



INSTITUTO TECNOLÓGICO  
de saltillo

Congreso  
Internacional de  
Metalurgia y  
Materiales



ARTÍCULO 9

**COMPARATIVE STUDY BETWEEN  $\text{Sb}_2\text{O}_5$  AND  $\text{Nb}_2\text{O}_5$   
DOPING AND SINTERING TEMPERATURE ON VARISTOR  
PROPERTIES OF  $\text{SnO}_2$ - $\text{Co}_3\text{O}_4$ -BASED CERAMICS**

*J. A. Aguilar-Martínez<sup>1</sup>, A. Durán-Régules<sup>2</sup>, M.I. Pech-Canul<sup>5</sup>,  
A.B. Glot<sup>3</sup>, and M.B. Hernández<sup>4</sup>*

**UNIVERSIDAD TECNOLÓGICA DE LA MIXTECA:**

<sup>1</sup>INSTITUTO DE MINERÍA, <sup>2</sup>DEPARTAMENTO DE INGENIERÍA INDUSTRIAL,  
<sup>3</sup>DIVISIÓN DE ESTUDIOS DE POSTGRADO, <sup>4</sup>INSTITUTO DE DISEÑO;

<sup>5</sup>CENTRO DE INVESTIGACIÓN Y DE ESTUDIOS AVANZADOS DEL IPN-UNIDAD SALTILLO

SALTILLO, COAHUILA 17, 18 Y 19 DE OCTUBRE DEL 2007.

## Comparative study between $\text{Sb}_2\text{O}_5$ and $\text{Nb}_2\text{O}_5$ doping and sintering temperature on varistor properties of $\text{SnO}_2$ - $\text{Co}_3\text{O}_4$ -based ceramics

**J. A. Aguilar-Martínez**<sup>1</sup>, A. Durán-Régules<sup>2</sup>, M.I. Pech-Canul<sup>5</sup>, A.B. Glot<sup>3</sup>, and M.B. Hernández<sup>4</sup>

<sup>1</sup>Instituto de Minería, <sup>2</sup>Departamento de Ingeniería Industrial, <sup>3</sup>División de Estudios de Postgrado, <sup>4</sup>Instituto de Diseño; Universidad Tecnológica de la Mixteca, Carr. Acatlima Km. 2.5, Huajuapán de León, Oaxaca.

C.P. 69000

<sup>5</sup>Centro de Investigación y de Estudios Avanzados del IPN-Unidad Saltillo  
Carretera Saltillo-Monterrey Km. 13, Saltillo Coah., México, C.P. 25000.

Tel: (953) 5-32-02-14 Ext. 600, Fax: 5-32-03-99, E-mail address: [jaguilar@nuyoo.utm.mx](mailto:jaguilar@nuyoo.utm.mx)

### ABSTRACT

In this work a comparative study of the effects between antimony pentoxide ( $\text{Sb}_2\text{O}_5$ ) and niobium pentoxide ( $\text{Nb}_2\text{O}_5$ ) on microstructure and electrical properties for  $\text{SnO}_2$ - $\text{Co}_3\text{O}_4$ -based ceramics is reported. These ceramic materials were prepared using a non-conventional mixing method at two different sintering temperatures: 1350 and 1450 °C. The results show that the sintering temperature significantly affects the breakdown voltage value of our samples, being strongest for  $\text{Nb}_2\text{O}_5$ -doped ceramics. In addition, an outstanding grain growth is observed with no apparent total densification. The optimum sintering temperature to achieve the lowest breakdown voltages was 1450 °C for both dopants  $\text{Sb}_2\text{O}_5$  and  $\text{Nb}_2\text{O}_5$ , for which the  $\text{Nb}_2\text{O}_5$ -doped samples presented the smallest ones. The nonlinear coefficient was also modified by the sintering temperature, and the largest value we obtained was 10.7 corresponding to  $\text{Sb}_2\text{O}_5$ -doped ceramics at 1450 °C.

