# Characterization of ceramics materials mixed with $Co_3O_4$

**A F Guzmán[1], D A LandínezTéllez[2], J Roa-Rojas[2,*] and F Fajardo[1]**

[1] Grupo de Estudios de Materiales – GEMA, Departamento de Física, Universidad Nacional de Colombia, AA 5997, Bogotá DC, Colombia

[2] Grupo de Física de Nuevos Materiales, Departamento de Física, Universidad Nacional de Colombia, AA 5997, Bogotá DC, Colombia

E-mail: jroar@unal.edu.co

Received 4 October 2013, in final form XX Novembrer 2013

**Abstract**. We have performed the preparation, structural, electrical and mechanical characterizations of ceramic materials composed of kaolinite $Al_2(Si_2O_5)(OH)_4$ and alumina ($Al_2O_3$) mixed with different concentrations of cobalt oxide ($Co_3O_4$). Ceramic samples were prepared from a base concentration of alumina 30% and kaolinite 70%, mixed with various concentrations of cobalt oxide in steps of 4% up to a value of 20%. The samples were sintered by the standard solid-state reaction method at a temperature of 1350 $^oC$. In all samples with cobalt was found the presence of mullite. It was determined that alumina and cristobalite decreased when the cobalt concentration was increased due to the formation of the cobalt spinel. In order to determine the crystal structure of the samples, crystallographic analysis from X-ray diffraction experiments and also the semi-quantitative phase analysis were performed. Results were compared with theoretical parameters through the PowderCell 2.4 software. By increasing the concentration of cobalt oxide was found a significant increase in the resistance of materials to friction wear and a small decrease on the mean value of the dielectric constant. Through flexion measurements is observed the increases of the elasticity modulus by about 45% for the sample with 4% of cobalt oxide when compared with the samples without cobalt.

## 1. Introduction

Mullite ($3Al_2O_3.2SiO_2$) is a ceramic material of high resistance to thermal shock, which is characterized by very good physical and mechanical properties to be used in optical and electrical applications and as refractory, among others [1]. From the 80s the study of this material has been intensified in order to find an appropriate way to make the production process and sintering at a low cost and with high purity [2]. Different sintering processes have been used to achieve this goal, as for example, the methods of solid state reaction [3], sol-gel [4] and chemical vapor deposition [5]. These methods allow the sintering process but in most cases required high purity precursor oxides and the process is quite expensive, which is not viable for industrial production [6]. When it is done the sintering process of a low cost material such as kaolinite, primary mullite is obtained at specific

Journal of Physics: Conference Series **480** (2014) 012019 doi:10.1088/1742-6596/480/1/012019

temperatures and after the nucleation process the $SiO_2$ is released but different phases are present [7,8]. The interaction of cobalt oxide with zinc oxide on surface of kaolin is also interesting for applications as protective colour coatings [9]. Another important topic of study is to see how to modify the electrical, structural and morphological characteristics of ceramic materials when mixed with certain oxides such as $Co_3O_4$.

The aim of this work is to show the study of the reaction between the kaolinite and alumina at a sintering temperature of 1350 °C by the method of solid-state reaction and the effect of using cobalt oxide ($Co_3O_4$) as an additive in the mixture. The phase identification was performed from X-ray diffraction patters and the semi-quantitative analysis is carried out by considering the different concentrations of cobalt oxide. Electrical properties are measured by testing electric polarization. Mechanical properties of the material were investigated measuring the strength to flexion and hardness using the abrasive wear test.

## 2. Experimental

A fixed concentration of 70% kaolinite and 30% alumina was taken for the production of the samples in order to determine the effect of adding cobalt oxide in the sintering process of kaolinite and alumina. Then different percentages of $Co_3O_4$ were incorporated from 4 to 20% in increments of 4%. For all concentrations a total mass of *5 g* was used in the mixing process of the precursor oxides. Samples were pressed to form pellets of 2.5 cm diameter. For the flexion test some pellets with rectangular shape (0.3x2x8 cm) were prepared. Sintering of the samples was performed at 1350 °C during 4 hours, to reach this temperature a ramp with rise and fall times of 15 hours was employed in all cases. X-ray diffraction patters were obtained using the X-Pert PRO MPD Panalytical diffractometer, employing CuKα radiation (1.540598 Å). Crystallographic parameters were determined for each phase using the Rietveld refinement and compared with theoretical parameters through PowderCell software version 2.4. The weight concentration of each of the phases present in each sample depending on the concentration of $Co_3O_4$ was also determined. For measuring the bending of the sintered specimens an equipment SHIMADZU Universal Testing Machine was used, fitted with an AG-IS 5 kN load cell. For the abrasive wear test an experimental setup was used consisting of a motor with a disk on which is placed sandpaper having 180 aluminum oxide granules per square centimeter. When the disc is rotated at a determined angular velocity the sample is placed in contact with the abrasive surface for a period of 15 s. Polarization curves were measured through a Radiant Technologies Polarimeter applying electric fields from 10 to +10 kV/cm.

