CaTiO₃ RELATED MATERIALS FOR RESONATORS

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Ceramics of $Ca_{0.95}M_{0.05}(Ti_{0.95}Li_{0.05})O_{2.85}F_{0.15}$ (M = Ca, Sr, Pb) are prepared from mixtures of CaTiO₃, MF₂ and LiF powders by sintering at 950°C for 4 hours in free-air. The samples are investigated by X-ray diffraction, scanning electron microscopy , differential scanning calorimetry and dielectric measurements. The phase transitions of pure CaTiO₃ are strongly influenced by the incorporation of the fluoride mixture MF₂ + LiF into the host lattice whereas the orthorhombic symmetry at room temperature is not at all affected by the chemical substitutions Ca–M, Ti–Li and O–F. The dielectric permittivity ε'_r and losses $\tan\delta$ are slightly dependent of temperature between 20°C and 200°C. At room temperature, ε'_r is stable over a large frequency range with $\tan\delta < 1\%$. The $Ca_{0.95}M_{0.05}(Ti_{0.95}Li_{0.05})O_{2.85}F_{0.15}$ (M = Ca, Sr, Pb) oxyfluorides are promising materials to manufacture resonators.

INTRODUCTION

Calcium titanate is well known for the treatment of radioactive wastes since this perovskite forms a vast number of solid solutions with rare earth metals [1-4]. On the other hand, CaTiO₃ - based materials are used as catalysts for partial oxidation of light hydrocarbons [5]. However, the papers dealing with calcium titanate related electroceramics are limited in comparison with BaTiO₃ or SrTiO₃.

The structural phase transitions in pure CaTiO₃ have been investigated by a lot of authors by various techniques: heat capacity measurements, Raman spectroscopy, high temperature X-ray diffractometry, differential thermal analysis [6-9]. Irrespective of the method used, two phase transitions were detected at very high temperatures. After Redfern, the first one occurs in the range 1373-1423 K and the second one appears at 1523 ± 10 K [8]. These transformations correspond to the sequence of crystallographic changes orthorhombic (Pbnm) ↔ tetragonal (I4/mcm) ↔ cubic (Pm3m) [8].

Recently, calcium titanate entered the family of quantum paraelectrics like SrTiO₃ and KTaO₃ [10]. Moreover, Zelezny et al [11] reported a ferroelectric behavior of CaTiO₃ at very low temperature (TC ~ 105 K). According to Chandra et al [12], the (Ca₁₋ₓPbₓ)TiO₃ system exhibits an antiferroelectric phase transition in the temperature range 140-170 K, similar to that observed in (Ca₁₋ₓSrₓ)TiO₃ system by Ranjan et al [13].

Nowadays, advanced ceramics became the key of success for the development of integrated circuits in microelectronic industry. Calcium titanate could be of great usefulness in this field of applications in the future. Nevertheless, pure CaTiO₃ ceramics are difficult to densify and too fragile for many practical applications whereas compositionally modified ceramic bodies derived from calcium titanate could be of high interest in special applications such as capacitors and resonators.

In previous works we have dealt with successful preparations of $Ca_{1-x}M_x(Ti_{1-x}Li_x)O_{3-3x}F_{3x}$ solid solutions (M = Ca, Sr, Pb) [14-16] using rough CaTiO₃ with a disbribution grain size in the range 50-500 μm. The objective of the present study is the investigation of physical properties of ceramics with nominal compositions $Ca_{0.95}M_{0.05}(Ti_{0.95}Li_{0.05})O_{2.85}F_{0.15}$ prepared from calcium titanate with a selected granulometric class (450 μm ≤ grain size ≤ 500 μm). Emphasis is put on the dielectric characterizations.

EXPERIMENTAL

The starting products used in this study are CaCO₃, TiO₂, CaF₂, SrF₂, PbF₂ and LiF. Calcium carbonate and titanium dioxide are MERCK products of 99.9% purity

grade. They are previously dried in an oven at 300°C for 72 h. The fluorides are also MERCK products but of suprapur quality. They are carefully dried under vacuum at 150°C for 4 h.

