The obtaining of ZnO-Bi$_2$O$_3$-Sb$_2$O$_3$ (ZBS) based varistor thick films with high non-linear properties is constrained by the bismuth loss by vaporization that takes place during the sintering step of these ceramics, a process which is yet more critical in the thick film geometry due to its inherent high are/volume ratio. This volatilization can be controlled to a certain extent by modifying the proportions of the Bi and/or Sb precursors. Obviously this requires a clear knowledge of the different solid state compatibilities in the mentioned ZBS system. In this sense a detailed study of the thermal evolution of the ZnO-Bi$_2$O$_3$-Sb$_2$O$_3$ and ZnO-Bi$_2$O$_3$-Sb$_2$O$_5$ systems in the ZnO-rich region of interest for varistors, is presented in this contribution. A different behaviour is observed when using Sb$_2$O$_3$ or Sb$_2$O$_5$ as starting precursor, which should be attributed to the oxidation process experimented by Sb$_2$O$_3$ compound during the heating. On the other hand the use of high amounts of Bi in the starting formulation leads to the formation of a liquid phase at lower temperatures, which would allow the use of lower sintering temperatures.

**Keywords:** ZnO, varistor, Bi volatilization, solid state compatibility, thick film.

**Compatibilidad en estado sólido en la región rica en Zn de los sistemas ZnO-Bi$_2$O$_3$-Sb$_2$O$_3$ y ZnO-Bi$_2$O$_3$-Sb$_2$O$_5$**

La obtención de varistors en lámina gruesa basados en ZnO-Bi$_2$O$_3$-Sb$_2$O$_3$ (ZBS) y con propiedades altamente no-lineales está limitada por la pérdida de bismuto por volatilización durante la sinterización de estos cerámicos, un proceso que es todavía más crítico en la geometría de lámina gruesa debido a su elevada relación área/volumen inherente. Dicha volatilización puede ser no obstante controlada hasta cierta extensión modificando las proporciones de los precursores de Bi y/o Sb. Obviamente ello conlleva un amplio conocimiento de las diferentes compatibilidades en estado sólido en el mencionado sistema ZBS. En este sentido, en la presente contribución se presenta un estudio detallado de la evolución térmica de los sistemas ZnO-Bi$_2$O$_3$-Sb$_2$O$_3$ y ZnO-Bi$_2$O$_3$-Sb$_2$O$_5$ en la región rica en ZnO de interés para varistores. Como resultado se ha observado un comportamiento diferente al usar Sb$_2$O$_3$ o Sb$_2$O$_5$ como precursor de partida, lo cual debe atribuirse al proceso de oxidación experimentado por el compuesto Sb$_2$O$_3$ durante el calentamiento. Por otra parte, utilizando altas concentraciones de bismuto en la formulación de partida se llega a la formación de una fase líquida a temperaturas inferiores, lo que permitiría el empleo de temperaturas de sinterización más bajas.

**Palabras clave:** ZnO, varistor, volatilización de Bi, compatibilidad en estado sólido, lámina gruesa.

**1. INTRODUCTION**

Ceramic materials based in ZnO doped with Bi$_2$O$_3$ and Sb$_2$O$_3$ (ZBS system), exhibit high non-linear current-voltage responses which find application in the field of varistor surge-protective devices (1,2). Depending on the configuration, ZBS varistors can be made that protect different electric circuits, from electronic devices to power transmission lines. However in the particular case of high power applications such configurations are still restricted to bulk specimens, and for example the obtaining of thick films of ZBS ceramic varistors with an electrical response capable of repeatedly withstand high power pulses still represents a major challenge. The main obstacle to reach this goal is the unavoidable Bi loss by vaporization that takes place from the Bi-rich liquid phase formed during the sintering of these ceramics (3,4). This volatilization strongly depends on the area/volume ratio of the ceramic compact (5), so it is conceivable that the situation is particularly dramatic in the thick film geometry. Accordingly, in the last years different strategies have been proposed to overcome this drawback, and some interesting results have been reported acting over the preparation of the films and/or the sintering conditions (6-8). However the electrical properties thus obtained are still far from those of the bulk counterpart samples, because the Bi volatilization experimented by the films is still too high.