## 3. Results and discussion

Figure 1 shows the XRD pattern of the samples with different concentrations of $Co_3O_4$, the x-ray diffraction of the $Co_3O_4$ powder is also displayed. For the sample with 0% of cobalt oxide (70% kaolinite and 30% alumina) semi-quantitative analysis shows the presence of 64 wt% mullite which has an orthorhombic structure, 27 wt% alumina which has a rhombohedral structure and a 9 wt% of silicon oxide which correspond to a tetragonal crystal system. The characteristic peaks of mullite were found at the 2θ positions 16.44°, 26.33° and 35.27°. The characteristic peaks of alumina were found in the 2θ positions 25.58°, 35.27° and 43.34°. Peaks corresponding to cristobalite were identified at the 2θ positions 21.70°, 31.00° and 42.60°.

By comparing the diffraction patterns of samples with $Co_3O_4$ concentrations of 4, 8, 12, 16 and 20% as showed in figure 1, a reduction of the cristobalite peak located at the 21.70° was observed while the characteristic peak of mullite sited at 26.33° remains invariant. From the concentration of 8% of $Co_3O_4$ it was observed the appearance of three peaks at diffraction angles of 36.76°, 59.16° and 65.01° which are characteristics of the cobalt spinel. The results presented suggest that for $Co_3O_4$ concentrations higher than 4% the cobalt oxide in the mixture is highly reactive in the presence of alumina forming cobalt spinel which has a cubic crystal structure. Considering the peak of greatest

Journal of Physics: Conference Series **480** (2014) 012019 doi:10.1088/1742-6596/480/1/012019

intensity for each of the phases present in the samples, we obtained an average grain size of 54, 69 and 56 nm for the mullite, alumina and the cobalt spinel, respectively.

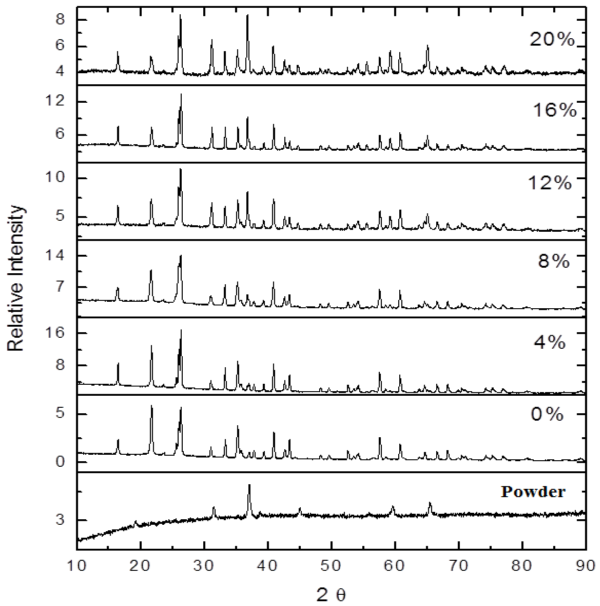


**Figure 1.** Comparison between the X-ray diffraction patterns of samples prepared at different $Co_3O_4$ percentages. The XRD for the $Co_3O_4$ powder is also displayed. The sample with 0% of $Co_3O_4$ corresponds to 70% of kaolinite and 30% of alumina.

From the semi-quantitative phase analysis is found that the weight percent of mullite after the nucleation process is approximately constant at all concentrations of cobalt oxide, as shown in figure 2. Note that the weight percentage of alumina and cristobalite phases decreases as cobalt oxide increases as a result of the formation of cobalt spinel.

