Evaluation of the reactivity of dense lanthanum-gadolinium zirconate ceramics with Colima volcanic ashes

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Abstract

The effects of ingestion of airborne particles from pyroclastic events of active volcanoes by aeronautical turbines and their subsequent reaction with thermal barrier coatings (TBCs) have attracted the attention of the scientific community in recent years. The reaction products of infiltration experiments of lanthanum-gadolinium zirconate (LGZO) ceramics with molten ashes from the active Colima volcano at 1250 °C for 10 h are presented and discussed as a function of the Gd^{+3} content. Five ceramic compositions, varying the Gd^{+3} content in solid solution were synthesized by the chemical coprecipitation and calcination method of pressed powders. These compositions include pure lanthanum and gadolinium zirconates, LZO, and GZO, respectively. Penetration depth and identification, and in some cases quantification of the reaction products between the molten ash and LGZO ceramics were performed by scanning electron microscopy (SEM), chemical composition with energy dispersive X-ray spectroscopy (EDS), grazing incident X-ray diffraction (GIXRD) as well as micro-Raman spectroscopy. Despite having the thinnest apatite layer compared to the other infiltrated LGZO compositions, the LZO ceramic exhibited the greatest infiltration resistance with an infiltration depth of approximately 23 µm from the surface. The phase characteristics of the reaction layers were dependent on the gadolinium content. LZO, LGZO25, and LGZO50 ($x=0$, 0.25, and 0.5) showed the presence of apatite as well as monoclinic and tetragonal zirconia, while LGZO75 and GZO ($x=0.75$ and 1), additionally showed the presence of cubic zirconia and anorthite. As the Gd^{+3} content increases in the LGZO solid solutions, the wavenumber value corresponding to the stretching vibrational mode of the silicon tetrahedra in apatite shifts from 862 to 877 cm^{-1}, which is associated to a decrease in Si-O bond lengths. These findings indicate that the amount of rare earth cations dissolved in the melt plays an important role in the precipitation of the reaction products.

Keywords: Rare-earth zirconates, reaction products, infiltration resistance, rare-earth apatite, Raman spectroscopy.

1. Introduction

The thermodynamic performance of aircraft turbines is enhanced by increasing the operating temperature at the turbine entry. Nonetheless, this increase can have a significant impact on the metallic components in the hot section of the turbines. Thermal barrier coatings (TBCs) are extensively used in the aerospace industry to protect such metallic components. For this purpose, 6-8 wt.% yttria stabilized zirconia (7YSZ) is the most prevalent thermal barrier material [1]. However, maximum operating temperatures for 7YSZ have been reached, due to the metastable character of the non-transformable tetragonal *t*'-phase. Such limits are observed at high temperatures, where destabilization of the *t*'-phase is induced by the transformation into a stable monoclinic phase during cooling [2], [3]. In addition, it has been extensively reported that 7YSZ degrades upon contact with molten calcium-magnesium-aluminosilicates (CMAS) compounds at similar temperatures [4], [5]. Some airborne Si-rich particles such as volcanic ashes (VAs) are ingested by the turbine, infiltrating through the porosity of the coating to finally solidify upon cooling to produce residual stresses that can cause the failure of the TBCs [6]. Thus, the working temperature and durability of TBCs are directly limited by the interplay of complex thermochemical and thermomechanical interactions with the molten siliceous particles [7]–[9]. Due to the potential damage, they can inflict on TBCs, siliceous residues pose a significant risk to aircraft turbomotors. The most well-known case occurred with the eruption of Eyjafjallökull volcano in 2010, which imposed severe limitations on European air traffic [9].

The interactions between TBCs and molten Si-based particles have been primarily studied using synthesized CMAS deposits. However, the composition of VAs can differ significantly from CMAS. VAs possess considerably more elements that are not present in CMAS [10]. For instance, the chemical composition of volcanoes such as Eyjafjallökull or Colima has been reported to contain Fe, K, Na, and Ti [5] thus generating important differences in Ca, Mg, Al and Si between CMAS and VAs. Consequently, these chemical contrasts can result in significant variations in thermal behavior and reactivity behavior of the molten glass with the thermal barrier ceramic during infiltration [10].

In Mexico, several active volcanoes constantly present eruptive activity and pose a constant threat to aircraft. Among them is the Colima volcano, which is located in a high-traffic air corridor and continuously emits significant amounts of siliceous debris into the atmosphere that can reach aircraft turbines and infiltrate TBCs. Although the effect of Colima VA on the integrity of aircraft TBCs has not been particularly reported, several studies have been conducted on the effect of VAs or CMAS on a wide range of siliceous particles compositions to understand the risk associated with their infiltration into 7YSZ TBCs [5], [10], [11].

