PZT consolidation by Spark Plasma Sintering (SPS).

Fausto Kenzo Chinen
faustochinen@gmail.com
Izabel Fernanda Machado
machadoi@usp.br
Julio Cezar Adamowski
jcadamow@usp.br
Departamento de Engenharia Mecatrônica e de Sistemas Mecânicos, Escola Politécnica da USP.

Eliana dos Santos Navarro Muccillo
enavarro@usp.br
Reginaldo Muccillo
muccillo@usp.br
Centro de Ciência e Tecnologia de Materiais do Instituto de Pesquisas Energéticas e Nucleares em S. Paulo

Abstract. *The lead zirconate titanate, also known as PZT, of formula $Pb[Zr_xTi_{1-x}]O_3$ is a ceramic material with marked piezoelectric effect and, therefore, it is used in the manufacture of ultrasound transducers and sensors. In this work, the Spark Plasma Sintering (SPS) technique was applied to sintering of PZT, which allows reaching the consolidation of powders at higher heating rates, lower temperatures and shorter dwell times than conventional methods, such as hot pressing. This sintering technique consists in applying electric current to a conductive die, directly heating it, which also reduces power consumption during the process. The main objective was to evaluate consolidation of the samples and loss of Pb during sintering process by SPS. Samples were processed in a Dr. Sinter machine model SPS1050 (SPS Syntex Inc.), using PZT powder ($Pb[Zr_{0.53}Ti_{0.47}]O_3$ doped with 1% of Nb) at different holding times (0, 1, 2 and 4 minutes). The other process parameters were kept the same in all samples (sintering temperature: 1000°C, heating rate: 100°C/min, axial pressure: 50MPa, diameter: 20mm, width: 2mm). Results showed it is possible to consolidate PZT samples even at 0min of holding time. The analysis carried out also showed almost the same results on density measurements, X-ray diffraction and carbon content evaluation for different samples. The other important result is related to the variation of chemical composition due to Pb evaporation. The energy dispersive analysis results did not show a significant difference in the levels of Pb near the surface.*

Keywords: *PZT, SPS, consolidation, chemical analysis, ultrasound transducers and sensors.*

1. INTRODUCTION

The lead zirconate titanate $Pb[Zr_xTi_{1-x}]O_3$ (PZT) has a strong piezoelectric response. PZT can be used to make ultrasound transducers and other sensors and actuators among other uses. PZT is conventionally sintered at approximately 1200-1250^{o}C (Araújo et al., 2001) for more than 1h (Orrù et al. 2009). The atmosphere should be saturated with PbO during sintering since there is an increase in PbO volatility at temperatures above 1100^{o}C (Sung-Gap Lee et al., 2006). The decrease in Pb concentration is detrimental because it strongly affect dielectric properties of $Pb(Zr_xTi_{1-x})O_3$ and causes environmental pollution (Yong Jun Wu et al, 2002). On the other hand, it is difficult to control the compositional fluctuation of PZT ceramics prepared by conventional sintering method, since high temperature and long sintering time were required.

Sintering process of PZT carried out at temperatures around 1000^{o}C and soaking time less than 10 min by means of Spark Plasma Sintering (hereafter SPS) showed very interesting results. Therefore, in other to solve the problems related to chemical fluctuation during conventional sinterization, some studies have been carried out to produce PZT using SPS. After sintering, the consolidated samples did not show significant change in composition and porosity (Orrù et al. 2009). The main reason is related to the low global thermal load of the process, causing the interaction between the materials during the sintering by SPS to be different with respect to conventional sintering technologies. SPS is a sintering method in which consolidation occurs at comparatively low temperatures. The powder is heated by a direct-pulsed current that flows through punches, die and the processed material. The Joule heat due to the electric current rapidly leads to the sintering of the powder particles under pressure. The advantages of the SPS process are known, although the diffusion and consolidation mechanisms remain to be understood (Cabibbo et al., 2008).

The main objective of this work was to evaluate the consolidation of the samples and loss of Pb during the sintering process by SPS of the lead zirconate titanate. The samples were processed in a Dr. Sinter machine model SPS1050 (SPS Syntex Inc.), using PZT powder ($Pb[Zr_{0.53}Ti_{0.47}]O_3$ doped with 1% of Nb) at 1000^{o}C at different holding times (0, 1, 2 and 4 minutes). A series of different tests and analysis were carried out to characterize PZT samples after SPS consolidation. The results showed it is possible to consolidate this material. However, some peculiarities of the process, such as carbon contamination and PbO volatilization have to be investigated.

