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DIELECTRIC MATERIALS OF THE Bi$_3$SbO$_7$ TYPE

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Résumé - Un oxyde mixte de bismuth et d'antimoine Bi$_3$SbO$_7$ a été isolé au sein du système Bi$_2$O$_3$-Sb$_2$O$_5$. L'étude par diffraction X et analyse thermique différentielle a montré que ce composé présente une transformation polymorphique vers 1050°C. Les deux variétés ont une structure cristalline dérivée de la fluorine et voisine de celle de Ln$_3$SbO$_7$. Leurs stabilités relatives ont été étudiées pour des solutions solides Bi$_3$-xLn$_x$SbO$_7$ avec Ln = La, Nd et Gd. Les caractéristiques diélectriques mesurées à basse fréquence et dans le domaine hyperfréquence montrent que Bi$_3$SbO$_7$ pourrait servir de composé de base pour la réalisation de nouveaux résonateurs diélectriques microondes.

Abstract - A bismuth antimony oxide Bi$_3$SbO$_7$ has been isolated in the Bi$_2$O$_3$-Sb$_2$O$_5$ system. DTA and X-ray diffraction analysis have shown that this compound undergoes a polymorphic transformation at about 1050°C. Both varieties have a fluorite related structure close to the Ln$_3$SbO$_7$ one. The relative stability of the two polymorphs has been studied for the Bi$_3$-xLn$_x$SbO$_7$ solid solutions where Ln = La, Nd and Gd. Low and hyperfrequency measurements of the dielectric constant, temperature coefficient and dielectric losses have been performed on sintered ceramics between room temperature and 100°C. The results show that Bi$_3$SbO$_7$ should be a basic compound for the elaboration of new microwave dielectric resonators.

INTRODUCTION

The constant development of microwave integrated circuits makes necessary the elaboration of systems which can be used in the millimetric or centimetric frequency range. Among these devices, dielectric resonators are more and more successful due to their relative small dimensions and their ability to be used both in passive and active systems. As an example, at 4 GHz a cylindrical metallic cavity must be 90 mm in diameter and 43 mm in height whereas the dimensions of a dielectric resonator with $\varepsilon_r = 38$ used at the same frequency would be 12.5 mm in diameter and 6.25 mm in height only.

However the elaboration of dielectric resonators needs materials with a good temperature stability of the resonant frequency (in the ppm/°C range) and low dielectric losses ($10^{-4}$) at high frequency. The number of presently available materials is quite small, e.g. Ba$_2$Ti$_4$O$_{12}$, (Zr,Sn)TiO$_4$, BaMg$_1$/3Ta$_2$/303, BaZr$_1$/3Ta$_2$/303, BaO-PbO-Nd$_2$O$_5$-TiO$_2$ /1,2,3,4,5,6,7/.

Investigations in the Bi$_2$O$_3$-Sb$_2$O$_5$ system led us to isolate a new bismuth antimony oxide with Bi$_3$SbO$_7$ formula /8/. Preliminary experiments have shown that the dielectric criteria of this compound should correspond to the above mentioned criteria for dielectric resonators. Moreover it seemed of interest to investigate some derivated compounds in order to modulate both dielectric constants and temperature coefficients.

Bi$_3$SbO$_7$ melts congruently at a temperature close to 1120°C. It undergoes a reversible...
polymorphic transformation $\alpha \rightarrow \beta$ at about 1050-1060°C. Nevertheless the high temperature $\beta$ phase can be stabilized in the metastable state by quenching. X-ray patterns of the two varieties, as do the orthorhombic Ln$_3$SbO$_7$ ones, show strong lines characteristic of a distorted fluorite-like sublattice of $\alpha$-Bi$_2$O$_3$ type /TAIRI, A., CHAMPARNAUD-MESJARD, J.C., MERCURIO, O. and FRIT, B., to be published/. For the two polymorphs, lanthanide substitution for bismuth is possible but in both cases rather low ($0 < x < 0.05$ for Bi$_3$-xLa$_x$SbO$_7$, $0 < x < 0.10$ for Bi$_3$-xLn$_x$SbO$_7$ with Ln = Nd, Sm, Gd, Eu). DTA experiments (500°C/h) showed that the transition temperature slightly decreases (max : 30°C) when the substitution contents increases but does not depend on the nature of the substituted lanthanide.

DIELECTRIC PROPERTIES

Dielectric properties of the synthesized compounds were measured both at low frequency and in the hyperfrequency range between room temperature and 100°C.