Calcium titanate is synthesized by solid state reaction in a platinium crucible. A stoichiometric mixture of $CaCO_3$ and TiO_2 is finely ground in an agate mortar then calcined in dry air at 850°C for 8 h. The powder obtained is re-ground and annealed for 2 h in the same conditions, then ground and separated in several granulometric classes.

Appropriate proportions of $CaTiO_3$ (95 mol. %) with granulometry 450-500 μm, MF_2 (5 mol. %) (M = Ca, Sr, Pb) and LiF (5 mol. %) are mixed thoroughly and dry-ground for 30 min in an agate mortar. After grinding, the various powders are cold-pressed to tablets of 13mm diameter and about 1mm thickness under an uniaxial pressure of 100 MPa. The disks thus obtained are heated under vacuum at 150 °C for 2 h to eliminate any water fixed during grinding then sintered in dry air 950°C for 4 h on platinum plates with a heating rate of 200°C/h.

The ceramics prepared are subjected to: measurement of shrinkage (ΔΦ/Φ) and density, X-ray diffraction (XRD) analysis, scanning electron microscopy (SEM) observations, differential scanning calorimetry (DSC) analysis, dielectric measurements.

XRD data are collected at room temperature on crushed ceramics into fine powders using a PHILPS PW 1710 diffractometer with the $K_{\alpha 1}$ copper radiation ($\lambda = 1.54051$ Å) in the angular range $5° \leq 2\theta \leq 120°$. The cell parameters are calculated then refined using a least squares method.

SEM observations are performed on polished surfaces and on fractured ceramics by means of a PHILIPS LX30 scanning electron microscope coupled with an energy dispersive X-ray spectrometer. The operating voltage is 20 kV.

