

Fabrication of near-zero thermal expansion of fully dense β -eucryptite ceramics by microwave sintering

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Abstract

Microwave heating is proposed as the non-conventional technique for the sintering of optimal lithium aluminosilicate compositions of the β -eucryptite system. The coefficient of thermal expansion and mechanical properties of the sintered samples has been studied under the influence of microwave heating.

The ad hoc synthesized β -eucryptite together with the microwave sintering technique developed in this work open the opportunity to produce breakthrough materials with low or negative coefficient of thermal expansion and excellent mechanical properties, as Young's modulus of 110 GPa. The combination of rapid heating with low energy applied by the microwave technology (eco-friendly process) and the dramatic reduction in cycle time allows densification without glass phase formation.

Results of the coefficient of thermal expansion of the β -eucryptite ceramics presented here under cryogenic conditions will be of value, for example, in the future design of new composite materials for space applications.

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1. Introduction

Over the past few decades, the lithium aluminosilicate (LAS) compositions have been extensively studied because its very low or even negative thermal expansion compounds have found a wide application field including cookware, bakeware, electronic devices, telescope mirror blanks, ring-laser gyroscopes and optically stable platforms [1,2].

Sintered negative thermal expansion materials have usually low mechanical strength because the expansion anisotropy causes microcracking. This is due to different extents of thermal expansion in different crystallographic orientations, which induces internal stress with temperature change. On the other hand, it has been reported by Pelletant et al. [3] that the

microcracking depends on the grain size, therefore, an increasing the β -eucryptite grain size causes a progressive microcracking and consequently a more negative bulk of thermal expansion coefficient.

Nevertheless, the usefulness of these thermal properties in the production of materials with null expansion has a wide range of potential engineering, photonic, electronic, and structural applications [4,5].

β -Eucryptite is the most negative thermal expansion phase in the lithium aluminosilicate system, and therefore, β -eucryptite has been thoroughly studied [6–8]. Compared with the number of studies of glass-ceramic materials, there are few studies in the literature, which deal with this system as a ceramic material in the solid state [6,9]. This is important because as far as possible obtaining 100% theoretically dense materials in this system in solid state would improve the mechanical properties as such modulus of elasticity compared with glass-ceramic

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materials with similar thermal shock characteristics. In the LAS system, the high temperatures required to fully densify ceramic powders result in large grain sizes due to Ostwald ripening when traditional sintering techniques are used [10]. This makes obtaining dense materials with nanometric and submicrometric grain sizes extremely difficult and, as a consequence, the sintered materials do not achieve high mechanical properties. To overcome the problem of grain growth, non-conventional sintering methods, have emerged as promising techniques [11].

Spark plasma sintering (SPS) was reported in [11] as a non-conventional sintering technique for LAS materials that can lead to high relative dense ceramics with no or with very low amounts of a glassy phase. However, SPS is restricted to materials with disk forms of different diameter, whereas materials with near-net-shape approach have still been not possible to obtain. Moreover, Vanmeensel et al. [12] reported that the temperature distribution inside the tool and specimen is not homogeneous during the field assisted sintering technique, especially, for electrical insulating samples (such as LAS ceramics), due to temperature gradient existing between the border and the center of the sample in the intermediate and final stage of sintering. Other important factor to consider is the high-energy consumption of the SPS technique.

Microwave heating is proposed in this paper as the non-conventional sintering technique to solve the difficulties found with previous techniques such as SPS. The microwave technique was specially designed to fabricate ceramic LAS bodies with high density, very low glass proportion and high mechanical properties (hardness and Young's modulus). 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 [13, 14]. The important characteristics associated to microwave process are such as rapid and uniform volumetric heating, improved production rate, enhancement in densification and grain growth prohibition of ceramics [15–17] and, most importantly it is possible to obtain directly materials without any carbon contamination. This supposes other significant advantage compared with the spark plasma sintering fast method [18].

The ceramic properties processed by microwaves have been evaluated by an analysis of their thermal expansion behavior over a wide temperature range, including cryogenic conditions, which is extremely important for some applications, such as space mirror blanks and other aerospace products.

The experimental control of the expansion properties and sintering conditions of these materials are presented and opens up the possibility of fine-tuning the properties of this kind of materials by adjusting the microwave conditions.

