INFLUENCE OF THE AMOUNT OF LI-CONTAINING FELDSPAR ON THE SINTERING OF A TRIAXIAL CERAMIC

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Abstract. *Traditional ceramics are in its majority based on triaxial bodies containing clay, quartz and feldspar. The feldspar is one of the minerals which most influences the mechanical characteristics of ceramic materials. Furthermore, Li-containing compounds may contribute to modify these characteristics. In this work, the influence of the feldspar content, using common feldspar containing Sodium (Na) and feldspar containing Lithium (Li) has been investigated. The overall amount of feldspar in the ceramic samples varied between 15 and 30 wt-%. Specimens were prepared by cold uniaxial pressing in a steel die under a pressure of 4 MPa. Sintering of the specimen was done in an electrical heated furnace in air at temperatures of 1000, 1100 and 1200 ºC for 1h. The samples were characterized by their mass loss, linear retraction, absorption and porosity. The phase composition of the sintered samples was investigated by X-ray diffraction analysis and the microstructure was observed by scanning electron microscopy of fracture surfaces. The best results were obtained by samples containing 30% spodumene sintered at 1200 °C with a linear shrinkage of 6,42%, a density of 2.01 g/cm3, an apparent porosity of 14.27% and a mechanical strength of 13.43 MPa while albite containing samples showed linear shrinkage of 5,78%, density of 1,91 g/cm3, apparent porosity of 9,79% and mechanical strength of 18,93 MPa respectively. Therefore, the use of spodumene in the triaxial ceramic resulted in a lower firing temperature, thus reducing production costs by saving energy.*

Keywords: *Feldspar, Lithium, triaxial ceramic, sintering.*

1. INTRODUCTION

Traditional ceramics are obtained from natural raw materials to fabricate products with pre-defined characteristics (Sacmi, 2003). In Brazil, the participation of the ceramic industry in the gross domestic product (GDP) is estimated in 1 %, corresponding to approximately six billion dollars. Due to the abundance of natural raw materials, alternative energy sources and availability of technologies, the Brazilian industry developed rapidly, producing and exporting high quality products (ABC, 2011).

The raw materials used to produce triaxial ceramic materials influence the properties of the final product such as porosity, density, fracture strength and surface quality. In this work, a ceramic body was formulated based on clay, kaolin, quartz and feldspar. Each of these compounds holds a specific task in the sintering of traditional ceramic materials. Clay forms gradually a liquid phase during sintering of the ceramic articles, producing mechanical strength (Navarro, J.E.E. *et al*., 1981 and Brusa; Contoli and Dardi, 1999). Kaolin increases the alumina content and helps to improve the whiteness of the final product (Rodrigues, M. Adriana. *et al*., 2004). Quartz participates in the fusion of the feldspar and equilibrates the viscosity of the liquid phase (Oliveira, 1998 and Drozda, 2003). Furthermore, feldspar decreases the sintering temperature, acting as flux, forming liquid phase and modifying the porosity of the pieces (Motta, J. F. M. *et al.,* 2002 e Llorens, G.F. *et al*., 2000). The importance of a flux in the in the ceramic samples consists in its capacity to lower the temperature of liquid phase formation during the process of sintering. The liquid formed tends to fill the voids of the ceramic body, reducing or eliminating the porosity (Worral, 1982).

The peculiarity of each of these compounds depends on its origin and requires an adjustment of the formulation, or even of the compounds used. In this way it may be possible to explore minerals situated closely to the ceramic industry, reducing transport costs (Verduch and Balmaseda, 1993 and Mussolin and Doneda, 1997).

The objective of this study is to compare the influence of the type and amount of feldspar (Lithium or Sodium containing feldspar) on the sintering of a triaxial ceramic and its resulting mechanical properties.

2. MATERIALS AND METHODS

2.1. Sample Preparation

The specimen was prepared by mixing the starting materials, quartz, kaolin, clay and feldspar in the proportions listed in table 1. The mixture 1 had a total weight of 100 g, the mixture 2 had 105 g, the mixture 3 had 110 g, and the mixture 4 had 115 g, the each mixture were made five specimens of 20 g, the rest of the mass was discarded.

Table 1. Sample compositions

Material	Standard Feldspar (g)				Feldspar Containing Lithium (g)			
	Mixture 1	Mixture 2	Mixture 3	Mixture 4	Mixture 1	Mixture 2	Mixture 3	Mixture 4
Clay	40	40	40	40	40	40	40	40
Kaolin	10	10	10	10	10	10	10	10
Feldspar	15	20	25	30	15	20	25	30
Quartz	35	35	35	35	35	35	35	35

The chemical analysis of Li-feldspar by X-ray fluorescence is listed in table 2, and the other compounds is listed in table 3.