Rare earth zirconates (REZs) have been studied due to their high resistance to Si-based molten particle infiltration, as well as their excellent features as thermal barrier materials, such as low thermal conductivity, sintering resistance, phase stability, etc. [12]. In the temperature range of turbine engines $La_2Zr_2O_7$ (LZO) and $Gd_2Zr_2O_7$ (GZO) ceramics have a particularly high infiltration resistance [9], [13]–[17]. During the infiltration of these ceramic materials, the molten silica-based particles dissolve the REZs, promoting their constituents to diffuse away from the dissolution front and forming local saturated regions that promote the precipitation of crystalline products from the melt. In REZs, the mechanism to stop infiltration is related to the precipitation of rare-earth apatites ($Ca_2RE_8(SiO_4)_6O_2$, Ap) with needle-like morphologies that can partially seal the infiltration channels and limit the thickness of the infiltrated layer [3], [9], [12], [15], [18].

On the other hand, it has been reported that lanthanum-gadolinium zirconate ceramics ($(La_{1-x}Gd_x)_2Zr_2O_7$, LGZO) demonstrate solid solutions over a broad range of compositions [14] and have lower thermal conductivity than pure LZO and GZO [16]. In addition, a previous study reported the formation of Ap and other Si-based phases as reaction products from LZO, LGZO, and GZO powder mixtures with three different VAs [13]. However, no study has yet been conducted on the behavior of these dense LGZO solid solutions under VAs infiltration from SiO_2-rich Mexican volcanoes. The study of the risk associated with VA damage inflicted by the Colima volcano on highly densified ceramics to evaluate the intrinsic resistance of LGZO materials to infiltration is another essentially unexplored aspect. The application of local characterization techniques to assess, at a micrometric scale, the reaction products and subsequently associate them with the risks posed by airborne VAs particles to LGZO ceramics is still needed.

This work provides information on the reaction products to elucidate the mechanism of Colima VAs infiltration in LGZO ceramics and thus, evaluate the level of risk associated with this interaction. For this purpose, highly densified LGZO ceramics were sintered from powders synthesized by coprecipitation in different ratios of La and Gd. Infiltration experiments were conducted with Colima VA at 1250 °C for 10 h. The infiltrated samples were characterized with different techniques seeking to identify characteristics as a function of infiltration depth such as such as scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM/EDS), grazing incident X-ray diffraction characterization (GIXRD), and micro-Raman spectroscopy. These results are intended to provide a fundamental understanding of the infiltration phenomena of Colima VAs by identifying their reaction products on LZGO ceramics.

2. Experimental procedure

2.1. Synthesis of powders and dense ceramics

$(La_{1-x}Gd_x)_2Zr_2O_7$ ceramics were prepared with molar fractions *x* of 0, 0.25, 0.5, 0.75, and 1, labeled as LZO, LGZO25, LGZO50, LGZO75, and GZO, respectively. The synthesis method was the reverse coprecipitation-calcination employing the following precursors : lanthanum oxide (La_2O_3, Alfa Aesar, 99.9 %), gadolinium oxide (Gd_2O_3, Alfa Aesar, 99.9 %) dissolved in an aqueous solution of nitric acid (HNO_3, Meyer, 70 %) and zirconium oxychloride ($ZrOCl_2 \cdot 8H_2O$, Alfa Aesar, 99.9 %) dissolved in water. To obtain the $(La_{1-x}Gd_x)_2Zr_2O_7$, 300 mL of solution was stoichiometrically prepared with the corresponding molar amounts. Each solution was carefully dropped over 21 mL of ammonium hydrate (NH_3, Sigma Aldrich, 30 % in water), and the pH value was maintained at 11 while stirring. After the reaction, the obtained gel-like precipitates were subsequently filtered using a filter paper of pore size of 0.45 μm and washed with deionized water. The washed precipitates were then dried at 110 °C for 24 h. Each $(La_{1-x}Gd_x)_2Zr_2O_7$ powder was calcined at 1300 °C in a box furnace (Thermo Scientific, f46110DCM-33) for 10 h and dry-milled (8000D mill, SpexSamplePrep) into fine powders with size between 0.2 μm to 1 μm with the characteristic pyrochlore phase.

Dense ceramics were prepared by weighing 0.3 g of the corresponding calcined powder and isostatically pressed under 194 MPa in a Cold isostatic press machine (MTI Corporation, YLJ-CIP-20B). The green bodies were sintered at 1450 °C for 10 h to obtain highly densified ceramics (relative density above 94%) ~~were obtained~~.

2.2. Infiltration experiments

The infiltration experiments were carried out, using ashes from the Colima volcano, collected from an eruption that occurred in 2015 and provided by the Geosciences Department of the National Autonomous University of Mexico (UNAM) REF. For the infiltration experiments, 20 mg of Colima VAs was deposited on each square centimeter of the ceramic surface by using an adhesive mask with a known area. The infiltration experiments were performed under isothermal conditions in air at 1250 °C for 10 h with heating and cooling rates of 10 °C/min. The infiltration temperature was chosen based on previous TGA-DSC analyses of these Colima VA [5] ensuring that the VA reached the melting range temperature so that molten glass could infiltrate through the ceramic volume.

2.3.Materials characterization

The crystalline characteristics of the VAs in their “as-received” condition as well as of the sintered ceramics of the LGZO system were determined by X-ray diffraction (XRD) using a diffractometer (Rigaku, SmartLab) with Cu $K\alpha 1$ = 1.54 Å, in the 2θ angle range of 20 ° to 70 °, a step size of 0.02 ° and recording time of 0.5 s.

