of $Bi_2O_3$.

As it is imperative to prevent the loss of $Bi_2O_3$ through evaporation in order to achieve good non-linear characteristics, attempts were made to prevent this by the addition of a small amount of CoO or $MnO_2$, because these oxides are known to prevent evaporation of $Bi_2O_3$ [5, 11]. The X-ray diffractogram shown in Fig. 14 provides evidence for the presence of



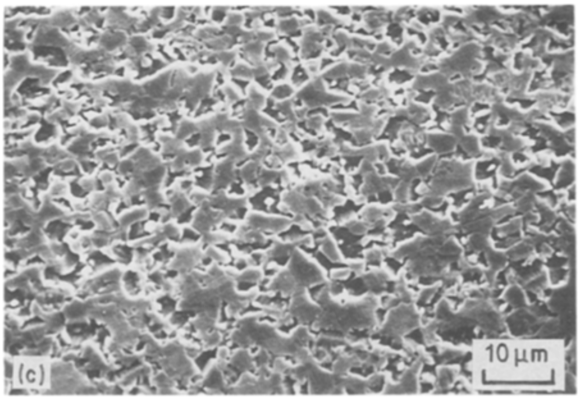
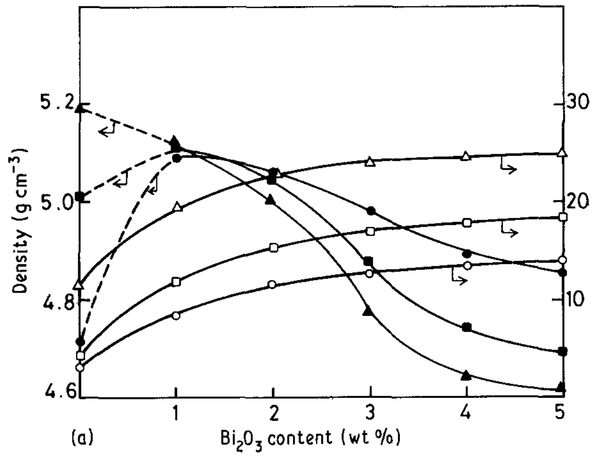


*Figure 10* Scanning electron micrographs of ZnO + $Nb_2O_5$ + $Sb_2O_3$ ternary systems sintered at 1300° C for 2 h. (a) ZnO + 0.2% $Nb_2O_5$ + 1% $Sb_2O_3$, (b) ZnO + 0.2% $Nb_2O_5$ + 2% $Sb_2O_3$, and (c) ZnO + 0.2% $Nb_2O_5$ + 3% $Sb_2O_3$.

$Bi_2O_3$ in the ZnO composite containing $Nb_2O_5$, $Sb_2O_3$, $Bi_2O_3$, CoO and $MnO_2$ sintered at 1300° C.

It is well known that the non-linearity index is a very important parameter to be considered in ZnO-based non-linear resistors. In addition, the breakdown voltage and energy handling capability of the composites are also important for surge-suppressing applications. It has been shown that a small addition of $Cr_2O_3$ and NiO to ZnO in the presence of other additive oxides increase the breakdown voltage by decreasing the grain size of the composite [7]. It was found that addition of $Cr_2O_3$ and NiO to ZnO in the presence of $Nb_2O_5$, $Bi_2O_3$, $Sb_2O_3$, CoO and $MnO_2$ control the grain size. The density of the above system was found to be around 92% theoretical density of ZnO. The decrease in density is due to the increase of pore volume. It has also been reported that addition of $Al_2O_3$ decreases the pore volume [7] which is an important parameter to be considered for the improvement of energy handling capability. In the present investigation $Al_2O_3$ was added in the form of $Al(NO_3)_3$ to ZnO in the presence of the other additive