One interesting possibility could be then to act over the sintering reactions. In a standard ZBS composition the oxidation upon heating of Sb$^{3+}$ to Sb$^{5+}$ first leads to the formation of an intermediate pyrochlore-type compound which at temperatures around 900°C decomposes into the Bi-rich liquid and a spinel-type phase (9). By slightly changing the starting proportion of Bi and/or Sb dopants, i.e., by changing the starting Bi/Sb ratio, these reactions can be
altered in such a way that the temperature at which the liquid is released could be decreased, so the subsequent volatilization could be somehow controlled and reduced. But obviously, prior to any modification, a detailed analysis of the solid state compatibility of the three components in the ZBS ternary system is absolutely compulsory, being this the main purpose of the present contribution.

So to face this goal, we have analyzed the thermal evolution of different ZnO-Bi₂O₃-Sb₂O₃ compositions for the temperature range between 700 and 900°C. The compositions were selected in the ZnO-rich region of the system, which represents the region of interest for varistors. But furthermore, we have also prepared and analyzed some compositions in the ZnO-rich region of the ZnO-Bi₂O₃-Sb₂O₅ system. By using Sb₂O₅ instead of Sb₂O₃ we are eluding the Sb³⁺ to Sb⁵⁺ oxidation that takes place upon heating and, although the final situation will be alike, the different reactivity of both antimony oxides will probably entail different reaction mechanisms than those mentioned above, so supposedly leading to a different control on the formation of the liquid phase.

2. EXPERIMENTAL PROCEDURE

The ceramics powders were prepared by a conventional solid state route in which the starting oxides ZnO, Bi₂O₃ and Sb₂O₃/Sb₂O₅ were mixed thoroughly including previous ball-milling for 2 hours in ethanol. Reagent-grade raw materials (Sigma-Aldrich) were used in all cases. As outlined in Table I, up to ten different compositions in the ZBS system were prepared, five using Sb₂O₃ as starting source of antimony and five more using Sb₂O₅. The prepared powders were pressed into pellets and heated at 700, 800 and 900°C with a dwell time of 72 hours at the maximum temperature. After this time, samples were rapidly quenched in air to avoid any parasitic or secondary reaction during cooling. Once quenched, the samples were grounded for further characterization.

The identification of the crystalline phases was carried out by X-Ray Diffraction (XRD) in a D5000 Siemens diffractometer with a fully computerized Kristalloflex 710 generator. CuKα radiation and polycrystalline Si as internal pattern were used to perform the XRD characterization. The analysis of the microstructure was carried out on a Field Emission Hitachi S-4700 FE-SEM microscope provided with a Noran EDS microprobe.

2. RESULTS AND DISCUSSION

XRD patterns of compositions 1 to 4 with Sb₂O₃ as raw oxide and treated at 700°C/72h are depicted in Figure 1. As observed, the equilibrium coexisting phases are ZnO (JCPDS file nº 36-1451), a ZnSb₂O₆ tri-rutile phase (JCPDS file nº 38-0453), and a third phase whose peaks correspond to a pyrochlore-like structure. Figure 2 on the other hand shows the XRD diffractogram of composition 5 prepared with Sb₂O₅ after 72 hours at 700°C. In this case a mixture of ZnO, the pyrochlore phase and the Bi₃ZnO₉ phase with a sillenite structure (10,11), can be observed. It is important to remark that, according to the literature, the observed pyrochlore compound could be ascribed to the stoichiometric Bi₃ZnSb₃O₁₄ compound suggested by Mergen et al (12) or to any of the non-stoichiometric phases more recently proposed by Miles et al (13), such as the solid solution BiₓSb₃-xZnₓSb₁₄ where 0 < x < 0.13 and 0 < y < 0.017 or the ZnₓBi₃-xSb₁₄O₁₄+y Phase. The fact is that all these structures show very similar XRD patterns and to accurately identify which one we are detecting is out of the scope of this contribution. So from now on we will simply refer to the pyrochlore phase, without any specification to the stoichiometry of the structure. When the compositions are prepared with Sb₂O₅ instead of Sb₂O₃, the thermal treatment of the samples at 700°C for 72 hours leads to the same distribution of phases, i.e., ZnO, ZnSb₂O₆ and pyrochlore for compositions 1 to 4 and, ZnO, pyrochlore and the sillenite Bi₃ZnO₉ for composition 5. Therefore, according to these first XRD analyses, the same triangle of solid state compatibility at 700°C can be proposed for the ZnO-rich region of both ZnO-Bi₂O₃-Sb₂O₃ and ZnO-Bi₂O₅-Sb₂O₅ systems. This triangle is illustrated in Figure 3.