Cross-sections of the infiltrated samples, prepared by standard metallographic techniques, were used to study the infiltration depth, reaction layers, and individual reaction products by SEM (JEOL, JSM-7610F) coupled with a back-scattering electrondetector (BSE). The chemical composition of the reaction products was measured by energy dispersive X-ray spectroscopy (EDS) coupled to the SEM. micro-Raman spectroscopy (WiTec, Alpha 300RA Raman Microscope) was carried out to identify the reaction products as a function of distance from the surface.

GIXRD in the 2θ angle range from 20 ° to 70 ° with a constant omega angle of 3 º, step size of 0.02 ° and a recording time of 0.5 s was carried out on infiltrated samples that were grinded with material removals of approximately 15 μm before each measurement. Finally, the XRD and GIXRD patterns were adjusted by the Rietveld method [19] to identify crystalline phases in VAs, the structural parameters in LGZO, and the contribution of reprecipitated phases, their amounts and distribution over the reaction layers of infiltrated LGZO50 and GZO samples. The data analysis was performed using the software FullProf Suite [20] (More details are presented in the supplementary material).

3. Results and discussion

3.1.Characterization Colima volcanic ash

Fig. 1a shows the XRD pattern for Colima VA in its as-received state. The XRD pattern of the Colima VA reveals the presence of several phases. The peaks at 22.2 º, 23.8 º, and 27.7 º of 2θ correspond to the (1-1-1), (012) and (2-1-1) planes of analbite, $NaAl(Si,Al)_3O_8$ [21], (ICSD collection code: 180328). The highest peak at 28.3 ° corresponds to the (011) plane of SiO_2 (ICSD collection code: 89658) [22]. The diffraction peak with low intensity at 35.5° can be assigned to (113) plane of Fe_3O_4 (ICSD collection code: 159973) and anorthite (ICSD collection code: 52343) with a peak at 22.2°.

Phase quantification by the Rietveld method, Fig. 1c, confirmed analbite as the main phase (63.5%), while the content of SiO_2 and Fe_3O_4 are 20.1 and 4.3 %, respectively. The albite phase is also found to be 5.9 %, which is consistent with similar experiments reported with Colima VAs [5]. Finally, anorthite was found in a 6.3 %. The chemical composition of Colima VAs determined by ICP as reported by Rivera-Gil et al. [5] showed SiO_2 (77.0 %), Al_2O_3 (4.3%), Na_2O (7.9%), CaO (4.3%), and Fe_2O_3 (4.1%). This VA also showed minor constituents such as TiO_2 (0.8%), K_2O (0.2%), and MgO (0.3%). It is worth mentioning that SiO_2, Fe_2O_3, CaO, and TiO_2 play the main role in infiltration kinetics and the formation of reaction products [15], [23], [24].

3.2. Characterization of $(La_{1-x}Gd_x)_2Zr_2O_7$ ceramics

Fig.2a shows the diffraction patterns of the sintered LGZO ceramics. The peaks at 29, 34, 48, and 61.5 ° of 2θ correspond to (222), (400), (440), and (444) planes of the pyrochlore phase, respectively. The peak around $2\theta = 37°$ corresponds to the (331) plane originates from the pyrochlore superstructure, and indicates ordering in the structure [13], [17]. The low intensity of the (331) in GZO evolves progressively as the La^{3+} content in LGZO solid solutions increases, suggesting that the structure becomes more ordered with La^{3+} substitution at the Gd^{3+} site. This behavior is consistent with the knowledge that the ordered-disordered state of pyrochlore-type REZs is mainly determined by the ratio of the average ion radius of the RE^{+3} site to the ion radius of Zr^{4+} [16]. In the case of LZO, the substitution of the La^{3+} site by Gd^{3+}, which is a smaller ion reduces the the average ionic radius, leading to disorder of the structure as Gd^{3+} increases in the solid solution [25]. Fig.2b shows a magnified section of the LGZO peaks corresponding to the diffractions of the (622) plane diffractions and reveals the shift of these peaks towards higher values of 2θ as Gd^{3+} in LGZO solid solutions increases. Fig. 2c shows the linear shift of the lattice parameter, obtained from Rietveld refinement (see supporting information for details). The lattice parameter values change with the variation of the solid solution composition from 10.80 Å for LZO to 10.53 Å for GZO. The values obtained are consistent with those reported by Wan et al. [16] shown with square symbols in Fig 2c. The changes in the crystal lattice parameters indicate that Gd^{3+} has occupied the La^{3+} site to form the LGZO with different compositions. According to the results, all LGZO compositions comprise the pyrochlore phase and no additional phase was observed.

Raman spectroscopy was performed on the LGZO samples to confirm the formation of the pyrochlore phase in the ceramics. It has been reported that fluorite, the precursor of the pyrochlore phase has only one Raman active mode F_{2g}. On the other hand, the ideal cubic pyrochlore structure, which belongs to the $Fd\bar{3}m$ space group has been reported to have four or even six active Raman modes, depending on the observed REZ [26]–[29]. Fig. 3a-e shows the different Raman spectra of the LGZO samples. For each composition, their corresponding modes were denoted as; E_g for O-La,Gd bending vibration, A_{1g} for La,Gd-O_{II} stretching vibration, one F_{2g} for O-Zr-O bending and two F_{2g} for Zr-O_{II}, and Zr-O_I stretching vibrations can be observed, respectively [26], [30] confirming that the precursor fluorite phase structure was completely transformed into pure pyrochlore under these calcination and sintering conditions.

