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Properties of SnO_2-based ceramics

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Some SnO_2-based ceramics of the ternary and binary systems SnO_2–Sb_2O_3–CuO have been prepared and some of their properties have been measured. It was observed that most of their properties, which include density, porosity, d.c. electrical conductivity, as well as the crystal occurrence, were dependent on the presence of CuO. Crystal phase occurrence was investigated using the X-ray diffraction technique and it was found that the phases were predominantly SnO_2 and Sb_2O_4 crystals. The d.c. conductivity at different sintering temperatures was found to be enhanced by the simultaneous presence of Sb_2O_3 and CuO.

1. Introduction

Highly porous tin dioxide has been known to exhibit semiconducting behaviour which is suitable for application as gas sensors [1–3]. On the other hand, highly dense SnO_2-based ceramic materials are now considered as potential candidates for many industrial applications, including stable electrodes in some glass-melting furnaces [4]. For these purposes, investigation of the influence of many dopants to ensure high conductivity and densification, is necessary. However, very little information is available in the literature, especially on the properties of such materials at higher sintering temperatures. It is therefore very important to determine the optimum composition of SnO_2 with other additives to fulfil the described purposes.

In the present work, ternary and binary systems of SnO_2–Sb_2O_3–CuO ceramics have been prepared and the properties discussed with respect to composition.

2. Experimental procedure

The sample was prepared from reagent-grade SnO_2 (purity 99.8%), Sb_2O_3 (purity 99.5%) and CuO (purity 99.5%). An appropriate amount of oxides with a particle size of less than 100 μm was well mixed to ensure homogeneity and then pressed into cylindrical pellets of 4 cm diameter and 1.5 cm high at a pressure of 33 kN m^{-2}. The pellets were then sintered in an electrical furnace at 700–1000 °C in air for 1 h before being allowed to cool down to room temperature. The sample density was determined using Archimedes' method while the porosity (%) was found by calculating the ratio of the sample weight before and after 24 h immersion in toluene.

For identification of the phases present, the samples were analysed by X-ray diffraction using a Philips PW 1390 goniometer with CuK_α radiation in the angle range of 10°–50°, 2θ deg.

For measurement of electrical conductivity, the flat surface of a clover-leaf shaped sample was well polished with a non-aqueous solution. Four ohmic contacts were made at the edge of the sample using platinum paste. The resistivity was measured using the van der Pauw method [5, 6].

3. Results and discussion

The starting compositions and some properties of the SnO_2-based ceramics are listed in Table I, from which it is observed that as the amount of Sb_2O_3 increases at the expense of SnO_2, the ceramics density decreases. On the other hand, increasing the amount of CuO at the expense of Sb_2O_3 results in an increase of ceramic density. These results suggest that an excess amount of Sb_2O_3 reduces the sample densification. However, with the simultaneous presence of at least a few mole per cent of CuO, the sample becomes more densified, reflecting that CuO may act as a densification promoting agent. Also, as can be seen, the porosity decreases with the addition of Sb_2O_3. This may be due to the substitution activity of antimony with tin in the SnO_2 crystal. On addition of CuO, the effect seems to be more obvious. This may indicate that CuO has the capability of enhancing the substitution process in a similar manner to the sample density.

From the phase identification using the JCPDS data card, it is found that there are two phases existing in the ceramics, i.e. SnO_2 (major phase) and Sb_2O_4

TABLE I Starting compositions and some properties of SnO_2-based ceramics at 800 °C

Sample	Composition (mol %)			Density (g cm^{-3})	Porosity (%)
	SnO_2	Sb_2O_3	CuO		
S_1	96	4	–	5.99	8.0
S_2	90	10	–	5.95	7.9
S_3	85	15	–	5.30	7.8
S_4	80	20	–	4.32	7.5
S_5	96	3	1	6.31	7.3
S_6	96	2	2	6.41	7.1
S_7	96	1	3	6.38	6.7
S_8	96	–	4	6.48	5.7

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TABLE II Phase content and conductivity of SnO_2-based ceramics at 800 °C (w, weak peaks; vs., very strong peak; vw, very weak peak)

Sample	Phase content	Conductivity ($S\ cm^{-1}$)
S_1	SnO_2,Sb_2O_4 (vw)	0.68
S_2	SnO_2,Sb_2O_4 (vs)	0.63
S_3	SnO_2,Sb_2O_4 (vs)	0.62
S_4	SnO_2,Sb_2O_4 (vs)	0.60
S_5	SnO_2,Sb_2O_4 (vw)	0.72
S_6	SnO_2	0.74
S_7	SnO_2	0.75
S_8	SnO_2	0.71