DSC analysis are carried out under nitrogen gas (N_2) with a PERKIN-ELMER apparatus on crushed ceramics into fine powders from room temperature up to 600°C. The heating rate is 10°C/min.
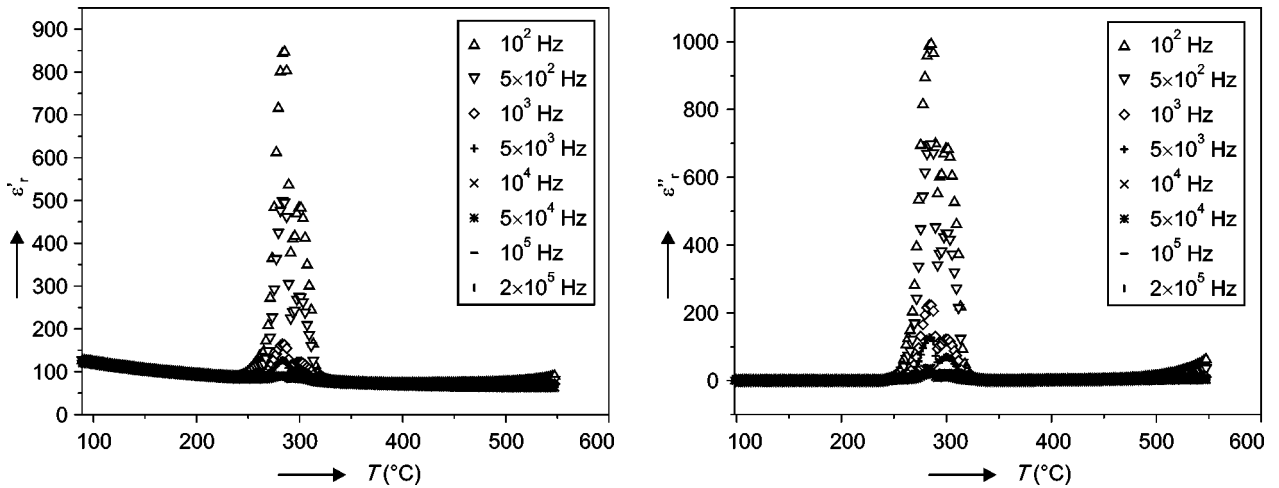
For dielectric measurements, both faces of the sintered pellets are polished then electroded by sputter deposition of gold. The real and the imaginary dielectric permittivities (ε'_r, ε''_r) are measured under helium gas (He), firstly as a function of temperature between room temperature and 600°C at various frequencies (10^2 Hz, 5×10^2 Hz, 10^3 Hz, 5×10^3 Hz, 10^4 Hz, 5×10^4 Hz, 10^5 Hz, 2×10^5 Hz) using a WAYNE-KERR capacitance bridge. Dielectric measurements are then performed at room temperature versus frequency in the range 10^5-4×10^7 Hz by means of a HEWLETT PACKARD impedance analyzer HP 4194A. All measurements are computer controlled and, before each measurement, the ceramic is heated in the cell under vacuum at 150°C for 2 h to eliminate any contribution of water vapor on the dielectric characteristics.
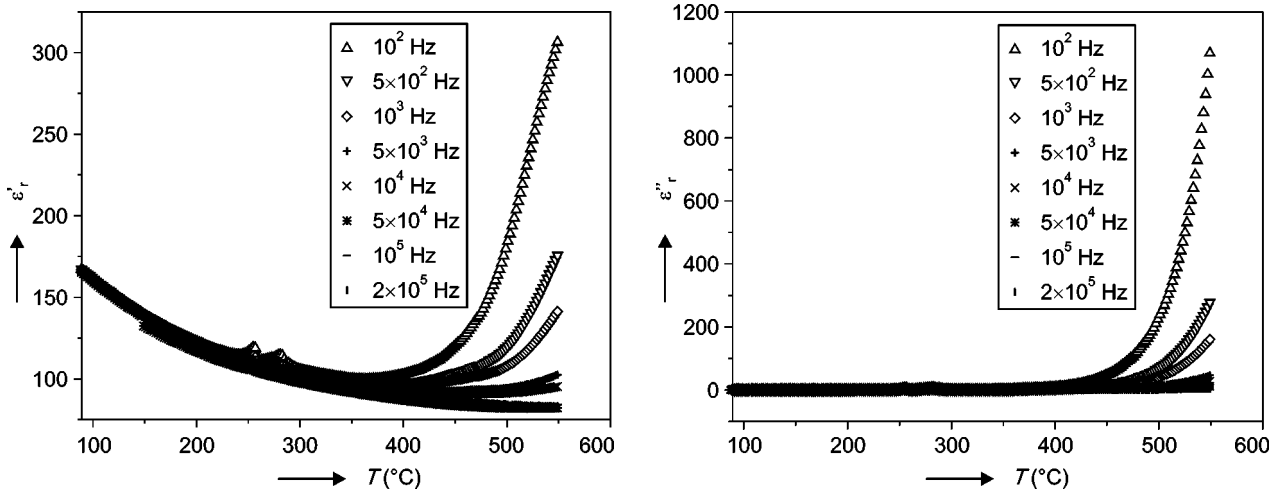
RESULTS AND DISCUSSION

The shrinkage, the relative density, the cell parameters, the spontaneous deformation , the grain size, the phase transitions temperatures obtained by DSC and dielectric characteristics are reported in table 1.

Table 1. Shrinkage, relative density, cell parameters, spontaneous deformation (e_s), grain size, phase transitions temperatures obtained by DSC and dielectric characteristics.

Composition		$CaTiO_3$	$Ca(Ti_{0.95}Li_{0.05})O_{2.85} F_{0.15}$	$Ca_{0.95}Sr_{0.05}(Ti_{0.95} Li_{0.05})O_{2.85}F_{0.15}$	$Ca_{0.95}Pb_{0.05}(Ti_{0.95}Li_{0.05})O_{2.85}F_{0.15}$
Shrinkage		1.9 %	22.5 %	21.7 %	16.8 %
Relative density		—	98 %	96 %	92 %
Cell parameters	$a = 5.443$ Å		5.446 Å	5.447 Å	5.446 Å
	$b = 7.653$ Å		7.644 Å	7.670 Å	7.654 Å
	$c = 5.376$ Å		5.385 Å	5.387 Å	5.379 Å
Spontaneous deformation: $e_s = b - a/b + a$		0.168	0.167	0.169	0.168
Grain size		—	1 - 4 μm	1 - 1.5 μm	1 - 2 μm
Phase transitions		—	$T_1 = 191$ °C	279 °C	405 °C
			$T_2 = 380$ °C	410 °C	442 °C
			$T_3 = 487$ °C	550 °C	469 °C
Dielectric permittivity		—	ε'_r (20°C) = 120	ε'_r (20°C) = 160	ε'_r (20°C) = 60
			ε'_r (200°C) = 100	ε'_r (200°C) = 125	ε'_r (200°C) = 45
Dielectric losses		—	tanδ < 1%	tanδ < 1%	tanδ < 1%

