



Influence of Li_2CO_3 and V_2O_5 combined additions on the sintering and dielectric properties of $\text{Ca}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$ ceramics prepared from powders synthesized by sol-gel method

Nouara Lamrani^{1,*}, Ahcène Chaouchi¹, Jérôme Bernard², Brahim Itaalit², David Houivet², Jean Marie Haussonne², Mohamed Aliouat¹

¹Laboratoire de Chimie Appliquée et Génie chimique de l'Université Mouloud Mammeri de Tizi-Ouzou. Route de Hasnaoua BP. 17 RP 15000, Tizi-Ouzou, Algeria

²Laboratoire Universitaire des Sciences Appliquées de Cherbourg (LUSAC) EA4253, Université de Caen Basse-Normandie (UCBN), Site Universitaire, B.P. 78, 50130 Cherbourg-Octeville, France

Received 20 February 2014; Received in revised form 3 April 2014; Received in revised form 18 May 2014;

Accepted 20 June 2014

Abstract

In this work, we have studied the influence of lithium carbonate (Li_2CO_3) associated with the vanadium oxide (V_2O_5) on sintering and dielectrics properties of $\text{Ca}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$ ceramic materials obtained from nanopowder synthesized by sol-gel method. The nanopowder was obtained by controlled mixing of titanium butoxide dissolved in butanol-2 and acetic acid with a saturated aqueous solution of calcium acetate and strontium carbonate and subsequent drying of the formed gel at 80 °C and calcination at 1100 °C. The synthesized nanopowder was mixed with different amount of additives, and then uniaxally pressed and sintered in air atmosphere at temperature determined by dilatometric measurements. The pure $\text{Ca}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$ sample obtained by this process required a sintering temperature around 1500 °C. The addition of Li_2CO_3 combined with V_2O_5 improved sinterability and caused a shift of dilatometric shrinkage curve to much lower temperatures. Thus, dense ceramics (98% of theoretical density) were obtained at sintering temperature ≤ 1300 °C. The effect of adding Li_2CO_3 - V_2O_5 on the structure of ceramics and the dielectric properties is discussed and show that type I dielectric properties (linear variation of the permittivity) are conserved, but with an increase of dielectric loss.

Keywords: perovskite $\text{Ca}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$ ceramic, sol-gel synthesis, sintering aids, dielectric properties

1. Introduction

Perovskite type oxides of general formula ABO_3 [1] are well known in material sciences due to their good electrical properties, magneto-resistivity and ability to immobilize high-activity radioactive waste [2–5]. They are also known for their phase transitions which may strongly affect the physical and chemical properties [5]. Several authors have also studied the system CaTiO_3 - SrTiO_3 [5–12]. According to the results of Ball *et al.* [6] and Ceh *et al.* [7] these two perovskite oxides are completely miscible and form $\text{Ca}_{1-x}\text{Sr}_x\text{TiO}_3$ (CST) solid solution. CaTiO_3 exhibits the orthorhombic structure with

space group $Pbnm$ or $Pnma$ [8], while SrTiO_3 has a cubic structure with space group $Pm3m$ [9] at room temperature. Recently, Ball *et al.* [6] reported the following phase transitions with increasing the amount of Sr in CST: orthorhombic $Pnma$ for $0 \leq x \leq 0.40$ to orthorhombic $Bmmb$ for $0.45 \leq x \leq 0.6$, then to tetragonal $I4/mcm$ for $0.65 \leq x \leq 0.90$ and finally to cubic $Pm3m$ for $x \geq 0.95$. However, Ranjan *et al.* [10] confirmed that the structure remains orthorhombic at $x \leq 0.88$. Recently, Carpenter *et al.* [11,12] proposed phase diagram of CST solution showing the sample compositions at different room temperatures.

Many researchers have investigated transition phases of $\text{Ca}_{1-x}\text{Sr}_x\text{TiO}_3$ synthesized by the solid state route and sintered at high temperature. It is known that the

* Corresponding author: tel: +213 779 357 486
e-mail: nouara7402@gmail.com

high sintering temperature can be decreased by a liquid phase sintering with sintering agents such as lithium salts, vanadium oxide etc. [13–15]. Thus, previous studies [16–18] have shown the important role of lithium for a low sintering temperature of BaTiO_3 , SrTiO_3 or generally all ABO_3 perovskites. Two mechanisms can occur simultaneously [16]. In the first, lithium might be, together with fluorine, introduced into the perovskite BaTiO_3 lattice, and form solid solution with the general formula $\text{BaTi}_{1-x}\text{Li}_x\text{O}_{3-3x}\text{F}_{3x}$. According to the second, it has been stated that lithium might be introduced in the perovskite structure and it can be described by the formula $\text{A}(\text{B}_{1-x}\text{Li}_x)\text{O}_{3-3x/2}$. Thus, LiO_4 tetrahedra can be created by simple elimination of rows of oxygen atoms along the $\langle 110 \rangle$ direction. Moreover, the ability of titanium to take a square pyramidal coordination suggests that oxygen vacancies might also appear in the TiO_6 octahedra, due to the introduction of lithium. It is most probable that isolated LiO_4 tetrahedra as well as TiO_5 pyramids are formed simultaneously in the structure and that anionic vacancies are randomly distributed, leading to a low temperature densification of the material. Vanadium, can also have two effects: the first one is the low melting point of V_2O_5 ($T_m = 690^\circ\text{C}$) which can lead to a lowering of sintering temperature; the second one is the small radius in coordination 6 of V^{5+} ($r_{\text{V}^{5+}} = 0.54 \text{ \AA}$) [16–18] which could facilitate its inclusion in the $\text{Ca}_{1-x}\text{Sr}_x\text{TiO}_3$ structure and enhance diffusion in the cationic B sublattice ($r_{\text{Ti}^{4+}} = 0.72 \text{ \AA}$). In addition, a combined effect of vanadium with lithium cannot be excluded. The literature [19–24] suggests V_2O_5 to be a promising sintering aid for the densification at relatively low temperatures. For example, it allows the sintering of $\text{Li}_2\text{O}-\text{Nb}_2\text{O}_5-5\text{TiO}_2$ at 900°C , $\text{Li}_{1+x-y}\text{Nb}_{1-x-3y}\text{Ti}_{x+4y}\text{O}_3$ at 900°C , $5\text{Li}_2\text{O}-0.583\text{Nb}_2\text{O}_5-3.248\text{TiO}_2$ at 920°C , and $\text{MgTiO}_3-\text{CaTiO}_3$ at 1300°C . Its effectiveness has been also demonstrated, when associated with Bi_2O_3 and CuO in ZnNb_2O_6 system by Huang *et al.* [20] and Gu *et al.* [21].