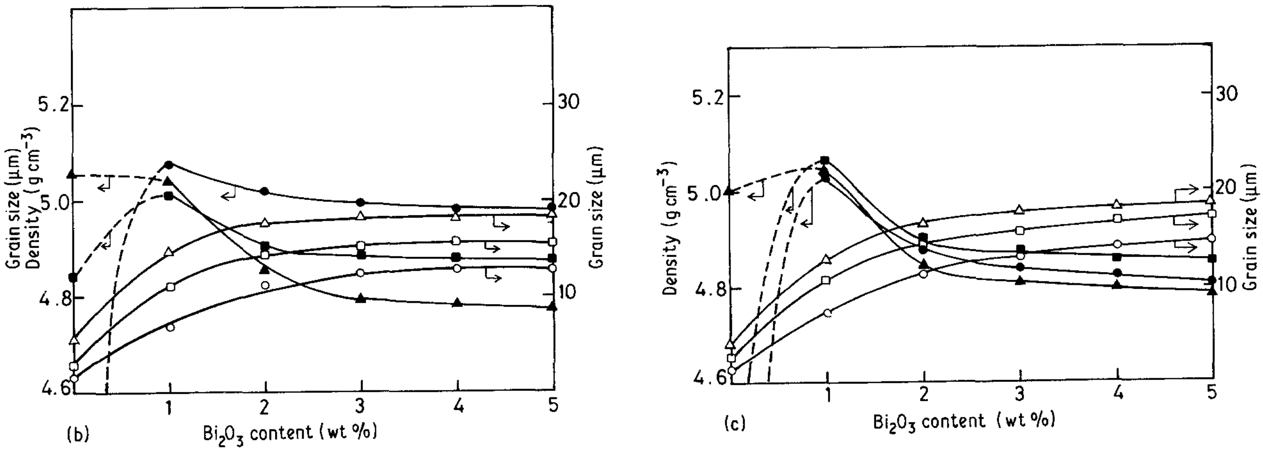


*Figure 11* Variation of bulk density and grain size in ZnO + 0.2% $Nb_2O_5$ + $Sb_2O_3$ + $Bi_2O_3$ system with $Sb_2O_3$ and $Bi_2O_3$ content at different sintering temperatures. (a) ZnO + 0.2% $Nb_2O_5$ + 1% $Sb_2O_3$ + $Bi_2O_3$, (b) ZnO + 0.2% $Nb_2O_5$ + 3% $Sb_2O_3$ + $Bi_2O_3$, (c) ZnO + 0.2% $Nb_2O_5$ + 5% $Sb_2O_3$ + $Bi_2O_3$. (○, ●) 1100° C, (□, ■) 1200° C, (△, ▲) 1300° C.