1. Synthesis and sample elaboration Bi$_3$SbO$_7$ and Bi$_3$-xLn$_x$SbO$_7$ ($\text{Ln} = \text{La}, \text{Nd} \text{and Gd}; \ 0 < x < 0.1$) solid solutions were synthesized using two methods.

a) Solid state reaction from oxides

Weighed quantities of reagent grade Bi$_2$O$_3$, Sb$_2$O$_3$ and rare-earth oxides were mixed and ground in an agate mortar and calcined for 48 hours at 600°C. After grinding the reacted mixtures were heated again for 20 hours at 850°C.

b) Thermal treatment of co-precipitated oxalate powders

The weighed oxides were dissolved in HCl 6 M and the mixed oxalates were co-precipitate by adding an excess of an aqueous solution of oxalic acid at pH 10. After washing with distilled water and drying for several hours at 110°C, the coprecipitated powders were calcined at 500-700°C for 3 hours and then heated for 15 hours at 800-900°C.

Fig. 1. Scanning electron micrographs of polished (left) and chemically etched (right) ceramics obtained by solid state reaction (a) and from co-precipitated powders (b).
It must be noticed that obtaining either the α or the β polymorph strongly depends on the experimental conditions: the α polymorph was obtained pure for temperatures lower than about 950°C by solid state reactions, and for temperatures lower than 870°C only by the wet method.

The large differences between the phase transformation temperatures given by DTA and the temperatures used in the thermal treatments are obviously kinetic in character.

Ceramic samples for dielectric measurements were prepared by natural sintering. After grinding, the powders were uniaxially cold-pressed at 2 kbar in a steel die. The as-obtained disks or cylinders were then sintered in air for 20 hours at 900-970°C. Typical dimensions of the sintered bodies were 8-10 mm in diameter, 1 and 8 mm thick for low and high frequency characterization respectively. The apparent densities calculated from dimension measurements or by the hydrostatic method are in the range 90-96% of theoretical densities and depend only slightly on the composition.

Scanning electron microscopy observations of polished and etched Bi₃SbO₇ samples are given in figure 1. All the samples present holes on their surfaces, the origin of which is certainly related to some Bi₂O₃ or Sb₂O₅ loss although no significant weight loss was observed after sintering. Micrographs of chemically etched ceramics show that for samples obtained by solid state reaction the grains are well crystallized and separated; those obtained from coprecipitated powders show lesser grain growth in relation with a lower porosity.

2. Dielectric measurements

In the low frequency range, dielectric constants ε₀ and dielectric losses tan δ were measured between room temperature and 100°C with a R 905 Wayne Kerr RLC automatic bridge at 10³ and 10⁴ Hz. After being electroded with a low temperature silver paste coating, the samples were heated up to 110°C overnight.

Table I. Low frequency (10 kHz) characteristics of Bi₃SbO₇ and Bi₃₋ₓLnₓSbO₇ ceramics. (CO and VS refer to the coprecipitation and the solid state methods respectively).

<table>
<thead>
<tr>
<th>Compound</th>
<th>Sample</th>
<th>Relative density % (±0.1)</th>
<th>Dielectric constant ε₀ (±0.1)</th>
<th>Dielectric loss 10⁴ tan δ (±1)</th>
<th>Temperature coeff. of capacitance τc (ppm/°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bi₃SbO₇</td>
<td>CO 5</td>
<td>93.7</td>
<td>30.0</td>
<td>25</td>
<td>110</td>
</tr>
<tr>
<td></td>
<td>CO 6</td>
<td>94.0</td>
<td>36.6</td>
<td>20</td>
<td>106</td>
</tr>
<tr>
<td></td>
<td>VS 13</td>
<td>94.8</td>
<td>36.3</td>
<td>14</td>
<td>58</td>
</tr>
<tr>
<td>Bi₁.₉₅La₀.₀₅SbO₇</td>
<td>VS 15</td>
<td>91.1</td>
<td>27.7</td>
<td>20</td>
<td>91</td>
</tr>
<tr>
<td>Bi₁.₉₅La₀.₀₅SbO₇</td>
<td>VS 11</td>
<td>87.4</td>
<td>30.9</td>
<td>20</td>
<td>105</td>
</tr>
<tr>
<td>Bi₁.₉₅Nd₀.₀₅SbO₇</td>
<td>CO 2</td>
<td>92.3</td>
<td>35.0</td>
<td>35</td>
<td>92</td>
</tr>
<tr>
<td>Bi₁.₉₅Nd₀.₀₅SbO₇</td>
<td>CO 3</td>
<td>87.0</td>
<td>30.5</td>
<td>30</td>
<td>160</td>
</tr>
<tr>
<td>Bi₂.₉₀Nd₀.₁₀SbO₇</td>
<td>CO 5</td>
<td>89.3</td>
<td>31.2</td>
<td>40</td>
<td>180</td>
</tr>
<tr>
<td>Bi₂.₉₀Gd₀.₁₀SbO₇</td>
<td>CO 1</td>
<td>92.5</td>
<td>31.1</td>
<td>20</td>
<td>105</td>
</tr>
<tr>
<td>Bi₂.₉₀Gd₀.₁₀SbO₇</td>
<td>CO 5</td>
<td>91.3</td>
<td>34.6</td>
<td>20</td>
<td>300</td>
</tr>
</tbody>
</table>