2. MATERIAL AND EXPERIMENTAL PROCEDURE

2.1. Material

The material used in this study was PZT ($Pb[Zr_{0.53}Ti_{0.47}]O_3$ doped with 1% of Nb), which was provided by Grupo de Cerâmicas Ferroelétricas, Universidade Federal de S. Carlos. The effect of slightly differences in the composition or the impurity level was not analyzed and/or measured.

2.2. SPS Processing

The SPS consolidation was carried out using a SPS-1050 system, produced by SPS Syntex Inc. The samples were disks with 20 mm diameter and 2 to 3 mm height. The processing parameters were as follows:

– graphite die with an inside diameter of 20 mm;
– heating rate: 100^{o}C/min
– axial pressure: 50MPa;
– holding time: 0, 1, 2 and 4 min at 1000^{o}C;
– free cooling in the die;
– sintering was done under vacuum ranging from 10 to 20 Pa.

The SPS-1050 is connected to an acquisition system. Hence, the processing parameters control and measurements are carried out throughout the SPS consolidation. The data, such as vacuum level, displacement and pressure applied, is recorded as function of time. Therefore, changes during the consolidation process, such as gas formation, causing a decrease in the vacuum level, and displacements due to consolidation and phase transformations, can be detected and recorded for later evaluation. A schematic of SPS apparatus is shown in Zhao et al. (2009).

2.3. Sample characterization

The first evaluation carried out was the density by Archimedes principle. Therefore, the consolidation process could be verified. Secondly, samples were evaluated by means of different complementary techniques: X-ray diffraction, microstructural observation (scanning electron microscopy), EDS analysis (scanning electron microscopy) and carbon chemical analysis (LECO). As a result, chemical composition changes during consolidation and their effects in the polarization process could be evaluated.

3. RESULTS AND DISCUSSION

3.1 Density.

Density of the samples was measured by Archimedes principle. The results are displayed in Tab. 1.

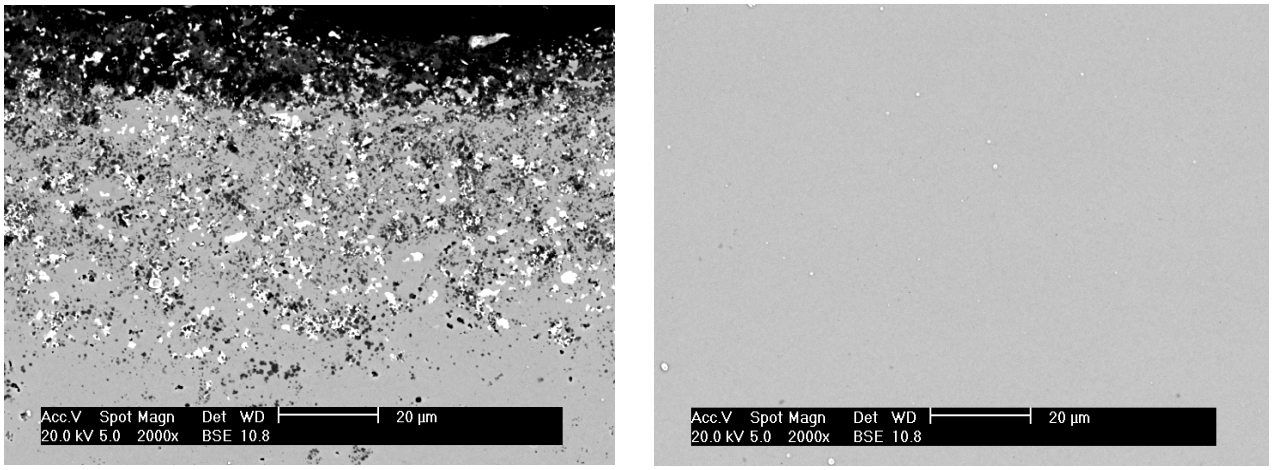
Table 1. Density of the materials consolidated by SPS.