The effects of combined addition of Li_2CO_3 and V_2O_5 on the sintering behaviour of $\text{Ca}_{1-x}\text{Sr}_x\text{TiO}_3$ have not yet been thoroughly investigated. In this paper, we report on the possibility of lowering the sintering temperature of $\text{Ca}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$ ceramics by co-addition of Li_2CO_3 ($T_m = 720^\circ\text{C}$) and V_2O_5 ($T_m = 690^\circ\text{C}$) with equal amount of two oxides or by addition of the eutectic $0.38\text{Li}_2\text{O}-0.62\text{V}_2\text{O}_5$ composition ($T_m = 550^\circ\text{C}$

[25]). In the first one, the sintering will occur with an excess of lithium, however with the eutectic composition the sintering process will be held with an excess of vanadium. The effect of those sintering aids on sinterability and dielectric properties of $\text{Ca}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$ ceramics were investigated in terms of microstructure and structure analysis.

II. Experimental

The pure $\text{Ca}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$ (denoted as CST50) powder was prepared by the sol-gel method. It is well known that titanium alkoxides are highly reactive in the presence of water and under uncontrolled conditions might cause rapid formation of hydrated titanium oxide by condensation between $\text{Ti}-\text{OH}$ or $\text{Ti}-\text{O}-\text{Ti}$. Because of that titanium butoxide (97%, Aldrich) was diluted in butanol-2 (98%, Prolabo) and acetic acid (96%, Prolabo), then a saturated aqueous solution of calcium acetate (99%, Merck) and strontium carbonate (99%, Merck) were added quickly to increase the number of hydrolysis centres and therefore prevent crystallization. The precursors ($\text{Ti}(\text{Bu}-\text{O})_4$, $\text{Ca}(\text{C}_2\text{H}_3\text{O}_2)_2$ and SrCO_3) were mixed in stoichiometric amounts, i.e. $(\text{Ca}+\text{Sr})/\text{Ti} = 1$. Acetic acid was also added to stabilize the titanium precursor by increasing the Ti coordination and delay the hydrolysis of acetate groups and thus activate reactions with different cations from Ca- and Sr-precursors and formation of $\text{Ti}-\text{O}-\text{M}$ bonds. The increase of the viscosity of the mixture, maintained at 60°C , led to the formation of homogeneous gel which was dried in an oven for 24 hours at 80°C . After drying, the product was calcined at 1100°C in order to obtain the $\text{Ca}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$ phase. The calcined $\text{Ca}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$ ceramic powder was milled with different amounts of Li_2CO_3 and V_2O_5 in alcohol for 1 h with a Fritsch Pulverisette. Two types of samples were prepared (Table 1): the first one with equivalent mass of Li_2CO_3 and V_2O_5 and the second one with the eutectic $0.38\text{Li}_2\text{O}-0.62\text{V}_2\text{O}_5$ composition. After drying, an organic binder (polyvinyl alcohol APV 7.5% aqueous) was added and powders were then uniaxially pressed with a force of 20 kN, into pellets with diameter of 10 mm and thickness of 2–3 mm. Sintering was performed in a Pyrox furnace in air atmosphere at temperature determined according to dilatometric measurements with a ramp rate of $150^\circ\text{C}/\text{h}$ and a dwell time of 2 hours.

Table 1. Composition of $\text{Ca}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$ samples containing different amounts of additives: Li_2CO_3 , V_2O_5 and eutectic mixture ($0.38\text{Li}_2\text{O}-0.62\text{V}_2\text{O}_5$)

Sample notation	Li_2CO_3 [wt.%]	V_2O_5 [wt.%]	$0.38\text{Li}_2\text{O}-0.62\text{V}_2\text{O}_5$ [wt.%]	Li [at.%]	V [at.%]
CTS50					
CTS50-1.5	1.5	1.5		6.5	2.6
CTS50-2.5	2.5	2.5		10.8	4.4
CTS50-5	5	5		21.6	8.8
CTS50-E1.65			1.65	1.6	2.6
CTS50-E5			5	4.7	8.4

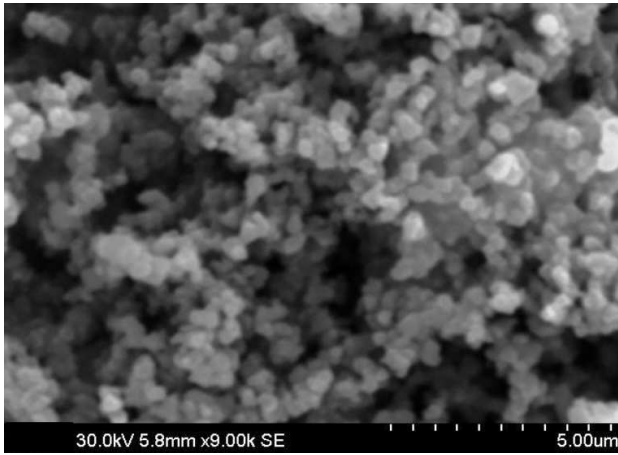


Figure 1. SEM micrograph of calcined $\text{Ca}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$ powder