### RESUMEN

En este trabajo un estudio comparativo de los efectos entre el pentóxido de antimonio ( $\text{Sb}_2\text{O}_5$ ) y el pentóxido de niobio ( $\text{Nb}_2\text{O}_5$ ) sobre las propiedades eléctricas y microestructurales de cerámicas a base de  $\text{SnO}_2$ - $\text{Co}_3\text{O}_4$  es reportado. Estos materiales cerámicos fueron preparados usando un mezclado no convencional a dos temperaturas de sinterización: 1350 °C y 1450 °C. Los resultados muestran que la temperatura de sinterización afecta significativamente el valor del voltaje de ruptura de nuestras muestras, siendo más fuerte en los cerámicos dopados con  $\text{Nb}_2\text{O}_5$ . Además, se produce un crecimiento de grano notable pero sin una densificación total aparente. La temperatura de sinterización óptima para obtener los voltajes de ruptura más bajos fue de 1450 °C con ambos dopantes  $\text{Sb}_2\text{O}_5$  y  $\text{Nb}_2\text{O}_5$ , para los cuales las muestras dopadas con  $\text{Nb}_2\text{O}_5$  presentaron los valores más pequeños. El coeficiente de no-linealidad fue también modificado por la temperatura de sinterización y el valor más grande obtenido fue de 10.7 correspondiendo a los cerámicos dopados con  $\text{Sb}_2\text{O}_5$  a 1450 °C.

## 1. Introduction

Varistors are materials with nonlinear current-voltage characteristics, these materials are commonly used as over-voltage and surge absorbers in electronic circuits and electrical systems [1-4]. The nonlinear features of current and voltage derive from the existence of potential barriers between the grain boundaries of the ceramic polycrystalline microstructure of varistor devices [5]. The electrical behavior of a varistor is represented by the non-ohmic relationship:

$$J = kE^\alpha \quad (1)$$

where  $J$  is the current density,  $E$  is the applied electric field,  $k$  is a constant related to the microstructure of the material and  $\alpha$  is the coefficient that is a vital parameter used to scale the nonlinearity ( $\alpha > 1$ ).

Since it was introduced by Matsuoka back in 1971, zinc oxide (ZnO) has been the most extensively studied material (as the base for a ceramic system) and consequently became the most important ceramic for the commercial production of varistors [3, 6]. Due to the need for better properties, recently there has been an increased interest in other ceramic materials like TiO<sub>2</sub> [7], SrTiO<sub>3</sub> [8] and SnO<sub>2</sub> [9].

Tin dioxide (SnO<sub>2</sub>) is a n-type semiconductor with a rutile-type tetragonal crystalline structure [10] and has a low densification rate due to its high surface tension as diffusion coefficient at low temperature and high SnO<sub>2</sub> partial pressure at high temperatures [11]. Because this material presents low densification after sintering, it is used mostly in gas sensor applications [12, 13]. Dense SnO<sub>2</sub> based ceramics can be achieved by introducing dopants [14, 15] or by hot isostatic pressure processing [16]. Dopants with valence +2 can promote densification of SnO<sub>2</sub> ceramics due formation of a solid solution with creation of oxygen vacancies. The processing of SnO<sub>2</sub> based material with high density enables its use in other types of electronic devices such varistors.

In this work, it was studied the influence sintering temperature and the inclusion of the niobium and antimony oxides in the doping of one system ceramics: SnO<sub>2</sub> - 1% Co<sub>3</sub>O<sub>4</sub> - 0.05% (Nb<sub>2</sub>O<sub>5</sub> and Sb<sub>2</sub>O<sub>5</sub>) with the objective of verifying the physical and electrical characteristics of these systems.