Soaking time (min)	Density (g/cm^3)
0	7.95
1	7.95
2	7.92
3	7.95

Theoretical density of PZT ceramics is 8.002g/cm^3 for $Pb(Zr_{0.517}Ti_{0.483})O_3$) (Hiroshi et al., 2005). Even though the chemical composition of the material used in this work is slightly different ($Pb[Zr_{0.53}Ti_{0.47}]O_3$ doped with 1% of Nb), one can consider the material obtained is almost full density even with 0 min of holding time.

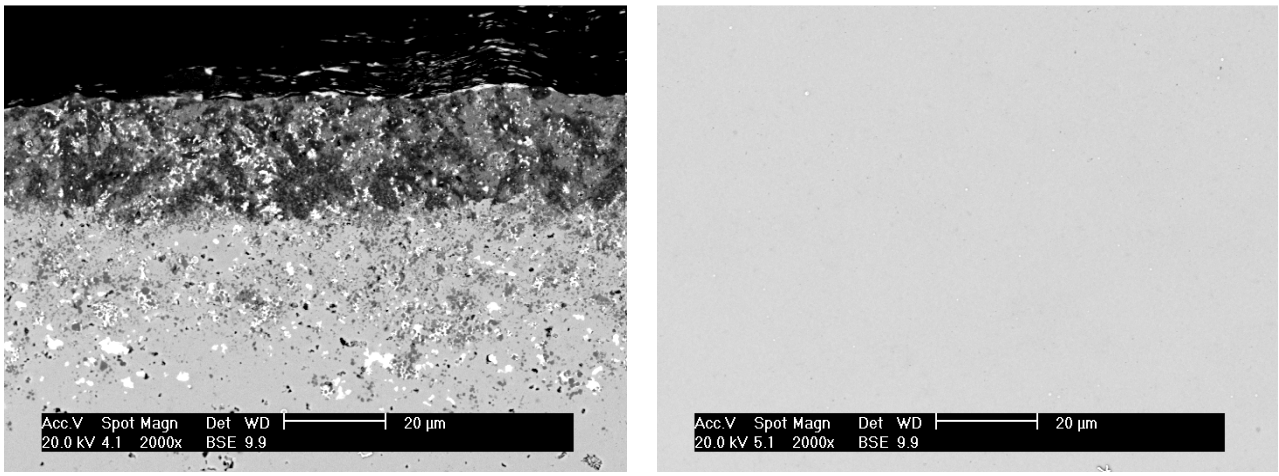
3.1 PZT microstructure and chemical analysis.

Fig. 1 and Fig. 2 depict microstructures of the sample consolidated by SPS for 2 min and 4 min (holding time), respectively. Some different features are observed, mainly in the region near the surface, in the samples consolidated for 2 and 4 min. Chemical analyses, carried out by means EDS displayed in Fig. 3 to 6 show greater impoverishment of Pb near the surface in the sample consolidated for 4min. However, this impoverishment was barely 50 μm. The chemical composition remained stable in the inner of the sample. As a conclusion, no significant differences were observed.



(a) (b)

Figure 1. Sample consolidated by SPS, 2 min. (a) indicates the region near to the surface which was in contact with the graphite die and (b) indicates the inner of the sample.



(a) (b)

Figure 2. Sample consolidated by SPS, 4 min. (a) indicates the region near to the surface which was in contact with the graphite die and (b) indicates the inner of the sample.

