

# Laminated object manufacturing of LZSA glass-ceramics

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## Abstract

**Purpose** – This paper seeks to detail the fabrication of a glass-ceramic substrate, based on the  $\text{LiO}_2\text{-ZrO}_2\text{-SiO}_2\text{-Al}_2\text{O}_3$  (LZSA) system, by laminated object manufacturing (LOM) using water-based cast tapes.

**Design/methodology/approach** – Small amounts of  $\text{ZrSiO}_4$  were added to control the thermal expansion coefficient (TEC) of the original glass-ceramic (LZSA5Zr: LZSA + 5 wt%  $\text{ZrSiO}_4$ ). In order to verify the influence of the amount and nature of crystalline phases on the thermal and dielectric behavior of the material, LZSA and LZSA5Zr laminates were sintered at 700°C for 30 min and crystallized at either 800 or 850°C for 30 min.

**Findings** – LZSA laminates (sintered and crystallized at 700 and 800°C, respectively) exhibited a relative density of ~90 percent, a dielectric constant of 8.39, a dielectric loss tangent of 0.031 and TEC of  $5.5 \times 10^{-6} \text{ K}^{-1}$  (25-550°C). The addition of 5 wt%  $\text{ZrSiO}_4$  to original LZSA glass-ceramics led to a nearly constant TEC value of  $6 \times 10^{-6} \text{ K}^{-1}$  throughout the whole temperature interval (25-800°C). Dielectric properties of LZSA5Zr did not show any remarkable change when compared to original LZSA.

**Originality/value** – The thermal, mechanical and electrical properties of LZSA glass-ceramic laminates fabricated by LOM makes them potential candidates for substrate applications.

**Keywords** Ceramics and glass, Thermal expansion, Dielectric properties, Laminated object manufacturing

**Paper type** Research paper

## 1. Introduction

Among other applications, glass-ceramic substrates may be employed for microelectronic packages, using the so-called low-temperature co-fired ceramic (LTCC) approach (Pannhorst, 1995; Moulson and Herbert, 2003; Birol *et al.*, 2006). The substrates used in microelectronic packages must fulfill several requirements such as: low dielectric constant for optimized transmission of signals, high dielectric strength, compatible thermal expansion coefficient (TEC) with the printed components, high mechanical strength, smooth surfaces free of distortion and of visual defects, and low cost/high production (Prudenziati, 1994; Shimada *et al.*, 1983).

The majority of the ceramic substrates used in microelectronics are based on alumina, beryllia, magnesia,

zirconia, and glass-ceramics (Prudenziati, 1994; Shimada *et al.*, 1983). The selection of the substrate is related to the application area of interest. It requires a careful evaluation of the chemical, mechanical, thermal, and electrical properties of the potential candidate. LTCC substrates based on glass-ceramic fulfill most of these conditions, whilst providing other benefits such as flexibility of design and fabrication in addition to reduced sintering temperatures. However, the production of these components demand fundamental and advanced ceramics processing techniques like powder preparation (Reed, 1995; Lange, 1989), colloidal processing (Lewis, 2000; Horn, 1990), and tape casting (Mistler, 1998; Hellebrand, 1996).

Sintering of the  $\text{LiO}_2\text{-ZrO}_2\text{-SiO}_2\text{-Al}_2\text{O}_3$  (LZSA) glass-ceramic system occurs by viscous flow (Montedo *et al.*, 2008). The effect of  $\text{ZrO}_2$  substitution by  $\text{Al}_2\text{O}_3$  in the  $\text{LiO}_2\text{-ZrO}_2\text{-SiO}_2$  (LZS) system (de Oliveira *et al.*, 2000) resulted in decrease of the glass transition temperature ( $T_g$ ) and consequently increase of the material sinterability.

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A 10 wt% substitution of  $ZrO_2$  for  $Al_2O_3$  led to a reduction on the  $T_g$  of this materials from 558 to 504°C (Montedo *et al.*, 2008).

Laminated glass-ceramic produced by laminated object manufacturing (LOM) (Gomes *et al.*, 2008) exhibited high values of flexural strength at relatively high porosities when compared to LZSA bodies obtained by other processing techniques such as injection molding (Giassi *et al.*, 2005), extrusion (Bertan *et al.*, 2009) or roll pressing (Reitz *et al.*, 2006). Compared to other processing techniques, LOM can combine adequate values of mechanical strength with the possibility to produce complex 3D parts.

In previous works, the colloidal processing parameters of LZSA suspensions (Gomes *et al.*, 2009) as well as correlations between green and sintered laminate properties (Gomes *et al.*, 2008) were presented. The purpose of this work is to investigate thermal, mechanical and electrical properties of LZSA glass-ceramic laminates fabricated by LOM, as potential candidates for substrate applications.

## II. Materials and methods

Table I shows the optimized processing parameters to fabricate LZSA materials from water-based tapes laminated by LOM. Further details are given elsewhere (Gomes *et al.*, 2008, 2009). Parent glass tapes of LZSA have been produced by aqueous tape casting and laminated by LOM. LZSA substrates were obtained after sintering at 700°C for 60 min and crystallization at either 800 or 850°C, respectively, for 30 min. Moreover, laminates based on LZSA system have been fabricated by addition of 5 wt%  $ZrSiO_4$  (average particle size of 4.5  $\mu m$ ) to the original system (here named LZSA5Zr).