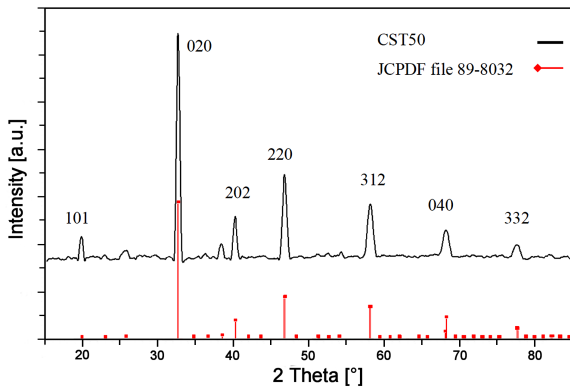


Figure 2. Diffractogram of calcined $\text{Ca}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$ powder

The crystalline phases of the sintered ceramics were determined by X-ray diffractometry (SIEMENS D5005 X-Ray Diffractometer) using $\text{Cu K}\alpha 1$ radiation and a step of 0.02 for 2θ with an acquisition time of 5 second per step. The shrinkage behaviour was studied in situ by TMA using a Setaram TMA92. Surface and cross-section microstructure of the sintered samples were observed by SEM (Hitachi S-3400N). The sample compositions were measured with EDX ThermoFinnigan system six. The porosity is calculated from the apparent density (ρ_{app}) relative to the absolute density (ρ_{abs}), which is determined with helium pycnometer (Accupyc 1330, Micrometric).

Gold electrodes are deposited using a brush on both sides of the pellets. To promote adherence the ceramic

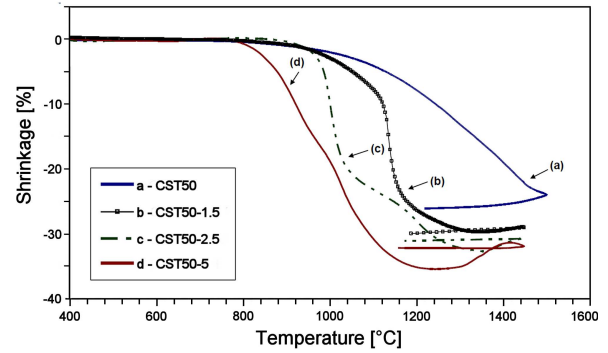


Figure 3. Dilatometric curves of $\text{Ca}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$ prepared with various amounts of Li_2CO_3 and V_2O_5 : CST50 (a), CST50-1.5 (b), CST50-2.5 (c) and CST50-5 (d)

samples coated with gold are annealed at 850°C . The dielectric properties were measured as a function of temperature using a RLC meter (Fluka PM306) and resistivity is determined by using a Megohmmeter (Sefelec).

III. Results and discussion

3.1. Structural characterization

Mean particle diameter of the calcined CST50 powder, measured by laser granulometry, is around 70 nm. When observed by SEM (Fig. 1) the CST50 powder (calcined at 1100°C) seems to be agglomerated. X-ray diffraction pattern (Fig. 2) indicates the presence of perovskite $\text{Ca}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$ phase (JCPDF 89-8032) with an orthorhombic structure and a surprisingly intensive 101 peak at $2\theta = 19.744^\circ$. Even the intensity of this peak might indicate incomplete phase formation we have not heated the powder at higher temperature in order to prevent the increasing of grains size.

Figure 3 shows the shrinkage behaviour of $\text{Ca}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$ ceramics with various amounts of Li_2O and V_2O_5 . For the CST50 sample without any sintering aids (Fig. 3, curve a), it can be seen that densification starts around 900°C and is nearly completed at 1500°C (Table 2). An attempt of sintering at this temperature indicates a value of densification of 97 %TD (theoretical value).

TMA curves of $\text{Ca}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$ with addition of equivalent mass of Li_2CO_3 and V_2O_5 (Fig. 3, curves b-d) show a real efficiency of the additions. The beginning of the shrinkage is shifted to lower temperatures when the amount of Li_2CO_3 and V_2O_5 is increased. More pre-

Table 2. Summary of sintering conditions and densification properties

Sample notation	Starting temperature of shrinkage [$^\circ\text{C}$]	Sintering temperature [$^\circ\text{C}$]	Shrinkage [%]	Porosity [%]
CTS50	900	1500	12	10
CTS50-1.5	890	1300	15.1	10
CTS50-2.5	850	1300	15	7
CTS50-5	750	1200	16.8	6
CTS50-E1.65	890	1300	11.5	10
CTS50-E5	700	1200	16.5	5