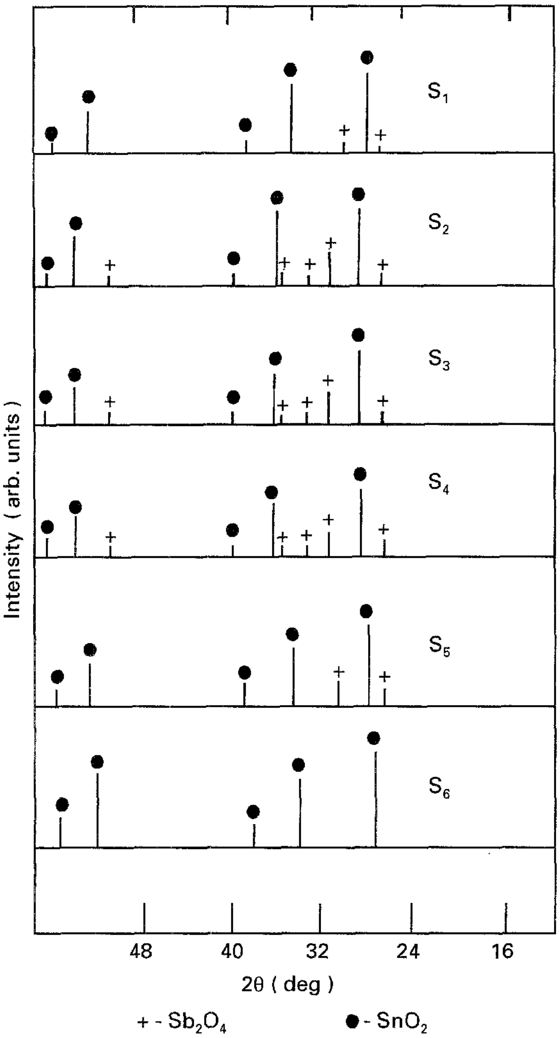

Figure 1 X-ray diffraction pattern of SnO_2–Sb_2O_3–CuO ceramics. (+) Sb_2O_4, (●) SnO_2.

(minor phase). The phase content of all the samples can be seen in Table II.

An interesting feature can be noted from the X-ray diffraction pattern (Fig. 1) : a peak of Sb_2O_4 begins to emerge very strongly as the Sb_2O_3 content is increased to 10 mol %, i.e. in sample S_2. In samples S_3 and S_4, the Sb_2O_4 peak is observed to be very strong. However, in S_5, the peak becomes very weak, presumably because the amount of Sb_2O_3 has been reduced to only 3 mol %. When the Sb_2O_3 content is further reduced, as in S_6 and S_7, the Sb_2O_3 peak is not apparent. Meanwhile, at the same time, it is observed that the SnO_2 peak region in samples S_2–S_5 has shifted slightly towards a higher angle. This indicates that the structure of SnO_2 has changed slightly. This may also indicate that substitution of antimony for tin in the SnO_2 crystal has occurred. The effect becomes more obvious when the content of Sb_2O_3 is increased to more than 10 mol %. Calculations from the X-ray diffraction peaks of the tetragonal lattice parameters of SnO_2 and the orthorhombic parameters of Sb_2O_4 crystal using the usual method [7], show that there are variations in the parameters. Plotting the parameter, a (nm) against the Sb_2O_3 content shows that as the concentration of Sb_2O_3 is increased, the parameter a will decrease. This kind of behaviour would support the above argument. These results can clearly be seen in Fig. 2 and Table III.

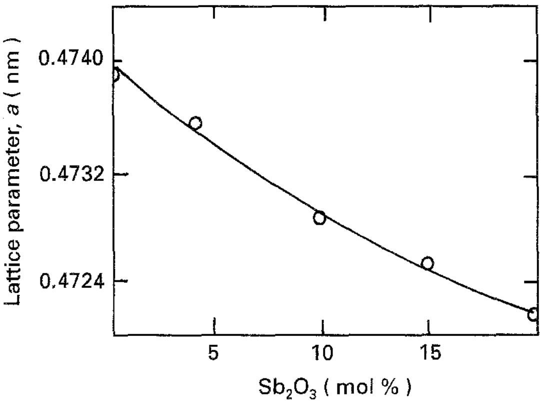

Figure 2 The variation of lattice parameter, a(nm) with composition.

TABLE III The variation of lattice parameters of the crystals found in SnO_2–Sb_2O_3–CuO ceramics at 800 °C

Sample	Lattice parameter (nm)					Reference
	SnO_2		Sb_2O_4			
	a	c	a	b	c	
SnO_2	0.4738	0.3188				[8]
Sb_2O_4			0.5436	0.4810	1.176	[9]
S_1	0.4736	0.3186				
S_4	0.4722	0.3183	0.5430	0.4782	1.168	
S_5	0.4730	0.3184				
S_8	0.4737	0.3188				

It should also be noted that CuO alone does not contribute to any significant variation in lattice parameters. This is true because investigations on S_6 and S_7 show no clear evidence of phases other than SnO_2 and Sb_2O_4 being present. This may confirm that copper ions do not enter the crystal structure of SnO_2.

The d.c. conductivity of various SnO_2-based ceramic materials prepared at various temperatures are shown in Table IV. It is observed that most values are higher than that reported earlier by Paria *et al.* [10], apparently due to the effect of oxygen pressure on the sample.