Table 2. Chemical analysis of Li-feldpsar (*CIA Industrial Fluminense – MIBRA)*

Compounds	Wt %
SiO_2	76.36
Al_2O_3	16.09
Fe_2O_3	2.05
CaO	1.42
Na_2O	4.10
K_2O	2.31
MnO	0.15
TiO_2	0.0003
MgO	0.68
P_2O_5	0.14
Li_2O	0.91
loss	0.35

Table 3. Chemical analysis of others compounds

Compounds	SiO_2 (wt%)	Al_2O_3 (wt%)	Alkalis*(wt%)
Na-feldspar	65.92	19.31	14.77
Kaolin	52.74	45.83	1.44
São Simão Clay	63.76	35.03	1.21
Quartz	99.23	0.50	0.27

** contents of CaO + Na2O + K2O + MgO; the origin of raw material: MINASOLO Comércio e Representação Ltda., (2)UFSCar, (3)TALMAG PP-325 - Magnesita S.A.*

The mixing of the powders was done by dry milling of the starting materials in a ball mill for 2h. The specimens were fabricated by cold uniaxial pressing in a steel die, under a pressure of 28.5 MPa for 30 seconds, SIWA Press PH 15 ton. For each composition studied, 20 specimens were pressed with dimensions of 70 x 20 x 7 mm and approximately 20g weight. After pressing, the green density of the samples was determined by measuring their volume and weight.

2.2. Sintering

The specimen were sintered at temperatures of 1000, 1100, and 1200 °C, in an electrical heated furnace in air, using a heating rate of 3 °C/min and an isothermal soaking time of 1hour at maximum temperature, Lavoisier Furnace Model 4020. After this cycle, the oven was switched off, allowing natural cooling of the samples inside the furnace.

2.3. Characterization of the Sintered Samples

The sintered samples were characterized by the weight loss, linear shrinkage, absorption of water and porosity.

2.4. Linear Shrinkage

The linear shrinkage represents the change of the length of the sample after sintering, according Eq. (1):

$$RL(\%) = \frac{l_o - l_f}{l_o} \times 100 \qquad (1)$$

Where: *RL* is the linear shrinkage and l_o and l_f the initial and final length of the sample, respectively.

2.5. Absorption

In order to determine the open porosity, the absorption of water by the samples was measured by soaking the samples in boiling water for 60 min. The water absorption is calculated by Eq. (2) by the weight difference of the dry and humid samples.

$$AA(\%) = \frac{P_h - P_d}{P_d} \times 100 \qquad (2)$$

Where: *AA* is the water absorption, P_h and P_d the humid and dry mass of the samples, respectively.

2.6. Apparent porosity

The apparent porosity, which is the apparent pore volume in relation to the total volume of the body, was calculated by Eq. (3):

$$PA(\%) = \frac{P_h - P_s}{P_h - P_i} \times 100 \qquad (3)$$

Where: P_h is the humid, P_s the dry and P_i is the immersed mass of the samples.

The immersed weight of the samples was determined by immersing the samples completely in water and measuring their weight.

2.7. Apparent density

The apparent density was calculated by the following relationship, according Eq. (4):

$$DA(g/cm^3) = \frac{PA}{AA} = \frac{P_s}{P_h - P_i} \quad (4)$$

Where: P_h is the humid, P_s the dry and P_i is the immersed mass of the samples.

3. RESULTS AND DISCUSSION

In all compositions studied and even after sintering at 1200 ^oC large faceted particles of size up to 70 µm have been observed, probably residual quartz. Furthermore, it can be noted that with increasing sintering temperatures a glassy phase is formed, which exhibits a smooth fracture surface. With increasing sintering temperature and increasing feldspar content of the samples higher amounts of glassy phase are detected. The formation of the glass phase is more pronounced in samples sintered at 1200 ^oC, due to the reactions between feldspar, quartz and meta-kaolinite.

With increasing amount of glassy phase formed the fractured surface is smoother, still exhibiting residual porosity, indicating that densification during sintering has not been completed, even when using 30 % of feldspar in the triaxial mixture and sintering at 1200 ^oC, according figure 5 and 6.