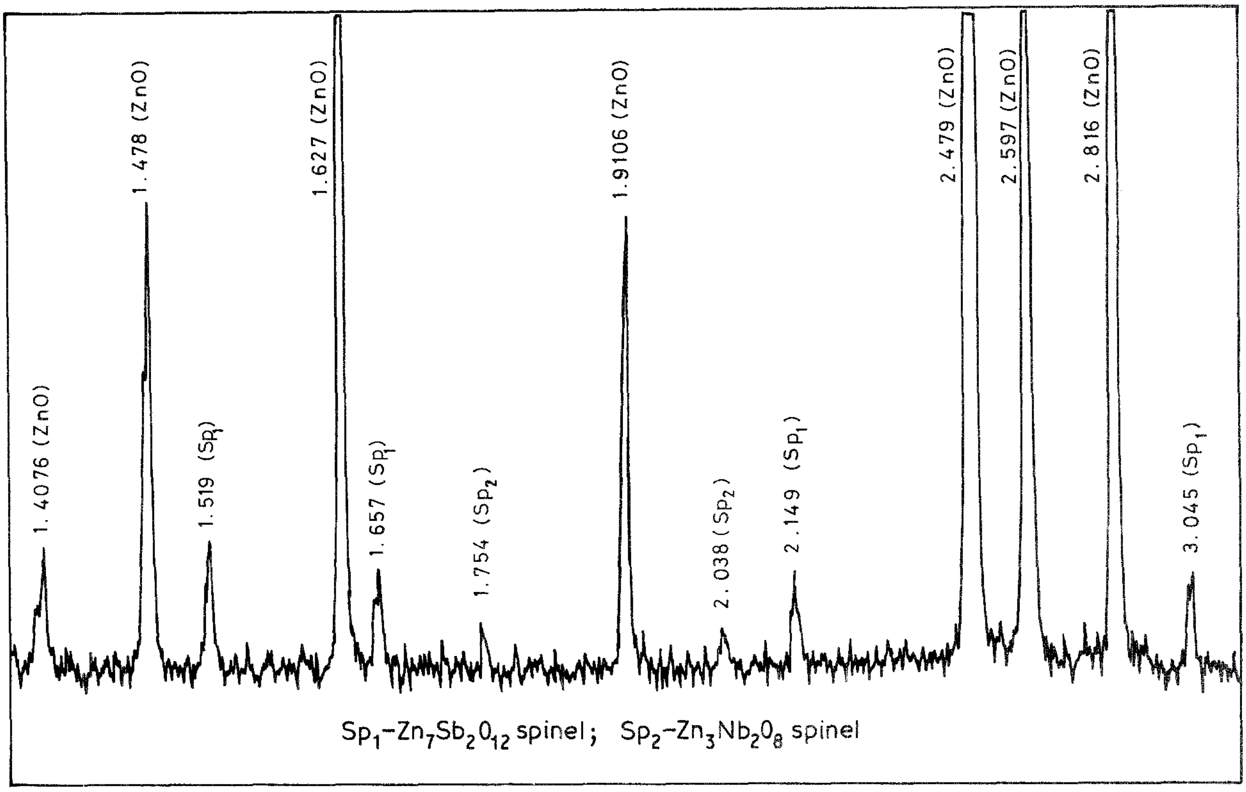


*Figure 12* X-ray diffractogram of ZnO + 0.2% $Nb_2O_5$ + 3% $Sb_2O_3$ + 5% $Bi_2O_3$ sample sintered at 1300° C for 2 h.

oxides mentioned above. The typical scanning electron micrograph of the sintered ZnO containing the above additives shown in Fig. 15 reveals minimum porosity in the sintered compact. The density of the sample was found to be 96% theoretical density of ZnO.

On the basis of the above microstructural and X-ray studies of a multicomponent ZnO system containing small amounts of additive oxides of niobium, bismuth, antimony, cobalt, manganese, chromium and nickel, and from the information available in the literature, it can be concluded that the following four phases are present in the sintered polycrystalline ZnO based composite.

1. ZnO matrix doped with $Co^{2+}$ and $Mn^{4+}$.
2. The ZnO grains are separated from one another by $Bi_2O_3$-rich pyrochlore network [12].
3. $Zn_7Sb_2O_{12}$ spinel constitutes the third phase and forms well faceted octahedral crystals present usually at grain boundaries.
4. $Zn_3Nb_2O_8$ spinel phase constitutes the minor phase. In addition, cobalt and manganese oxides dissolve in ZnO grains as well as in the $Zn_7Sb_2O_{12}$ phase.