<table>
<thead>
<tr>
<th>Composition</th>
<th>ZnO</th>
<th>Bi₂O₃</th>
<th>Sb₂O₃/Sb₂O₅</th>
<th>Sb/Bi ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>92.5</td>
<td>2.5</td>
<td>5</td>
<td>2</td>
</tr>
<tr>
<td>2</td>
<td>85</td>
<td>5</td>
<td>10</td>
<td>2</td>
</tr>
<tr>
<td>3</td>
<td>70</td>
<td>10</td>
<td>20</td>
<td>2</td>
</tr>
<tr>
<td>4</td>
<td>50</td>
<td>10</td>
<td>40</td>
<td>4</td>
</tr>
<tr>
<td>5</td>
<td>77.25</td>
<td>17.25</td>
<td>5.5</td>
<td>0.3</td>
</tr>
</tbody>
</table>

Table I. Experimental compositions prepared in this study.
The situation however changes when samples are treated at 800ºC and now some differences appear when Sb$_2$O$_3$ or Sb$_2$O$_5$ are used starting materials. For example at this temperature, the compositions 1 to 4 prepared with Sb$_2$O$_5$ show the same solid phases than in the experiment at 700ºC: ZnO, ZnSb$_2$O$_6$, and the pyrochlore phase. But when these four compositions are prepared with Sb$_2$O$_3$, different stability fields are obtained at 800ºC than those observed at 700ºC. Table II summarizes the equilibrium phases identified by XRD for the compositions 1 to 4 prepared with Sb$_2$O$_3$ and thermally treated at 800ºC, and as can be seen new phases with a spinel-like structure are now detected. As happened before with the pyrochlore structure, this spinel phase can be ascribed to stoichiometric compound Zn$_7$Sb$_2$O$_{12}$ (JCPDS file nº 36-1445), or to the non-stoichiometric one, Zn$_{2.33}$Sb$_{0.67}$O$_4$ (JCPDS file nº 15-0687) (9,14). With regards to composition 5, the treatment at 800ºC however leads to the same equilibrium phases independently of the use of Sb$_2$O$_3$ or Sb$_2$O$_5$: ZnO, the pyrochlore and a new β-Bi$_2$O$_3$ phase, as inferred from XRD diffractograms (not depicted here). It happens that at temperatures above 753ºC the sillenite Bi$_{38}$ZnO$_{58}$ phase melts incongruently (10), so at 800ºC the compositions number 5 are both characterized by the presence of a liquid phase which on cooling crystallizes into the metastable phase β-Bi$_2$O$_3$. The SEM image in Figure 4 corresponds to composition 5 prepared with Sb$_2$O$_3$ treated at 800ºC (same microstructure was observed for composition 5 with Sb$_2$O$_5$) and the corresponding EDS analyses confirm the results of XRD characterization: together with the rounded dark grains of ZnO (a) and the octahedral crystals of the pyrochlore phase (b), an intergranular phase is observed (c) which can be ascribed to the β-Bi$_2$O$_3$ compound. So according to all these results, at 800ºC two new triangles of solid state compatibility can be drawn for the ZnO-rich region of the ZnO-Bi$_2$O$_3$-Sb$_2$O$_3$ and the ZnO-Bi$_2$O$_3$-Sb$_2$O$_5$ systems.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Equilibrium Phases</th>
</tr>
</thead>
<tbody>
<tr>
<td>1, 2</td>
<td>ZnO, pyrochlore, ZnSb$<em>2$O$</em>{12}$</td>
</tr>
<tr>
<td>3</td>
<td>ZnSb$<em>2$O$<em>6$, pyrochlore, Zn$</em>{1.33}$Sb$</em>{0.67}$O$_4$</td>
</tr>
<tr>
<td>4</td>
<td>ZnSb$_2$O$_6$, pyrochlore, Zn$_7$Sb$<em>2$O$</em>{12}$</td>
</tr>
</tbody>
</table>

Table II. Solid state equilibrium phases for compositions 1 to 4 prepared with Sb$_2$O$_3$, and thermally treated at 800ºC/72h.