a) $Ca(Ti_{0.95}Li_{0.05})O_{2.85}F_{0.15}$

b) $Ca_{0.95}Sr_{0.05}(Ti_{0.95}Li_{0.05})O_{2.85}F_{0.15}$
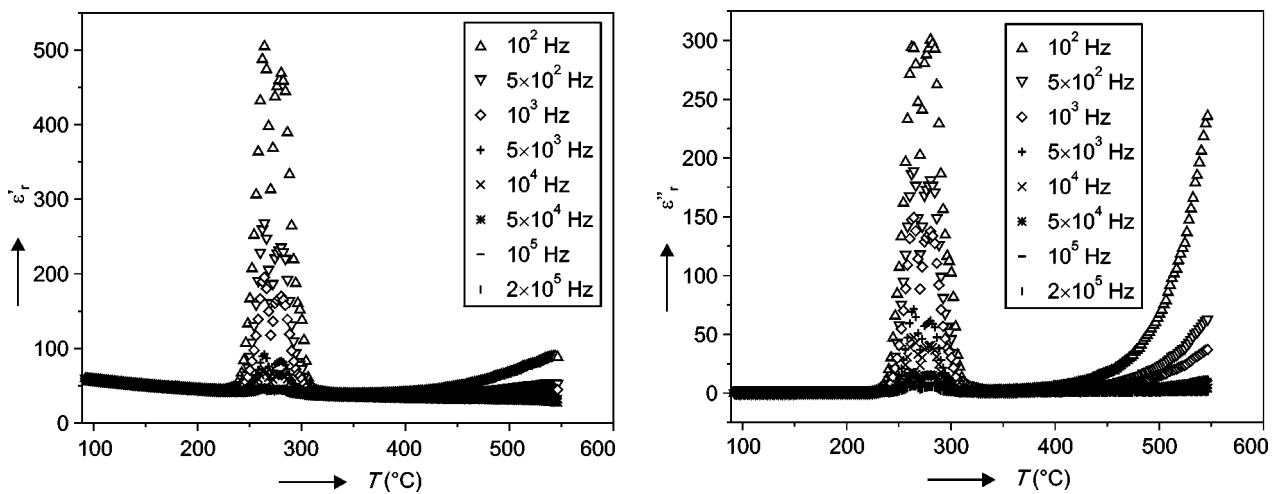
c) $Ca_{0.95}Pb_{0.05}(Ti_{0.95}Li_{0.05})O_{2.85}F_{0.15}$

Figure 1. Temperature dependence of ε'_r and ε''_r at various frequencies.

Structure and microstructure

The shrinkage is very low (1.9 %) for pure CaTiO$_3$ after sintering at 950°C. On the other hand, strong shrinkage occurs in (Ca,M)(Ti,Li)(O,F)$_3$ ceramics at the same sintering temperature (16 % < ΔΦ/Φ < 23 %). To achieve similar shrinking in pure calcium titanate, a sintering at 1400-1500°C is necessary. Such results, already observed for BaTiO$_3$ and SrTiO$_3$ [17], are interesting for the sintering of good quality ceramics at low temperature with the aid of metallic fluorides for several electronic applications.

The CaTiO$_3$ ceramic is very brittle whereas the fluorinated ceramics are very hard and therefore very difficult to crush. The maximum of relative density (98 %) is obtained with CaF$_2$ additive whereas only 92 % of the theoretical density is achieved for ceramic containing Pb.