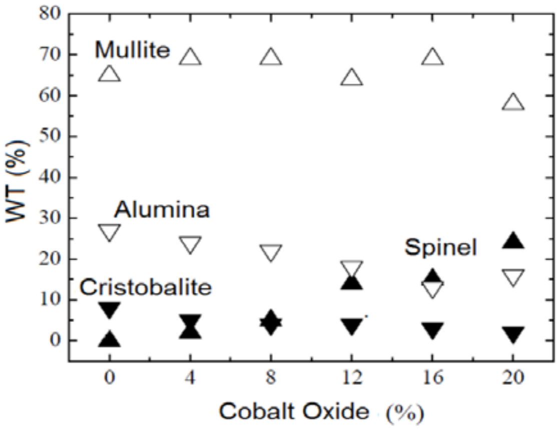


**Figure 2.** Quantitative analysis of the weight percentage of the phases present as a function of the concentration of cobalt oxide in samples sintered at 1350 °C.

Figure 3 shows the hysteresis behavior of polarization curves obtained for the sample with a concentration of 12% of cobalt oxide, showing a typical ferroelectric feature. A similar behavior was observed for all the percentages of cobalt oxide used in this work. Based on the applied voltage and the saturation polarization we obtained an average value of 26.50 for the relative dielectric constant. We found that with the increase of the $Co_3O_4$ in the samples is observed a small change in the dielectric constant, going from 27.82 to 26.30 for the samples with 0% and 20% of $Co_3O_4$, respectively.

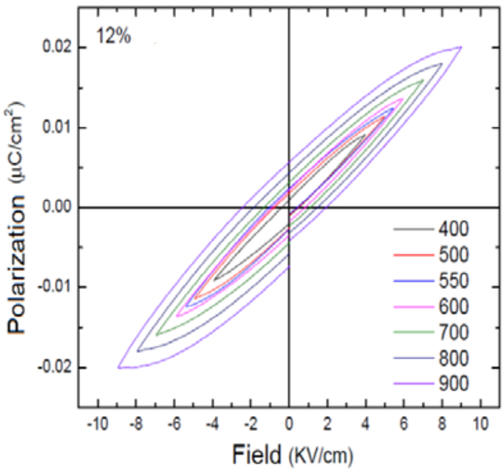


**Figure 3.** Hysteretic behavior of polarization as a function of applied field for a sample with 12% of cobalt oxide (Co3O4). The inset shows the applied voltage.

The analysis of the material hardness was done by means of a friction wear test for each of the samples. Figure 4 shows the wear of the ceramic pieces as a function of the percentage of cobalt oxide in the mixture. It was observed that there is a significant increase in the hardness of the material when the cobalt oxide is introduce in the mixtures as compared to the sample with 0% (70% kaolinite and 30% alumina). One can infer that the increased wear resistance occurs because the reaction of alumina and cristobalite with the $Co_3O_4$ during the sintering process produce the formation of the cobalt spinel.

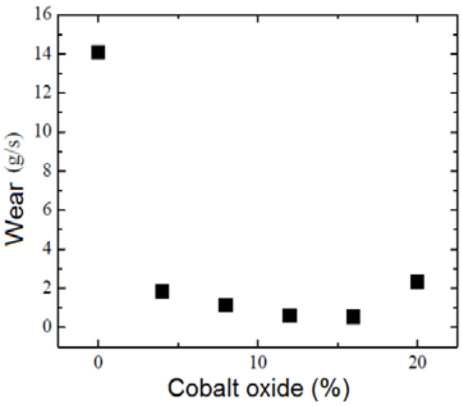


**Figure 4.** Frictional wear as a function of percentage of cobalt used to manufacture samples at a sintering temperature of 1350°C.

For the flexion test we used the three-point method. The distance between the supports was *40 mm*, the lower supports having a diameter of *5 mm* and the upper support has a diameter of *4 mm*. The pre-charge used for calibration of the equipment was 0.6 N. Bending measurement was performed for sintered samples with 0 and 4% of cobalt oxide.