Table III. Solid state equilibrium phases after the treating the samples at 900ºC/72h.

<table>
<thead>
<tr>
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<th>Equilibrium Phases</th>
</tr>
</thead>
<tbody>
<tr>
<td>1, 2</td>
<td>ZnO, pyrochlore, ZnSb$<em>2$O$</em>{12}$</td>
</tr>
<tr>
<td>3, 4</td>
<td>ZnSb$_2$O$_6$, pyrochlore, Zn$_7$Sb$<em>2$O$</em>{12}$</td>
</tr>
</tbody>
</table>

Figure 5. Solid state compatibility at 800ºC for A) ZnO-Bi$_2$O$_3$-Sb$_2$O$_3$ system and B) ZnO-Bi$_2$O$_3$-Sb$_2$O$_5$ system.

Figure 4. SEM analysis of composition 5 treated at 800ºC/72h; a) ZnO grains, b) octahedral crystals of pyrochlore phase and c) β-Bi$_2$O$_3$ intergranular phase.
These triangles are shown in Figure 5 and evidence a different reactivity when the powder is formulated with Sb₂O₅ or with Sb₂O₃. The origin of this different behaviour should be attributed to the oxidation process experimented by Sb₂O₃ compound on heating; actually, the ZnO-Bi₂O₃-Sb₂O₃ system may be expressed as the quaternary ZnO-Bi₂O₃-Sb₂O₃O₂ where the oxygen partial pressure would be taking into account. As a consequence more intermediate compounds can be formed when Sb₂O₃ is used, so leading to a more complex microstructure that could finally make more difficult to have an efficient control over the vaporization process.

However the differences observed between both systems at 800°C come to disappear when the samples are treated at 900°C/72h (Table III). Now the same crystalline phases are observed in both groups of compositions, independently of the starting antimony oxide. In particular, XRD analyses of compositions 1 and 2 show the presence of ZnO, the pyrochlore phase and the stoichiometric spinel Zn₇Sb₂O₁₂ whereas in compositions 3 and 4 the compatible phases are the tri-rutile ZnSb₂O₆, the stoichiometric Zn₇Sb₂O₁₂ spinel and the pyrochlore. These results indicate that the increase in temperature contributes to the stabilization of the stoichiometric spinel, Zn₇Sb₂O₁₂ instead of the non stoichiometric one, ZnₓSb₂O₇₋ₓ which was previously observed in some compositions at 800°C (Table II). On the other hand the treatment of both compositions 5 and 9 at 900°C show the same phases already observed at 800°C: ZnO, the pyrochlore and the β-Bi₂O₃. Figure 6 thus shows the triangle of solid state compatibility for the thermal treatment at 900°C, which as happened before at 700°C is again the same one for both the ZnO-Bi₂O₃-Sb₂O₃ and the ZnO-Bi₂O₃-Sb₂O₅ systems.

4. CONCLUSIONS

Different solid state fields of compatibility have been described for the ZnO-rich region of the ZnO-Bi₂O₃-Sb₂O₃ and the ZnO-Bi₂O₃-Sb₂O₅ systems. According to them, some relevant differences are obtained when using Sb₂O₃ or Sb₂O₅ as precursors of antimony in the starting formulation. These differences should find their origin on the oxidation process experimented by Sb₂O₃ compound, which leads to the stabilization of several intermediate compounds. But from the point of view of the obtaining of thick films of ceramic varistors, the most interesting finding is the lower temperature of liquid formation obtained in those compositions with the higher amount of bismuth (compositions number 5). Such compositions lead to the formation of a Bi₃⁻ZnO₅ sillenite phase which already melts at 753°C. This phase could be used then as a Bi precursor in the starting varistor formulation, allowing the use of lower sintering temperatures, reducing the subsequent Bi loss by volatilization and therefore leading to a high non-linear varistor response in the thick film devices.

ACKNOWLEDGMENTS

The present work has been conducted within the CICYT MAT 2007-66845-C02-01 project.

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Recibido: 12/02/2010
Aceptado: 23/03/2010