ISSN : 0974 - 7486 Volume 7 Issue 1

Trade Science Inc.

Materials Science

An Indian Journal

Full Paper

MSAIJ, 7(1), 2011 [12-16]

Structural, temperature comportment and electrical study of the ceramic matrix system (SiO_2-Fe_2O_3-MoO_3):Nb_2O_5

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Received: 11th August, 2010 ; Accepted: 21st August, 2010

ABSTRACT

In this paper we present a study the structural, temperature comportment and electrical properties of the ceramic system SiO_2–MoO_3–Fe_2O_3:Nb_2O_5. The phases **A** (SiO_2-Fe_2O_3-MoO_3), **B** (SiO_2-Fe_2O_3-MoO_3 + 0.3% weight molar Nb_2O_5) and **C** (SiO_2-Fe_2O_3-MoO_3 + 0.5% weight molar Nb_2O_5) was prepared through the solid state reaction. The samples were analyzed by X-Ray Powder Diffraction (XRD) together with the Rietveld refinement, Scanning Electron Microscopy (SEM), Energy-Dispersive Spectroscopy (EDS) analysis. The dielectric properties were measured in the frequency range 1Hz–1MHz as a function of temperature. The Temperature Capacitance Coefficient (TCC) was measured for all samples. The obtained results are discussed and correlated with the preparation method. The obtained results suggest that this ceramic matrix is a good candidate for temperature sensing.

KEYWORDS

Temperature comportment;
Structural measurements;
Electrical measurements.

INTRODUCTION

The sensitivity characteristics of metal–oxide ceramics[1,2] have been extensively investigated in recent years. The metal tin dioxide (SnO_2) is well-known material for various applications including preparation of semiconductor devices such as gas sensors[3,4], humidity sensors[4,5] and varistors[6-11]. SnO_2-Co_3O_4-Nb_2O_5-Cr_2O_3 ceramic material exhibits not only varistor properties discussed in the literature but also humidity-sensitive properties. In this work we will study the properties of the ceramic system SiO_2-MoO_3-Fe_2O_3:Nb_2O_5 for possible applications as a thermal sensor. Temperature sensing in particular has received great attention[12]. The silicon has been used a lot as thermal sensor in the substrates form with oxides and polymers deposited formed of thin films[13]. The temperature can have such a significant effect on materials and processes at the molecular level, it is the most widely sensed of all variables. Temperature is defined as a specific degree of hotness or coldness as referenced to a specific scale. It can also be defined as the amount of heat energy in an object or system[14].

MATERIALS AND METHODS

Samples preparation

Silicon Oxide (SiO_2) (Aldrich, 99.8%), Iron Oxide (Vetec, 97%), Molybdenum Oxide (MoO_3) (Vetec, 99%) and Niobium Oxide (Nb_2O_5) (Aldrich, 99.9%) were used in the ceramic system preparation. The samples **A** (SiO_2-Fe_2O_3-MoO_3), **B** (SiO_2-Fe_2O_3-MoO_3 + 0.3% weigh Nb_2O_5) and **C** (SiO_2-Fe_2O_3-MoO_3 + 0.5% weigh Nb_2O_5) was ground on a Fritsch Pulverisette 7 planetary mill. Milling was performed in steel vials and balls under air. Mechanical alloying was performed for 3 hours of milling in alcohol media. In this case the milling was used only to give a good homogeneity to the powder. All samples were calcinated for 1 hour to 1300°C with rate of 5°C/min. The obtained material was sinterizated in a two step process: 450°C for 1 hour and after to 1300°C for 1 hour.

X-Ray diffraction (XRD) and rietveld refinement

The X-ray diffraction (XRD) patterns data were obtained at room temperature using powder samples in an X'Pert MPD Philips diffractometer (with K_α radiation, λ = 1.54056 A°) at 40 KV and 30 mA. Intensity data were collected by the step counting method (step 0.02° and a time per step of 1s) between 20 and 60° (2θ). The analysis of formation of system SiO_2-MoO_3-Fe_2O_3:Nb_2O_5 was investigated by X-ray Diffraction using the Rietveld method[15].