The TEC was determined by the dilatometric analysis of sintered samples in air with a heating rate of 10°C/min (DIL402C, Netzsch, Germany). Flexural strength was measured by three-point test (4204, Instron, Germany) using prismatic specimens with 27.0  $\times$  3.5  $\times$  2.5 mm<sup>3</sup> after lamination of 20 tapes. The measurements were conducted at ambient temperature and a grip separation speed of 5 mm/min while the fracture surface of the laminates after flexural tests has been analyzed by scanning electronic microscopy, SEM (FEI, Quanta, Czech Republic).

Dielectric constant ( $\epsilon$ ) and dielectric loss ( $\tan \delta$ ) data have been measured at a frequency of 1 MHz on laminates in the form of pellets of 20 mm diameter and 1.2 mm thickness after lamination of ten tapes and submitted to the same thermal treatment conditions already described above. The planar surfaces of the samples have been coated by a thin layer of

Au for 45 s at constant tension of 190 V and current of 35 mA (SCD 040, Balzers Union, Switzerland).

The crystalline phases of the LZSA system with and without  $ZrSiO_4$  were identified by X-ray diffraction analysis (Kristalloflex D500, Siemens, Germany) using the  $CuK_{\alpha}$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ) at 40 kV and 30 mA with a divergence slit of 1°. Samples were rotated to minimize the effect of preferential orientation and analyzed in powder form with particle size smaller than 45  $\mu m$ , using a step size of 0.02°, dwell time of 2 s per step and  $2\theta$  between 10 and 90°. ICSD and JCPDS data banks were used for identification of the resulting crystalline phases. The quantitative analysis of the crystalline phases has been performed by the Rietveld method (Kemethmüller *et al.*, 2006; Wiles and Young, 1981). The refinement of the X-ray patterns as well as the simulation and quantification of the crystalline phases were performed by the X'Pert HighScore Plus program (Philips, The Netherlands).

## III. Results and discussion

### III. 1 Thermal expansion behavior of laminates

The thermal expansion behavior of the LZSA laminates changes significantly with the temperature. The system is characterized by two main TEC regions:  $3.5\text{-}5.5 \times 10^{-6} \text{ K}^{-1}$  (25-550°C) and  $5.5\text{-}14.3 \times 10^{-6} \text{ K}^{-1}$  (550-800°C). The increase of TEC at temperatures above 550°C could be attributed to some changes in the crystalline phases. In the particular case of  $ZrSiO_4$ , there is anisotropy in thermal behavior: the thermal expansion in c-direction is higher than that in a-direction, which is more pronounced at temperatures above 520°C (Bayer, 1972, 1973).

Two approaches were used to optimize the thermal expansion behavior of the LZSA system. First, the system has been submitted to crystallization at 800°C for 30 min. The crystallization at lower temperatures should induce the formation of crystalline phases with lower thermal expansion, such as  $\beta$ -spodumene ( $2.0 \times 10^{-6} \text{ K}^{-1}$ ) (Pannhorst, 1995) and  $ZrSiO_4$  ( $4.1 \times 10^{-6} \text{ K}^{-1}$ ) (Bayer, 1972). In a second approach, LZSA5Zr laminates were produced by adding 5 wt%  $ZrSiO_4$  to the LZSA glass precursor and then submitted to same thermal treatment: sintering at 700°C for 60 min and crystallization for 30 min at 800 and 850°C.

The crystallization of LZSA5Zr both at 800 and 850°C resulted in a material with nearly constant TEC value of  $\sim 6 \times 10^{-6} \text{ K}^{-1}$  throughout the temperature range from 25 to 850°C. Nearly constant values of TEC for LZSA5Zr when compared to LZSA may be explained by phase

**Table I** Optimized processing parameters for manufacturing of LZSA laminates from tapes produced by aqueous tape casting

	Process parameters				
	Tape casting	LOM		Thermal treatment	
<b>Composition (wt%)</b>	Dispersant: 1.5 (Darvan CN)	Roll temperature (°C)	80	Debinding	22-215°C: 9.5°C/min
	Binder: 33.3 (PVA, 31.5 wt% solution)	Lamination speed (cm/s)	25		215-261°C: 0.3°C/min
	Plasticizer: 0.8 (PEG, 400 g/mol)				261-433°C: 1.3°C/min
	Anti-foamer: 0.50 (Agitan 357)				433-700°C: 3.2°C/min
	Content of solids: 47.8	Retract	0.10	Sintering temperature (°C)	700
<b>Casting speed (mm/min)</b>	450	Laser power (%)	100	Dwell time (min)	60
<b>Blades gap (<math>\mu m</math>)</b>	600 and 400	Laser speed (cm/s)	50	Crystallization temperature (°C)	850
<b>Casting substrate</b>	PET uncoated film	Tape orientation	0°/90°	Dwell time (min)	30

stabilization in LZSA5Zr material due to presence of  $ZrSiO_4$  (Table II).