Table I gives the dielectric characteristics at 10 kHz obtained for several Bi₃SbO₇ samples as well as for some selected rare-earth substituted solid solutions. The ceramics always correspond to the low-temperature Bi₃SbO₇ polymorph.

All the samples have dielectric constants lying in the range 28-38 and dielectric losses between 20 and 40·10⁻⁴. Temperature coefficients of capacitance, calculated between room temperature and 100°C are all positive and show quite a large disper-
sion which seems to be related as for the dielectric constants to the porosity of
the samples.

Dielectric characteristics at microwave frequency were measured by the dielectric
resonator method. Dielectric constants were calculated from the resonant frequency
of the TE_{015} resonant mode and the dielectric losses were derived from the reso-
nant curve /9/. Table II gives the microwave characteristics of some Bi_{3}Sb_{07} ceramic
resonators.

Table II. Microwave characteristics of some Bi_{3}Sb_{07} ceramics (CO and VS refer to the
coprecipitation and the solid state methods respectively).

<table>
<thead>
<tr>
<th>Bi_{3}Sb_{07}</th>
<th>resonant frequency</th>
<th>Temperature coefficient of resonant frequency ( \tau_F ) (ppm/°C)</th>
<th>Dielectric constant ( \varepsilon_r )</th>
<th>Dielectric loss tg ( \delta ) (± 2.10^{-5})</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO 6</td>
<td>20° C, 6876 MHz</td>
<td>-69.2</td>
<td>40.1</td>
<td>7.10^{-4}</td>
</tr>
<tr>
<td>VS 11</td>
<td>30° C, 6645.7 MHz</td>
<td>-31.3</td>
<td>42.1</td>
<td>7.10^{-4}</td>
</tr>
<tr>
<td>VS 13</td>
<td>35° C, 6618 MHz</td>
<td>-32.0</td>
<td>41.6</td>
<td>7.10^{-4}</td>
</tr>
<tr>
<td>VS 15</td>
<td>25°C, 7280 MHz</td>
<td>-88.0</td>
<td>34.6</td>
<td>5.10^{-4}</td>
</tr>
</tbody>
</table>

At about 6.6 GHz the dielectric constants are close to 40 (the absolute values of \( \varepsilon \) at microwave frequency cannot be compared to those obtained at low frequency) and
the dielectric losses in the range 5.10^{-4} - 7.10^{-4}. The temperature coefficients of
the resonant frequency \( \tau_F \) strongly depend on the ceramic elaboration. Nevertheless
these results fit quite well the relation between \( \tau_F, \tau_C \) and \( \tau_e \) (respectively tem-
perature coefficients of capacitance and dielectric constant) and the linear thermal
expansion coefficient \( \alpha \) (= 10 - 20 ppm/°C)

\[
\tau_e + 2 \tau_F + 2\alpha = 0 \quad \text{and} \quad \tau_C = \tau_e + \alpha
\]

CONCLUSIONS

Ceramics with dielectric constants lying in the range 28-40 and with low losses at
microwave frequencies, were obtained by sintering Bi_{3}Sb_{07} powders at temperature
below 1000°C. Rare-earth substitutions for bismuth do not strongly affect the die-
lectric characteristics.

Experiments in order to improve the microwave properties (hot-pressing, use of
some additives with suitable characteristics) are now in progress.

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crowave measurements.
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/9/ Hakki, B.W. and Coleman, P.D., IRE Microwave Theory Tech. MTT-8, 10 (1960) 402.