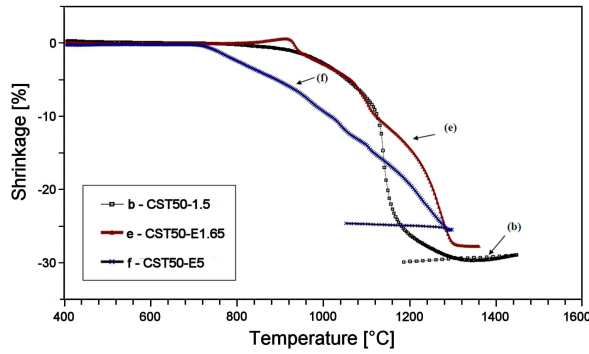
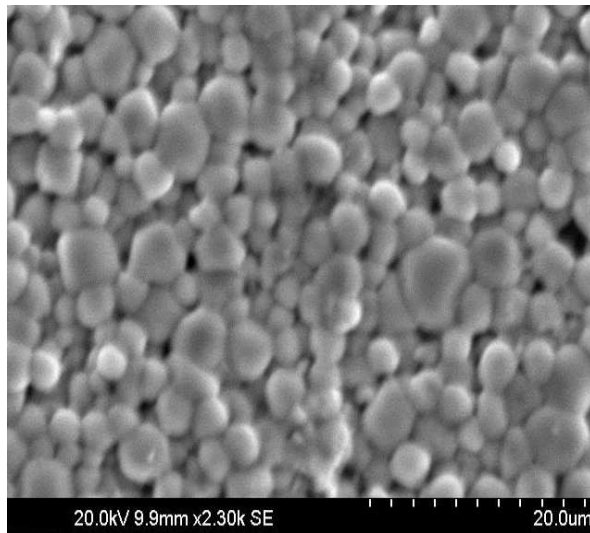


Figure 4. Dilatometric curves of $\text{Ca}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$ prepared with various amounts of eutectic mixture: CST50-1.5 (b), CST50-E1.65 (e) and CST50-E5 (f)

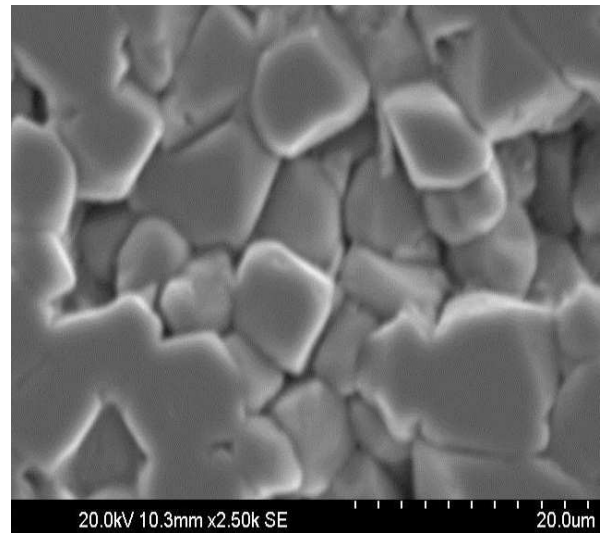
cisely we can notice that with addition of 1.5 wt.% of Li_2CO_3 and V_2O_5 (the sample CST50-1.5) the shrinkage starts at 890 °C and continues slowly until 1000 °C.

The shrinkage rate reaches a maximum at 1150 °C and the densification is completed at 1300 °C. At higher temperatures secondary porosity appears. Concerning the addition of 2.5 wt.% of Li_2CO_3 and V_2O_5 (the sample CST50-2.5) shrinkage begins at around 850 °C and strongly accelerates from this temperature up to 1000 °C where shrinkage slows down. Full densification occurs around 1300 °C. According to the obtained results the ceramics prepared with addition of 1.5 and 2.5 wt.% of Li_2CO_3 and V_2O_5 were sintered at 1300 °C (Table 2).

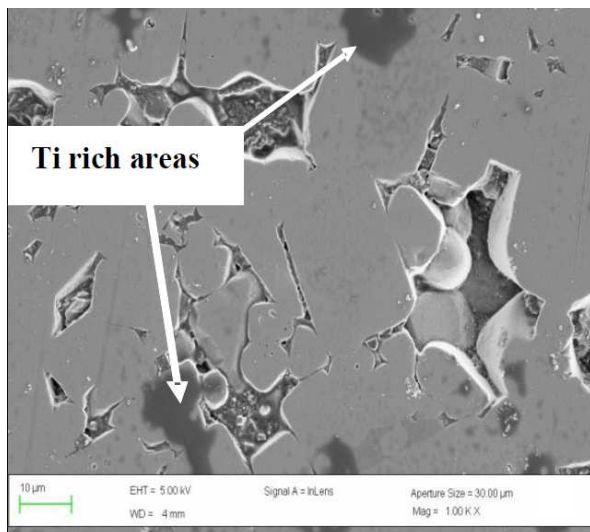
In the case of the sample with addition of 5 wt.% of Li_2CO_3 and V_2O_5 (CST50-5) the TMA exhibits a beginning of densification at 750 °C. Then the shrinkage continues until 1250 °C where full densification is obtained. Thus, the sample CST50-5 was sintered at a slightly lower temperature, i.e. at 1200 °C (Table 2) in order to avoid coarsening of grains and the appearance of secondary porosity.



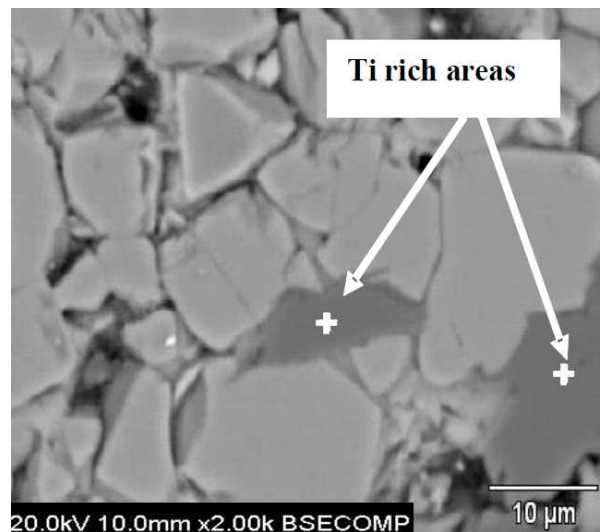
(a)