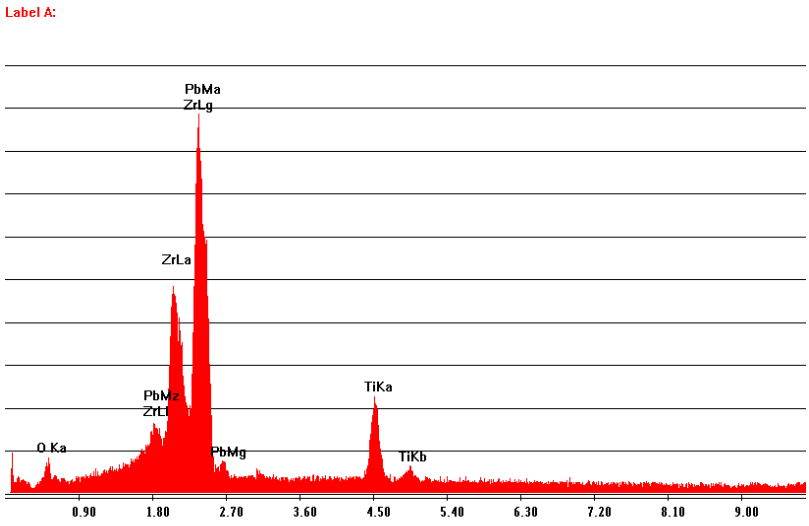


Figure 3. Sample consolidated by SPS, 2 min. The chemical analysis carried out by means EDS in the region near to the surface which was in contact with the graphite die. Chemical composition measured (wt%): 4.64%O, 19.96%Zr, 65.77%Pb and 9.63%Ti measured by EDS.

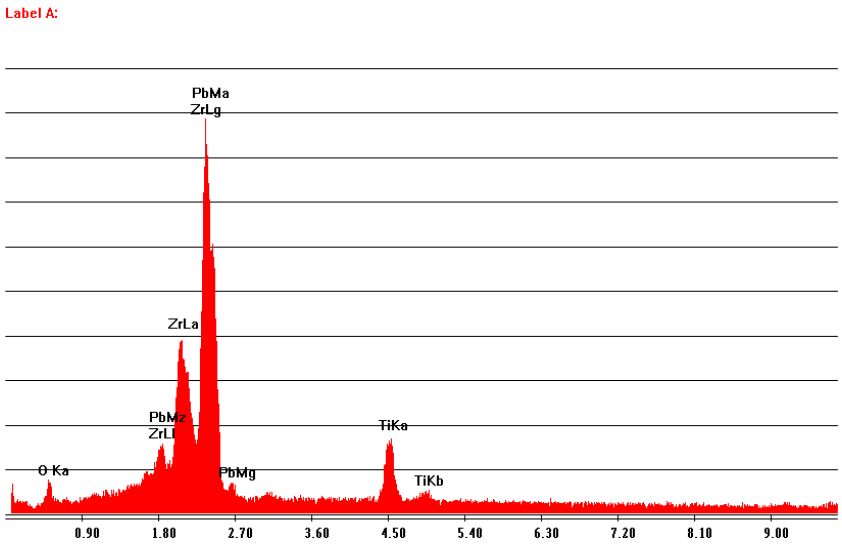


Figure 4. Sample consolidated by SPS, 2 min. The chemical analysis carried out by means EDS in the inner zone of the sample. Chemical composition measured (wt%): 4.50%O, 17.13%Zr, 70.14%Pb and 8.23%Ti measured by EDS.

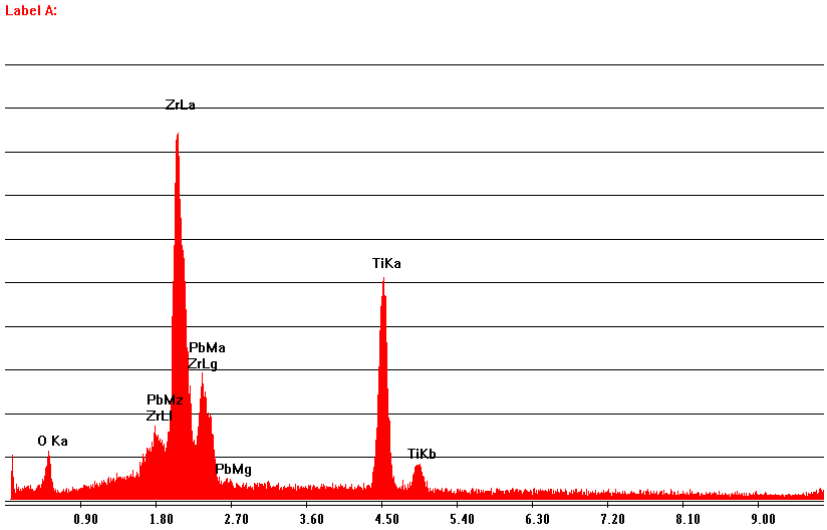


Figure 5. Sample consolidated by SPS, 4 min. The chemical analysis carried out by means EDS in the region near to the surface which was in contact with the graphite die. Chemical composition measured (wt%): 9.43%O, 39.24%Zr, 26.05%Pb and 25.28%Ti measured by EDS.