## 2. Experimental Procedure

Analytical grade SnO<sub>2</sub> (Aldrich), Co<sub>3</sub>O<sub>4</sub> (Aldrich), Nb<sub>2</sub>O<sub>5</sub> (Aldrich), Sb<sub>2</sub>O<sub>5</sub> (Aldrich) and CaCO<sub>3</sub> (Baker) powders were used as raw materials for the preparation of a series of mixtures with compositions given by (98.95-X) % SnO<sub>2</sub> + 1.00% Co<sub>3</sub>O<sub>4</sub> + 0.05% Sb<sub>2</sub>O<sub>5</sub> + x% CaCO<sub>3</sub> and (98.95-x) % SnO<sub>2</sub> + 1.00% Co<sub>3</sub>O<sub>4</sub> + 0.05% Nb<sub>2</sub>O<sub>5</sub> + x% CaCO<sub>3</sub>, being X equal to 0 and 0.5 (mol. %). The powders were processed by a non conventional method of mixture, through high-energy milling performed in a planetary ball-mill Restch PM-100 using vials

and balls of agate for 20 minutes. The resulting powders were uniaxially pressed in the form of tablets (10.0 mm diameter and about 1.2 mm thickness) at 230 MPa without using any kind of binder. The tablets were sintered in ambient atmosphere at 1350 and 1450 °C for 1 hour with a heating and cooling rate of 6°C/min in a tube furnace (Lindberg/Blue STF55433C-1). For electrical characterization, silver electrodes were placed on both faces of the ceramic sintered samples followed by thermal treatment at 800°C for 6 minutes. Current-voltage measurements were taken using a High Voltage Measure Unit (Keithley 237). The non linear coefficient  $\alpha$  was evaluated in terms of the relation:

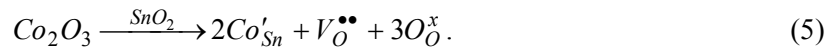
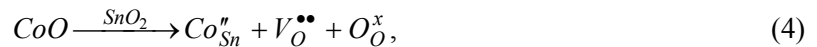
$$\alpha = \frac{\log(J_2 / J_1)}{\log(E_2 / E_1)} \quad (2)$$

where  $E_1$  and  $E_2$  are the applied electrical field corresponding to the current densities  $J_1$  and  $J_2$  respectively. The breakdown voltage ( $E_b$ ) was obtained at 1 mA/cm<sup>2</sup>. Values of  $J$  and  $E$  are obtained by  $I/s$  and  $V/t$ , where  $s$  is the area of silver electrode and  $t$  is the thickness of the tested sample.

Density measurements of the sintered samples were made using the Archimedes' method and related to the theoretical density of SnO<sub>2</sub> (6.95 g/cm<sup>3</sup>). Microstructure characterization was carried out using scanning electron microscopy (SEM, Philips XL30 ESEM).

### 3. Results and discussion

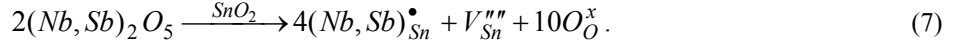
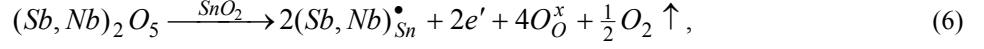
The addition of Co<sub>3</sub>O<sub>4</sub> to SnO<sub>2</sub> induced modifications in the oxygen vacancies concentration responsible for high densities attained. These changes can be explained with the aid of replacement equations representing phenomena occurring in the tin oxide lattice. Possible substitution equations, in terms of the Kröger-Vink standard notation are as follows:



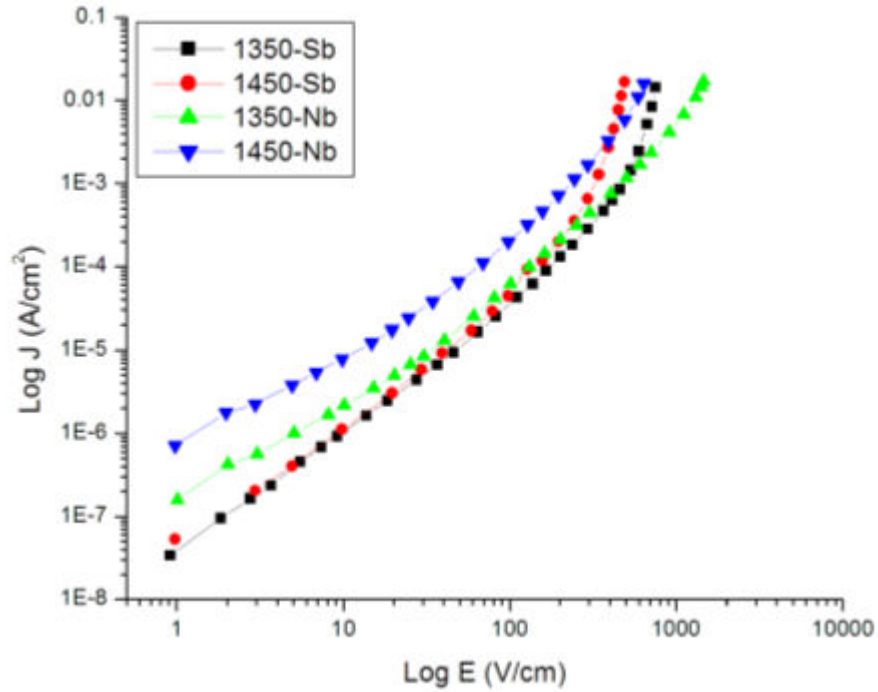
Cobalt ions bring about an increase in the oxygen vacancies concentration allowing solid state diffusion and material densification.

Without the dopants of antimony and niobium oxides, the sample appears as an insulator, because of the ultrahigh grain resistivity. The addition of Sb<sup>+5</sup> and Nb<sup>+5</sup> in small amounts to the SnO<sub>2</sub> ceramics leads to the concentration

of  $e'$  and  $V_{Sn}'''$ , owing to the substitution of  $Sn^{+4}$  for  $Sb^{+5}$  and  $Nb^{+5}$ , which increases the electronic conductivity in the  $SnO_2$  lattice and leads to the semiconductivity of the grains, according to the equation:



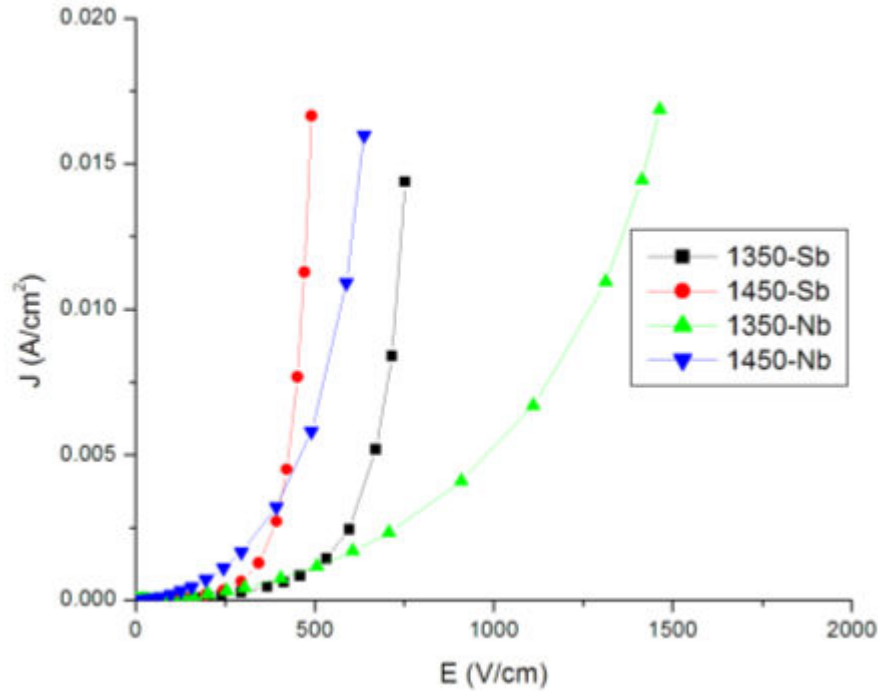
The electrical characteristics of (Co, Sb or Nb)-doped  $SnO_2$  varistors are shown in Figure 1, where all samples present nonlinear behavior. It is found from Figure 1 that the samples doped with Sb have the best nonlinear electrical property when it is compared with those obtained for Nb-doped samples at their correspondingly sintering temperatures. The largest nonlinear coefficient was 10.7 associated with that Sb-doped ceramic at 1350 °C, whereas the lowest electric field breakdown was 299 V/cm attained for Nb-doped samples at a sintering temperature of 1450 °C.