Fig. 3f shows the wavenumber for each vibrational mode of pyrochlore as a function of x in $(La_{1-x}Gd_x)_2Zr_2O_7$. As x increases, the Raman active modes of the pyrochlore tend to shift slightly toward higher values, indicating that the bond lengths become shorter as La^{+3} is replaced by Gd^{+3}, due to the radius of La^{+3} (1.95 Å) being larger than that of Gd^{+3} (1.80 Å), which is consistent with the decrease in the lattice parameter shown at Fig. 2c.

3.3. Infiltration and interactions between Colima volcanic ashes and dense ceramics

In this section, the reaction products precipitating from the infiltrated ceramics are discussed. The phases precipitated their morphologies and distribution changes as a function of the infiltrated rare earth zirconate. The characteristics of the reaction layer were studied by different techniques to comprehend the interplay of the reaction products in the infiltration.

3.3.1. SEM, elemental composition and mapping of infiltrated ceramic cross sections

An overview of the cross-section of LGZO ceramics infiltrated at 1250 °C for 10 h is shown in Fig. 4a-e. Interactions between Colima VA and LGZO samples reveal variations in the reaction products, their morphologies, and their distribution. For infiltrated LZO, LGZO25, and LGZO50 ceramics, two zones, labeled as Z1 and Z2 are observed. Z1 shows globular phases distributed at the top of the reaction layer, with a size around 1-4 μm for LZO and decreases in size until less than 1 μm is observed for LGZO50. On the other hand, Z2 exhibits a dense layer of about 15 μm for LZO and increases to 20-25 μm for LGZO25 and LGZ50. Unlike Z1, Z2 exhibits a mixture of globular and needle like morphologies, which have been previously identified as m, t, c-ZrO2 and RE-apatite phases, respectively REF. For Colima VA interactions with LGZO75 and GZO, similar microstructures are observed. However, both LGZO75 and GZO exhibit an additional zone at the bottom, labeled Z3 with a thickness of about 25 μm; these zones show the presence of a scattered thin phase embedded in a dense matrix. As Gd content in LGZO ceramics increases, the distance from the surface tends to be greater as shown in Fig. 4f. Colima VA infiltration depths appear to follow a linear trend as Gd^{3+} content increases. The distance for LZO was only 22.9 μm, while for GZO the infiltration reached 84.2 μm. This result is affected by several factors that will be discussed below.

Elemental mappings of the cross sections of the infiltrated ceramics, Fig. 5a-e, reveal the distribution of the principal elements involved in the chemical reactions during infiltration. Al is predominantly distributed in the glass above and within the Z1 regions of all samples. However, the Z3 regions of the infiltrated LGZO75 and GZO ceramics also exhibit the presence of Al at the bottom although with a different distribution, suggesting the presence of an Al-rich phase within this zone [31]. Ca is detected in the Z2 and Z3 regions of the glass, in all infiltrated samples. Si is present in the Z1, Z2, and Z3 regions of the glass in all the infiltrated samples. Zr is observed in the REZ ceramics and in the reprecipitated phases in Z1, Z2, and Z3 regions.

The elemental compositions of the reaction products (Fig. 6a-c) match the stoichiometric values of zirconia in its monoclinic (*m*-ZrO_2), tetragonal (*t*-ZrO_2), and cubic (*c*-ZrO_2) phases as well as Ap, and anorthite ($CaAl_2Si_2O_8$, An) [13], [32]. These phases are commonly reported as reaction products in infiltrated REZs [10]. Additionally, reprecipitated phases were also identified by GIXRD (discussed in section 3.3.3). Fig. 6a shows that *c*-ZrO_2, of which the highest amount of RE element reported in solid solution (around 5-10 at.%) [13][33][14], is more likely to reprecipitate in infiltrated Gd-rich zirconates such as LGZO75 and GZO [14]. In contrast, *m*-ZrO_2, which dissolves a negligible amount of La or Gd in solid solution (up to 2 at.%) [13] [33][14] predominantly reprecipitates in infiltrated LZO. The elemental composition of the reprecipitated zirconia from Colima VA interactions with LGZO25 and LGZO50 is largely identical to that of *m*-ZrO_2 and *t*-ZrO_2, which dissolves approximately 2-5 at.% of La or Gd [33], [34]. RE element composition in reprecipitated zirconia phases tends to increase as Gd content in infiltrated LGZO ceramics increases, while Zr element composition decreases. This trend enables the definition of the locations where *m*-ZrO_2, *t*-ZrO_2, and *c*-ZrO_2 are favorable to reprecipitate based on their compositions and infiltrated LGZO (Fig. 6a).