2. Experimental procedure

2.1. Materials

β -Eucryptite solid solution powders with a composition between eucryptite and spodumene were synthesized for this

study following the route proposed in a previous work (see [9] for details). The chemical compositions of the LAS powder correspond to a $\text{Li}_2\text{O}:\text{Al}_2\text{O}_3:\text{SiO}_2$ relation of 1:1.1:2.5 (compositions LAS8 in [9]). Green samples were prepared by cold isostatic pressing (CIP) at 200 MPa of pressure (15 mm height, 10 mm \varnothing). The green density was approximately 1.2 g cm^{-3} , i.e. 49% of theoretical density (2.39 g cm^{-3}).

2.2. Microwave setup

2.2.1. Design of the microwave cavity

A single mode cylindrical cavity operating in the TE₁₁₁ 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. 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 [19]. 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.

Fig. 1 shows the EM fields in the cavity with holes and sample holder given by the EM simulator.

2.2.2. Experimental set-up and microwave components

Fig. 2 shows the schematic diagram of the developed apparatus for microwave sintering.

A rectangular waveguide (not shown in figure) 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 [19].

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.

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).

The fracture surface sections of the sintered samples have been observed using a field emission gun scanning electron microscope (FESEM, HITACHI S-4800, Japan). Nanomechanical properties such as hardness and Young's modulus of samples were obtained by the 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, giving a surface roughness in the nanometer range. The nanomechanical properties of the LAS ceramics were evaluated from the load–displacement nanoindentation data using the widely accepted Oliver and Pharr method [20].

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

The coefficient of thermal expansion was checked in a Netzsch DIL-402-C between –150 and 450 °C.

3. Results and discussion

By using the experimental setup described above, LAS ceramic powder samples were placed in quartz tubes and inserted in the microwave cavity for sintering. No susceptors

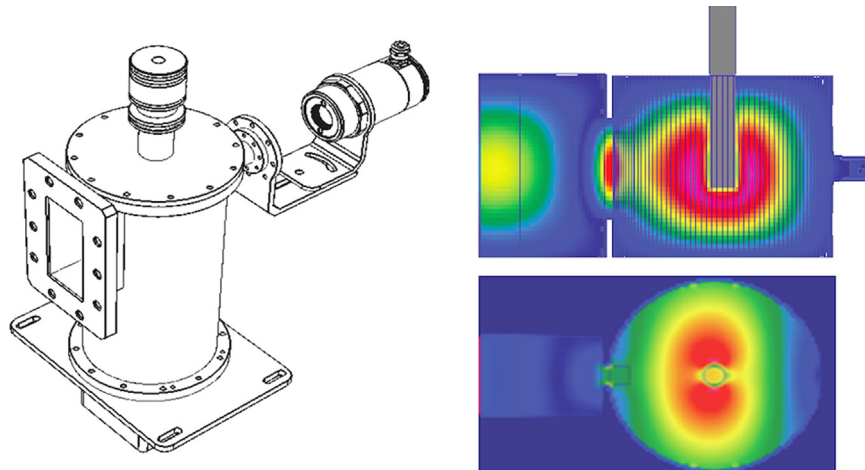


Fig. 1. Microwave E field magnitude distribution in the cavity heating cell.

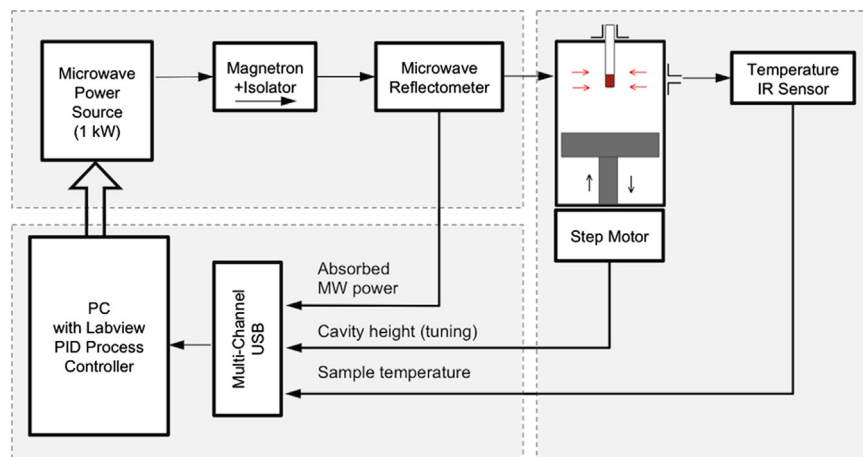


Fig. 2. Schematic of the developed apparatus for microwave sintering.