**Figure 1** Current density-electric field logarithmic plots of Sb and Nb samples sintered at two different temperatures

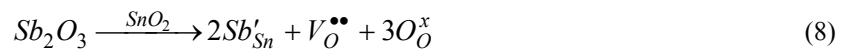
The effect of Sb and Nb dopants and sintering temperature on breakdown electrical field magnitude can be clearly seen in Figure 2, where the largest breakdown electric field occurs at 1350 °C whether Sb or Nb are utilized. On the other hand, the lowest  $E_B$  values are obtained at 1450 °C. Moreover, the breakdown electric

field values for Nb-doped samples are always lesser than those attained for Sb-ceramics at their respective sintering temperatures.



**Figure 2**  $J$  vs.  $E$  curves for Sb and Nb samples sintered at two different temperatures

The best electrical properties results obtained using antimony dopants are due to the existence of two stable oxidation states:  $Sb^{+3}$  and  $Sb^{+5}$ , while for niobium there is only one:  $Nb^{+5}$  [17]. It has been reported that  $Sb_2O_5$  is the stable phase from room temperature up to  $970^\circ C$ , and at higher temperature  $Sb_2O_3$  is the most stable one. However, the  $Sb^{+5}/Sb^{+3}$  ratio depends on both temperature and their concentrations in an oxygen ambient [18], and it is then possible that during cooling process the transformation of  $Sb^{+3}$  into  $Sb^{+5}$  takes place. At lower concentrations, antimony presents as pentavalent, and acts as a donor. The defect reaction may be described as the equations 6 and 8