Table II shows the relative percentages of the detected phases after the Rietveld refinement using powder data as well as the respective parameters of the unit cell. The theoretical structural data of each phase were extracted from the ICSD data bank (GMELIN, 2007). The main crystalline phases formed were  $\beta$ -spodumene and  $ZrSiO_4$ . Considerably low content of lithium metasilicate and zirconium oxide were also detected.

The variation in the crystallization temperature of the material from 800 to 850°C led to an increase in the relative content of the crystalline phase  $ZrSiO_4$  from 5 to 16 percent and consequently a reduction in the content of  $ZrO_2$  from 5 to 2 percent. Concerning the LZSA materials, an increase was observed in the formation of the crystalline phase  $Li_2SiO_3$  from 10 to 13 percent. On the other hand, the variation in the crystallization temperature from 800 to 850°C in LZSA5Zr did not promote a significant effect in the formation of the crystalline phase  $\beta$ -spodumene and  $ZrSiO_4$  (68-66 and 19-22 percent, respectively).

### III. 2 Microstructure and mechanical properties of glass-ceramic laminates

Table III shows the properties of the laminated glass-ceramics after sintering at 700°C for 60 min and crystallization at 800 and 850°C for 30 min.

It can be observed that the presence of  $ZrSiO_4$  particles decreases the strength of the glass-ceramic material due to the development of higher porosities on the final material. Strength values were reduced from 127 and 125 to 96 and 80 MPa, while relative densities drop around 3-7 percent, for crystallization temperatures at 800 and 850°C, respectively.

The flexural strength of LZSA and LZSA5Zr glass-ceramics has shown the same tendency in relation to porosity and temperature of crystallization. The increase in the porosity and crystallization temperature led to decrease on the flexural strength. Nevertheless, the bending strength of the laminated LZSA produced by LOM was higher than those of samples fabricated by roll pressing (Reitz *et al.*, 2006), at similar relative densities (Figure 1). For LOM laminates, the highest values of flexural strength (~127 MPa) obtained for the LZSA system have been found for samples with relatively high porosity (~11 percent) (Reitz *et al.*, 2006). These strength values are higher than the most of those strengths assigned to injection-molded (Giassi *et al.*, 2005) and extruded (Bertan *et al.*, 2009) LZSA samples at higher relative densities. The scattered data in those cases are due to different sintering and crystallization conditions, such as temperature, time, and heating rate.

The SEM microstructures in Figure 2(a) and (b) reveal the fracture surface of the LZSA and LZSA5Zr laminates, respectively. Porosity was mainly located at the interfaces between the layers, shown by arrows in Figure 2(a) and (b), which may be explained by incomplete fusion of the adjacent tapes during the LOM process. This interlayer porosity, however, has not conducted to a deleterious effect on the mechanical strength as observed also elsewhere (Ma *et al.*, 2004). Ma *et al.* (2004) investigated the effect of porous interlayers on crack deflection in  $Al_2O_3$  laminates. The assumption of no elastic mismatch on the layered material is also herein valid since the composition of the layers has not been changed. It has been observed that the improvement on the fracture toughness of  $Al_2O_3$  laminates through crack deflection mechanism is not only dependent of the amount of “weak” interfaces but also from the amount of

**Table II** Relative percentages of the crystalline phases of LZSA and the refined cell parameters

Crystalline phase	Chemical formula	Unit cell parameters (Å)	Relative crystalline phases (wt%) <sup>a</sup>			
			LZSA 800	LZSA 850	LZSA5Zr 800	LZSA5Zr 850
$\beta$ -spodumene (ICSD 14235)	$LiAlSi_2O_6$	a = 7.51010 b = 7.51010 c = 9.13927	80	69	68	66
Zirconium silicate (ICSD 100248)	$ZrSiO_4$	a = 6.60292 b = 6.60292 c = 5.97663	5	16	19	22
Lithium metasilicate (ICSD 28192)	$Li_2SiO_3$	a = 9.40565 b = 5.40416 c = 4.66885	10	13	11	11
Zirconium oxide (ICSD 172161)	$ZrO_2$	a = 5.15221 b = 5.19120 c = 5.33381	5	2	2	1

Note: <sup>a</sup>LZSA800, LZSA5Zr800, LZSA850 and LZSA5Zr850 are referred to the materials crystallized for 30 min at 800 or 850°C, respectively

**Table III** Physical and mechanical properties of glass-ceramic laminates

Material	Crystallization temperature (°C)	Apparent density (g/cm <sup>3</sup> )	Theoretical density (g/cm <sup>3</sup> )	Relative density (%)	Flexural strength (MPa)
LZSA	800	2.32 ± 0.03	2.62 ± 0.04	88.55	127 ± 6
	850	2.17 ± 0.08	2.69 ± 0.01	80.67	125 ± 21
LZSA5Zr	800	2.25 ± 0.08	2.62 ± 0.01	85.87	96 ± 15
	850	2.06 ± 0.02	2.73 ± 0.02	75.45	80 ± 17



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