Effect of perovskite and spinel additives on zinc oxide varistors by sol-gel route

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Synthesis of zinc oxide (ZnO) varistors using sol-gel (SG) route is reported here. Multicomponent oxides, perovskites and spinels have been used as dopants in various mole percentages. Nonlinear coefficients for the three types of dopants are of the order 25, 35 and 18, respectively. SEM characterization of the samples prepared by SG route indicates a change in the grain-size of the order 4-30 μm with respect to the sintering temperature 1000-1200 °C. Similarly, perovskite and spinel dopants show a variation in the grain-size of the varistors as characteristic of temperature. Also, there is an improvement in the bulk density at lower sintering temperatures for the powders prepared by SG route.

Zinc oxide varistors have been widely used as surge arrestors and stabilisers in electric power systems and electric circuits because of their non-ohmic behaviour and other useful properties. The varistors contain Bi₂O₃ as one of the forming constituents although single addition of Bi₂O₃, BaO or CuO are also reported to produce high nonlinear coefficients.

The properties of polycrystalline voltage-variable resistors based on the ZnO-Bi₂O₃ system have been discussed by other investigators. Many authors have reported electrical properties of ZnO varistors in order to elucidate the mechanism of nonlinear resistivity.

The present investigations are aimed at: (i) synthesizing structural additives and ZnO by SG route, specially by citrate precursor route, as compared to the conventional SS route, and (ii) comparative study of the two methods with respect to the multi-component additives to evaluate the samples for their sinterability, nonlinear coefficients and microstructure.

Experimental Procedure

The synthesis of ZnO varistors with multicomponent oxides was done using analar grades of ZnO, Bi₂O₃, Co₃O₄, NiO, MnO and Sb₂O₃ in the mole percentage ratio 97:1:0.5:0.5:0.5:0.5. These compositions were prepared by SG and SS routes, and pressed in the form of pellets (12 mm diameter and 2-3 mm thick) for further sintering at different temperatures. The materials were characterized by XRD using Siemens X-ray powder diffractometer with filtered CuKα radiation. SEM studies were carried out by Hitachi S-520 scanning electron microscope.

Synthesis of ZnO, perovskite and spinel materials by sol-gel route

Zinc oxide was reacted with 1:1 HNO₃. One mole of citric acid solution in water was used for every one mole of Zn, and the corresponding amount of ethylene glycol (1.2 mole) was added to it. The transparent solution was heated on water bath to form the gel. The gel so obtained was heated in an oven at 150°C to form powder, which was further heated to 550°C to get white powder of zinc oxide.

SrBaMnO₃₋₄, SrBaNiO₃₋₄ and SrBaCoO₃₋₄ perovskites were also synthesized using corresponding amounts of carbonates/oxides. The fine powders obtained 150°C were calcined in oxygen atmosphere at 900°C for 6h, cooled to 600°C at the rate of 60°C/h, soaked for 72 h in oxygen atmosphere, and further cooled to room temperature. XRD studies at room temperature on these samples indicate the formation of single phase compounds.

The spinel compounds (MgAl₂O₄, CoAl₂O₄, NiAl₂O₄, MnAl₂O₄ and CuAl₂O₄) were also prepared similarly using corresponding stoichiometric quantities of various compositions in the form of carbonates/oxides/acetates. Fine powders of the compositions obtained at 150°C were calcined at 1150°C for 5 h. XRD studies of these samples indicated the formation of single-phase compounds, as shown in Fig. 1.

Green shapes prepared by sol-gel route, made from ZnO, perovskite and spinel additives (1, 2 and 3
mole%) were pressed in the form of pellets and sintered at 1000/1050/1100/1150/1200°C after soaking for 4 h.

Synthesis of perovskite materials by solid-state route
Requisite stoichiometric quantities of corresponding carbonates/oxides (99.5%) were weighed, wet mixed for 2 h, dried and calcined under the conditions as described for sol-gel route, using commercially available ZnO.