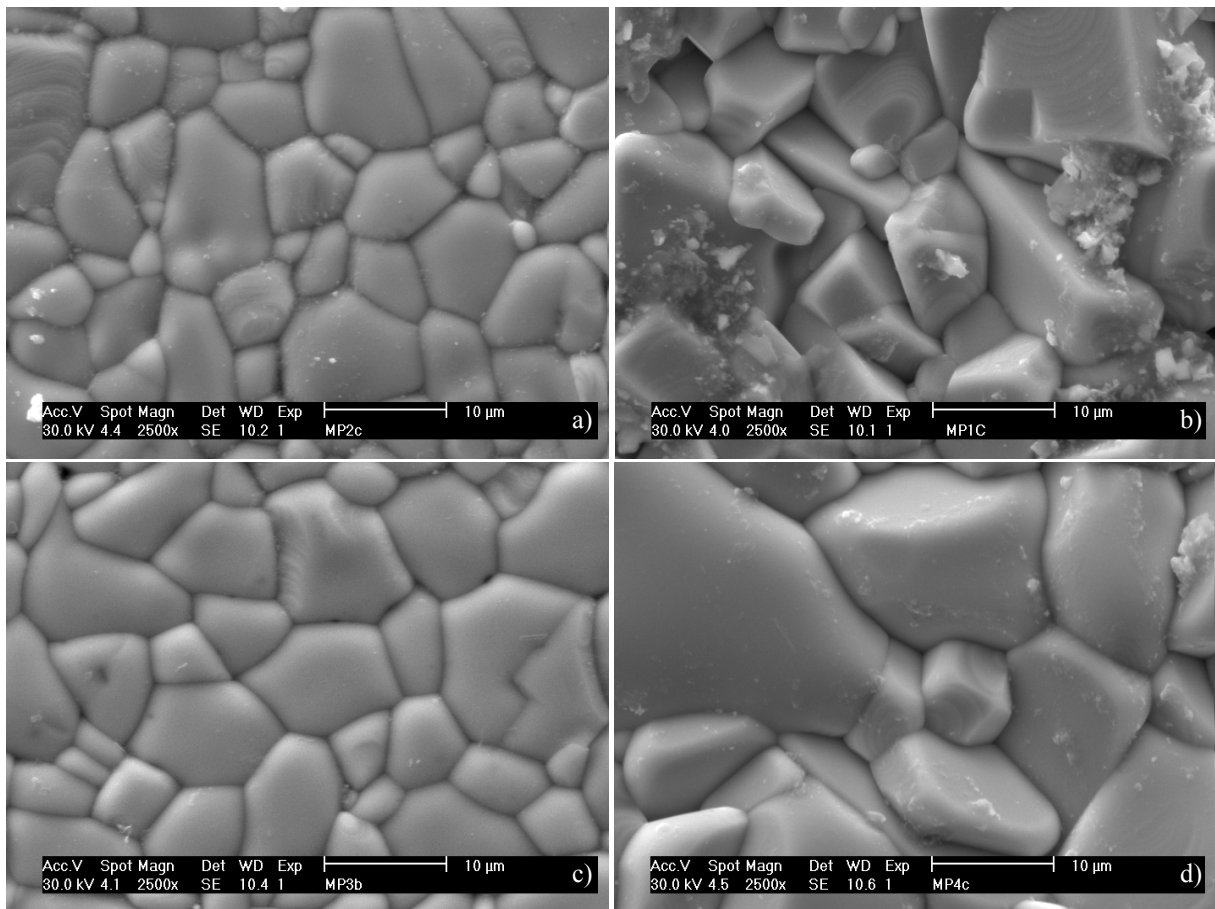
The higher conductivity of the ceramics with Sb as compared to those with Nb must be the result of Sb segregation on the grain boundary, which decreases the potential barrier. It is also the result of the fact that Sb introduces electrons directly in the conduction band, what seems not to occur with Nb.

Figure 4 shows SEM photomicrographs of all specimens studied at 1350 and 1450 °C: a) 1350-Sb, b) 1450-Sb, c) 1350-Nb and d) 1450-Nb. It can be observed that whether  $Sb_2O_5$  or  $Nb_2O_5$  are employed the grain size significantly increases when the sintering temperature is raised. Nevertheless, if one uses  $Nb_2O_5$  as dopant then

the grain size is more significant. The smallest breakdown electric fields were obtained when the sintering temperature was higher, which could be explained due to the grain size increased and therefore the potential barriers lowered. This should be well described by the following equation, which represents the breakdown electrical field of varistors:

$$E_B = n * V_B \quad (9)$$

where  $n$  is the average grain number per unit length and  $V_B$  the breakdown voltage of a grain boundary. Equation (9) indicates that  $E_B$  is mainly determined by  $V_B$ , the average grain size and by the relative density of ceramics, considering that the average grain number per unit length is related to the average grain size and the relative density of ceramics.



**Figure 4** SEM photomicrographs of specimens with the composition  $98.95\%SnO_2+1\%Co_3O_4+0.05\%X$ , where  $X=Sb_2O_5$  and  $Nb_2O_5$  sintered at  $1350\text{ }^\circ\text{C}$  and  $1450\text{ }^\circ\text{C}$ , a) 1350-Sb, b) 1450-Sb, c) 1350-Nb and d) 1450-Nb.

Table 1 summarizes the processing conditions as well as the values of physical and electrical parameters of the varistor systems studied. The best nonlinearity coefficient ( $\alpha = 10.7$ ) was obtained when the  $\text{Sb}_2\text{O}_5$  was utilized at the sintering temperature of 1350 °C.

