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Non-linear *I–V* characteristics of doped $Sn_{1-x}Ti_xO_2$ ($0·0 < x < 0·25$) system

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Abstract. **The solid solutions of $Sn_{1-x}Ti_xO_2$ ($0·0 < x < 0·25$) were prepared by the usual high temperature ceramic processing techniques with small amounts of dopants such as Nb, Co, Al. The electrical measurements (log *I*–log *V*) on the ohmically metal electroded sintered pellets showed the non-linear behaviour. The non-linear coefficient was found to decrease from 12 to 3 with increase in x. On the other hand, the breakdown voltage (E_b) showed the increase with the increase in x. This complex electrical behaviour is explained on the effects of the three dopants (as varistor former, performance enhancer and highlighter) on the microstructural features of the dense pellet.**

Keywords. **Varistors; SnO_2; TiO_2; nonlinear coefficient; breakdown voltage.**

1. Introduction

Voltage dependent resistors (varistors) are used to protect the electrical/electronic circuits from transient voltage surges (Matsuoka 1971; Einzinger 1987; Gupta 1990; Clarke 1999). The most commonly used varistors are ZnO-based and their non-linear electrical properties were well studied and documented (Clarke 1999). An important characteristic of ZnO-based varistors is their high break-down voltage (3 V per grain boundary) which precludes them for low voltage applications. The search for low voltage varistors, i.e. lower E_b with high a values, are based on following guidelines: The material must be a doped high bandgap polycrystalline semiconductor. Further, as in ZnO ceramics two types of dopants are necessary: one that is soluble in the grains to affect the grain resistivity and the other a large insoluble ion that segregates at the grain boundaries. The search has resulted in the discovery of nonlinear *I–V* characteristics in $SrTiO_3$ (Fujimoto *et al* 1985), TiO_2 (Yan and Rhodes 1982) and SnO_2 (Santhosh *et al* 1997) based materials. For example, in the case of SnO_2-based varistor, Nb and Co were used as varistor formers and Al acts as a per-formance enhancer. The various important parameters of the above varistors are given in table 1.

Although the dopants used were different in TiO_2 and SnO_2, both show nonlinear *I–V* characteristics. Both crys-tallize in rutile (tetragonal) structure. Further, SnO_2 has a higher breakdown voltage (E_b = 700 V/mm) value whereas TiO_2 has a lower E_b (200 V/mm). Hence we have attempted to prepare a series of solid solution, $Sn_{1-x}Ti_xO_2$, with common additives to get an optimum E_b value. We report here the results obtained from the investigations carried out on doped SnO_2–TiO_2 system.

2. Experimental

The solid solution $Sn_{1-x}Ti_xO_2$ containing additives was prepared by the standard ceramic technique. The SnO_2, TiO_2 along with dopants such as $Al_2(SO_4)_3·16\,H_2O$, CoO and Nb_2O_5 in the stoichiometric ratio were mixed and ground well and calcined at 1473 K for 24 h. The calcined powders were again ground and fired at 1473 K for another 24 h. The compositional formula for the series is $Co_{0·01}Nb_{0·0005}Al_{0·0005}Sn_{0·989-x}Ti_xO_2$. The calcined powders were mixed with a binder (polyvinyl alcohol 2 wt%) and pelletized (12 mm dia, 1 mm thick) at 2–3 tons. The pellets were sintered at 1573 K for 2 h. The sintered pellets were polished and silver contacts were obtained by curing Ag-paste and annealed at 873 K for 30 min. The structure related phase determination was studied by Philip 1730 X-ray diffractometer. The change in lattice parameters in the solid solution was also recorded using slow scan. The microstructure of the sintered pellets was observed using a Leica Cambridge 440 microscope. The *I–V* characteristics were measured by using Keithley ele-ctrometer (610 C) and APLab (761 and 7323) power supply.

The current–voltage relation of a varistor is given by the equation,

$$J = (E/C)^a, \tag{1}$$

where J is the current density, E the applied field, C the proportionality constant and a the nonlinear coefficient. The current–voltage curves were plotted on log–log scale from which the slope of the curve gives the value of a.

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The another important parameter, E_b breakdown voltage is taken as the field applied when current flowing through the varistor is 1 mA.

3. Results and discussion

The variation of the unit cell parameters of doped $Sn_{1-x}Ti_xO_2$ system is shown in figure 1. Both the cell parameters of the tetragonal rutile structure decreases with increase in TiO_2 content. The '*a*' values decrease from 4·738 A to 4·658 A and '*c*' decreases from 3·188 A to 3·108 A as x varies from 0·0 to 0·25. This is in accordance with decrease in the ionic radius as Sn^{4+} (0·71 A) is substituted by Ti^{4+} (0·68 A). When $x > 0{\cdot}25$, rutile TiO_2 segregates as a second phase as revealed by XRD. The dopants being added in small quantities do not show up as second phase in XRD.