Dielectric spectroscopy

The samples (bulks) for the dielectric measurements have diameters of 2 cm. The bulks were placed between two metallic electrodes. The thicknesses obtained were of the order of 1mm. Measurements of the complex impedance were carried out using an impedance analyzer Solartron 1260A over the frequency range of 1Hz-1MHz at room temperature (300K). The TCC describes the maximum change in capacitance over a specified temperature range. The TCC was calculated using the following formula:

$$TCC = \frac{[(C_P(T_2) - C_P(T)_1)]}{[C_P(T_1)(T_2 - T_1)]} \quad (1)$$

where $C_P(T_1)$ is the measured capacitance at T_1 (40°C) and $C_P(T_2)$ is the measured capacitance at T_2 (90°C).

Scanning electronic microscopy (SEM) and energy-dispersive spectroscopy (EDS)

The microstructure of the free surface samples was performed using the Scanning Electron Microscopy (SEM), Hitachi S4100-1 system operating with beans of primary electrons ranging from 25 KeV. The pellets were covered with a layer of carbon of around 30 nm in thickness.

RESULTS AND DISCUSSION

Figure 1-3 showed the XRD (Rietveld Refinement) of sample A, B and C respectively, confirm a good crystallinity of the different phases[16]. As can be observed in figure 1 the XRD of the sample A indicates that the peak at X-Ray diffraction show that one has the formation of two phases of SiO_2[16] with 82.20 % mass (Tetragonal) and 8.42 % (Hexagonal) and Fe_2O_3 with 9.38% (rhombohedra phase) mass in the ceramic system (TABLE 1). The R-WP found to A sample was 17.13 % become satisfactory, because typical values are between 10 at 20%[17]. R-WP is the factor with most statistical significance and it reflects the progress of the refinement. Some factors that are not related to the quality of the used model can increase or reduce the value of R-WP; for instance, the presence of other phases in the material increases the value of R-WP, where as a high background reduces it[15]. In figure 2 and 3 the XRD of the samples B and C indicates that the X-Ray diffraction show the presence of two phases of SiO_2, with 79.29 % mass (Tetragonal) and 8.57 % (Hexagonal) for B sample and 81.27 % mass (Tetragonal) and 7.97% (Hexagonal) for C sample. For both samples one has Fe_2O_3 phase (rhombohedra) with 10.42% (B sample) and 8.57% in sample C. Besides Fe_2O_3, the growth of a monoclinic phase of $FeNbO_4$ was observed with 1.71% in B sample and 2.20% in C due the doped of Nb_2O_5 in the ceramic system (TABLE 1). The R-WP found to B and C sample was 15.27 % and 15.25%, which is satisfactory.

In figure 4 one can observe that the sample resistivity is decreasing with the temperature for all samples until 160°C when it begins to increase in direct association with the increase in the thermal energy of the atoms in the dielectric. With the addition of Nb_2O_5, the