It has also been reported that the Ap phase is a common reaction product as siliceous debris reacts with different REZs [9], [13], [29], [35], [36]. This phase exhibits a fine needle-like hexagonal morphology that prevents infiltration by forming a dense sealing layer at the REZs [9], [13]. Fig. 4a-exhibits Ap among the reprecipitated phases in the Z2 and Z3 regions. The elemental compositions of the Ap phases in Z2 and Z3 regions are identical to that of the rare-earth Ap ($Ca_2(La,Gd,Zr)_8((Si,Al)O_4)_6O_2$), with Zr^{+4} and Al^{+3} cations occupying the RE^{+3} (La^{+3},Gd^{+3}) and Si^{+4} sites, respectively [9], [13]. The quantity of RE elemental composition that Ap can incorporate tends to increase as the Gd^{+3} content of LGZO ceramics raises (Fig. 6b). In contrast, the elemental composition of Si and Ca remains practically constant. On the other hand, the elemental composition of Al tends to decrease in Ap reprecipitated from Gd-rich zirconates.

The elemental composition of the embedded Al-rich phase, observed in the Z3 region is depicted in Fig. 6c. This composition corresponds to the An phase, and GIXRD (discussed in section 3.3.3) has also confirmed this phase. As indicated by the elemental map in Fig. 5e, the An phase is an intrinsic crystallization product rich in Al, and Si. The An phase exists in LGZO75 and GZO and contains Ca, Al, and Si. LGZO75 has a larger Al content (68.4 %) than GZO (47.9 %), while the GZO has a higher Si content (41.7 vs. 25.6 %). In contrast, the Ca content of LGZO75 and GZO is 6.0 % and 10.4%, respectively.

3.3.2. Phase identification by Raman spectroscopy

Several bands, corresponding to reprecipitated *m*-ZrO_2, *t*-ZrO_2, *c*-ZrO_2, Ap, and An phases, are visible in Raman spectra as a function of distance from the surface of the infiltrated ceramics (Fig. 7a-e). The bands centered around 190, 484, 613, and 635 cm^{-1} match with those observed in *m*-ZrO_2 phase [37], [38]. Consequently, their presence exposes the distribution of *m*-ZrO_2 throughout the reaction layers of all the infiltrated samples. These bands are predominantly observed as Colima VA infiltrate null or low-Gd^{3+}-content LGZO ceramics, such as LZO, LGZO25, and LGZO50. Moreover, these bands are most likely to be found at low infiltration depths of the reaction layer.

The bands centered at 292 and 324 cm^{-1} correspond to *t*-ZrO_2. These bands appear to increase with increasing distances from the surface and are present in all interactions. The LGZO75 and GZO infiltrated ceramics predominantly exhibit bands corresponding to *c*-ZrO_2 along with An phase. *c*-ZrO_2 has been reported to present an amorphous-like Raman spectrum showing a broad band around 670 cm^{-1} [38]. The bands at 503 and 770 cm^{-1} correspond to An phase, which has been reported to be reprecipitated frequently in infiltrated GZO [39]. The band around 850 cm^{-1} observed in the Z2 and Z3 regions in all the interactions corresponds to the symmetric stretching mode of SiO_4 tetrahedra in Ap [40] and crystallizes with all interactions involving Colima VA and LGZO.

As shown in Fig. 8a, the wavenumber values of the planar bending vibrational mode of *t*-ZrO_2 and the symmetric stretching vibrational mode of Ap were analyzed as a function of Gd^{+3} content in infiltrated LGZO to better understand the reaction products resulting from interactions between LGZO and VA. It was observed that the wavenumber of the planar bending vibrational mode of *t*-ZrO_2 increases with increasing Gd^{3+} content in the infiltrated LGZO ceramics. This shift toward higher wavenumber values indicates that the bond lengths of the atoms involved in these vibration modes become shorter as the Gd^{3+} concentration in the solid solutions of the infiltrated LGZO ceramics increases.

Fig. 8b shows the correlation between the wavenumber values of these two vibrational modes as a function of the Gd^{3+} content in LGZO solid solutions and the range of distance from the surface at which they appear. According to the results, the wavenumber values for each infiltrated LGZO ceramic remained constant as the distance from the surface increased. However, it was also observed that infiltrated GZO reprecipitated as *t*-ZrO_2 exhibited this vibrational mode at the highest wavenumber value and the highest range in distance from the surface where this phase was present. In contrast, infiltrated LZO reprecipitated a *t*-ZrO_2 that exhibited this vibrational mode at the lowest wavenumber value and the lowest range in distance from the surface.

The shift to higher wavenumber values indicates a decrease in bond length of atoms associated with the concerned vibrational mode, which is associated with a decreasing lattice parameter of the phase. Therefore, LGZO ceramics with a low-Gd^{3+} content reprecipitate more t-ZrO_2 than LGZO solid solutions with high-Gd^{3+} content.