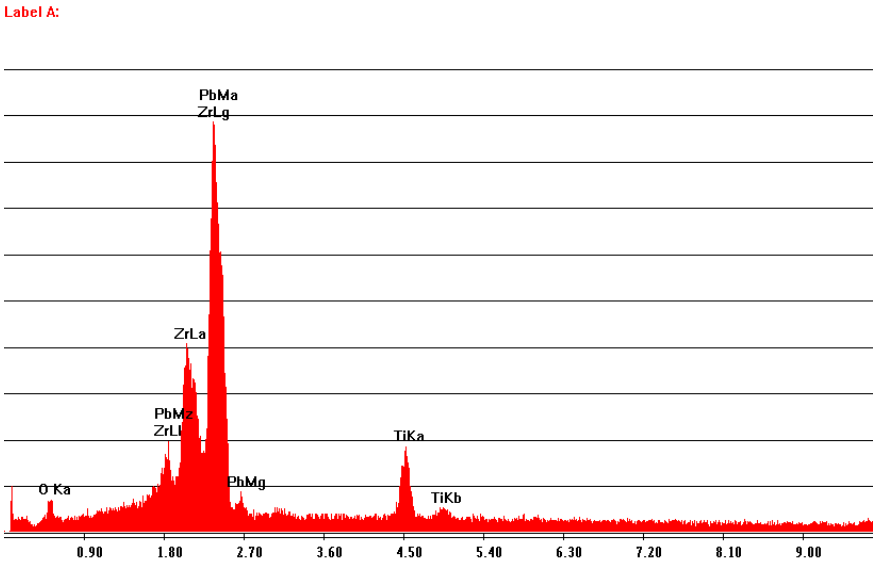
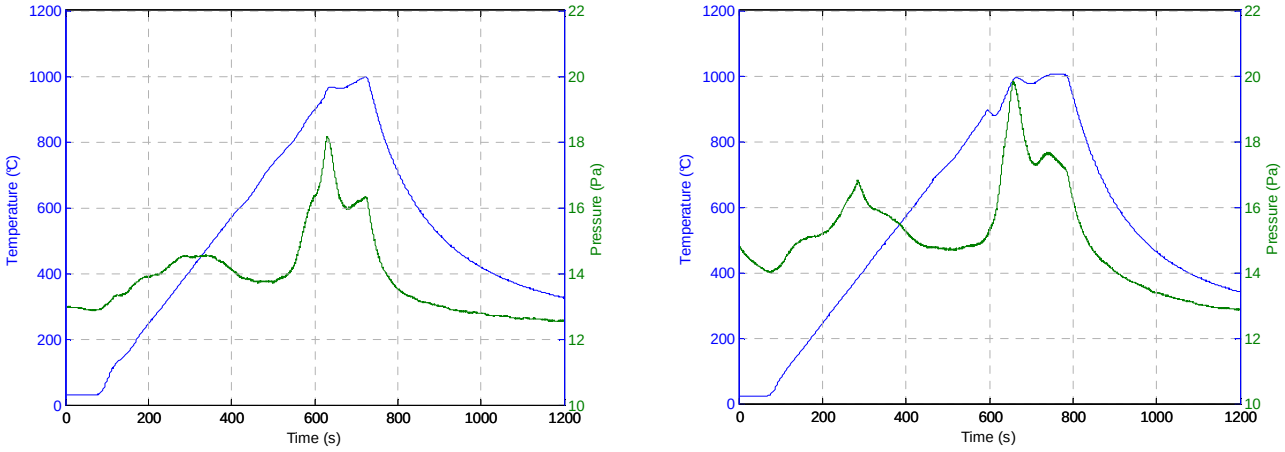


Figure 6. Sample consolidated by SPS, 4 min. The chemical analysis carried out by means EDS in the inner zone of the sample. Chemical composition measured (wt%): 4.17%O, 17.36%Zr, 70.10%Pb and 8.38%Ti.

