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Microwave, spark plasma and conventional sintering to obtain controlled-thermal-expansion β- eucryptite materials

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Abstract

Lithium aluminosilicate was fabricated by conventional and non-conventional sintering: microwave and spark plasma sintering, from 1200 to 1300 ºC. A considerable difference in densification, microstructure, coefficient of thermal expansion behavior and hardness and Young's modulus was observed. Microwave technology made possible to obtain fully dense glass-free lithium aluminosilicate bulk material (>99%) with near-zero and controlled coefficient of thermal expansion and relatively high mechanical properties

(7.1 GPa of hardness and 110 GPa of Young's modulus) compared to the other two processes. It is believed that the heating mode and effective particle packing by microwave sintering are responsible to improve these properties.

1. Introduction

Thermal expansion, the increase in volume upon heating under constant pressure, is assumed to be normal from experience in the realm of research and in daily life. Thermal expansion behavior is easily understood from well-known examples: the joints of rails or bridge girders contain spaces, and precision optical instruments are placed under strict temperature control to reduce the effects of thermal [1]. Therefore, the usefulness of these thermal properties in the production of materials with null expansion [2] has a wide range of potential engineering applications, as photonic, electronic, aeronautical or structural applications [3,4].

β- eucryptite is the most negative thermal expansion phase in the lithium aluminosilicate ceramic system and, consequently, β- eucryptite has been thoroughly studied [5,6]. However, the study has focused on glass-ceramic materials [7,8], due to the difficulty in obtaining this system as a fully dense ceramic material in the solid state [3,9]. This is important because as far as possible obtaining glass-free dense materials would improve the mechanical properties such as modulus of elasticity compared with glass-ceramic. This improvement is very relevant to advanced technological applications of this material. Therefore, a variety of approaches in the field of sintering techniques have arisen due to the widespread demand of innovative materials in recent years. Hence, understanding how the processing variables affect microstructural evolution is the key to initiating a proper sintering procedure. Various sintering

methodologies based on diverse mechanisms are currently available to engineer the densification kinetics enabling the realization of above cited objectives. Applying a promising sintering procedure is, therefore, great importance for the superior performance of bulk ceramic materials.

Non-conventional sintering techniques; spark plasma sintering and microwave sintering, represent an alternative approach to the densification of nanoparticles [10,11]. In ceramic materials, the high temperatures required to fully densify ceramic powders result in large grain sizes due to Ostwald ripening when traditional sintering techniques are used. This makes it extremely difficult to obtain dense materials with nanometric and submicrometric grain sizes. To overcome the problem of grain growth, non-conventional sintering methods has been proposed in this work.

Spark plasma sintering simultaneously applies pulsed electrical current and pressure directly on the sample leading to densification at relatively lower temperatures and short retention times [12,13]. The mechanisms responsible for high rate densification were identified as grain rotation and sliding, aided by partial melting of the particle surface or plastic deformation in materials with low yield stress [14,15].

Microwave radiation of ceramic components has recently gained new relevance in the field of sintering and joining of ceramics due to its advantages against conventional heating techniques [16]. Microwave sintering has several advantages such as rapid and volumetric heating, improved production rate, enhancement in densification and grain growth prohibition of ceramics [17,18].

The scientific development of new products and technical processes has traditionally been of vital importance to advance in materials science and design. Nowadays, to go further, they require new techniques "*breakthrough*" to fabricate materials with different multifunctional applications.

The objective of the present study is, therefore, a comparative evaluation of the densification, microstructural behavior, thermal expansion coefficient and mechanical properties in fully dense glass-free LAS bulk materials by the different non-conventional sintering methodologies: microwave and spark plasma sintering. A comparison between the conventional processing is also represented within the results.

2. Experimental Procedure

2.1. Materials

β- Eucryptite solid solution powders were synthesized for this study following the route proposed in a previous work (see [19] for details). The chemical compositions of the LAS powder correspond to a Li_2O:Al_2O_3:SiO_2 relation of 1:1.1:2.5 (Compositions LAS8 in [19]). Green samples were prepared by cold isostatic pressing (CIP) at 200 MPa of pressure (15 mm height, 10 mm diameter). The green density was approximately 1.2 g cm^{-3}, i.e. 49% of theoretical density (2.39 g cm^{-3}).