3.3.3. Crystalline phases according to the depth of infiltration

To identify the reprecipitated phases, GIXRD was performed as a function of distance from the surface on the LGZO50 and GZO samples interacting with Colima VA, as shown in Fig. 9a-c and Fig. 9d-f, respectively. The cross-section microstructure of the infiltrated LGZO50 sample, which exhibits the morphology of the reprecipitated products along the reaction layer is depicted in Fig. 9a. Fig. 9b shows the corresponding GIXRD patterns and phases identified by Rietveld fitting at different distances from the surface. The dashed gray and orange lines, labeled as Y_{obs} and Y_{calc}, are the GIXRD patterns and their calculated Rietveld fittings, respectively, while the colored lines represent the reprecipitated identified phases. The cyan line observed at the bottom corresponds to the Rietveld fitting for LGZO50 ceramic. Fig. 9**Error! Reference source not found.**c shows the phase percentage obtained from the Rietveld fitting for each observed phase as a function of distance from the surface. The m-ZrO_2 phase is in the majority and reprecipitates with t-ZrO_2 and c-ZrO_2 in traces in the outermost layer of reaction products. It can be observed that as the distance to the surface increases, the m-ZrO_2 phase decreases from 43% to 16%, but t-ZrO_2 and Ap phases increase from 31 to 60 % and 3 to 15 %, respectively, confirming the presence of Ap in the dense layer right above LGZO50. However, c-ZrO_2 can also be observed with an 8 % at 35 µm. This reveals that the interaction between LGZO50 with Colima VA reprecipitates mainly m-ZrO_2 (43-50 %) near the glass (solidified VA reservoir) with lower amounts of t-ZrO_2 (26-31 %), but as the distance from the surface increases t-ZrO_2 and Ap reprecipitate in higher amounts (60 % and 15 % respectively).

Fig. 9d. shows the microstructure in cross-section of the infiltrated GZO ceramic and the morphology of the reprecipitated products along the reaction layer. In Fig. 9e, the corresponding GIXRD patterns and phases identified by the Rietveld method at different distances from the surface are presented. Fig. 9f shows the phase percentages obtained by the Rietveld method from each GIXRD pattern. For this interaction, GZO and Colima VA, c-ZrO_2 with a 57 % is the majority reprecipitated phase throughout the infiltrated region and decreases slightly up to 48 %, as the distance from the surface increases. The Ap phase with 12-7 % remains almost unchanged throughout a large part of the infiltrated region. Similarly, the *t*-ZrO_2 phase was identified, which seems to increase as the distance from the surface increases from 16 % to 32 %. Also, *m*-ZrO_2 can be observed reprecipitating in higher amounts just in the vicinity of the glass contact, at shallow depths from the surface. These results indicate that in the infiltrated GZO ceramic, the percentage of the Ap phase remains constant over a wide range of distances from the surface (25 to 84 µm) and reprecipitates along with a higher percentage of the *c*-ZrO_2 phase (around 57 %).

3.4. Insight of the crystallization mechanism of the reaction products

The infiltrated LZO shows not only the shortest infiltration distance from the surface (23 µm) but two zones with different morphology in the reaction layer (Fig.4a). Z1 shows mainly reprecipitated *m*-ZrO_2 while Z2 shows a thin dense layer of Ap. However, traces of *t*-ZrO_2 phase in Z1 and Z2 were also confirmed by Raman spectroscopy (Fig. 7a), where characteristic bands at 484, 313, and 862 cm^{-1} from *m*-ZrO_2, *t*-ZrO_2 and Ap were observed at 19 µm distance from the surface, falling within the zone labeled as Z2 (see Fig. 4a). EDS analysis allowed the identification of precipitated zirconia, with the composition of *m*-ZrO_2, corroborated by the Raman spectra (Fig. 7a and Fig. 8a). The presence of *m*-ZrO_2 and traces of *t*-ZrO_2 can be explained by the equilibrium phase diagram for lanthanum and zirconium oxides, in which LZO and *t*-ZrO_2 phases are in equilibrium at 1250 °C but upon cooling the *t*-ZrO_2 transforms into *m*- ZrO_2 at temperatures around 1000 °C [13], [33]. Therefore, *t*-ZrO_2 bands observed by Raman spectroscopy (Fig. 7a and Fig. 8a) are associated with this metastable phase.

On the other hand, the thin Z2 region shown by the infiltrated LZO suggests a rapid crystallization of the Ap phase, which is favored by two facts. Firstly, Ap has been reported to crystallize faster as the RE radius increases in some REZ, such as in infiltrated GZO and $Y_4Zr_2O_7$ (YZO), where Gd^{+3} ionic radius is larger than Y^{+3} [12], [35]. Thus, the crystallization of Ap in the infiltrated LZO is favored because La^{+3} possesses the largest ionic radius of the lanthanide series [10], [41]. Secondly, *m*-ZrO_2 can only incorporate a low or no RE cation content in solid solution [13]. Consequently, a significant amount of dissolved RE^{+3} ions is available to promote rapid crystallization of the stable Ap phase that effectively mitigates the infiltration.