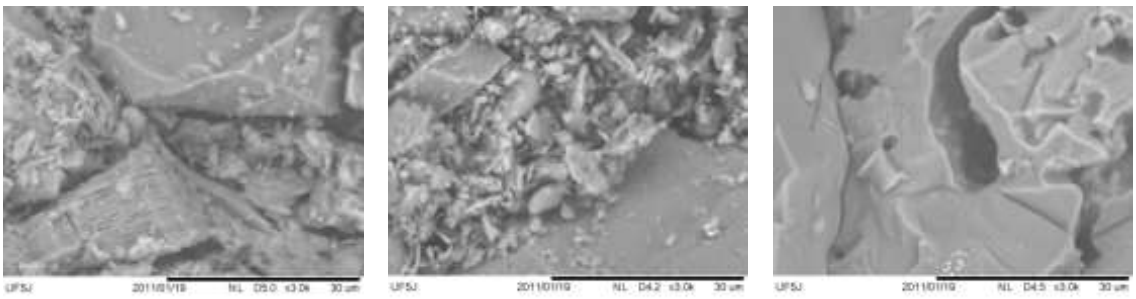

Fig.5: Micrographs of samples containing 30% Li-feldspar sintered at 1000, 1100 and 1200 ^oC

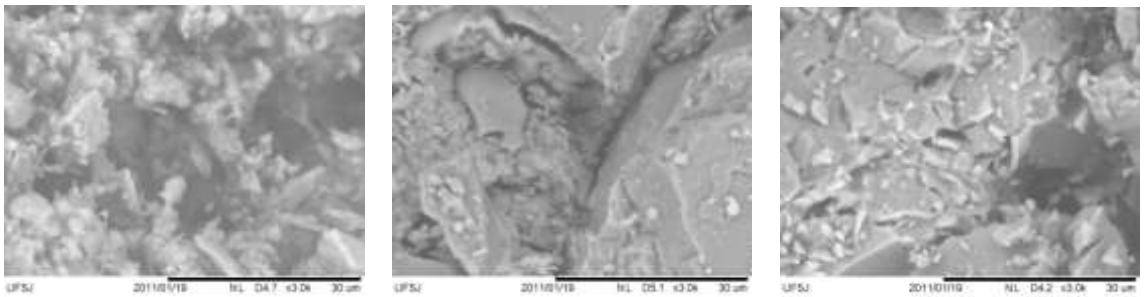

Fig. 6: Micrographs of samples containing 30% Na-feldspar sintered at 1000, 1100 and 1200 ^oC

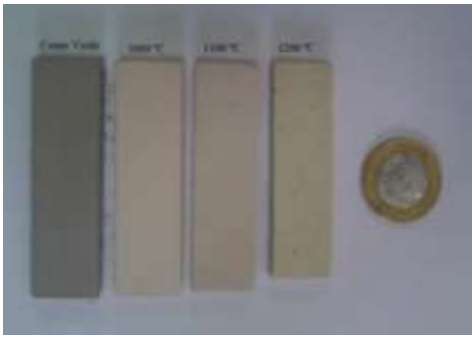

Fig. 7: Samples containing Li-feldspar, after sintering

Fig. 8: Samples containing Na-feldspar, after sintering

Comparing the samples after sintering, as shown in the photographs shown in Fig. 7 and 8, samples containing Na-feldspar exhibited a brighter coloring in comparison to the samples prepared with Li-based feldspar, specifically at the higher sintering temperatures of 1100 and 1200 °C. Otherwise, both sample compositions showed very similar shrinkage in regard to the sinter temperature, according Fig. 9 and 10.

