Influence of Li$_2$CO$_3$ and V$_2$O$_5$ combined additions on the sintering and dielectric properties of Ca$_{0.5}$Sr$_{0.5}$TiO$_3$ ceramics prepared from powders synthesized by sol-gel method

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Abstract

In this work, we have studied the influence of lithium carbonate (Li$_2$CO$_3$) associated with the vanadium oxide (V$_2$O$_5$) on sintering and dielectrics properties of Ca$_{0.5}$Sr$_{0.5}$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 uniaxially pressed and sintered in air atmosphere at temperature determined by dilatomeric measurements. The pure Ca$_{0.5}$Sr$_{0.5}$TiO$_3$ sample obtained by this process required a sintering temperature around 1500 °C. The addition of Li$_2$CO$_3$ combined with V$_2$O$_5$ improved sinterability and caused a shift of dilatomeric shrinkage curve to much lower temperatures. Thus, dense ceramics (98% of theoretical density) were obtained at sintering temperature $\leq$ 1300 °C. The effect of adding Li$_2$CO$_3$-V$_2$O$_5$ on the structure of ceramics and the dielectric properties is discussed and show that type 1 dielectric properties (linear variation of the permittivity) are conserved, but with an increase of dielectric loss.

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

I. 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 Ca$_{1-x}$Sr$_x$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 $Bnnm$ 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 Ca$_{1-x}$Sr$_x$TiO$_3$ synthesized by the solid state route and sintered at high temperature. It is known that the
high sintering temperature can be decreased by a li-
quid phase sintering with sintering agents such as lithium
salts, vanadium oxide etc. [13–15]. Thus, previous stud-
ies [16–18] have shown the important role of lithium for a
low sintering temperature of BaTiO₃, SrTiO₃ or gener-
ally all ABO₃ perovskites. Two mechanisms can oc-
cur simultaneously [16]. In the first, lithium might be,
together with fluorine, introduced into the perovskite
BaTiO₃ lattice, and form solid solution with the gen-
eral formula BaTi₁ₓLiₓO₃₋ₓFₓ. According to the sec-
ond, it has been stated that lithium might be introduced
in the perovskite structure and it can be described by the
formula A(BₓLiₓ)O₃₋ₓ. Thus, LiO₄ tetrahedra can be
created by simple elimination of rows of oxygen atoms
along the <110> direction. Moreover, the ability of ti-
tanium to take a square pyramidal coordination sug-
gests that oxygen vacancies might also appear in the
TiO₆ octahedra, due to the introduction of lithium. It is
most probable that isolated LiO₄ tetrahedra as well as
TiO₃ pyramids are formed simultaneously in the struc-
ture and that anionic vacancies are randomly distributed,
leading to a low temperature densification of the ma-
terial. Vanadium, can also have two effects: the first one is
the low melting point of V₂O₅ (Tₚ = 690 °C) which can
lead to a lowering of sintering temperature; the second
one is the small radius in coordinence 6 of V
⁵⁺ (r_V⁵⁺ = 0.54 Å) [18]. Which could facilitate its inclusion
in the Ca₁₋ₓSrₓTiO₃ structure and enhance diffusion in the
cationic B sublattice (r_B⁴⁺ = 0.72 Å). In addition,
a combined effect of vanadium with lithium cannot be
excluded. The literature [19–24] suggests V₂O₅ to be a
promising sintering aid for the densification of oxide at relatively
low temperatures. For example, it allows the sintering of
Li₂O-Nb₂O₅-5TiO₂ at 900 °C, Li₁₋ₓNbₓO₋ₓ₋₂TiₓO₅ at 900 °C, 5Li₂O-0.583Nb₂O₅-3.248TiO₂ at 920 °C, and
MgTiO₃-CaTiO₃ at 1300 °C. Its effectiveness has been also demonstrated,
when associated with Br₃O and CuO in ZnNb₂O₆ system by Huang et al. [20] and Gu et al. [21].