(b)



(c)



(d)

Figure 5. SEM micrographs of polished surface of $\text{Ca}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$ with various amounts of Li_2O and V_2O_5 : a) CST50 (sintered at 1500 °C), b) CST50-2.5 (sintered at 1300 °C), c) CST50-1.5 (sintered at 1300 °C) and d) CST50-E1.65 (sintered at 1300 °C)

Table 3. Pointed EDS analyses (from Fig. 5d)

Element line	Li-K	Ca-K	Ti-K	V-K	Sr-K
Cation content [at.%]	0.00	0.62	99.16	0.19	0.03
Error, +/ – 1 Sigma	0.00	0.13	0.53	0.17	0.09

Figure 4 shows the TMA curves of $\text{Ca}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$ ceramics obtained with different amounts of the eutectic $0.38\text{Li}_2\text{O}-0.62\text{V}_2\text{O}_5$ composition. The shrinkage of the sample CST50-E1.65 with 1.65 wt.% of the eutectic composition (curve e) starts at 950°C . The samples CST50-E1.65 and CST50-1.5 have the same amount of vanadium and similar TMA curves in temperature interval between 950°C and 1135°C (Fig. 4 curves b and e). However, at higher temperature the sintering of the CST50-E1.65 is slower. Thus, the sample CST50-E1.65 was sintered at 1300°C (Table 2).

High amount of the eutectic mixture (5 wt.%) leads to a premature shrinkage compared to the previous ones. It starts at 700°C and continues progressively until 1200°C where full densification is obtained. According to this, sintering temperature of the sample CST50-E5 was 1200°C (Table 2).

SEM micrographs of polished surface of the sintered samples are presented in Fig. 5. All ceramics have a dense structure and small amount of intergranular porosity (Table 2). It is clear that the grains have different sizes and shapes (2–12 microns). The small grains are inserted properly between large grains thus reducing porosity.

Pointed EDS analyses show the presence of titanium very rich phase (Fig. 5c,d) with more than 98 at.% Ti as showing in the pointed analysis data illustrated in Table 3. This indicates that Ti could be expelled from perovskite cell. It is not surprising when considering the mechanism of densification in the perovskite in the presence of Li [16]. Because of the very close energy of Ti and V lines, EDS analyses can't be helpful to study the repartition of V. We can't reject the hypothesis that V^{5+} can enter in the perovskite cell, especially as the radius of V^{5+} in 6 coordination is 0.54Å and 0.61Å for Ti^{4+} in the same coordination [30–32]. These substitutions

could lead to some compensation phenomenon. If Li^+ substitutes Ti^{4+} it can play the role of acceptor and if V^{5+} also substitutes Ti^{4+} it can be considered as a donor. These substitutions can limit the number of oxygen vacancies in the perovskite structure and may allow the obtaining of good dielectric properties [26]. The presence of Ti rich phase is also revealed for the samples with additives with the eutectic composition (Fig. 5d), but in that case we observe an increasing of grain size may be due to too high sintering temperature.

X-ray diffraction patterns of the sintered ceramics with various amounts of Li_2CO_3 and V_2O_5 (Fig. 6) are similar and can be indexed in perovskite cubic cell according to JCPDF: 35-0734. Not any secondary phase was observed. It confirms that additives don't destabilize the structure. If we index the cell according to cubic $Pm\bar{3}m$ it leads to: $a = 3.872\text{Å}$ instead of 3.905Å for the pure SrTiO_3 (JCPDF: 35-0734). The amounts of additives don't modify the cell parameter. It let us think that if Li^+ or (and) V^{5+} enter the perovskite cell it may be in very limited amount otherwise parameters cell will be different for each amount and secondary phase(s) will certainly be observed for high amount of additives. The cell with the same lattice parameter ($a = 3.872\text{Å}$) is also observed for eutectic additives (Fig. 7), so even if EDS analyses present a Ti rich phase, it doesn't seem to be demonstrated that cations Li^+ and V^{5+} replace Ti^{4+} in the perovskite cell. The densification of these samples could also be due to some liquid phases as shown in phase diagram $\text{Li}_2\text{O}/\text{V}_2\text{O}_5$ or in systems Ca/Sr/V oxides [25].

3.2. Dielectric properties

Dielectric properties of $\text{Ca}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$ ceramics prepared with addition of equivalent mass of Li_2CO_3 and V_2O_5 are presented in Fig. 8. The pure $\text{Ca}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$

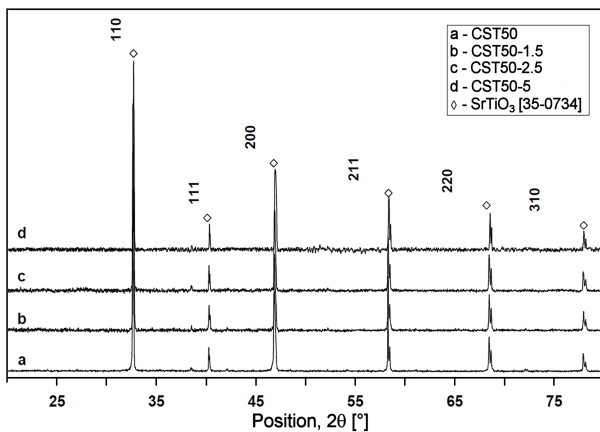


Figure 6. Diffraction pattern of $\text{Ca}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$ prepared with different amount of Li_2CO_3 and V_2O_5