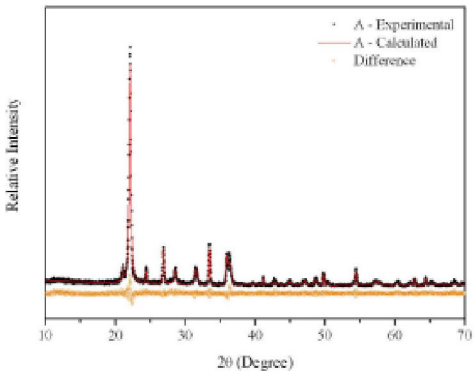

Figure 1 : Rietveld refinement of the sample A

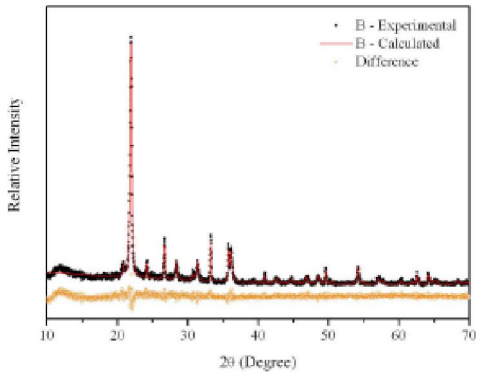

Figure 2 : Rietveld refinement of the sample B

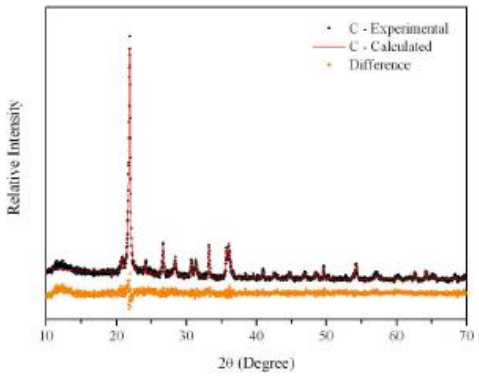

Figure 3 : Rietveld refinement of the sample C

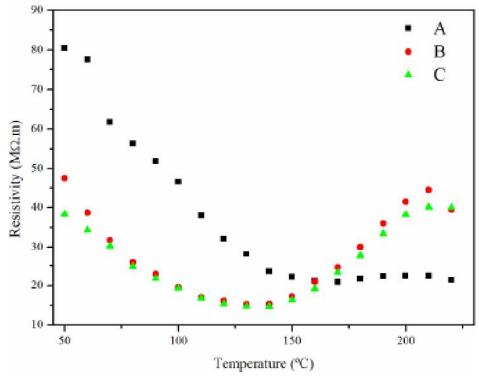

Figure 4 : Resistivity (MΩ.m) versus Temperature (°C) of the samples A (■), B (●) and C (▲) at 10 KHz of Frequency

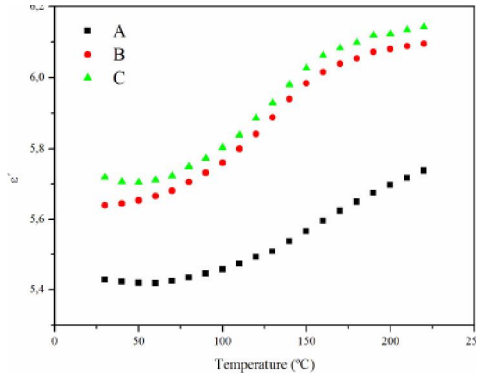

Figure 5 : ε′ versus Temperature (°C) of the samples A (■), B (●) and C (▲) at 10 KHz of Frequency

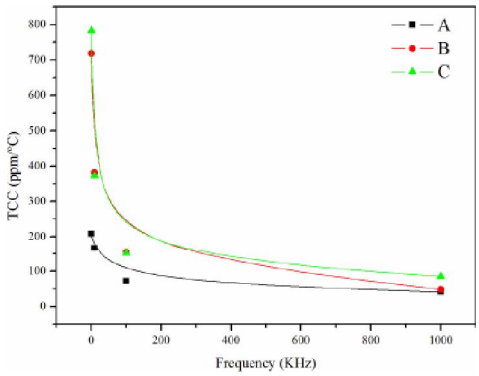

Figure 6 : The temperature capacitance coefficient (TCC) versus frequency of samples A (-■-), B (-●-) and C (-▲-)