Figure 2 illustrates the J vs E plot for the compositions $Co_{0{\cdot}01}Nb_{0{\cdot}0005}Al_{0{\cdot}0005}Sn_{0{\cdot}989-x}Ti_xO_2$ ($0{\cdot}0 < x < 0{\cdot}25$). The nonlinear coefficient decreases with increase in Ti content whereas the breakdown voltage increases with Ti. The low current in the pre-breakdown region implies that the grain boundary resistance is high for the solid solutions. However, the grain boundary barrier or energy barrier is not effective as shown by low a values. The dopants used for the end member SnO_2 to improve the grain boundary barrier were not ideal for the solid solutions. The dopant Nb acts as a donor both in SnO_2 or TiO_2. The Nb^{5+} added in small quantities dissolves in the lattice, replaces Ti^{4+} or Sn^{4+} to give an extra electron to the conduction process as

$$Nb_2O_5 + TiO_2 \text{ (or } SnO_2) \rightarrow 2\,Nb_{Ti} \text{ (or } 2Nb_{Sn}) + 2e + 4O_O + 1/2\,O_2\,(g). \quad (2)$$

Thus Nb^{5+} ions are also expected to increase the conductivity in the solid solution. The addition of Co^{2+} ions was mainly responsible for the densification of SnO_2 and in the presence of TiO_2 may form oxygen ion vacancies due to its lower valency. The third dopant, Al^{3+} ions, added as performance enhancer (i.e. to increase the a value in SnO_2), is not effective in the case of $Sn_{1-x}Ti_xO_2$ as they exhibit low a values. The variation of the nonlinear coefficient (a) and the breakdown voltage (E_b) with TiO_2 incorporation were depicted in figure 3. The a decreases whereas E_b increases with increase in x.

Table 1. Various varistor systems.

System	Dopants	α	E_b (V/mm)	Reference
$SrTiO_3$	Nb, Na, Si	20	100	Fujimoto *et al* (1985)
TiO_2	Nb, Ba	7	200	Yan and Rhodes (1982)
SnO_2	Nb, Co, Al	15	700	Santhosh *et al* (1997)

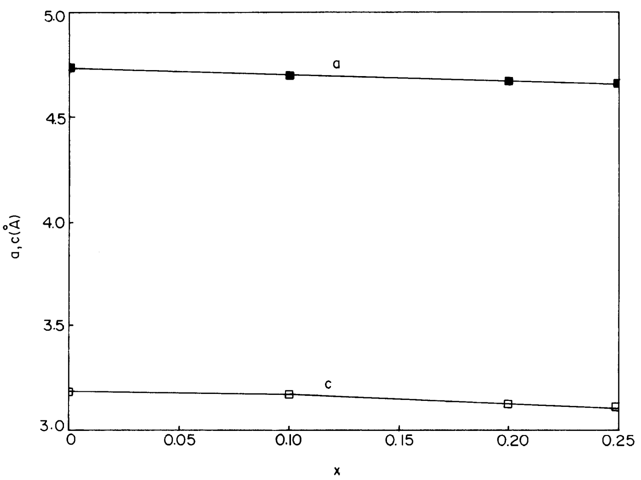

Figure 1. The variation of lattice parameters with x in $Co_{0{\cdot}01}Nb_{0{\cdot}0005}Al_{0{\cdot}0005}Sn_{0{\cdot}989-x}Ti_xO_2$.

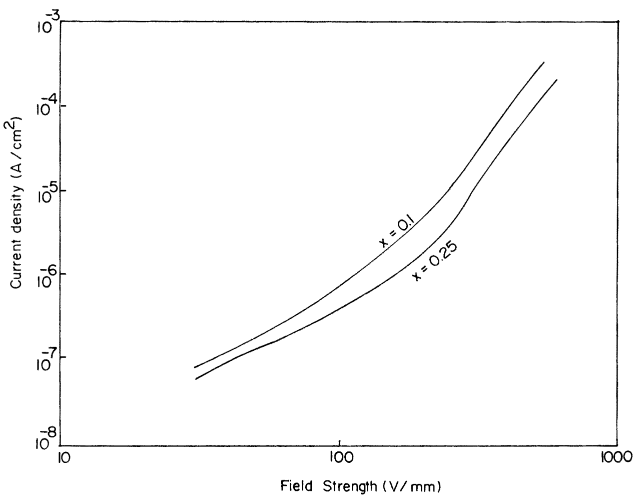

Figure 2. *I–V* characteristics of $Co_{0{\cdot}01}Nb_{0{\cdot}0005}Al_{0{\cdot}0005}Sn_{0{\cdot}989-x}Ti_xO_2$.