were required to assist the initial heating period during the trials. The samples were fired in air atmosphere at a heating rate of $100\text{ }^{\circ}\text{C min}^{-1}$ to temperatures between 1200 and $1250\text{ }^{\circ}\text{C}$ with a short dwell time of 5 and 10 min. Overheating of the samples was avoided by an exhaustive control of the heating rate. The cooling rate of the microwave-heated samples was also controlled by reducing the amount of power supplied to the controller. As a result, the samples were exposed to the microwave field during the cooling process, as well as during heating. Fig. 3 shows the temperature profile and microwave absorbed power during the sintering process of a LAS specimen. The figure shows a microwave experiment with a resident time of the ceramic sample of 10 min around $1200\text{ }^{\circ}\text{C}$.

Table 1 summarizes the results in terms of density and coefficient of thermal expansion (CTE) of the microwave sintering (MW) samples.

Dense ceramic bodies with low volumetric proportion of vitreous phase ($<2\text{ vol}\%$) were obtained after sintering at temperatures of 1200 and $1250\text{ }^{\circ}\text{C}$. Density values were very high and close to theoretical values for all materials. Even for relatively low temperature ($1200\text{ }^{\circ}\text{C}$) density increased remarkably in comparison with density values obtained by means of pressureless conventional sintering [9]. In this work it is necessary to elevate the temperature up to $1300\text{ }^{\circ}\text{C}$ to obtain materials with only 96% of density.

Fig. 4 shows the elongation vs. temperature curves for each of the sintered samples. These data allow calculation of the thermal expansion coefficient data (or technical α values) in the temperature ranges described in Table 1.

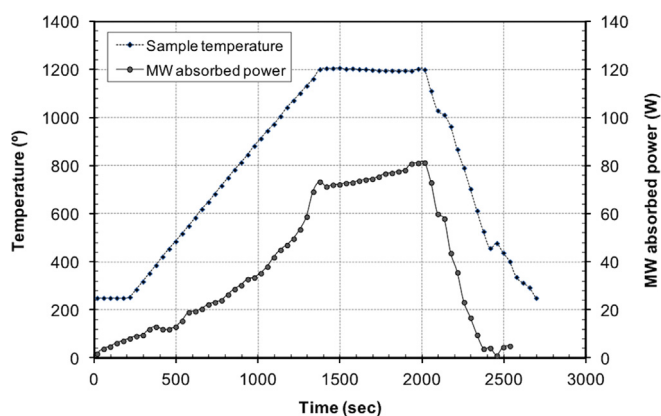


Fig. 3. Temperature profile and microwave absorbed power during the sintering process of the LAS specimen.

Table 1
Density and CTE values of the sintered samples by microwave sintering.

Temperature ($^{\circ}\text{C}$)	Dwell time (min)	Density (%)	CTE -150 to $+150\text{ }^{\circ}\text{C}$ ($\times 10^{-6}$) (K^{-1})	CTE -150 to $+450\text{ }^{\circ}\text{C}$ ($\times 10^{-6}$) (K^{-1})
1200	5	99.0	-3.01 ± 0.05	-2.62 ± 0.05
1200	10	99.1	-2.41 ± 0.05	-1.44 ± 0.05
1250	5	99.2	-1.22 ± 0.05	0.41 ± 0.05
1250	10	99.2	-2.04 ± 0.05	-1.30 ± 0.05

The coefficient of thermal expansion (CTE) was very low for all the samples, with values between -3.01 and $+0.41 \times 10^{-6}\text{ K}^{-1}$, depending on the final sintering temperatures and the temperature interval of the measurement. In general, as can be seen in Fig. 4, the sintered LAS samples have negative expansion behavior in the low temperature range, which slightly changed to positive in the high temperature range for some samples. In sample sintered at $1250\text{ }^{\circ}\text{C}$ with 5 min, a roughly flat curve can be observed between room temperature and $+150\text{ }^{\circ}\text{C}$, with almost null elongation. In general, the CTE of all samples in range of -150 to $+150\text{ }^{\circ}\text{C}$