3.3 SPS pressure analysis.

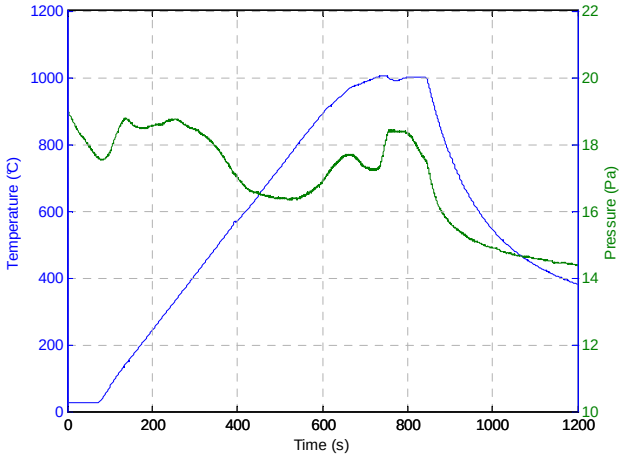
The processing parameters control and measurements are carried out throughout the SPS consolidation. The vacuum level is recorded as function of time. Therefore, changes during the consolidation process can be detected and they are recorded for later evaluation, such as gas formation, causing a decrease in the vacuum level. Fig. 7 and Fig. 8 show these results for the different samples consolidated.

In Fig. 7 and Fig. 8 it can be observed a decrease of vacuum level between 600s and 800s. There is a peak just about 650s, which is higher than the peak at 700s. There was no information about the chemical composition of the gases, although, probably the peaks are related to Pb volatilization, since it was detected in some samples. The other peaks observed, mainly that occurred before 600s of processing, should be related with humidity of powder. This observation is very common during SPS consolidation.

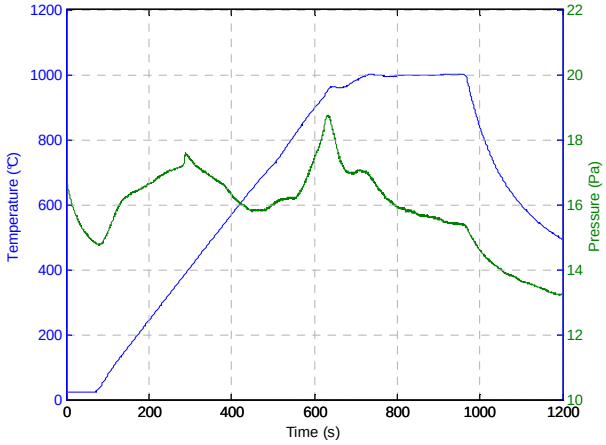


(a) (b)

Figure 7. Results of Vacuum level (Pa) due to degassing during the SPS consolidation as function of SPS process time (green curve) and temperature (^{o}C) versus time (s) throughout SPS consolidation of all the samples (blue curve). (a) Indicates 0 min, (b) 1 min, respectively.



(c)

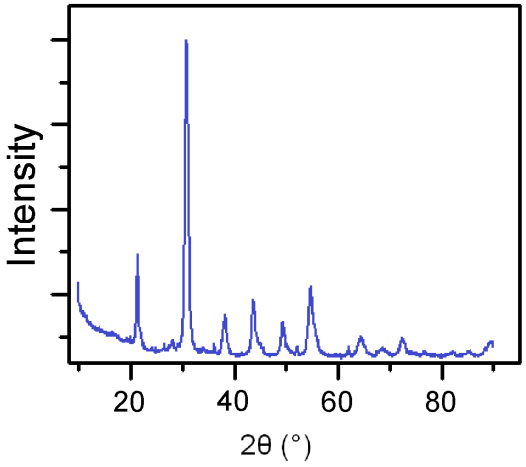


(d)

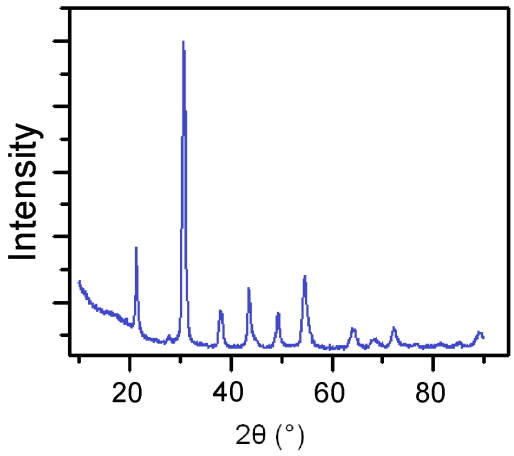
Figure 8. Results of Vacuum level (Pa) due to degassing during the SPS consolidation as function of SPS process time (green curve) and temperature (^{o}C) versus time (s) throughout SPS consolidation of all the samples (blue curve). (a) 2 min and (b) 4 min of holding time, respectively.