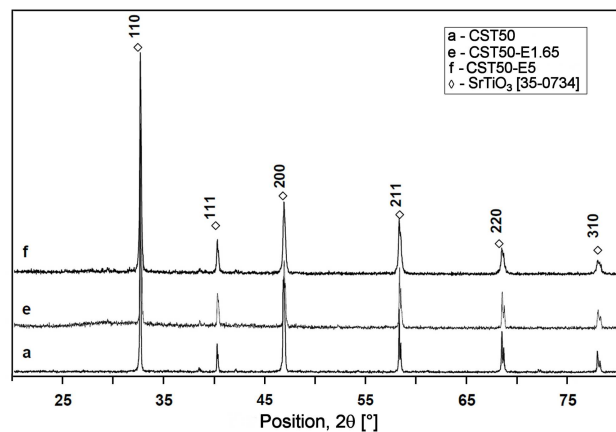


Figure 7. Diffraction pattern of $\text{Ca}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$ prepared with different amount of eutectic composition

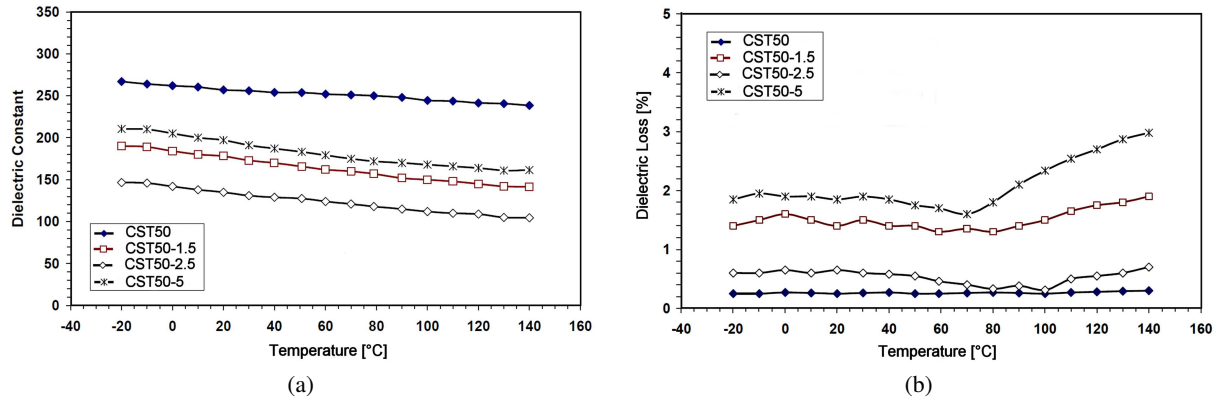


Figure 8. Dielectric properties of $\text{Ca}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$ prepared with different amounts of Li_2CO_3 and V_2O_5 : a) dielectric constant and b) dielectric loss

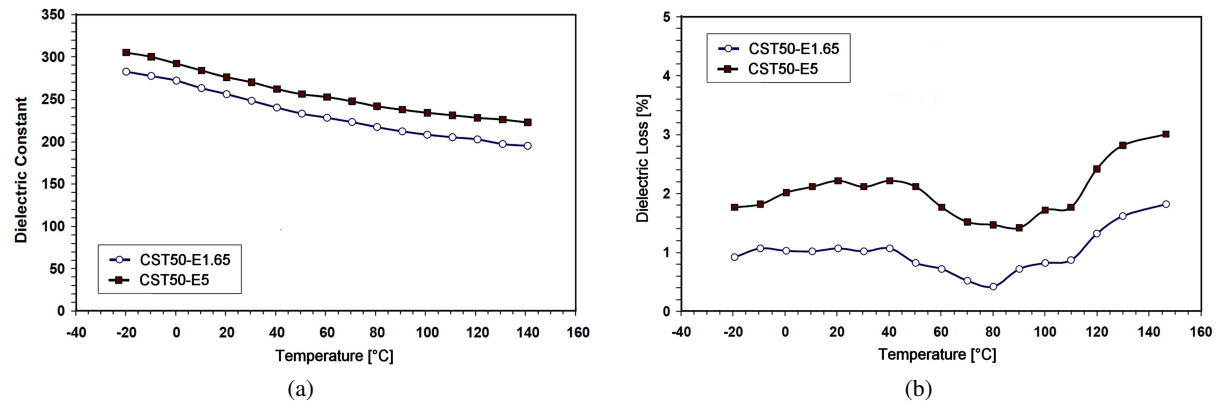


Figure 9. Dielectric properties of $\text{Ca}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$ prepared with different amounts of eutectic composition: a) dielectric constant and b) dielectric loss

ceramic (CST50) has the highest dielectric constant at all investigated temperatures. With 1.5 and 2.5 wt.% of Li_2CO_3 and V_2O_5 (the samples CST50-1.5 and CST50-2.5) dielectric constant decreases, but addition of 5 wt.% of Li_2CO_3 and V_2O_5 (the sample CST50-5) cause an increase of permittivity. This lowering of the permittivity value is accompanied by an increase of dielectric loss, indicating the increased conductivity. It is noteworthy that increase of dielectric loss is also not directly correlated to the amount of Li_2CO_3 and V_2O_5 .

Concerning the $\text{Ca}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$ with addition of the eutectic composition an increase of dielectric constant at lower temperatures, and its decreases at higher temperatures are observed (Fig. 9a). However, addition of the eutectic composition cause considerable increase of dielectric loss (Fig. 9b). Dielectric loss also indicates the presence of semi-conduction at high temperature similar to the $\text{Ca}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$ ceramics obtained with addition of Li_2CO_3 and V_2O_5 . These properties might be optimised by adjustment of appropriate sample composition and one interesting way would be the study of addition of those sintering additives which could form structure with Ti vacancies. This could improve densification and make easier the insertion of acceptor/donor pair in Ti site [17].