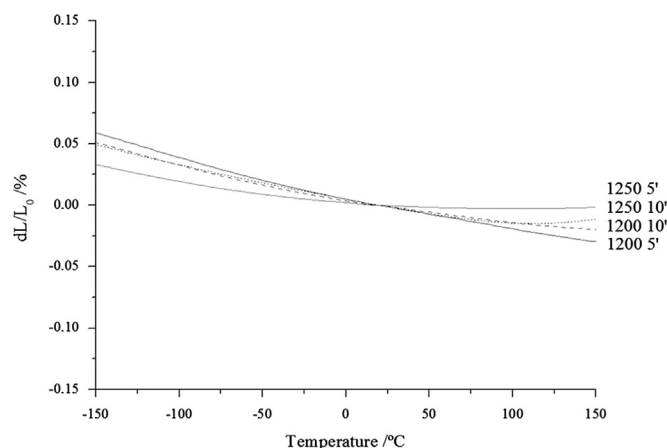


Fig. 4. Elongation vs. temperature of the sintered samples by MW at different temperatures.

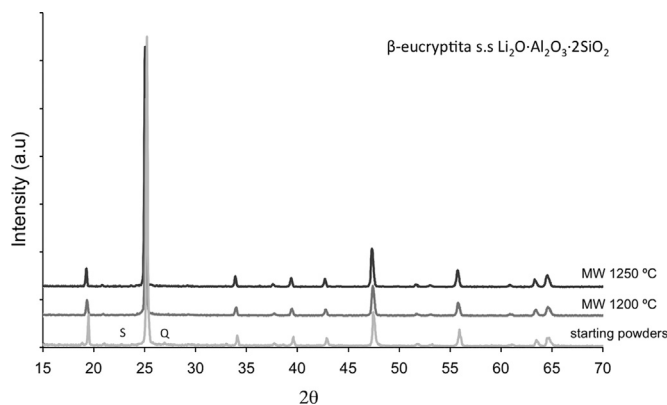


Fig. 5. Diffractogram of the starting material powder and sintered materials at 1200 and $1250\text{ }^{\circ}\text{C}$ with 10 min of dwell time. The diffraction maxima correspond to β -eucryptite phase (PDF file #870602 and 251183), traces of quartz and spodumene in the starting powder are marked by Q and S, respectively.

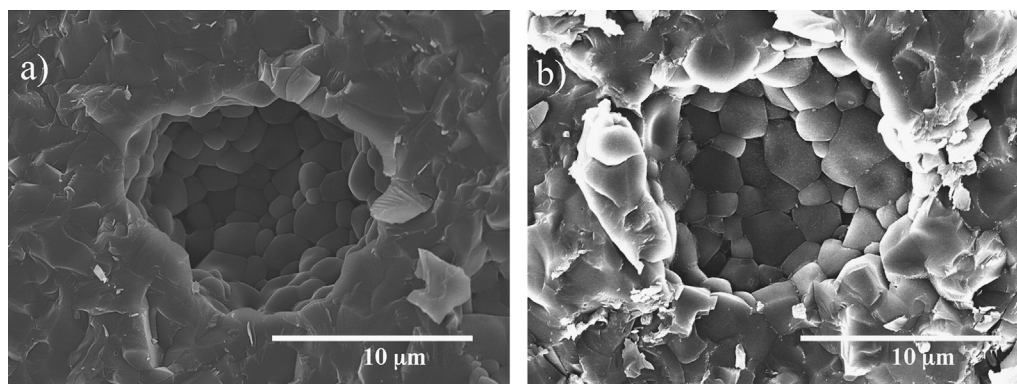


Fig. 6. FE-SEM images of fracture surface of samples sintered by microwave sintering at (a) 1200 °C/10 min and (b) 1250 °C/10 min.

Table 2
Hardness and Young's modulus values of the sintered samples by the microwave technique.

Temperature (°C)	Dwell time (min)	Hardness (GPa)	Young's modulus (GPa)
1200	5	6.7 ± 0.4	101 ± 4.5
1200	10	7.1 ± 0.4	110 ± 3.4
1250	5	6.0 ± 0.4	100 ± 4.2
1250	10	5.9 ± 0.4	86 ± 3.1

is near-zero and controlled, this fact, is necessary for a wide range of industrial applications.

The mineral phases present in each of the sintered samples were identified by XRD. The major phase identified in both, starting powder material and sintered by the microwave technique at different temperatures, is β -eucryptite LAS phase (Fig. 5). Therefore, it was observed that the composition $\text{Li}_2\text{O}:1.1\text{Al}_2\text{O}_3:2.5\text{SiO}_2$ corresponded to a solid solution of eucryptite. It is noticeable that β -eucryptite was stable without any need for additives like ZrO_2 [21]. The estimated glass proportions in all cases for the sintered samples were below 2 wt%.