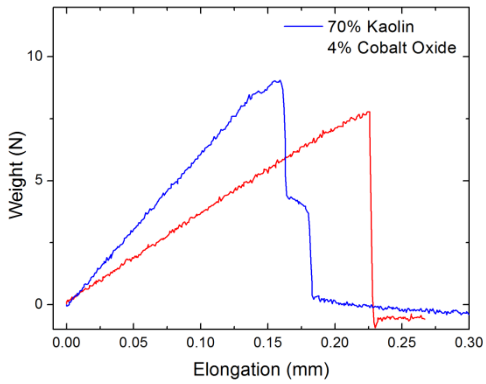


**Figure 5.** Applied load as a function of elongation for samples with O% (red) and 4% (blue) of $Co_3O_4$. The sample with 0% corresponds to 70% of kaolinite and 30% of alumina.

Figure 5 shows the applied load as a function of the elongation for two of the ceramic samples. Note that for the samples with 0 and 4% of $Co_3O_4$ in the mixture the maximum load that resists is 7.78 N and 11.28 N, respectively. This small increment on the maximum load is consistent with the increases of the material hardness when the percentage of $Co_3O_4$ is increased. Table 1 shows the maximum load applied, the maximum displacement and the value of the elasticity modulus for the samples shown in figure 5. We found that the sample with 4% of $Co_3O_4$ shows an increase of 45% in the elastic modulus as compared with the sample without cobalt oxide.

**Table 1**. Values of the maximum applied load, the maximum displacement and the elastic modulus for the characterized samples.

| $Co_3O_4$ (%) | $F_{Max}$ (N) | $D_{Max}$ (mm) | Elas. Mod. ($N/mm^2$) |
|---|---|---|---|
| **0** | 7.78 | 0.225 | 3774 |
| **4** | 11.28 | 0.205 | 5496 |

## 4. Conclusions

Was made a study of the effect of adding cobalt oxide on the structural, electrical and mechanical properties of samples prepared from a mullite matrix at a sintering temperature of 1350 °C. By XRD technique was determined the formation of cobalt spinel with a cubic structure when the $Co_3O_4$ cobalt oxide on percentages greater than 4% is incorporated on a ceramic matrix of 70% of kaolinite and 30% of alumina. The weight percent of mullite phase remained relatively constant when the percentage of $C0_3O_4$ varies from 4 to 20%. From the polarization curves we found a typical ferroelectric feature. Mechanical properties of the material, such as hardness and elastic modulus, are improved considerably when the cobalt oxide is incorporated on the ceramic.

## 5. Acknowledgments

This work was partially financed by DIB (Hermes code 13893) and “El Patrimonio Autónomo Fondo Nacional de Financiamiento para la Ciencia, la Tecnología y la Innovación Francisco José de Caldas” Contract RC No. 0850-2012”.

## References

[1] L. Aksay, D. Dabbs, Mullite for Structural, Electronic, and Optical Applications. *J. Am. Ceram. Soc.***74**, 2344 (1991).
[2] R. Heimann, Classic and Advanced Ceramics, Wiley-VCH Verlag, Weinheim, Germany (2010).
[3] C. Chen, G. Lan, W. Tuan, Preparation of mullite by the reaction sintering of kaolinite and alumina. *J. Eur. Ceram. Soc*. **20**, 2519 (2000).
[4] D. Amutharani, F. Gnanam, Low temperature pressureless sintering of sol–gel derived mullite, *Mater. Sci. Eng.* A **264**, 254 (1999).
[5] Y. Hirata, I.A. Aksay, Processing of mullite powders processed by CVD, in Ceramic Transaction: Mullite and Mullite Matrix Composites, *Am. Ceramic Society*, Westerville, OH, **6** 287 (1990).
[6] H. Schneider, J. Schreuer, B. Hildman. Structure and properties of mullite. *J. Eur. Ceram. Soc*. **28**, 329 (2008).
[7] A. Rossíni, S. Arazi, Mullitización de Mezclas de Arcilla Caolinítica e Hidróxido de Aluminio. *Boletín de la Sociedad Española de Cerámica***5**, 579 (1970).
[8] B. Meng, J. Peng, J. Effects of in Situ Synthesized Mullite Whiskers on Flexural Strength and Fracture Toughness of Corundum-Mullite Refractory Materials, *Ceramics International***39**, 1525 (2013).
[9] Nivin M. Ahmed, Hesham T. Abdel-Fatah, Elham A. Youssef, Corrosion studies on tailored ZnCo aluminate/caolin core-shell pigments in alkyd based paints. *Progress in Organic Coatings***73** 76 (2012).