The addition of Li-compound to dielectric materials can exacerbate moisture sensitivity [27–29]. In order to investigate this behaviour, we have measured dielectric properties of the same samples but without any regulation of humidity in the measuring unit. In dry atmosphere the samples with addition of eutectic composition (CTS50-E1.65 and CTS50-E5) indicate a resistivity greater than $10^{11} \Omega\cdot\text{cm}$. However, dielectric loss of the $\text{Ca}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$ ceramics prepared with addition of

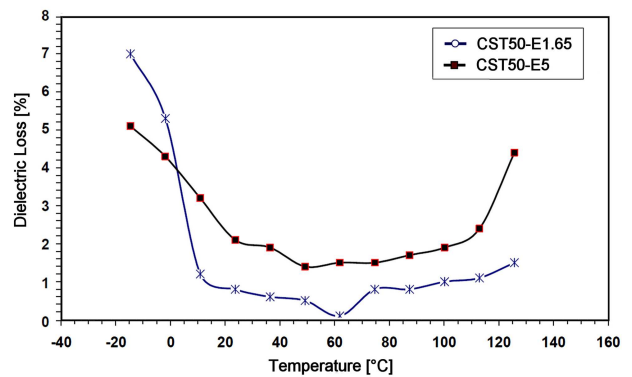


Figure 10. Dielectric loss measured at uncontrolled humidity of $\text{Ca}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$ prepared with different amounts of eutectic mixture

the eutectic composition (Fig. 10) clearly shows an increase, which might be correlated to the increase of humidity in the oven. This clearly confirms that the studied samples with additives are sensitive to humidity levels in air.

This fact can also be amplified by porosity (ratio of geometric density and helium pycnometry density) of these materials. It is observed that porosity decreases with increasing the amounts of Li_2CO_3 and V_2O_5 (Table 2). In addition, according to dielectric measurements, given in Fig. 10, the sample CTS50-E1.65 with addition of 1.65 wt.% of the eutectic composition is more sensitive to humidity than the sample CTS50-E5 with 5 wt.% of the eutectic composition. However, this sample is also more porous: about 10% for the sample CTS50-E1.65 in comparison to 5% for the sample CTS50-E5. So sensitivity to humidity is not simply correlated with the amount of Li and V [27].

IV. Conclusions

This study clearly shows the efficiency of $\text{Li}_2\text{O}/\text{V}_2\text{O}_5$ addition on the densification of $\text{Ca}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$ since sintering temperature can be lowered to 1200 °C for the ceramic prepared with 5 wt.% Li_2CO_3 and 5 wt.% V_2O_5 . Dense samples with little porosity were obtained with this co-addition. Best results are obtained with the addition of these elements in the form of the eutectic mixture (0.38 Li_2O -0.62 V_2O_5). The addition of 5 wt.% of the eutectic mixture allows the obtaining of material with only 5% of porosity. The cubic structure seems to be stabilised by the addition. In both cases type I dielectric properties are conserved with dielectric constant around 240 ($R_i > 10^{11} \Omega\cdot\text{cm}$) and an increase of dielectric loss. The Li_2CO_3 and V_2O_5 addition leads also to an increase of sensitivity to humidity. This sensitivity is correlated to the presence of residual porosity. The study of densification optimisation by adjusting the Ti amount and sensitivity to humidity is in progress and will be published soon.