Another way to obtain fully dense eucryptite ceramics was using $\text{Li}_2\text{O}-\text{GeO}_2$ as a sintering additive [22]. Using the microwave sintering method, high densities and comparable mechanical properties are obtained in a more simple method.

Fig. 6 represents the FE-SEM fracture surface of LAS samples sintered by microwave at 1200 °C and 1250 °C with 10 min of dwelling time. There is a clear difference in the grain size between samples sintered at 1200 °C with respect to the obtained at 1250 °C. The studied microstructures reveal that the grain size in the sintered samples was usually between 1 and 4 μm . Samples obtained show a low porosity, this data also verify the densities values.

In Fig. 6, it can be seen quite clearly that there is no glass-phase, as XRD analysis has been demonstrated. García-Moreno et al. found some details of the glass phase for the LAS compositions sintered by conventional sintering at 1100 °C and at 1250 °C [9]. At these temperatures, the authors have been

reported a grain size between 5 and 10 μm , respectively. Therefore, by the microwave technique it is possible to achieve a smaller grain size than conventional sintering.

For space applications such as mirrors or structural systems where high dimensional stability is needed, low thermal expansion and good mechanical properties are demanded together. Table 2 lists the hardness and Young's modulus of the LAS materials sintered at different temperatures and dwelling time by the microwave technique.

The hardness and Young's modulus significantly increase with sintering temperature to 1200 °C. Mechanical properties appeared highly dependent on sintering conditions. Young's modulus of 110 GPa and hardness of 7.1 GPa measured on LAS material sintered at 1200 °C allow the use of this material in some existing spatial applications. These, highly dense materials were prepared at relatively low sintering temperatures hindered the formation of a glassy phase in the LAS system. The presence of glass phase may affect the mechanical properties of those materials [23].

The relatively low sintering temperatures needed to obtain theoretical density values in our materials are essential, as they make the mechanical values increase due to the low proportion of glassy phase formed during microwave sintering. All these features can be combined for special-designing an ultra low CTE material. This had already been achieved by using glass-ceramic materials such as Zerodur [24] or even pure LAS ceramics obtained by the conventional method [10] and the $\text{NaZr}_2\text{P}_3\text{O}_{12}$ (NZP) family [25–27], but the high mechanical values of these LAS materials presented here fulfill more demanding requirements for the final application of these materials. The ad hoc synthesized β -eucryptite together with the microwave sintering technique developed in this work open the opportunity to produce breakthrough materials with low or negative CTE and excellent mechanical properties, as a Young's modulus of 110 GPa. The combination of rapid heating with low energy applied by the microwave method (*eco-friendly process*) and the dramatic reduction in cycle time allows densification without glass phase formation.

It is important to remark that materials with close to zero CTE value commonly used for different applications are glass-

ceramic materials with poor mechanical properties or reinforced with carbides such as SiC or TiC. This kind of reinforcements limits the use of these materials to non-oxidizing atmospheres. The materials presented in this work have improved mechanical properties and stability in oxidizing conditions.

4. Conclusions

A microwave system has been developed to investigate microwave heating as the non-conventional sintering technique of β -eucryptite ceramic powders. An important advantage found for this technique is the fabrication of complex parts (near-net-shape components) directly in the microwave furnace without the application of pressure. This point is essential in order to use this sintering technology where the final dimension of the sintered component has to be almost constant in order to reduce the final machining cost of nanocomposites.

This study confirmed the possibility of successfully obtaining for the first time well-densified β -eucryptite ceramics by using the microwave sintering technology. The use of this technology allows the densification of the β -eucryptite with glass-free at relatively low temperatures (1200 °C) and time (5 min of dwell time).

The dilatometric data presented for the cryogenic temperature interval is essential in order to design these kinds of materials for space applications in which controlled and very low thermal expansion behavior are needed at very low temperatures. This is the case of mirror blanks in satellites, where exceptional thermal properties are demanded together with exceptional mechanical properties, i.e., the β -eucryptite sample sintered at 1200 °C with 10 min of dwell time shows Young's modulus of 110 MPa and hardness of 7.1 GPa values. Compared with others heating modes, conventional and spark plasma sintering, the most important characteristics associated to microwave process are the rapid and volumetric heating, which improves the final properties of the materials.

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