From Table IV, it can clearly be seen that as the amount of Sb_2O_3 increases, the d.c. conductivity

TABLE IV Electrical conductivity of SnO_2-based ceramics prepared at various sintering temperatures

Sample	Electrical conductivity (S cm^{-1})				Activation energy
	700 °C	800 °C	900 °C	1000 °C	(eV)
S_1	0.55	0.68	0.78	0.90	0.18
S_2	0.52	0.63	0.73	0.87	0.19
S_3	0.50	0.62	0.70	0.85	0.20
S_4	0.48	0.60	0.68	0.81	0.21
S_5	0.64	0.72	0.82	0.95	0.17
S_6	0.65	0.74	0.85	0.97	0.16
S_7	0.66	0.75	0.88	0.99	0.14
S_8	0.63	0.71	0.81	0.92	0.16

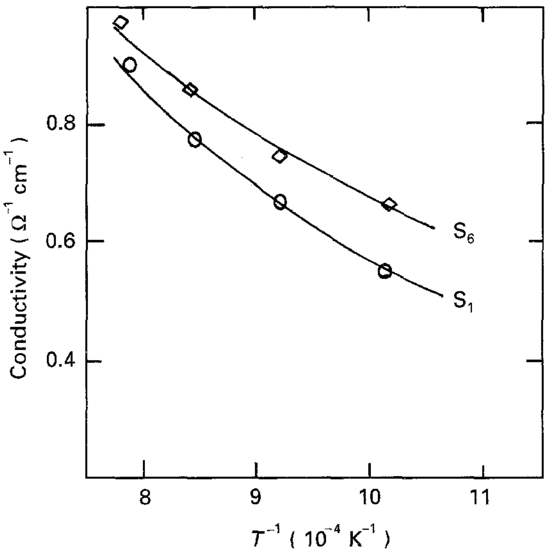

Figure 3 Dependence of conductivity on sintering temperature for S_1 and S_6.

slightly decreases. However, when the CuO content is added (a few mol %), there is a marked increase in the conductivity. It is also observed that the magnitudes of conductivity in the ternary system with CuO are always higher than that of the binary system without CuO. These results may be explained by considering that the addition of CuO may cause the densification process to become greater which means that fewer pores are created in the ceramic matrix. In other words, the sample may become more densified and more compact. As has been discussed earlier, the presence of CuO in the ceramic mixture may cause the substitution activity of Sb_2O_3 for tin in the ceramic matrix to become very active. This mechanism would simply cause the electrical conduction to become higher.

The dependence of conductivity as a function of sintering temperature is shown in Fig. 3. From this figure, it can clearly be seen that the conductivity slowly increases with temperature and is in good agreement with the normal Arrhenius equation of conductivity. Despite the fact that an increase in sintering temperature would also contribute to an increase in the densification of the ceramics materials [11], thus resulting in an increase in the conductivity, it can also be said that an increase in conductivity might also be attributed to the increase in charge carrier concentration in SnO_2-based ceramics.

From Fig. 3, the activation energies for conduction can be calculated and values ranging from 0.14–0.21 eV were obtained; these are shown in Table IV. From this table, it can be said that the simultaneous presence of oxide additives such as Sb_2O_3 and CuO will enhance the activation energy. These oxides must correspond to the main activity of an extrinsic conductivity in the SnO_2-based ceramics materials.

4. Conclusion

Most properties of the SnO_2-based ceramics are dependent on the composition. The X-ray diffraction study shows that after sintering, two phases occur. The major phase is tetragonal SnO_2 while the minor phase is orthorhombic Sb_2O_4. While CuO oxide enhances the densification (and hence conductivity capability), Sb_2O_3 can be promoted to substitute for tin in the SnO_2 crystal. The activation energy of this ceramic is also controlled by the simultaneous presence of oxide additives of Sb_2O_3 and CuO.

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References

1. T. SEIYAMA, N. YAMAZAE and H. ARAI, *Sensors Actuators* **4** (1983) 85.
2. K. IHOKURA, K. TANAKA and, N. MURAKAMI, *ibid.* **4** (1983) 607.
3. M. FORSTER, J. EBERLE, S. STRASSLER and G. PFISTER, *Inst. Phys. Ser. III* (1990) 479.
4. S. ZUCA, M. TERZI, M. ZAHRESCU and K. M. TIASOUSKY, *J. Mater. Sci.* **26** (1991) 1673.
5. L. J. VAN DER PAUW, *Philips Res. Rep.* **13** (1958) 1.
6. M. K. SAIDIN, PhD thesis, University of Durham (1987).
7. L. V. AZAROFF; “Elements of X-ray crystallography” (McGraw-Hill, New York, 1968) p. 483.
8. JCPDS powder diffraction data; Entry 21–1250 (1974).
9. JCPDS powder diffraction data; Entry 11–694 (1974).
10. M. K. PARIA and H. S. MAITI, *J. Mater. Sci.* **17** (1982) 3275.
11. M. P. LOW, *ibid.* **15** (1980) 2947.

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