Nonlinear coefficient (α) of varistors is defined as the slope of the graph of log current density (log I/A) vs log field strength (log V/t). Thus,

\[ \alpha = \log \left( \frac{I}{A} \right) / \log \left( \frac{V}{t} \right) \]

where \( I \) is the current, \( A \) is the cross-sectional area of the sample, \( V \) is the voltage and \( t \) is the thickness of the sample, \( I/A \) is the current density and \( V/t \) is the field strength. The current-voltage (I-V) characteristics were measured in the range of 5-110V using Keithley 236 instrument.

Results and Discussion
Multicomponent oxide additives
Based on the XRD studies, ZnO based varistors, when prepared by SS or SG route, did not indicate the presence of the various components used as additive. This may be due to the very small mole percentages of these components in the varistors. The actual value of theoretical density of zinc oxide from the literature is 5.61 g/cm³. Table 1 indicates the variation of theoretical density of ZnO varistors at different sintering temperatures. It is seen that there is a slight variation of density at higher temperature for SG studies. The table also indicates that the multicomponent oxide addition by SG route gives better density at lower temperature as compared to SS method. Regarding the uniformity and grain size, SEM micrographs of polished and etched surfaces of varistors by SS and SG routes sintered at 1100/1150/1200/1250/1300/1350°C indicate approximately 10 to 20 μm grain size.

It is also observed that by SG route, the nonlinear coefficient is 50% and 80% higher at 1050°C and 1100°C respectively as compared to that by SS route sintering at the same temperatures.

Perovskite additives
Preparation of various perovskites, namely Sr/BaMnO₃, Sr/BaNiO₃, and Sr/BaCoO₃ prepared by the SS and SG routes indicated the presence of single phase character. XRD studies indicated the

![X-ray diffraction patterns](image-url)

Fig. 1—X-ray diffraction patterns of: (a) NiAl₂O₄, (b) MgAl₂O₄, (c) CoAl₂O₄ spinel materials
Fig. 2—X-ray diffraction patterns of: (a) ZnO (b) ZnO+3 mole% of BaMnO$_{3.8}$, and (c) BaMnO$_{3.8}$ (SG)

Table 1—Variation of theoretical density of ZnO varistors at different sintering temperatures

<table>
<thead>
<tr>
<th>Method of preparation</th>
<th>Theoretical density (%) at</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1000°C</td>
</tr>
<tr>
<td>Solid-state (SS)</td>
<td>77</td>
</tr>
<tr>
<td>Sol-gel (SG)</td>
<td>83</td>
</tr>
</tbody>
</table>

Table 2—Variation of per cent theoretical density of zinc oxide varistors at different sintering temperatures doped with 3 mole% of perovskites

<table>
<thead>
<tr>
<th>Dopant</th>
<th>Theoretical density (%) at</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>1100°C</td>
</tr>
<tr>
<td></td>
<td>SS</td>
</tr>
<tr>
<td>BaMnO$_{3.8}$</td>
<td>72</td>
</tr>
<tr>
<td>BaCoO$_{3.8}$</td>
<td>80</td>
</tr>
<tr>
<td>BaNiO$_{3.8}$</td>
<td>65</td>
</tr>
<tr>
<td>SrMnO$_{3.8}$</td>
<td>70</td>
</tr>
<tr>
<td>SrCoO$_{3.8}$</td>
<td>63</td>
</tr>
<tr>
<td>SrNiO$_{3.8}$</td>
<td>65</td>
</tr>
</tbody>
</table>

The variation of theoretical density (%) of ZnO varistors doped with 3 mole% perovskite dopants by SS and SG routes as a function of sintering temperature is reported in Table 2. The samples prepared by SG route are found to be sintered at 90-91% theoretical density at a maximum of 1150°C whereas by SS route, sintering at 1350°C is needed to attain the same density. Thus, the sintering temperature is lowered by 200°C to attain the ~90% density by using SG route. Similarly, the percent presence of all the lines as reported earlier. Addition of 1/2/3 mole% of BaMnO$_{3.8}$ in zinc oxide by SG route did not show any XRD lines except that for 3 mole% (Fig.2). This might be due to the presence of 7.5 wt% of BaMnO$_{3.8}$ corresponding to its 3 mole%. It is interesting to note that intensity of 2.600 d-line is suppressed by the addition of 3 mole% BaMnO$_{3.8}$. Also, the intensities of both lines of ZnO (2.813 and 2.607Å) are suppressed considerably by the addition of 3 mole% SrMnO$_{3.8}$.}