The effects of combined addition of Li₃CO₃ and
V₂O₅ on the sintering behaviour of Ca₁₋ₓSrₓTiO₃ have not yet been thoroughly investigated. In this paper, we
report on the possibility of lowering the sintering tem-
perature of Ca₀.₅Sr₀.₅TiO₃ ceramics by co-addition of
Li₃CO₃ (Tₚ = 720 °C) and V₂O₅ (Tₚ = 690 °C) with
equal amount of two oxides or by addition of the eu-
tectic 0.38 Li₂O-0.62 V₂O₅ composition (Tₚ = 550 °C
[25]). In the first one, the sintering will occur with an
excess of lithium, however with the eutectic composi-
tion the sintering process will be held with an excess of
vanadium. The effect of those sintering aids on sin-
terability and dielectric properties of Ca₀.₅Sr₀.₅TiO₃ cer-
amics were investigated in terms of microstructure and
structure analysis.

II. Experimental

The pure Ca₀.₅Sr₀.₅TiO₃ (denoted as CST50) powder was prepared by the sol-gel method. It is well known
that titanium alkoxides are highly reactive in the pres-
ence of water and under uncontrolled conditions might
cause rapid formation of hydrated titanium oxide by
condensation between Ti-OH or Ti-O-Ti. Because of
that titanium butoxide (97%, Aldrich) was diluted in
butanol-2 (98%, Prolabo) and acetic acid (96%, Pro-
labo), then a saturated aqueous solution of calcium
acetate (99%, Merck) and stearonate (99%, Merck)
were added quickly to increase the number of hydrolysis centres and therefore prevent crystallization.
The precursors (Ti(Bu-O)₄, Ca(C₂H₃O₂)₂ and SrCO₃)
were mixed in stoichiometric amounts, i.e. (Ca+Sr)/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 Ti-O-M bonds. The increase of the viscos-
ity of the mixture, maintained at 60 °C, led to the for-
mation of homogeneous gel which was dried in an oven
for 24 hours at 80 °C. After drying, the product was cal-
cined at 1100 °C in order to obtain the Ca₀.₅Sr₀.₅TiO₃
phase. The calcined Ca₀.₅Sr₀.₅TiO₃ ceramic powder was
milled with different amounts of Li₂CO₃ and V₂O₅ in
alcohol for 1 h with a Fritsch Pulverisette. Two types of
samples were prepared (Table 1): the first one with
equivalent mass of Li₂CO₃ and V₂O₅ and the second one with the eutectic 0.38 Li₂O-0.62 V₂O₅ composition.
After drying, an organic binder (polyvinyl alcohol APV
7.5% aqueous) was added and powders were then un-
axially 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 mea-
surements with a ramp rate of 150 °C/h and a dwell time of
2 hours.

<table>
<thead>
<tr>
<th>Sample notation</th>
<th>Li₃CO₃ [wt.%]</th>
<th>V₂O₅ [wt.%]</th>
<th>0.38 Li₂O-0.62 V₂O₅ [wt.%]</th>
<th>Li [at.%]</th>
<th>V [at.%]</th>
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The crystalline phases of the sintered ceramics were determined by X-ray diffraction (SIEMENS D5005 X-Ray Diffractometer) using Cu Kα1 radiation and a step of 0.02 for 2θ with an acquisition time of 5 seconds 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 Thermonoran 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 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 Megohmeter (Sefelec).

### III. Results and discussion

#### 3.1. Structural characterization

Mean particle diameter of the calcined CTS50 powder, measured by laser granulometry, is around 70 nm. When observed by SEM (Fig. 1) the CTS50 powder (calcined at 1100 °C) seems to be agglomerated. X-ray diffraction pattern (Fig. 2) indicates the presence of perovskite Ca_{0.5}Sr_{0.5}TiO_{3} phase (JCPDF 89-8032) with an orthorhombic structure and a surprisingly intensive 101 peak at 2θ = 19.744°. 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. Dilatometric curves of Ca_{0.5}Sr_{0.5}TiO_{3} prepared with various amounts of Li_{2}CO_{3} and V_{2}O_{5}: CTS50 (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 Megohmeter (Sefelec).](image)

<table>
<thead>
<tr>
<th>Sample notation</th>
<th>Starting temperature of shrinkage [°C]</th>
<th>Sintering temperature [°C]</th>
<th>Shrinkage [%]</th>
<th>Porosity [%]</th>
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cisely we can notice that with addition of 1.5 wt.% of Li$_2$CO$_3$ and V$_2$O$_5$ (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$_2$CO$_3$ and V$_2$O$_5$ (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$_2$CO$_3$ and V$_2$O$_5$ were sintered at 1300 °C (Table 2).

