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High thermal stability of β-eucryptite materials with low-ε_r obtained by microwave technology

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ABSTRACT

Low-temperature sinterable microwave $LiAlSiO_4$ solid-state material-based was investigated with regard to microwave dielectric properties as functions of the sintering temperature. β-eucryptite materials and alumina-reinforced β-eucryptite composites were sintered by microwave technology at 1100 ºC and 1200 °C. The combination of fast heating and the dramatic reduction in cycle time along with the non-conventional heating source, open the opportunity to produce materials with multifunctional desired properties.

The microstructure and crystalline composition of the materials were characterized, and the mechanical, thermal and microwave dielectric behavior were analyzed. XRD showed good chemical stability materials without reaction between phases during microwave sintering process. The excellent mechanical (~ 8 GPa of hardness and ~ 100 GPa of Young's modulus) thermal ($-0.23 \cdot 10^{-6}$ K^{-1}) and microwave dielectric properties (ε_r = 4.10, Q = 1494), were obtained from the LAS/Al_2O_3 composites sintered at very low temperature (1100 ºC). The results achieved show the possibility of designing ceramic nanocomposites at low sintering temperature using microwave technology with near-zero thermal expansion coefficients, high mechanical and chemical stability and low dielectric properties.

Keywords: A. Microwave processing; B. Microstructure-final; C. Dielectric properties; C. Thermal expansion; Ceramics.

1. INTRODUCTION

Over the past half-century low dielectric materials have been intensively researched by ceramic and polymer scientists. However, these materials possess a vast myriad of electrical, thermal, chemical, and mechanical properties that are just as crucial as the name that classifies them. Therefore, in many cases, the applications of low dielectric constant materials are dictated by these other properties, and the choice of low dielectric material may have a tremendous effect on a device's performance and lifetime [1].

Many investigations have been conducted to develop advanced ceramic substrate materials which can be used as microwave integrated circuits (MICs) for applications related to satellite communications, wireless local area networks, and car collision

avoidance systems [2-4]. These materials must meet stringent requirements, such as a low dielectric constant (ε_r), a high quality factor (Q), dimensional, thermal and chemical stability, and excellent mechanical properties (hardness and Young's modulus). Therefore, the main challenge for researchers in the microelectronic industry is not only to develop materials with the lowest dielectric constant, but also to find materials that satisfy all of the electrical, thermal, chemical, and mechanical properties required for optimal device performance.

Many ceramic materials have been widely investigated as candidates for advanced microwave dielectric materials, i.e, Al_2O_3 [5], $Mg_xNb_2O_9$ [6,7], Zn_2SiO_4 [8], $Sm_3Ga_5O_{12}$ [9] and complex perovskite compounds [10, 11]. Although good microwave dielectric properties were obtained, the other properties were not satisfactory. Other negative factor is the high sintering temperature needed to obtain these materials and, accordingly, the high cost added, which has restricted its use [12,13]. Therefore, it is necessary to develop new advanced materials with exceptional properties that satisfy minimum requirements.

In order to reduce the sintering temperature and therefore lower economic cost without impairing the other properties, the microwave sintering technique has been used in this research. 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 [14-17]. Benavente and coworkers [18] have developed a microwave equipment that has been specially designed to fabricate ceramic materials of lithium aluminosilicate (LAS) stable in solid state with high density, and high mechanical properties (hardness and Young's modulus). The important characteristics associated with the microwave sintering process of ceramic materials are, e.g. rapid and uniform volumetric heating, improved production rate, enhancement in densification

and inhibition of the grain growth. Since the last years, a wide variety of ceramics ranging from dielectric materials to transparent ceramics have been obtained by this technique [19-21].

The $LiAlSiO_4$ ceramics have been known to have negative thermal coefficient [22], but have very poor intrinsic mechanical properties and low elastic modulus. Alumina-reinforced LAS materials are proposed as a solution to obtain composites with improved mechanical, thermal and microwave dielectric properties compared to the LAS monolithic ceramics. The results of García-Moreno et al. [23] have demonstrated experimentally that alumina and β-eucryptite are compatible in solid-state, which opens the opportunity of designing new advanced materials. For these purposes, Alumina powders and an *ad-hoc* synthesized β-eucryptite solid-state, were used to fabricate LAS/Al_2O_3 composites by microwave sintering method. The sintering capability of this composite at low temperature by microwave and their mechanical and dielectric properties, and thermal stability are presented and discussed.

2. MATERIALS AND METHODS

2.1. Microwave setup

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 (Fig 1). The *E* field has a maximum (E_r and E_φ components) in the center, where the samples are located in a quartz tube [18]. A movable short-circuit at the bottom of the cavity allows to tune the cavity dynamically, due to the changes in the dielectric constant of the heated test sample during the sintering process [24]. The possibility to tune the cavity also permits to follow a heating slope previously defined by the user to avoid too fast or

too slow heating speed.