2.2. Sintering procedure

A single mode cylindrical cavity operating in the TE_{111} mode with a resonant frequency of 2.45 GHz was selected as the heating cell for microwave sintering. The cavity has two 12 mm diameter holes in the top and lateral walls, which allows access for a quartz tube containing the specimen (radius = 10 mm, height = 15 mm) and a temperature

sensor, respectively (Fig. 1). The dimension and position of these holes were designed to ensure that there was no microwave leakage from the cavity and there was negligible perturbation of the resonant mode. The *E* field vectors are perpendicular to the cavity axis with the maximum electric field magnitude at the center, where the samples are located. Preliminary dimensions of the cavity (radius = 52 mm, height = 85 mm) were determined analytically and afterwards optimized with the use of a commercial EM simulator QuickWave 3D [20]. A movable short-circuit at the bottom of the cavity permits to track the cavity heating mode resonant variations caused by changes in the dielectric constant of the heated test sample during the sintering process.

A rectangular waveguide is used to launch microwaves to the cylindrical cavity through a coupling aperture. A switching power supply (Magdrive1000) circuit for driving a magnetron (Panasonic 2M244, 1200 W) operating at 2.45 GHz delivers a continuous variable 1 kW of microwave power. A compact isolator (Valvo VZU1234 isolauncher) protects the magnetron from undesirable reflections. Incident, reflected and absorbed microwave energy, as well as complex impedance of the cylindrical cavity, are measured by a waveguide reflectometer [20].

The temperature of the sample is monitored by an infrared radiation thermometer (Optris CT-Laser LT, 8-14 μm), which is focused on the test sample via the small circular aperture in the wall of the cavity. The emissivity of the LAS material at different temperatures was calculated previously to sintering. A stepper motor placed at the bottom of the cavity permits the mechanical tuning of the cavity by changing the height to adjust such that the new resonant frequency of the cavity test cell is modified back to the frequency of the magnetron.

The power supplied to the magnetron, tuning by the stepped motor, and sample temperature are recorded using serial links. A programmable proportional integral differential (PID) controller has been implemented in the PC under a Labview code to control the sample temperature. The PID control parameters were optimized for each sample using an in-built auto-tune routine. This automatic procedure fixes the amounts of microwave energy being supplied to the sample to operate under the desired heating rate. The samples were heated at a rate of 100 ºC min^{-1} to temperatures between 1200 and 1250 ºC with a short holding time of 10 min.

Other non-conventional technique is spark plasma sintering, where the powder was placed into a graphite die with an inner diameter of 20 mm and cold uniaxially pressed at 30 MPa. Then, they were introduced in a spark plasma sintering device HP D25/1 (FCT Systeme GmbH, Germany) under low vacuum (10^{-2} mbar). The sintering temperatures were 1200 and 1300 ºC with a holding time of 2 min at the maximum temperature under an applied pressure of 50 MPa and a heating rate of 100 ºC min^{-1}.
The conventional heating process was carried out in an electrical furnace (Thermolyne type 46100, Thermo Fisher Scientific, USA) in air at 1200 and 1300 ºC with 10 ºC min^{-1} of heating rate and 2 h of holding time.

2.3. Characterization methods

The bulk density of the sintered samples was measured by Archimedes' principle by immersing the sample into water based liquid (ASTM C373-88). Nanomechanical properties such as hardness and Young's modulus of samples were obtained by nanoindentation technique (Model G200, MTS Company, USA). To carry out

indentations at very low depths, a brand new Berkovich diamond tip was used with radius less than 20 nm as certified by the manufacturing company. In order to ensure the quality of the tip throughout the work, pre- and post- calibration procedures were performed for this indenter ensuring the correct calibration of its function area and correct machine compliance. Previous to the nanoindenter testing, the samples were prepared by metallographic techniques. After cutting, the surface was lapped and then polished, with a final step with 0.25 μm diamond paste. The nanomechanical properties of the LAS ceramics were evaluated from the load-displacement nanoindentation data using the widely accepted Oliver and Pharr method [21].

The crystalline phases of the bulk ceramic composites were determined by X-ray diffraction (XRD, BRUKER AXS D5005, Germany). The measurements were performed in the 15º-70º range and the step size and time of reading were 0.02º and 0.3 s, respectively.

The coefficient of thermal expansion was checked in a Netzsch DIL-402-C between -150 and +150 ºC.

The fracture surface sections of the sintered samples have been observed using a field emission gun scanning electron microscope (FESEM, HITACHI S-4800, Japan).

3. Results and Discussion

Table 1 shows the sintering parameters and relative densities of β- eucryptite densified powders using the sintering methodologies of conventional sintering (CS), microwave sintering (MW) and spark plasma sintering (SPS). It can be observed, a meaningful

difference between the relative densities of the conventionally sintered samples and those prepared by MW and SPS.