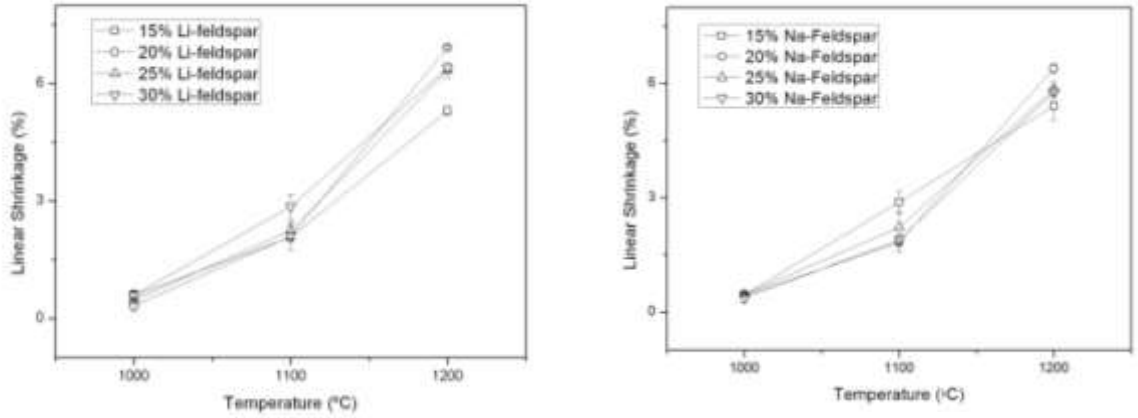

Fig.9: Linear Shrinkage x Temperature graphs of samples, containing 15, 20, 25 and 30 % Li-feldspar

Fig.10: Linear Shrinkage x Temperature graphs of samples, containing 15, 20, 25 and 30 % Na-feldspar

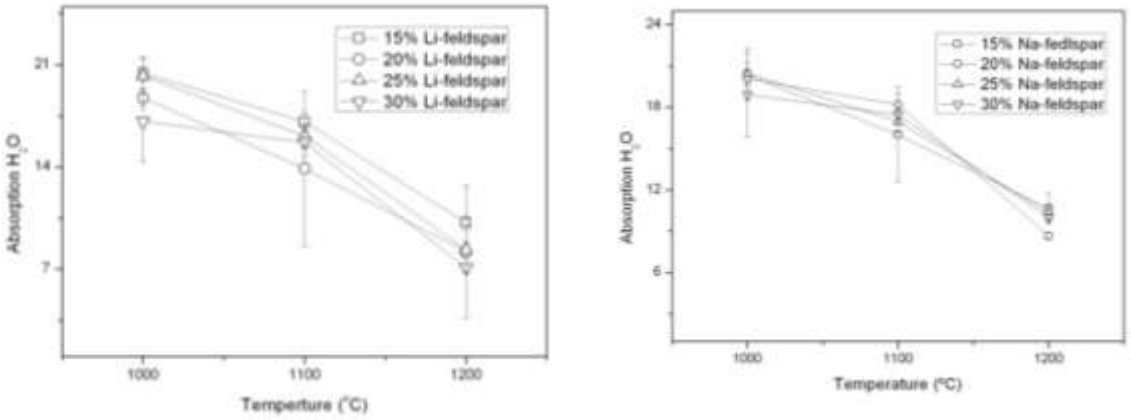

Fig.11: Absorption H_2O x Temperature graphs of samples, containing 15, 20, 25 and 30 % Li-feldspar

Fig.12: Absorption H_2O x Temperature graphs of samples, containing 15, 20, 25 and 30 % Na-feldspar

With increasing sintering temperature densification increased and, consequently, absorption and porosity decreased, since density and porosity are related inversely, as shown in the figures 11 to 16.

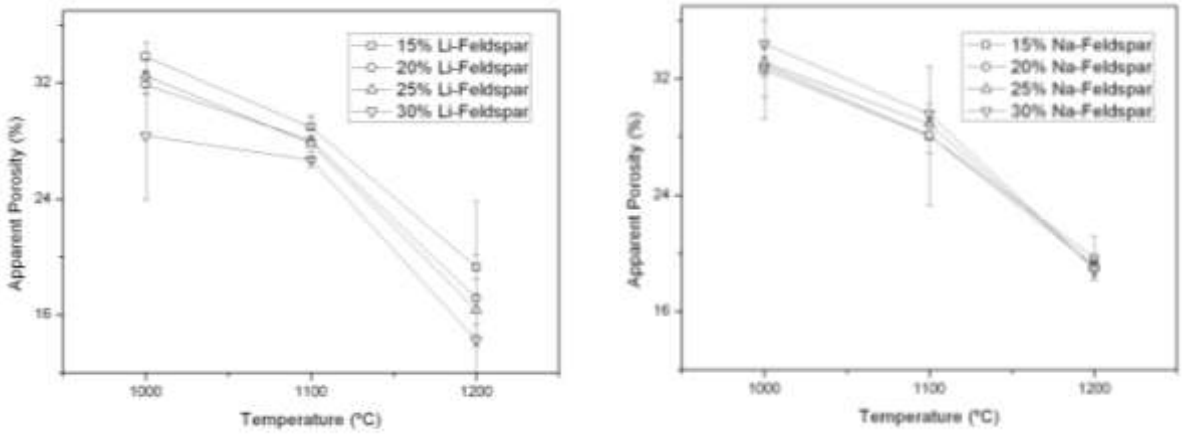

Fig.13: Apparent Porosity x Temperature graphs of samples, containing 15, 20, 25 and 30 % Li-feldspar