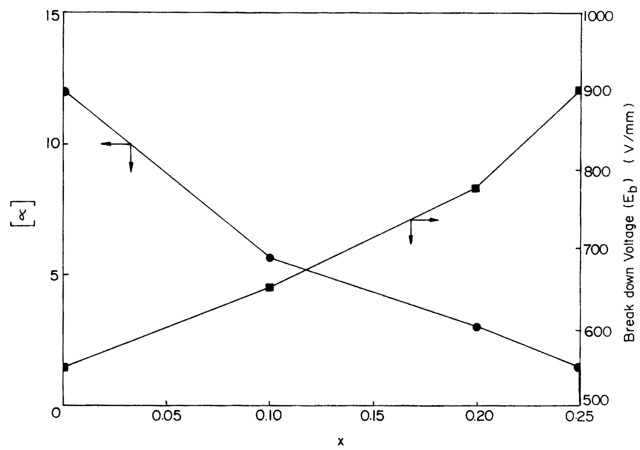

Figure 3. The variation of nonlinear coefficient (a) and breakdown voltage (E_b) with x in $Co_{0{\cdot}01}Nb_{0{\cdot}0005}Al_{0{\cdot}0005}Sn_{0{\cdot}989-x}Ti_xO_2$.

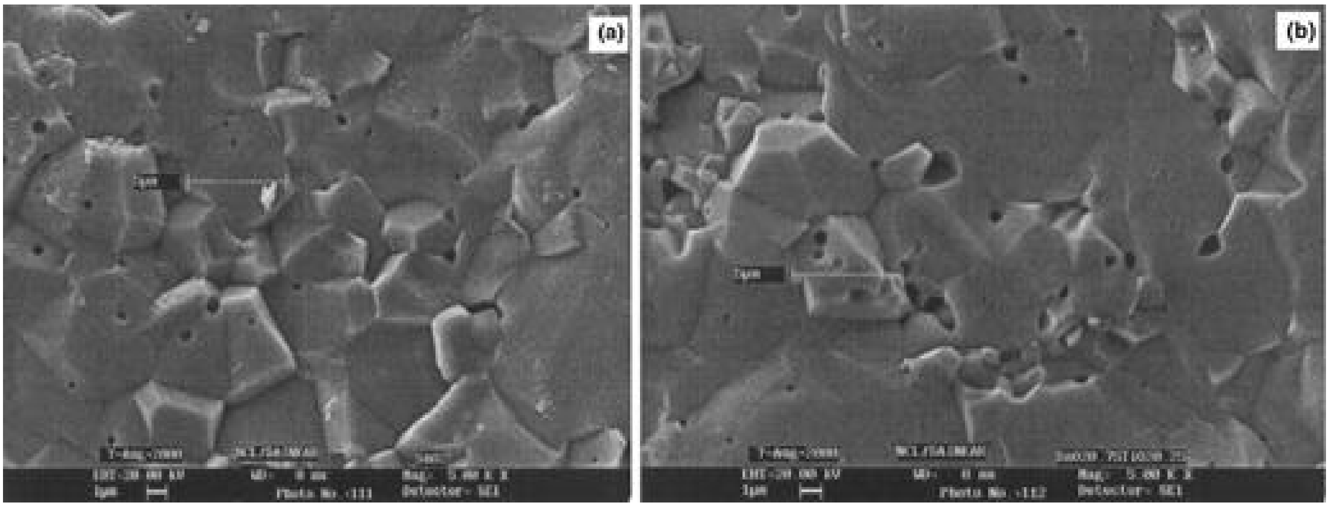

Figure 4. The microstructure of $Co_{0\cdot01}Nb_{0\cdot0005}Al_{0\cdot0005}Sn_{0\cdot989-x}Ti_xO_2$ for (**a**) $x = 0\cdot0$ and (**b**) $x = 0\cdot25$.

Figure 4 shows the microstructure recorded for the compositions $x = 0$ and $0\cdot25$, sintered in identical conditions. The morphological features were well defined for the end member $x = 0$, whereas grain boundaries and triple points were not sharply defined for $x = 0\cdot25$. This may be the possible reason for the low a values observed for the solid solutions. The average grain size was found to be 4 μ in both cases. The substitution of Ti^{4+} for Sn^{4+} does not affect the grain growth characteristics as observed from micrographs.

4. Conclusions

The influence of isovalent ion such as Ti^{4+} on the *I–V* curves of doped SnO_2 was investigated in detail. The solubility of Ti^{4+} in SnO_2 is up to 25 mole%. The results show that a decreases for the solid solution whereas E_b increases with Ti^{4+} content. Presently systematic investigations are on for other compositions to obtain optimum nonlinear coefficient and breakdown voltage.

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