3.4 PZT X-ray diffraction

Results of X-ray diffraction (CuKα radiation) for the samples consolidated for 0 min and 4 min (holding time) are shown in Fig. 9a and Fig 9b, respectively.



(a)



(b)

Figure 9. X-ray diffraction patterns for spark plasma sintered. (a) Holding time 0 min and (b) 4 min.

Comparing the results of X-ray diffraction of Fig. 9 with the results presented in the literature (Fig 10.), it can be observed that the peaks of X-ray diffraction are in the same positions (2θ angles). A slightly difference is expected since the composition is different. It can be noted from Fig. 9 that the holding time does not have any significant effect on the phases nor lead to different phase transformation.

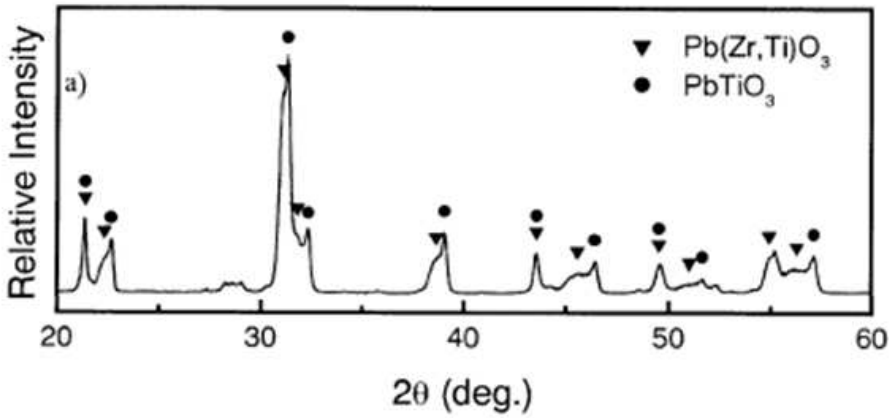


Figure 10. X-ray diffraction patterns for spark plasma sintered $Pb(Zr_{0.3}Ti_{0.7})O_3$, as-SPS sintered (Yong Jun Wu et al, 2002).

3.5 Carbon contamination

After sintering, samples are frequently annealed to recover from a potential reduction that may occur due to reducing atmosphere; to relieve residual stress and to eliminate carbon contamination caused by the use of graphite die (Orrù et al. 2009). The contamination with carbon is detrimental since it causes conductance, preventing polarization of the PZT sample. This contamination is easily identified by observing the sample. The PZT becomes gray, as can be seem in Fig. 11.

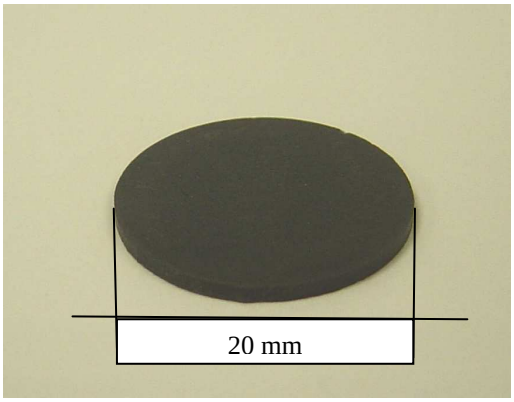


Figure 11. Main features of PZT samples after SPS consolidation.

Results of carbon analysis after SPS consolidation are displayed in Tab. 2. Different results of carbon content are observed in the samples after sintered. However, the carbon content does not increase when the holding time increases. Therefore, it can be considered qualitative, since some graphite residue from the die can be present in the sample, even after surface grinding.

Table 2. wt% of carbon in the samples after consolidation by means of SPS. (Carbon analysis by Infrared Technique).