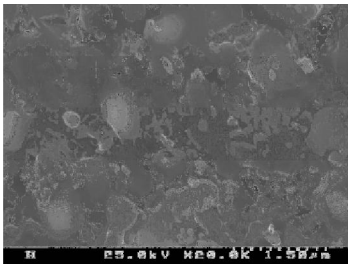

Figure 7 : SEM micrograph of the sample A with 20,000 X

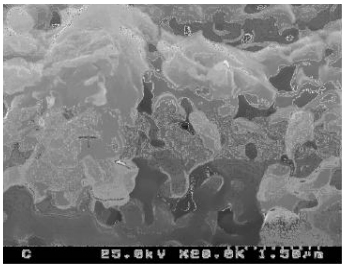

Figure 8 : SEM micrograph of the sample C with 20,000 X

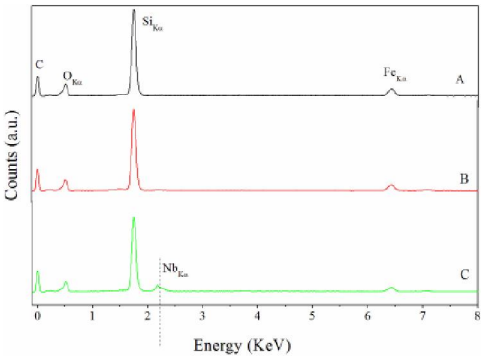

Figure 9 : EDS of the samples A, B and C

ceramic system presented a higher temperature sensitivity (dR(Ω)/dT(°C)). Thermal response times are determined by physical construction material and mass of the temperature-sensing element[18], being the same behavior observed in figure 5 with the increase of the dielectric permittivity as a function of temperature variation. The ceramic systems are good thermal conductors, then becoming a very effective sensor. We measured the thermal response of the samples in the temperature range of 30°C to 220°C. The samples presented a relatively fast thermal response. This fact becomes more important if we are taking into account that the electrical contacts geometry and the size (and mass) of the sensor were not optimized for the construction of a device ready for use. At 1 KHz, 10 KHz, 100 KHz and 1 MHz the samples A, B and C showed values for the TCC parameters of 783ppm/°C (1 KHz sample C) and 41ppm/°C (1 MHz sample A) (TABLE 2). The TCC parameters decrease with the increase of frequency (Figure 6). These results indicate that interfacial effects play an important role in the electrical properties of the samples, especially at low frequency ranges[19].

The morphology of the ceramic system was investigated by means of SEM. In Figures 7-8 one has the samples A and C with a 20,000X amplification factor respectively. Comparing the SEM figures one can notice that the scanning electron photomicrograph of the ceramics revealed that the presence of the Nb_2O_5 (cross mark in figure 8) decrease to a spherical morphology. With the increase of the presence of the Nb_2O_5 the grains are aggregating together forming plates. The kind of grain clustering behavior will be very critical in the electrical properties of the ceramics. Energy dispersive spectroscopy (EDS) analysis (Figure 9) showed that

TABLE 1 : Rietveld Refinement of the samples A, B and C with R-WP (%), R-Exp (%) and weight (%) of phases

Samples	R-WP (%)	R-Exp (%)	% weight			
			SiO_2 (1)	SiO_2 (2)	Fe_2O_3	$FeNbO_4$
A	17.13	14.08	82.20	8.42	9.38	----
B	15.27	11.30	79.29	8.57	10.42	1.71
C	15.25	12.46	81.27	7.97	8.57	2.20

TABLE 2 : The Temperature Capacitance Coefficient (TCC) at 1 KHz, 10 KHz, 100 KHz and 1 MHz for Samples A, B and C

Samples	1 KHz TCC (ppm/°C)	10 KHz TCC (ppm/°C)	100 KHz TCC (ppm/°C)	1 MHz TCC (ppm/°C)
A	208	167	72	41
B	718	381	155	48
C	783	373	151	85

the main elements of the samples A, B and C powder were carbon, oxygen, silicon, iron and niobium. We just observed niobium in sample C probably due to % in weight of $FeNbO_4$ found in B to be smaller.

CONCLUSIONS

In this paper we present a study the structural and electrical properties of the ceramic system SiO_2-MoO_3-Fe_2O_3:Nb_2O_5 for temperature sensor applications. The phases **A** (SiO_2-Fe_2O_3-MoO_3), **B** (SiO_2-Fe_2O_3-MoO_3 + 0.3% weight molar Nb_2O_5) and **C** (SiO_2-Fe_2O_3-MoO_3 + 0.5% weight molar Nb_2O_5) was prepared through the solid state reaction. The X-Ray diffractions show a good crystallinity of the different phases. The values of R-WP found to samples A, B e C was satisfactory (17.13; 15.27 and 15.25 respectively), because the typical values are between 10 at 20%. With the addition of Nb_2O_5, the ceramic system presented a higher temperature sensitivity (dR(Ω)/dT(°C)) causing larger sensibility to the temperature variation and increase in the dielectric permittivity (Figure 5), and showing that the studied ceramic system can be used as sensor of temperature. With the increase of the presence of the Nb_2O_5 the grains are aggregating together forming plates. The kind of grain clustering behavior will be very critical in the electrical properties of the ceramics because the dielectric permittivity decreasing slowly in sample C with the increase of temperature demonstrating behavior of ionic jump effect and space load, resulting in growth of the concentration of load transport

with addition of niobium oxide.

ACKNOLEDGEMENTS

The authors thank this work to LOCEM (Physics Department, Federal University of Ceara-Brazil) for the use of theirs laboratories for samples preparation and X-Ray analysis, CNPq-CT-Petro (Brazilian Agency).

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