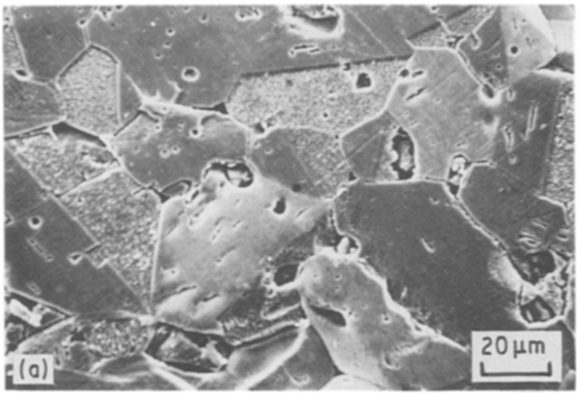
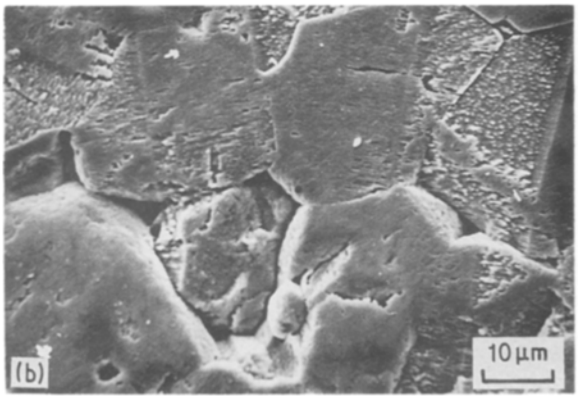
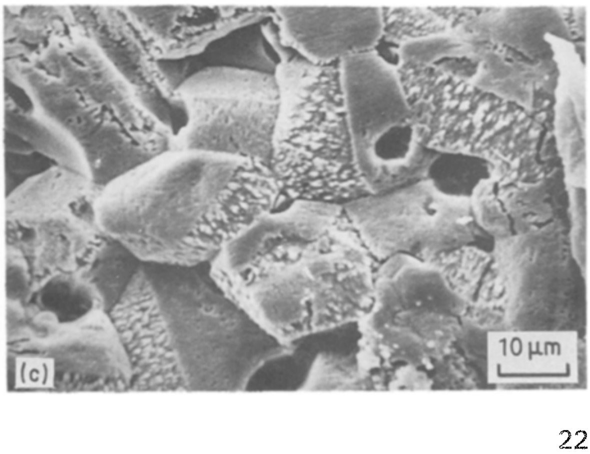


*Figure 13* Scanning electron micrographs of four-component systems sintered at 1300° C for 2 h. (a) ZnO + 0.2% $Nb_2O_5$ + 1% $Sb_2O_3$ + 3% $Bi_2O_3$, (b) ZnO + 0.2% $Nb_2O_5$ + 3% $Sb_2O_3$ + 3% $Bi_2O_3$, (c) ZnO + 0.2% $Nb_2O_5$ + 5% $Sb_2O_3$ + 3% $Bi_2O_3$.