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 and transmissivity of the composites at different temperatures was calculated before sintering process.

The microwave dielectric values were measured, before sintering and once the samples were sintered, in a TM_{0np} cavity with the circuit analysis method as described in [25].

2.2. Experimental procedure

β-eucryptite solid solution (hereafter referred to as LAS) with chemical composition 1:1.01:3.11 Li_2O:Al_2O_3:SiO_2 was synthesized as described in a previous work [22]. The resulting powder was composed of β-eucryptite with an average grain size of 2 μm. The raw material used in this study as a second phase was commercial α-Al_2O_3 nanopowder (Taimei TM-DAR Chemicals Co. Ltd, Japan) with an average particle size of 160 nm. The powder mixtures were dispersed in ethanol and processed by a high-energy attrition mill (Union Process, USA) for 1 h at 400 rpm. The composition of the mixture was LAS/10vol.% Al_2O_3.

Cylindrical specimens of 10 mm diameter and about 15 mm height were prepared by isostatic pressing (200 MPa).

The bulk density of the sintered samples was measured by Archimedes' principle (ASTM C373-88).

The crystalline phase composition of the bulk ceramic composites was determined by X-ray diffraction (XRD, BRUKER AXS D5005, Karlsruhe, Germany). The

measurements were taken in the 15-60 º range and the step size and time of reading were 0.02 º and 0.3 s, respectively.

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 nanoindentation technique (Model G200, MTS Company, USA). Tests were performed under maximum depth control, 2000 nm, using a Berkovich diamond tip previously calibrated with silica. The contact stiffness (S) was determined by the Continuous Stiffness Measurement technique (CSM) to calculate the profiles of hardness (H) and elastic modulus (E) [26]. Amplitude was programmed to 2 nm with 45 Hz frequencies. A matrix of 25 indentations was made on each sample. Previous to the nanoindenter testing, the samples were prepared by metallographic techniques.

The coefficient of thermal expansion, CTE, was checked in a Netzsch DIL-402-C between -150 and 400 ºC.

3. RESULTS AND DISCUSSION

Table 1 presents the relative density and mechanical values of the sintered LAS materials and LAS/Al_2O_3 composites fabricated by microwave sintering.

As can be observed, the density of LAS materials increased strongly with sintering temperature. The relative density rises from 91% to 99% T.D. by increasing the sintering temperature 100 ºC. This temperature increment has been very important to close residual porosity. Density values of LAS/Al_2O_3 composites are very high and close to theoretical values. It is important to appreciate that full densification of LAS/Al_2O_3 composites is achieved at a rather low temperature (1100 ºC) for

pressureless sintering method (microwave). In previous studies, the temperature needed to reach full densification of LAS/Al_2O_3 composites was ~ 1350 ºC for pressureless method (conventional sintering) and 1150 ºC for pressure method (spark plasma sintering) [27]. Reducing sintering temperatures avoids formation of glassy phase, with a positive effect on the final mechanical properties of the materials, as described in Table 1.

The phase composition of the materials was studied by XRD. Fig 2 show the diffractograms of the LAS and LAS/Al_2O_3 composites obtained at the maximum sintering temperature. In LAS material, the major phase identified corresponds to a solid solution of β-eucryptite (PDF 870602). There remain some small traces of β-spodumene (PDF 350797) that have already been in the initial powders. LAS/Al_2O_3 composite shows two crystalline phases: β-eucryptite and α-alumina (PDF 77-2135). This result indicates that reaction between two phases has not occurred during sintering heating.

Young's modulus (E) and hardness (H) values are summarized in Table 1. Values are averaged from 250 nm to 1500 nm of depth. LAS/Al_2O_3 composites show mechanical properties substantially higher than those for LAS materials. Adding 10 vol.% of alumina to LAS matrix leads to an increment of the mechanical properties of ~ 350% for hardness values and ~ 160% for Young's Modulus, in the material obtained at 1100 ºC. The composite obtained at 1200 ºC improved the H values by ~ 40% and E values by ~ 60% with respect to monolithic material values at the same temperature. The E and H values that were achieved in the LAS/Al_2O_3 composites are excellent, for both temperatures, but the ones obtained at 1000 ºC are extraordinary. It is remarkable that the temperature needed to achieve maximum mechanical values by SPS was 1200 ºC [27]. The exceptional value of Young's modulus reached at low temperature, allows the

ability to design and make materials with particular desired properties, as use in some space applications. In contrast to LAS/Al_2O_3 composites mechanical behavior, LAS materials exhibit an improvement in E and H with the increasing sintering temperature. Microstructure of surface fracture of LAS and LAS/Al_2O_3 composites sintered at 1100 ºC and 1200 ºC are shown in Fig 3.