Table 1 Physical and electrical parameters of the ceramic-mix systems investigated.

$\text{Sb}_2\text{O}_5$ Dopant	Temperature (°C)	$\rho$ (g/cm <sup>3</sup> )	Relative density (%)	$\alpha$	$E_B$ (V/cm)
$\text{Sb}_2\text{O}_5$	1350	6.64	95.53	10.7	481
	1450	6.71	96.54	10.6	378
$\text{Nb}_2\text{O}_5$	1350	6.68	96.11	2.9	467
	1450	6.69	96.25	6.00	299

$\text{SnO}_2$  theoretical density: 6.95 g/cm<sup>3</sup>

#### 4. Conclusions

In this work we show that better nonlinear coefficients are obtained when  $\text{Sb}_2\text{O}_5$  is used than those values determined for  $\text{Nb}_2\text{O}_5$ -doped samples. However, the difference between the breakdown electric fields for both dopants is not very significant. In addition, if the sintering temperature is increased the breakdown electric field decreases for both dopants, and the densities are almost equal in these materials. In summary, the best results are obtained when  $\text{Sb}_2\text{O}_5$  dopant is employed at a sintering temperature of 1350° C.

#### 5. Acknowledgements

This study was performed in the frames of the project SEP-2003-C02-42821, CONACYT, México. Authors gratefully acknowledge Mr. Felipe Márquez Torres for assistance in the microstructure characterization by SEM and Dr. Jaime Castillo Torres for supervising the manuscript.

#### REFERENCES

1. L. Levinson., H. Philipp. IEEE Trans. Parts, Hybrids, and Packaging, 13 (1977) 338.
2. T.K. Gupta. Application of Zinc Oxide Varistors. J. Am. Ceram. Soc., 73 (1990) 1817.
3. D.R. Clarke. J. Am. Ceram. Soc., 82 (1999) 485.
4. M. Peiteado. Bol. Soc. Esp. Ceram. V., 44 (2005) 77.
5. M.S Castro, and C.M. Aldao. *Appl. Phys. Lett.*, **63** (1992) 1077.
6. M. Matsuoka. Jpn. J. Appl. Phys., 10 (1971) 736.
7. L. Kong, L. Zhang, X. Yao. *Mater. Lett.*, 32 (1997) 5.
8. J. Li, S. Li, F. Liu, M.A. Alim, G. Chen. *J. Mater. Sci.: Mater. Electr.*, 14 (2003) 483.



9. A.B. Glot, and A.P. Zlobin. *Inorg. Mater.* 25 (1989) 274.
10. É.V. Degtyareva, I.I. Kabakova, and V.I. Drozd. *Refractories and Industrial Ceramics*, 18 (1977) 5.
11. Z.M. Jarzebski, and J.P. Marton. *J. Electrochem. Soc.* 123 81976) 199C.
12. I.T. Weber, E.R. Leite, E. Longo, and J.A. Varela. *Cerâmica*, 46 (2000) 156.
13. P.S. More, Y.B. Khollam, S.B. Deshpande, S.K. Date, R.N. Karekar, and R.C. Aiyer. *Mater. Lett.*, 58 (2003) 205.
14. J.A. Cerri, E.R. Leite, D. Gouvêa, E. Longo, and J.A. Varela. *J. Am. Ceram. Soc.*, 79 81996) 579.
15. C.R. Foschini, L. Perazolli, and J.A. Varela, *J. Mater. Sci.* 39 (2004) 5825.
16. S.J. Park, K. Hirota, and H. Yamamura, *Ceram. Int.*, 10 (1984) 116.
17. D. R. Leite, I. O. Mazali, E. C. Aguiar, W. C. Las, and M. Cilense. *J. Mater. Sci.*, 41 (2006) 6256.
18. A. Ovenston, D. Sprinceana, J. R. Walls and M. Caldhararu. *J. Mater. Sci.* 29 (1994) 4946.