Sample (holding time – min)	**%C**
0	0.0099
1	0.0122
2	0.0071
4	0.0046

As suggested in other work (Orrù et al. 2009), one of the samples was annealed at 1000°C for 3 hours. After annealing the polarization tests were carried out and they show good results, besides the change in the color of the sample (2 min of holding time) which had become yellow (Fig. 12), as the PZT powder. The results of polarization will be analyzed in future work, since the first evaluation showed only qualitative results.

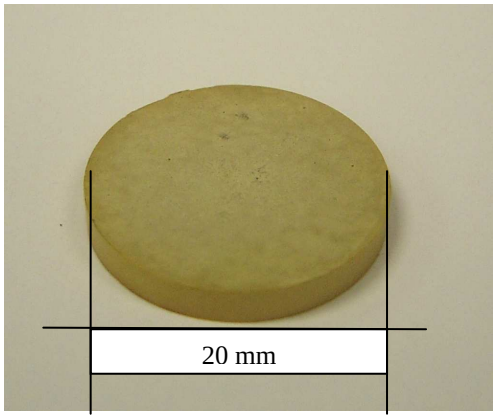


Figure 12. Main features of PZT sample after SPS consolidation and annealing at 1000^{o}C for 3 hours .

4. CONCLUSIONS

Results of this work allow the following conclusions:

1. PZT powder was sintering by means of SPS and almost a 100% of density was reached even at 100^{o}C/min heating rate and 0 min of holding time, and X-ray diffraction analysis showed no significant differences in the phases formed during consolidation process.
2. No significant loss of Pb was observed in the samples sintered by SPS. This result is one of the most important, since the loss in Pb is detrimental because it strongly affects dielectric properties.
3. Sample contamination with carbon could be observed and measured in the samples sintered by SPS, although it can be eliminated by annealing.
4. Vacuum level showed that some transformation and/or Pb volatilization occurred when the highest temperature of processing was reached.

5. ACKNOWLEDGEMENTS

The authors are thankful to CNPq, CAPES, FAPESP and Petrobras for financial support and Prof. J.A. Eiras from Grupo de Cerâmicas Ferroelétricas, Departamento de Física, Universidade Federal de S. Carlos for providing the PZT powder.

6. REFERENCES

Araújo, E. B.; Eiras, J. A. 2001. “Otimização de parâmetros estruturais, dielétricos e ferroelétricos de filmes finos de PZT”. Cerâmica. Vol. 74, pp. 9-12.

Cabibbo M, Paternoster C, Cecchini R, Fabrizi A, Molinari A, Libardi S, et al. 2008 “A microstructure study of nanostructured Fe–Mo + 1.5wt%SiO_2 and + 1.5wt%TiO_2 powders compacted by spark plasma sintering”. Mater Science Engineering. Vol A496, pp. 121–32.

Maiwa, H.; Kimura, O.; Shoji, K.; Ochiai, H. 2005. “Low temperature sintering of PZT ceramics without additives via an ordinary ceramic route”. Journal of the European Ceramic Society. Vol. 25, pp. 2383–2385

Orrù, R.; Licheri, R.; Locci, A. M.; Cincotti, A.; Cao, G. , 2009, “Consolidation/synthesis of materials by electric current activated/assisted sintering”. Materials Science and Engineering. Vol 63, pp. 127–287.

Sung-Gap Lee; Young-Hie, 2006 “Dieletric properties of PZT (20/80)PZT(20/80) heterolayered thick films fabricated by screen-printed method”. Transactions on Eletrical and Eletronic Materials. Vol. 7.pp. 129-133.

Yong Jun Wu; Uekawa, N.; Kakegawa, K.; Sasaki, Y. 2002 “Compositional fluctuation and dielectric properties of $Pb(Zr_{0.3}Ti_{0.7})O_3$ ceramics prepared by spark plasma sintering”. Materials Letters. Vol. 57, pp. 771–775

Zhao J, Hollad T, Unuvar C, Munir ZA. 2009 ”Spark plasma sintering of nanometric tungsten carbide”. International Journal of Refractory Metals and Hard Materials. Vol. 27, pp.130–139.

7. RESPONSIBILITY NOTICE

The authors are the only responsible for the printed material in this paper