Preparation, characterization and dielectric behaviour of some yttrium doped strontium stannates

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Abstract. Samples of $\text{Sr}_{(1-3x/2)}\text{Y}_x\text{SnO}_3$ are prepared by usual solid state reaction route. X-ray diffraction studies confirm the formation of single cubic perovskite single phase. The dielectric constant and dielectric loss at 1 kHz were measured in the temperature range from room temperature up to $\cong 150^\circ\text{C}$. The dielectric constant decreases and losses increase with increased yttrium content in the samples. The percentage porosity and unit cell parameters are also calculated for the samples.

Keywords. Electronic ceramics; sensors; dielectric constant; strontium stannate.

1. Introduction

Sensors have become important devices because they provide information about physical and chemical signals, which could otherwise be difficult to perceive directly. BaSnO_3 and SrSnO_3 have been widely investigated as sensor materials along with their solid solutions with BaTiO_3 (Sze *et al* 1998). In semiconductor sensors, the adsorption of gases on the surface of the material can bring significant change in the electrical resistance of the material. The mechanism of semiconductor gas sensors can be distinguished in two different classes. The first involves the change in the surface conductance while the second involves change in bulk conductance. The materials, which sense small concentration of reactive gases in air, rely by the change in the surface conductance and detect the displacement from equilibrium condition.

This class of compounds having cubic perovskite structure (CaTiO_3 , SrSnO_3 , BaSnO_3 , etc) show paraelectric behaviour at room temperature and are found to be semiconductors exhibiting relaxor behaviour when doped with more than 1% Y_2O_3 and sintered in an inert atmosphere at very low oxygen partial pressure (Neirman and Burn 1984). The same compound, when sintered in an oxygen rich atmosphere, exhibits dielectric behaviour similar to pure compound (Buchanan 1986). When Y^{3+} ions are substituted at A site of SrSnO_3 , two types of changes are expected. The ionic size will be affected resulting into change in the unit cell dimension. Secondly, substitution of Y^{3+} ions at A site (divalent site) will not bring the charge neutrality, and electrical conductivity is expected to increase.

The ceramic compounds are sintered to approach the equivalent single crystal behaviour as far as possible. Sintering increases density and in some cases it may reach up to 99.9%. However, for sensor materials, loosely sintered particles or thin films give better response as it increases the effective surface area and/or makes gas particle percolation into bulk easy. Therefore, one of the objectives of material modification for sensors is to increase porosity of the material. Further, earlier reports on charge compensated perovskites show sintering in a nitrogen atmosphere, oxygen lost from these ceramics according to relation, $\text{O}_0 = 1/2\text{O}_2 + V_0 \pm 2e'$ (Prakash *et al* 1987). On cooling from the firing temperature, reoxidation of the product takes place. However, sufficient time is not available for the reoxidation of the grains. Only grain boundaries are reoxidized and become insulating, thus enveloping the semiconductor grains. This gives rise to barrier layer at grain/grain boundary interfaces imparting very high dielectric constant to the resulting material. One therefore expects high dielectric constant and porosity in doped stannates.

In this paper, we report the preparation, structural characterization and dielectric behaviour of $\text{Sr}_{(1-3x/2)}\text{Y}_x\text{SnO}_3$ ceramics for $x = 0.0, 0.01, 0.03$ and 0.05 with a view to develop newer materials for semiconductor sensors.

2. Experimental

The starting materials, SrCO_3 (SD fine, 99%), SnO_2 (BDH, 99.5%) and Y_2O_3 (Indian Rare Earth, 99.9%) were mixed together in appropriate molar ratio as per the equation

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with x being 0, 0.01, 0.03 and 0.05, respectively. The finely grinded powders were kept for calcination in the silicon carbide furnace at 1200°C for 24 h. The calcined powders were homogenized and again calcinated at 1225°C for 16 h. The finally calcinated powders were finely grinded and used to make pellets of 10 mm diameter and 1–2 mm thickness and were sintered at 1275°C for 24 h. Sintered pellets were polished and electroded with silver conducting paint. These pellets were used for dielectric measurement. The calcined powder was characterized by XRD using Cu-K α X-ray radiation. The XRD pattern is shown in figure 1, which was indexed on the basis of cubic perovskite structure (table 1). The indexed peaks clearly show single-phase formation. The lattice parameter deduced from XRD data are given in table 2. The data show that Y³⁺ doping decreases the lattice constant. The dielectric measurements were performed at 1 kHz using HP-4263B LCR meter and a home made temperature dependent measurement setup from room temperature up to 150°C.