The materials obtained by non-conventional techniques, at the maximum sintering temperature, achieved higher density compare to the samples sintered by CS. An increasing of the temperature does not mean a significant improvement in densification observed in all samples. The samples sintered at 1200 ºC by MW with 10 min of dwelling time has a density enhancement up to 9% compared with CS samples sintered at the same temperature and with 2 h of dwelling time. The employed time in conventional cycle is, approximately, 360 min and non-conventional cycle is 30 min. The economic and time cost is remarkable. According to previous reports [11], microwave heating has been recognized as a promising method to improve the densification in ceramic materials.

During microwave heating, the energy is transferred electro-magnetically to the material and not as a thermal heat flux, enabling the material to be heated at fastest rates and shortest sintering times. The rapid densification of samples by SPS is attributed to the enhanced densification rate due to mechanisms such as particle rearrangement and the breaking up of agglomerates aided by applied pressure and faster heating rates. By rearrangement of particles, the SPS process also impedes the pore size increasing which was generally observed in the first and intermediate stages of sintering [22]. In this method, the sintering of the compact is taking place in a graphite die, the carbon diffuses into the sample from the die where is promoted by the applied pressure. This is an important problem, as the carbon diffusion is linked to the carbon rich atmosphere in which it is performed. Removing this contamination is possible, but this implies high

temperatures (>800 ºC) and a long time inside a furnace (>2 h), resulting in high economic costs.

The phase composition of raw material and sintered samples were studied by XRD. Fig. 2 shows the diffractograms of the starting powders and sintered samples at maximum temperature for each different sintering method. In all cases, glass-free materials have obtained. It can be observed that the major phase identified corresponds to a solid solution of β- eucryptite (PDF file #870602 and 251183). Traces of quartz and spodumene present in the starting powder disappear with heat treatment.

Fig. 3 represents the FE-SEM fracture surface of LAS samples sintered by MW, SPS and CS at highest sintering temperature. Samples obtained by CS (Fig. 3c) show a high porosity compared to MW and SPS samples, this data are consistent with density values.

On the one hand, the uniaxial pressure applied (50 MPa) by SPS device during the sintering cycle promotes the densification. Therefore, these samples exhibit lower porosity and higher density. In SPS, the materials are heated by Joule effect, which causes the surface of particles to receive all the heat and, therefore, are more reactive. The presence of an electrical field can potentially affect surface phenomena by modifying the grain boundary energy and interface kinetics [23]. This high energy induces the formation of sintering neck at an early stage of densification (first sintering step) between adjacent grains [24,25]. This can produce a larger grain size, compared to the microwave technique, in the final stage of sintering.

On the other hand, in contrast to thermal radiation, electromagnetic waves in the microwave spectrum and millimeter-wave range penetrate more in dielectric materials and are absorbed in their volume. In this work, the β- eucryptite besides being a dielectric material is also an absorbent material of the microwave from low temperature (room temperature ~25 ºC) to high temperature (>1400 ºC). This fact is a great advantage because it allows the material to heat itself without the necessity of a susceptor or others external factors. When heating materials with microwave energy, the sintering occurs due to a self-heating of the material and the maximum temperature is found in the core of the material. Therefore, the most energetic area is located within grain center. Consequently, the grain boundary diffusion and subsequent formation of sintering neck is less favored. This effect can lead directly to the second stage of the sintering process; densification and microstructural change [24], skipping the first phase, which causes the neck between grains and thickening. Microwave heating could lead to a delay in the grain growth process (more pronounced than for SPS), resulting enhanced sinterability and involving changes in the final properties of samples, as discussed below.

Other significant difference observed in Fig. 3 is the grain size between the samples sintered by the different methods. The larger the grain size the more important the microcracking phenomenon, leading to a significant and progressive decrease of the bulk β- eucryptite CTE. Microcracks can be readily observed in the FE-SEM images for the CS samples (Fig. 3c). The samples obtained by non-conventional sintering techniques are free of microcracks. The grain size is lower than 8 μm for all the materials obtained; MW 1250 ºC: 2-3 μm; SPS 1300 ºC: 4-5 μm and CS 1300 ºC: 6-7 μm, approximately. Pelletant et al. [26] reported the dependence between the mean

grain size and the quantity of microcracks and located the threshold of microcracks formation in 2.8 μm. In the Bruno et al. [27] study the small grain size material (< 4μm) is nominally free of microcracks. In this novel study, the results indicated that the microcracks formation depends on the technique used, and therefore, to the different mechanisms of heat diffusion, which are responsible of the grain size and microcraks formation.