The infiltrated LGZO25 and LGZO50 show a similar microstructure in the reaction layers and an infiltration distance from the surface of 40 µm on average. In these two ceramics, Z1 and Z2 extend to a greater depth of infiltration from the surface. Gadolinium oxide preferentially stabilizes *c*-ZrO_2 while lanthanum oxide stabilizes *t*-ZrO_2, which subsequently transforms to *m*-ZrO_2 upon cooling. In LGZO solid solutions, these two dissolved rare-earth oxides compete to precipitate in one or the other zirconia phase. In the case of infiltrated LGZO50, Raman spectra (Fig. 7c) and the GIXRD diffraction pattern (Fig. 9c) confirm that all three zirconia phases coexist in the Z1 region near the glass. However, *m*-ZrO_2 appears to be the dominant phase. This result suggests that at this distance from the surface, on average there is a slightly higher concentration of La^{+3} than Gd^{+3} cations dissolved in the melt, which promotes the crystallization of *m*-ZrO_2 just below the glass. Z2, on the other hand, has a higher presence of *t*-ZrO_2 which reprecipitates along with Ap, (Fig. 7c and Fig. 10c). The following hypothesis is proposed to explain the majority percentage of this phase in Z2. La^{+3} and Gd^{+3} are two rare-earth cations dissolved in the melt that compete with each other. Under equilibrium conditions at 1250 °C, La^{+3} dissolved in the melt tends to precipitate in *m*-ZrO_2. However, traces of *t*-ZrO_2 can be observed, as mentioned, and explained previously for infiltrated LZO samples. Gd^{+3} dissolved into the melt, otherwise, induces *c*-ZrO_2 reprecipitation as previous works have shown [12].

Furthermore, considering the Gd_2O_3-ZrO_2 phase diagram for simplicity, despite the complexity of the overall system due to all the stringent oxides involved, *c*-ZrO_2 and *t*-ZrO_2 coexist in equilibrium at 1250 °C [34], so *t*-ZrO_2 is also feasible to reprecipitate under cooling such as those carried out in this work (10 °C/min) and as it will be discussed further below for infiltrated GZO sample. EDS (Fig. 6a) reveals that for infiltrated LGZO50, the measured composition of the zirconia matches the composition of *t*-ZrO_2 for this interaction as prior works have also confirmed [5], [9].

Ap reprecipitated from infiltrated LGZO50 (Fig. 4c) is less effective in stopping infiltration of molten VA than the Ap reprecipitated from the infiltrated LZO. Although the distance from the surface, Z2, at which this Ap reprecipitates is greater compared to the infiltrated LZO. The XRD pattern and Raman spectra (Fig. 9c and Fig. 7c) confirm that this Ap precipitates together *t*-ZrO_2, which can retain more RE^{+3} cations in solid solution compared to *m*-ZrO_2. Consequently, a smaller amount of RE^{+3} dissolved in the melt will be available to promote the crystallization of Ap compared to La-rich zirconate ceramics. Furthermore, it can be observed that this Ap is not as dense as that precipitated in the interaction between VA-LZO.

As shown in Fig.4f, the infiltrated LGZO 75 and GZO exhibit infiltration distances from the surface of 65 and 84 µm, respectively. Furthermore, Fig. 4d and Fig 4e show different phase distributions in the reaction layer compared to the infiltrated LZO, LGZO25, and LGZO50 ceramics, which can be explained by the mechanism in which these phases reprecipitate along the reaction layers. Only the infiltrated GZO samples will be explained in depth because the reaction layer of infiltrated LGZO75 ceramic presents a similar microstructure.

For infiltrated GZO, GIXRD patterns and phase percentages shown in Fig. 9b and Fig. 9c, respectively prove that the reprecipitated phases observed in Z1 correspond to a mixture of *m*-ZrO_2, *t*-ZrO_2, and *c*-ZrO_2, respectively. This latter appears as the majoritarian zirconia phase reprecipitated throughout the reaction layer; Z1, Z2, and Z3 regions. The predominance of *c*-ZrO_2 as molten siliceous debris interacts with GZO has been reported as a reprecipitated phase in previous works[12], [13]. Previous research has demonstrated that *c*-ZrO_2 can incorporate a larger amount of RE in solid solution than *m*-ZrO_2 and *t*-ZrO_2 [33], [34].

The Z2 in GZO (Fig. 4e), which is the region where Ap reprecipitates extends over a larger depth of infiltration compared to the other infiltrated LGZO solid solutions. The reprecipitated Ap in Z2 appears to be less efficient in stopping infiltration compared to La-rich zirconates. The GIXRD patterns and phase percentages shown in Fig. 8b and Fig. 8c reveal the presence of the Ap phase showing a phase percentage of about 7 %. It can also be seen that the Ap phase reprecipitates together with a considerable and majority amount of *c*-ZrO_2, which as mentioned can contain a large amount of RE cations in a solid solution. This finding implies that during the crystallization of this Gd-Ap, there is a smaller amount of dissolved RE^{+3} cations available in the melt to promote the crystallization of Ap compared to La-rich zirconates. Furthermore, other researchers have reported that additional silicate phases such as anorthite, garnet, and cuspidine can also reprecipitate together with Gd-Ap in GZO as infiltrated [10], [31].