3. Results and discussion

From the capacitance data, the dielectric constant at each temperature is calculated using

$$\epsilon = C \cdot d / \epsilon_0 A,$$

where C is capacitance, d the thickness and ϵ_0 the free space permittivity and A the area of the pellet. The temperature dependence of dielectric constant and dielectric loss for various Y³⁺ doped Sr_{1-3x/2}Y_xSnO₃ samples are shown in figures 2 and 3, respectively. The frequency dependent dielectric behaviour is shown in figures 4

and 5. From figure 2, it is clear that dielectric constant increases with yttrium substitution and remains almost constant in the entire temperature range studied. This indicates that the vacancies created due to inherent charge compensation are not fully reoxidized and grain/grain boundary interface is giving boundary layer capacitance, thus making them suitable materials for barrier layer capacitor application. The dielectric loss increases with temperature and the increase is almost exponential. This shows that the conductivity contribution is mainly due to hopping process. The frequency dependence of dielectric behaviour (figures 4–5) shows no dielectric dispersion. An important effect of Y³⁺ doping in these

Figure 1. XRD peaks observed in doped systems.

Table 1. X-ray diffraction data for yttrium doped strontium stannates.

$x = 0.01$			$x = 0.03$			$x = 0.05$		
d -values	I/O	hkl	d -values	I/O	hkl	d -values	I/O	hkl
4.0126	8.7	100	4.0081	8.7	100	4.0028	9.3	100
2.8422	100.0	110	2.8342	100.0	110	2.8373	100.0	110
2.0120	27.7	200	2.0086	25.1	200	2.0063	22.5	200
1.8044	2.0	210	1.7935	3.3	210	1.7968	2.5	210
1.6434	30.3	211	1.6394	26.6	211	1.6390	23.2	211
1.4240	9.3	220	1.4218	9.4	220	1.4219	8.5	220
1.2729	7.1	310	1.2692	8.2	310	1.2710	6.7	310

Table 2. Lattice constant, density data and percentage porosity for doped systems.

Sample doping percentage (x)	Experimental density (g/cm ³)	Theoretical density (g/cm ³)	% Porosity	Lattice constant
0.0	4.98	6.4868	86	4.042
0.01	3.285	6.5330	79	4.040
0.03	3.448	6.5340	68	4.023
0.05	2.863	6.5299	54	4.014

Figure 2. Dielectric constant as a function of temperature in $\text{Sr}_{(1-3x/2)}\text{Y}_x\text{SnO}_3$.

Figure 3. Dielectric loss as a function of temperature in $\text{Sr}_{(1-3x/2)}\text{Y}_x\text{SnO}_3$.

Figure 4. Effect of frequency on dielectric constant at room temperature in $\text{Sr}_{(1-3x/2)}\text{Y}_x\text{SnO}_3$.

compounds is the change in their porosity. We have calculated the densities of different samples theoretically and compared them with measured densities as shown in table 2. Whereas, in the pure SrSnO_3 pellets, the measured density being $\approx 86\%$ to that of theoretical density, it decreases with Y^{3+} substitution and becomes almost 50% in 5% Y^{3+} substituted samples. The preparation conditions

Figure 5. Effect of frequency on dielectric loss at room temperature in $\text{Sr}_{(1-3x/2)}\text{Y}_x\text{SnO}_3$.

being similar for all samples indicate that the different ion size of Y^{3+} decreases packing density, therefore, increasing the porosity. This means that the doped material will have more absorption, giving better response when used as sensor materials. Measuring their water retention capacity further checks the increase in porosity. Pellets were soaked in distilled water for 24 h and their weights were taken before and after water absorption. The results indicate increase in porosity with increasing Y^{3+} percentage in samples.

4. Conclusions

The present study shows that the inherent charge neutrality created by vacancies in the yttrium doped stannates makes them important materials from sensor application. These can be used as barrier layer capacitor. Also, the dielectric constant increases with A-site yttrium substitution and could be useful gas sensing material. In fact a number of systems with substitution of trivalent cation at A and B-sites simultaneously were studied earlier (Neirman and Burn 1984). However, the inherent charge compensated systems are very scant (Kulwfelti *et al* 1991).

The XRD results show that the prepared compounds have single phase. The lattice parameters calculated, show decrease in lattice constant with substitution. It is shown that dielectric constant and loss increases with Y^{3+} doping. The porosity factor also increases indicating that the yttrium-doped compound should be more sensitive for gas sensing in comparison to pure stannates. The frequency dependence of dielectric behaviour indicates dispersion free dielectric behaviour at audio frequencies.

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