In the case of the sample with addition of 5 wt.% of Li$_2$CO$_3$ and V$_2$O$_5$ (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.
Figure 4 shows the TMA curves of Ca$_{0.5}$Sr$_{0.5}$TiO$_3$ ceramics obtained with different amounts of the eutectic 0.38Li$_2$O-0.62V$_2$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 0.54 Å and 0.61 Å 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.

![Figure 6](image1.jpg) ![Figure 7](image2.jpg)

**Figure 6.** Diffraction pattern of Ca$_{0.5}$Sr$_{0.5}$TiO$_3$ prepared with different amount of Li$_2$CO$_3$ and V$_2$O$_5$.

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

X-ray diffraction patterns of the sintered ceramics with various amounts of Li$_2$CO$_3$ and V$_2$O$_5$ (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 $Pm3m$ it leads to: $a = 3.872$ Å instead of 3.905 Å 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 ($a = 3.872$ 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 Li$_2$O/V$_2$O$_5$ or in systems Ca/Str/N oxides [25].

### 3.2. Dielectric properties

Dielectric properties of Ca$_{0.5}$Sr$_{0.5}$TiO$_3$ ceramics prepared with addition of equivalent mass of Li$_2$CO$_3$ and V$_2$O$_5$ are presented in Fig. 8. The pure Ca$_{0.5}$Sr$_{0.5}$TiO$_3$
ceramic (CST50) has the highest dielectric constant at all investigated temperatures. With 1.5 and 2.5 wt.% of Li$_2$CO$_3$ and V$_2$O$_5$ (the samples CST50-1.5 and CST50-2.5) dielectric constant decreases, but addition of 5 wt.% of Li$_2$CO$_3$ and V$_2$O$_5$ (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$_2$CO$_3$ and V$_2$O$_5$.

Concerning the Ca$_{0.5}$Sr$_{0.5}$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 Ca$_{0.5}$Sr$_{0.5}$TiO$_3$ ceramics obtained with addition of Li$_2$CO$_3$ and V$_2$O$_5$. 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 $10^{13}$ Ω·cm. However, dielectric loss of the Ca$_{0.5}$Sr$_{0.5}$TiO$_3$ ceramics prepared with addition of

![Figure 8. Dielectric properties of Ca$_{0.5}$Sr$_{0.5}$TiO$_3$ prepared with different amounts of Li$_2$CO$_3$ and V$_2$O$_5$: a) dielectric constant and b) dielectric loss.](image1)

![Figure 9. Dielectric properties of Ca$_{0.5}$Sr$_{0.5}$TiO$_3$ prepared with different amounts of eutectic composition: a) dielectric constant and b) dielectric loss.](image2)

![Figure 10. Dielectric loss measured at uncontrolled humidity of Ca$_{0.5}$Sr$_{0.5}$TiO$_3$ prepared with different amounts of eutectic mixture.](image3)
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$_2$CO$_3$ and V$_2$O$_5$ (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 Li$_2$O/V$_2$O$_5$ addition on the densification of Ca$_{0.95}$Sr$_{0.05}$TiO$_3$ since sintering temperature can be lowered to 1200 °C for the ceramic prepared with 5 wt.% Li$_2$CO$_3$ and 5 wt.% V$_2$O$_5$. 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 (0.38Li$_2$O-0.62 V$_2$O$_5$). The addition of 5 wt.% of the eutectic mixture allows 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 (Ri > 10$^{11}$ Ω·cm) and an increase of dielectric loss. The Li$_2$CO$_3$ and V$_2$O$_5$ 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