Finally, EDS analysis (Fig. 6c) performed on Z3 embedded phases, GIXRD patterns, and phase percentages (Fig. 9b-c) confirm the presence of An, which is an Al-rich phase. The Z3 depicted in Fig. 4e shows that An phase is embedded in a dense reprecipitated layer of a mixture of *c*-ZrO_2, *t*-ZrO_2, *m*-ZrO_2, and Ap, as confirmed by phase percentages in Fig. 9f and

Raman spectra shown in Fig.7e. In addition, EDS analysis reveals that for this interaction, Ap contains a lesser amount of Al in solid solutions which may suggest that during infiltration local regions in the melt were saturated with this cation. On the other hand, several works have also reported that An phase can reprecipitate at the bottom of the infiltration region [18], [31].

4. Conclusions

The study of the Colima VAs, LGZO sintered ceramics, and the characterization of the cross-section infiltrated samples led to the following conclusions.

- Si-rich Colima VAs have phases such as SiO_2, (20.1 %), analbite (63.5 %), anorthite (6.2 %), albite (5.9 %), and small amounts of Fe oxides (4.3 %).
- The trend of increasing the Gd^{+3} content in LGZO was confirmed, in which the cell parameter linearly decreases from 10.80 Å to 10.52 Å for LZO and GZO, respectively.
- The main vibrational modes of the LGZO sintered ceramics shift to higher wavenumber values as Gd^{+3} content increases in their composition, for instance F_{2g} stretching vibrational mode. This shift to higher wavenumber, from 306.04 to 315 cm^{-1}, is related to a decrease in the bond distance, Zr-O associated to this mode, which in turn agrees with the decrease in the cell parameter.
- The Gd^{+3} content has an important effect on the infiltration depth. A high Gd^{+3} content in LGZO causes a large infiltration depth. In the reaction layer, distance from the surface as a function of the Gd^{+3} content shows an increasing linear trend, exhibiting 23 and 84 µm for LZO and GZO, respectively.
- LZO reprecipitates a thin packed La-Ap, embedded in a mixture of *m*-ZrO_2 and *t*-ZrO_2, which is more effective to stop infiltration, in comparison to the Ap reprecipitated by Gd-rich zirconates.
- As the gadolinium content in the lanthanum-gadolinium zirconate system increases, a less dense apatite is produced that is less effective in stopping infiltration compared to lanthanum-rich zirconates.
- An unknown?? phase seems to reprecipitate at the bottom of the infiltrated Gd-rich zirconate ceramics. This phase was detected by GIXRD performed on the grinded infiltration reaction layer of the infiltrated GZO samples showing a phase percentage of around 9.0 %.

- The distribution of the reprecipitated Aps in the reaction layers was identified by the mode associated with the stretching vibration of the silicon tetrahedra, which appears around 850 cm^{-1} and shifts to higher wavenumber as Gd^{+3} content increases in the LGZO samples.
- The higher wavenumber value of the corresponding reprecipitated Ap, the higher distance from the surface range in which this phase precipitates. This is associated with the amount and sort of atoms in solid solution that these Aps can retain.

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Figure caption

Fig. 1. a) X-ray diffraction patterns for Colima VA showing the main constituent phases, b) enlarged section of main Colima VA XRD pattern. Y_{obs} and Y_{cal} correspond to the experimental data and Rietveld fitting respectively, Colored lines correspond to the identified phases, c) cake chart with the phase percentages obtained from the Rietveld fitting.

Fig. 2. a) X ray diffraction patterns for LGZO ceramics. b) enlarged sections of the peak (622) shift and c) lattice parameter as function of LGZO ceramic. Wan results shown for comparison.

Fig. 3. Deconvoluted main peaks from Raman spectrum of a) LZO, b) LGZO25, c) LGZO50, d) LGZO75 and e) GZO ceramics. f) Wavenumber as a function of LGZO ceramic showing the vibrational modes shifts.

Fig. 4. SEM images of the cross-section infiltrated dense ceramics of a) LZO, b) LGZO25, c) LGZO50, d) LGZO75 and e) GZO. f) distance from surface as function of LGZO ceramic.

Fig. 5. Elemental mappings of Al, Ca, Si and Zr from the infiltrated LGZO ceramic. Yellow dashed rectangle in c) and d) corresponds to the infiltrated samples used for the GIXRD analysis.

Fig. 6. Elemental compositions of reprecipitate a) zirconia, b) apatite and c) anorthite phases as function of LGZO ceramic.

Fig. 7. Raman spectra as function of distance from surface for interactions between a) LZO, b) LGZO25, c) LGZO50, d) LGZO75 and e) GZO with Colima VA showing identified phases of Ap, *m*-ZrO_2, *t*-ZrO_2, and *c*-ZrO_2, An, and pyrochlore (P) and their distribution along the reaction layers.

Fig. 8. Wavenumber shift associated to the main vibrational mode of Ap and *t*-ZrO_2, respectively, a) as function of Gd^{+3} content in LGZO and b) as function of distance from surface range where this mode, associated to their corresponding phase, appears.

Fig. 9. For LGZO50 and GZO, respectively, a) and d) Cross-section SEM images. b) and e) GIXRD patterns, Y_{obs}, as a function of distance from surface, Y_{calc} from the Rietveld adjustment and colored lines for the identified phases. c) and f) Phase percentages obtained from Rietveld adjustment of the GIXRD patterns.