References

1. P.M. Woodward, "Octahedral tilting in perovskites, II. Structure stabilizing forces", *Acta Crystallogr. Sect.*, **B53** [1] (1997) 44–66.
2. H. Yoshioka, "Structure and electrical properties of A-site-deficient perovskite compounds in the $\text{La}_{2/3}\text{TiO}_3$ - $\text{La}_{1/3}\text{NbO}_3$ system", *J. Am. Ceram. Soc.*, **85** [5] (2002) 1339–1342.
3. L. Zhou, P.M. Vilarinho, J.L. Baptista, "Solubility of bismuth oxide in barium titanate", *J. Am. Ceram. Soc.*, **82** [4] (1999) 1064–1066.
4. D. Kolar, M. Trontelj, Z. Stadler, "Influence of inter-diffusion on solid solution formation and sintering in the system BaTiO_3 - SrTiO_3 ", *J. Am. Ceram. Soc.*, **65** [10] (1982) 470–474.
5. S. Qin, A.I. Becerro, F. Seifert, J. Gottsmann, J. Jiang, "Phase transitions in $\text{Ca}_{1-x}\text{Sr}_x\text{TiO}_3$ perovskites; effects of composition and temperature", *J. Mater. Chem.*, **10** [7] (2000) 1609–1615.
6. C.J. Ball, B.D. Begg, D.J. Cookson, G.J. Thoroughgood, E.R. Vance, "Structures in the system CaTiO_3 - SrTiO_3 ", *J. Solid State Chem.*, **139** [2] (1998) 238–247.
7. M. Ceh, D. Kolar, L. Golic, "The phase diagram of CaTiO_3 - SrTiO_3 ", *J. Solid State Chem.*, **68** [1] (1987) 68–72.
8. S. Sasaki, C.T. Prewitt, J.D. Bass, W.A. Schulze, "Orthorhombic perovskite CaTiO_3 and CdTiO_3 : structure and space group", *Acta Cryst.*, **C43** [9] (1987) 1668–1674.
9. R.H. Buttner, E.N. Maslen, "Structural study of the low-temperature phase transition in $\text{Cs}_3\text{D}(\text{SeO}_4)_2$ ", *Acta Crystal. Sect.*, **B48** [5] (1992) 633–639.
10. R. Ranjan, D. Pandey, V. Siruguri, P.S.R. Krishna, S.K. Paranjpe, "Novel structural features and phase transition behaviour of $(\text{Sr}_{1-x}\text{Ca}_x)\text{TiO}_3$ II. X-ray diffraction studies", *J. Phys. Condensed Matter*, **11** [10] (1999) 2247–2258.
11. J.N. Walsh, P.A. Taylor, A. Buckley, T.W. Darling, J. Schreuer, M.A. Carpenter, "Elastic and anelastic anomalies in $(\text{Ca},\text{Sr})\text{TiO}_3$ perovskites: Analogue behaviour for silicate perovskites", *Phys. Earth Planet. Int.*, **167** [1–2] (2008) 110–117.
12. M.A. Carpenter, C.J. Howard, K.S. Knight, Z. Zhang, "Structural relationships and a phase diagram for $(\text{Ca},\text{Sr})\text{TiO}_3$ perovskites", *J. Phys. Condens. Matter*, **18** [48] (2006) 10725–10749.
13. R. Li, Q. Tang, S. Yin, H. Yamane, T. Sato, "Sintering and characterization of $\text{Ca}_{0.9}\text{Sr}_{0.1}\text{TiO}_3$ ceramics with sintering additive", *Mater. Sci. Eng.*, **A373** [1–2] (2004) 175–179.
14. Q.L. Zhang, H. Yang, H.P. Sun, "A new microwave ceramic with low-permittivity for LTCC applications", *J. Eur. Ceram. Soc.*, **28** [3] (2008) 605–609.
15. M.J. Laurent, G. Desgardin, B. Raveau, J.M. Haussonne, J. Lostec, "Sintering of strontium titanate in the presence of lithium salts in a reducing atmosphere", *J. Mater. Sci.*, **23** [12] (1988) 4481–4486.
16. J.M. Haussonne, G. Desgardin, P.H. Bajolet, B. Raveau, "Barium titanate perovskite sintered with lithium fluoride", *J. Am. Ceram. Soc.*, **66** [11] (1983) 801–807.
17. J.M. Haussonne, O. Regreny, J. Lostec, G. Desgardin, M. Halmi, B. Raveau, "Sintering of various perovskites with lithium salts", *6th International Meeting on Modern Ceramics Technologies. (CIMTEC) World Congress on High Tech. Ceramics*, Milan, Italy, Elsevier, Amsterdam, Vol. 38 A-B-C [1–9] (1987) 1515–1524.
18. K. Cvetkovic, A. Petric, "Periodic table of the oxides", *Am. Ceram. Soc. Bul.*, **79** (2000) 65–69.
19. Y. Zhang, Z. Hue, Z. Gui, L. Li, "Low temperature sintered ZnNb_2O_6 microwave dielectric ceramics doped with $\text{CuO-Bi}_2\text{O}_3$ - V_2O_5 additions", *J. Mater. Sci. Lett.*, **22** [8] (2003) 595–597.

20. C.L. Huang, C.H. Shen, C.L. Pan, “Characterization and dielectric behavior of V_2O_5 -doped $MgTiO_3$ - $CaTiO_3$ ceramic system at microwave frequency”, *Mater. Sci. Eng.*, **B145** [1-3] (2007) 91–96.
21. Y.J. Gu, J.L. Huang, Q. Li, D.M. Sun, H. Xu, “Low-temperature firing and microwave dielectric properties of 16 CaO -9 Li_2O -12 Sm_2O_3 -63 TiO_2 ceramics with V_2O_5 addition”, *J. Eur. Ceram. Soc.*, **28** [16] (2008) 3149–3153.
22. Q. Zeng, W. Li, J.L. Shi, X.L. Dong, J.K. Guo, “Influence of V_2O_5 additions to 5 Li_2O -1 Nb_2O_5 -5 TiO_2 ceramics on sintering temperature and microwave dielectric properties”, *J. Am. Ceram. Soc.*, **90** [7] (2007) 2262–2265.
23. A.Y. Borisevich, P.K. Davies, “Effect of V_2O_5 doping on the sintering and dielectric properties of M-phase $Li_{1+x-y}Nb_{1-x-3y}Ti_{x+4y}O_3$ ceramics”, *J. Am. Ceram. Soc.*, **87** [6] (2004) 1047–1052.
24. Q. Zeng, W. Li, J.L. Shi, J.K. Guo, “Microwave dielectric properties of 5 Li_2O -0.583 Nb_2O_5 -3.248 TiO_2 ceramics with V_2O_5 ”, *J. Am. Ceram. Soc.*, **89** [10] (2006) 3305–3307.
25. A.A. Fotiev, “System V_2O_5 - $LiVO_3$ ”, *Russ. J. Inorg. Chem.*, **13** [7] (1968) 1007–1010.
26. K. Albertsen, D. Hennings, O. Steigelmann, “Donor-acceptor charge complex formation in barium titanate ceramics: role of firing atmosphere”, *J. Electroceram.*, **2** [3] (1998) 193–198.
27. J. Bernard, D. Houivet, M. Hervieu, J.M. Haussonne, “Evidence of the formation of a new rock-salt type compound Li_2MgTiO_4 and of its role on the properties of the Li doped $MgTiO_3$ ”, *Sol. State Sci.*, **8** (2006) 598–605.
28. E. Traversa, “Ceramic sensors for humidity detection: The state of the art and future developments”, *Sensors Actuators*, **B23** (1995) 135–156.
29. J. Bernard, D. Houivet, J.M. Haussonne, “Surface resistance and sensitivity to hygrometry of various ceramic compositions for multilayer capacitors”, *J. Eur. Ceram. Soc.*, **25** [12] (2005) 2977–2979.