There is a difference between the grain size of the β-eucryptite in LAS materials, 5-6 μm, and that obtained in the LAS/Al_2O_3 composite, 2-3 μm. Alumina, homogeneously dispersed in the LAS matrix, has performed as an inhibitor of the β-eucryptite grain size, even at very low sintering temperatures (1100 °C). The grain inhibition may be due, on one hand, to the position of the alumina particles at grain boundaries, which would promote a higher density and mechanical reinforcement at lower temperature. On the other hand, the homogeneous alumina particles dispersion, may improve the electromagnetic field distribution inside the sample, and lead to a more constant and uniform microwave energy absorption by both phases throughout the composite.

In terms of porosity, LAS/Al_2O_3 composites obtained at 1100 and 1200 ºC reveal complete elimination of residual porosity. LAS material, though, displays residual porosity between grains, at 1100 ºC.

Fig 4 displays the elongation vs. temperature curves for LAS materials and LAS/Al_2O_3 composites sintered by microwave technology. All the materials have stable dilatometric behavior and close to zero elongations in the measured temperature range. LAS materials exhibit a slight negative slope on the dilatometric curve with a change to negative values around 100 °C, for both materials. This negative slope is attenuated by

increasing the sintering temperature, showing greater stability data. The addition of alumina has lead to the higher stability in curves with less dispersion of dilatometric values throughout temperature range. Alumina has a dilatometric behavior involving dimensional expansion with temperature. This expansion has offset the slight contraction suffered by the LAS material in LAS/Al_2O_3 composite, showing a flat straight parallel to zero. Dilatometric values have no significant changes as sintering temperature is increased.

The coefficient of thermal expansion calculated from the dilatometrics curves (CTE referred to 25 ºC) is summarized in Table 2. CTE values are shown in two temperature ranges, one including cryogenic conditions, -150 to 400 ºC, and another from room temperature, 25 to 400 ºC. The reason for including cryogenic temperatures is due to the spatial applications of β-eucryptite materials as potential substrate in space satellites' mirrors [28]. CTE is close to zero over a wide temperature range, in all cases. The dilatometric behavior shown is numerically corroborated by CTE. LAS material stabilizes its CTE values with sintering temperature. However in LAS/Al_2O_3 composites, CTE is hardly influenced by the sintering temperature. This result indicates that it is not necessary to use high sintering temperatures to obtain LAS/Al_2O_3 composites with improved thermal properties, as it occurred with the mechanical properties.

Table 3 gives the microwave dielectric characteristics of all materials before and after sintering at different temperatures. Before sintering, dielectric parameters, measured in term of ε_r and Q, are closed for the different materials. After sintering, the values of ε_r increase while the Q value decreases, hence the importance of obtaining perfectly consolidated materials at low sintering temperature. The dielectric constant of all

materials depends mainly on the density of the samples. The ε_r value of the LAS sintered at 1100 °C was 3.91, probably due to the low relative density, and the ε_r increased with the sintering temperature to a maximum value of 4.1 for the LAS/Al_2O_3 sintered at 1100 °C. Therefore, the LAS/Al_2O_3 ceramics had a small ε_r value, which is required to minimize the cross-coupling effect with conductors ($\varepsilon_r < 10$) [5].

4. CONCLUSIONS

The microstructure of composites shown null porosity and fine grain size compared with monolithic LAS materials, which implies different thermal and mechanical behaviour. Fully dense LAS/Al_2O_3 composites sintered at very low temperature (1100 ºC) exhibit a good combination of low dielectric constant and excellent thermal and mechanical stability. This sintering temperature is the lowest it has been found so far in the literature, which implies a very high energy-savings and an economic cost and environment very attractive to many industrial applications.

The studied materials have suitable and interesting dielectric properties to be used in microwave integrated circuits (MICs), in applications related to telecommunications. Therefore, microwave sintering technology has demonstrated that is a good tool to obtain materials with exceptional characteristics, which make them promising for applications as multi-functional materials.

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Figure captions

Fig 1. Circular cavity of the developed microwave device.

Fig 2. Diffractogram of the LAS and LAS/Al_2O_3 sintered materials at maximum temperature.

Fig 3. FE-SEM images of fracture surface of the sintered samples at different temperatures.

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

Tables captions

Table 1. Sintering temperature, relative density, hardness and Young's modulus of materials obtained by microwave technique.

Table 2. Coefficient of thermal expansion of materials sintered by microwave technique at different temperatures.

Table 3. The microwave dielectric values at room temperature for the materials before and after microwave sintering.