The coefficient of thermal expansion (CTE) of samples sintered by CS at 1200 ºC, MW at 1200 ºC and SPS at 1300 ºC is visualized in Fig. 4. These samples have been chosen due to the best mechanical values obtained. The temperature range for these measures is from cryogenic temperatures at -150 ºC to 150 ºC. The interest of including cryogenic temperatures in this measurement lies in the spatial applications of β- eucryptite materials such as potential substrates in space satellites mirrors.

In all case, the trend of CTE values of sintered samples is the same: very low, controlled and closed to zero. The averaged values for that range of temperature are; CS (-0.84 ± 0.55)·10^{-6} K^{-1}, SPS (-0.44 ± 0.64)·10^{-6} K^{-1} and MW (-2.17 ± 0.50)·10^{-6} K^{-1}.
Indeed, sample obtained by CS show more negative values of CTE than SPS sample due to the evidence existence of microcracks [27]. Nevertheless, the sample obtained by MW shows the most negative values of CTE in all the range despite there is not evidence of microcracking. The presence of cracks, are not the only reason for the more negative CTE. As proposed by Ramalingam et al., [28] this effect may be attributed to stoichiometry/composition different, variation in processing conditions (sintering/crystallization parameters) and Li-disorder process, additionally to the grain size (and thereby microcracking). In this work, as mentioned above, the grain size is

very similar and the composition of raw powders is the same for all sintered samples, but the microcracking have been only observed in the CS samples. Thus, the most negative CTE values for microwave sintered samples, may be due to Li positional disordering and flattening of the tetrahedral sheets in the structure via tetrahedral tilting [19].

The negative CTE values in the materials obtained by MW will open a new possibility to obtain composites materials with improvement properties adjusting its CTE closed to zero with materials that show positive CTE.

Relationship between hardness and Young's modulus averaged from 250 nm to 750 nm of depth are presented in Fig. 5. The low mechanical values obtained in CS samples are due to the low density, the existence of microcraks in it and the vitreous phase formed around β-eucryptite grains. This amorphous phase has begun to have a significant influence on the mechanical properties. In the Fig. 3c, it can be seen quite clear that the glass-phase begins to form around the grains of β- eucryptite. The glassy content increases with sintering temperature, nevertheless, in this study the content is not very high at maximum temperature as XRD analysis have been demonstrated.

The non-conventional techniques offer a wide range of sintered samples with different hardness and Young's modulus values combinations. The maximum hardness value (7.5 GPa) is achieved for the sample sintered with SPS at 1300 ºC, with a 104 GPa of Young's modulus, whereas that the maximum Young's modulus value is achieved for the MW sample sintered at 1200 ºC (110 GPa) with a 7.1 GPa of hardness value.

A remarkable fact is that fully dense material with excellent mechanical properties can be obtained by microwave sintering at lower temperature (1200 °C). This is an important advance in terms of energy saving and reduction in process duration and, consequently, of the economic cost. This can help to improve the product quality, resulting in the final materials with finer and less defective microstructures and enhanced functional and structural properties [29].

Ultimately, an effective microwave sintering process should enable the manufacturing of components with controllable structure characteristics and macroscopic shape. In the future a possible scale-up to the microwave sintering technology open the possibility to develop new advanced materials with high-quality.

4. Conclusions

The behavior of the β- eucryptite materials obtained by different sintering techniques (CS, SPS and MW) has been carried out in the current investigation. The microwave sintering, compared to others techniques, has a lot of benefits in terms of mechanical properties and microstructural design, as well as in term of speed in the process. β-eucryptite materials sintered by the microwave technique show a full density with a small grain size compared to the specimens sintered by SPS and CS.

The dilatometric data presented for the cryogenic temperature interval, essential for different technological applications, show a controlled CTE and very low thermal expansion behavior in all range of temperatures.

As an important result for future work, is that it has been demonstrated that the role of

the electromagnetic field effect is very important to development and industrial mastering of a microwave sintering technology, capable of producing high-quality materials with unique properties.

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Figure captions

Fig. 1. Microwave cavity of the device and *E* field magnitude distribution in the cavity heating cell.

Fig. 2. Diffractogram of the raw material powder and sintered materials at maximum temperature for each sintered technique. Traces of quartz and spodumene in the starting powder are marked by Q and S, respectively.

Fig. 3. FE-SEM images of fracture surface of samples sintered by a) microwave sintering at 1250 ºC, b) spark plasma sintering at 1300 ºC and, c) conventional sintering at 1300 ºC.

Fig. 4. Coefficient of thermal expansion of materials with highest mechanical properties sintered by three methods; spark plasma sintering, conventional and microwave.

Fig. 5. Relationship between hardness and Young's modulus averaged from 250 nm to 750 nm depths for the sintered samples.