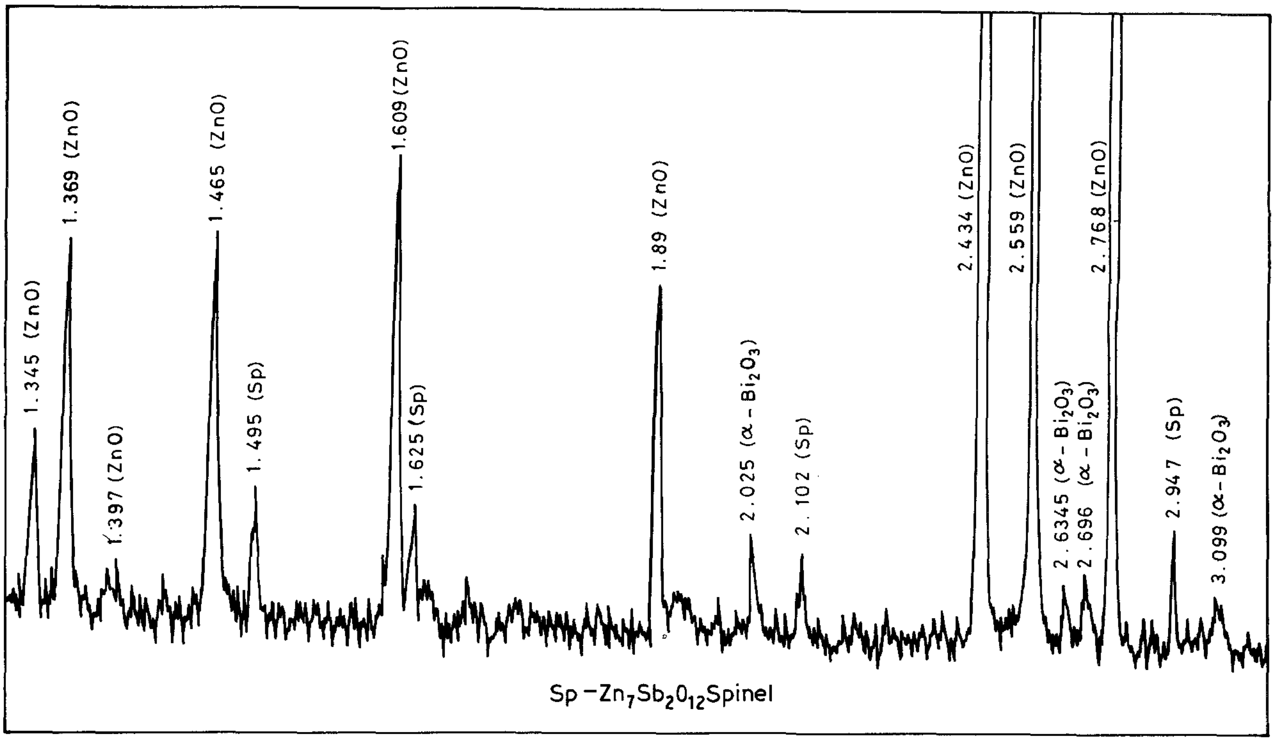


*Figure 14* X-ray diffractogram of ZnO + 0.2% $Nb_2O_5$ + 3% $Sb_2O_3$ + 5% $Bi_2O_3$ + 0.5% CoO sample sintered at 1300° C for 2 h.

## 4. Conclusions

1. Sintering behaviour and microstructural features of ZnO are found to be modified in the presence of additive oxides. Various types of sintering processes such as solid-state sintering, liquid-phase sintering and vapour transport are assumed to be responsible for the observed variations in the microstructure of ZnO-based composites.

2. The presence of $Sb_2O_3$ leads to the formation of $Zn_7Sb_2O_{12}$ spinel phase, which is present in the form of small inclusions in grain boundaries and inhibits the grain growth.

3. The presence of $Bi_2O_3$ in ZnO during sintering results in an enhanced grain growth. $Bi_2O_3$, being a low melting point oxide, forms a liquid phase along the grain boundaries which wets the ZnO grains thereby enhancing the grain growth. A grain size of about 20 to 30 $\mu$m can be achieved at higher sintering temperatures. In addition to the enhancement of grain growth, $Bi_2O_3$ also gives rise to a two-phase microstructure in which ZnO grains are surrounded by a thin intergranular layer of $Bi_2O_3$.

4. Addition of CoO or $MnO_2$ prevents the evaporation of $Bi_2O_3$ at higher sintering temperatures.

5. The grain size of the ZnO composites containing $Bi_2O_3$, $Nb_2O_5$, $Sb_2O_3$, CoO and $MnO_2$ can be controlled by the addition of small quantities of $Cr_2O_3$ and NiO.

6. Addition of $Al_2O_3$ in small quantities reduces the pore volume of the composite.

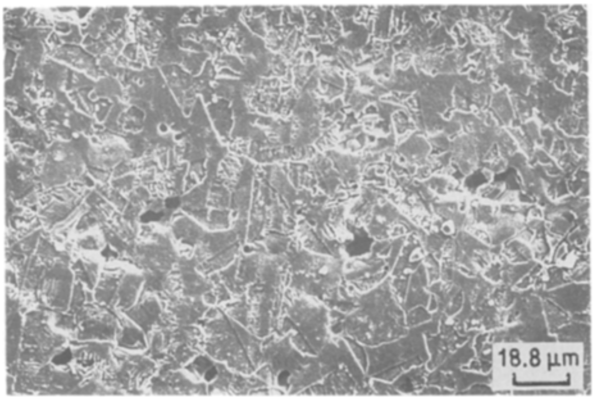


*Figure 15* Scanning electron micrograph of ZnO-based multicomponent system containing $Nb_2O_5$, $Bi_2O_3$, $Sb_2O_3$, CoO, $MnO_2$, $Cr_2O_3$, NiO and $Al(NO_3)_3$, sintered at 1300° C for 2 h.

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