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Table 3—Variation in theoretical density (%) of ZnO varistors with 3 mole% spinel additives as a function of sintering temperature

<table>
<thead>
<tr>
<th>Dopant</th>
<th>Theoretical density (%) at</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1000°C</td>
</tr>
<tr>
<td>MgAl₂O₄</td>
<td>77</td>
</tr>
<tr>
<td>CoAl₂O₄</td>
<td>77</td>
</tr>
<tr>
<td>NiAl₂O₄</td>
<td>78</td>
</tr>
<tr>
<td>MnAl₂O₄</td>
<td>79</td>
</tr>
<tr>
<td>CuAl₂O₄</td>
<td>79</td>
</tr>
</tbody>
</table>

**Fig. 3**—Graph of log current density vs log field strength of ZnO varistors with 3 mole% perovskite additives

Theoretical density increases by 3-5% for all the perovskite dopants by increasing the additives by 1-3 mole percent.

Non-linear coefficient values of 3 mole% of BaMnO₃₋₃, SrMnO₃₋₃ and SrNiO₃₋₃ prepared by SG route and sintered at 1150°C are of the order 34, 17 and 33 respectively (Fig. 3).

SEM studies of ZnO varistors with an addition of 1-3 mole% of perovskite additives show a rapid fall in grain size from 30-4 µm when sintered at 1100°C. In addition, the grain size distribution is also negligible as a function of sintering temperature on the above varistors. Similar observations are made from micrographs of ZnO varistors when doped with 3 mole% BaNiO₃₋₃ and BaCoO₃₋₃. In these cases, the grain sizes are of the order 2-8 µm and 1-3 µm, respectively.

ZnO varistors with spinel additives

Synthesis of various spinels (MgAl₂O₄, MnAl₂O₄, CoAl₂O₄, NiAl₂O₄, and CuAl₂O₄) by SG route, sintered at 1150°C, indicates the presence of single phase materials only. We have chosen aluminates as they are expected to be the insulators possessing very high electrical resistivity. Fig. 1 shows XRD patterns of MgAl₂O₄, CoAl₂O₄ and NiAl₂O₄. The presence of 2-3 mole% of these additives could be detected by XRD either because of minor presence (4.9 wt%) of these materials in ZnO or due to the overlapping of ZnO peaks (2.473) and highest intensity spinel peaks (2.472, 2.443 and 2.437 for Ni-Mg-Co aluminates).

ZnO varistor with 3 mole% spinel additives has shown considerable improvement in bulk density
when sintered at 1000-1150°C. The theoretical density (%) of these compositions, sintered at various sintering temperatures under air is given in Table 3.

Thus, the addition of spinel materials namely MnAl₂O₄ and CuAl₂O₄ to ZnO has increased their bulk density to 89 and 94% of theoretical density respectively when sintered at 1150°C. Hence, the synthesis of spinel materials by SG route is found to be better. In addition, the use of ZnO (SG) and spinel additives (SG) also reduced the sintering temperature considerably.

For 3 mole% spinel additive, the non-linear coefficient increases with the increase in sintering temperature. At 1150°C sintering temperature, the α values vary from 25 to 30 irrespective of spinel additives.

It is observed that the spinel additives (1-3 mole%) inhibit the grain growth of zinc oxide varistors when sintered at 1150°C, whereas with 3 mole% of CuAl₂O₄ spinel additive, the grain size appears to increase marginally from 2 µm to 4 µm and density increases from 79 to 94% when sintered at 1150°C.

Conclusions

Perovskite and spinel compounds have been prepared by SG route. The density of zinc oxide varistors has been found to improve significantly by the addition of these compounds (1-3 mole %). The nonlinear coefficient of zinc oxide varistors improved considerably with the addition of the perovskite compounds.

Acknowledgements

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References