Fig. 14: Apparent Porosity x Temperature graphs of samples, containing 15, 20, 25 and 30 % Na-feldspar

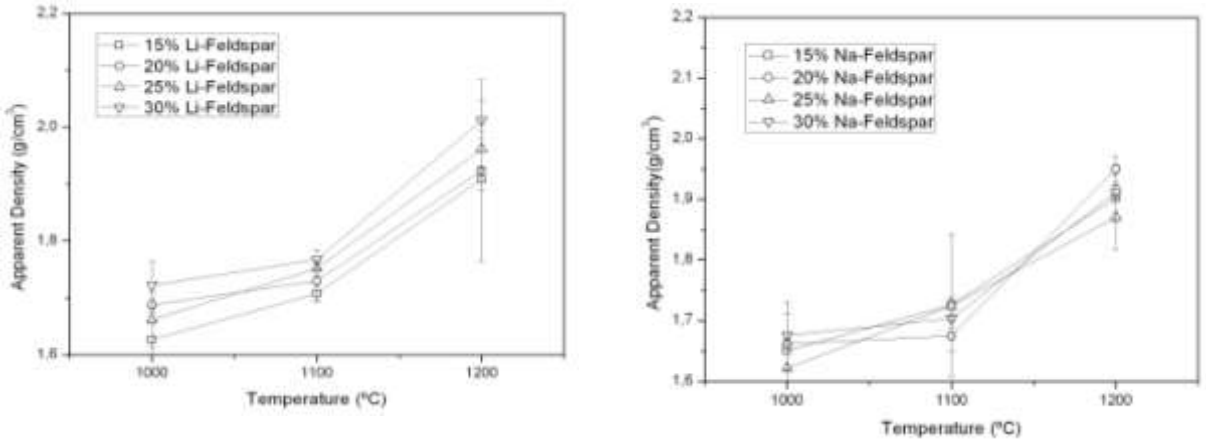

Fig. 15: Apparent Density x Temperature graphs of samples, containing 15, 20, 25 and 30 Li-feldspar

Fig. 16: Apparent Density x Temperature graphs of samples, containing 15, 20, 25 and 30 Na-feldspar

As can be seen from figure 13 and 14 the decrease of the porosity in the temperature range between 1100 and 1200 ^{o}C has been more pronounced than in the temperature range between 1000 and 1100 ^{o}C for all compositions studied, indicating that a higher amount of liquid phase is formed under a higher temperature. Even so, a porosity of approximately 18 % of the samples prepared with Na-containing feldspar after sintering may be considered unsatisfactory. In these samples no significant variation of the density in relation to the feldspar content has been observed.

In the case of samples prepared with Li-containing feldspar a higher decrease of the porosity in the temperature range between 1100 and 1200 ^{o}C is observed in relation to the samples containing Na-feldspar. Furthermore a dependency of the porosity with the feldspar content is observed; the porosity decreases with increasing amount of feldspar. Thus, samples prepared with 30 % Li-feldspar exhibited a porosity of 13 % after sintering at 1200 ^{o}C, while the samples containing only 15 % of Li-feldspar exhibited a porosity of 19 %, similar to the porosity determined in the samples containing 30 % Na-feldspar. Therefore, it may be concluded that the Li-containing feldspar is more efficient in the densification of triaxial ceramics than the common Na-based feldspar.

4. CONCLUSIONS

In order to improve the densification during sintering we suggest to use smaller quartz particles and/or increase the sintering temperature to 1300 ^{o}C or higher. In this way the diffusion paths are shortened and the diffusion coefficients increased, which should result in a higher densification.

No significant differences between the samples prepared with Na-feldspar and the samples with Li-Feldspar have been observed, confirming the possibility to substitute Na-feldspar by the Li containing feldspar in the triaxial mixtures, without prejudice for the properties of the sintered materials. Detailed sintering studies in a dilatometer will be conducted to closely monitor the shrinkage behavior during sintering and thus establish the best sintering program for each composition.

Considering the results obtained so far, we conclude that densification must be improved, for example by increasing the sintering temperature to 1250 or even 1300 ^{o}C and that the substitution of the Na-containing feldspar by the Li-containing feldspar has been viable. The lowest porosity of 13 % has been achieved using 30 % of Li-feldspar and sintering at 1200 ^{o}C.

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