The XRD patterns of all the samples are very similar to each other: a single perovskite-type phase is shown without any impurity. The peaks of (Ca,M)(Ti,Li)(O,F)$_3$ compounds are indexed by isotypy with CaTiO$_3$. Whatever the cationic Ca–M substitution is, the orthorhombic symmetry of pure calcium titanate persists at room temperature in (Ca,M)(Ti,Li)(O,F)$_3$ samples. As seen in table 1, the lattice parameters *a*, *b* and *c* are close to those of CaTiO$_3$. Consequently, the variation in the spontaneous deformation $e_s = b - a/b + a$ (*a,b* cell parameters) is insignificant.

However it was demonstrated that a liquid phase sintering occurs with fluoride additions [18], no secondary intergranular phases are present on the SEM micrographs. This result is in good agreement with the XRD data. Thus, we can deduce that the MF$_2$+LiF mixture simultaneously assists the densification and enters the host lattice during the sintering process to form oxyfluoride phases Ca$_{0.95}$M$_{0.05}$(Ti$_{0.95}$Li$_{0.05}$)O$_{2.85}$F$_{0.15}$ (M = Ca, Sr, Pb).

The ceramics microstructures are composed of fine grains with an open porosity which is more important in Ca$_{0.95}$Pb$_{0.05}$(Ti$_{0.95}$Li$_{0.05}$)O$_{2.85}$F$_{0.15}$. Small grains (~1 μm) and large grains (~4 μm) with various shapes are observed in Ca(Ti$_{0.95}$Li$_{0.05}$)O$_{2.85}$F$_{0.15}$. In the opposite, the morphology and the grain size are more homogeneous in ceramics with Sr or Pb content.

Phase transitions

The DSC results on CaTiO$_3$ and Ca$_{0.95}$M$_{0.05}$(Ti$_{0.95}$Li$_{0.05}$)O$_{2.85}$F$_{0.15}$ are summarized in table 1. No phase transition is detected in calcium titanate in the temperature range investigated (20-600°C). This result agrees quite well with previous works on this perovskite where two phase transitions are announced but above 600°C [6-9].

On the other hand, three phase transitions are pointed out in each oxyfluoride. Small enthalpy changes are associated with these thermal phenomena (ΔH < 0.07 kJ/mol). Therefore, these structural transformations are most likely second order transitions corresponding to various space group changes without any change in the crystallographic system.

Figure 1 shows the *T* - dependence of the dielectric permittivities ε'$_r$ (real component) and ε"$_r$ (imaginary part) at various frequencies for the three ceramics of CaTiO$_3$ chemically modified with 5 mol.% of MF$_2$+LiF. The first observation is both the ε'$_r$ - *T* and ε"$_r$ - *T* curves of samples with CaF$_2$ (figure 1a) or PbF$_2$ (figure 1c) contents exhibit practically the same profile whereas a little difference is observed for Ca$_{0.95}$Sr$_{0.05}$(Ti$_{0.95}$Li$_{0.05}$)O$_{2.85}$F$_{0.15}$ (figure 1b). Two dielectric peaks, very close one another, appear between 250 and 300°C in each ceramic but are less perceptible in sample containing Sr (figure 1b). Below ~200°C, the frequency dispersion in ε'$_r$ and ε"$_r$ is negligible with a slight temperature dependence and the dielectric losses are less than 1 %. Contrarly, a strong dispersion is observerd around the dielectric peaks.

In addition, the temperatures of ε'$_r$ maxima are coincident with those of ε"$_r$ without any shift to higher temperatures on increasing the measurement frequency. Therefore, these dielectric anomalies are due to thermodynamic phase transitions excluding any relaxor type transition.

The peaks correspond probably to the first phase transition observed by DSC. The splitting in two peaks could be ascribed to a gradient of composition in ceramic grains. The two other peaks detected by DSC are maybe masked by the conductivity. To check if the dielectric phenomena are related to ferroelectric transitions, polarization hysteresis loop measurements have to be carried out.
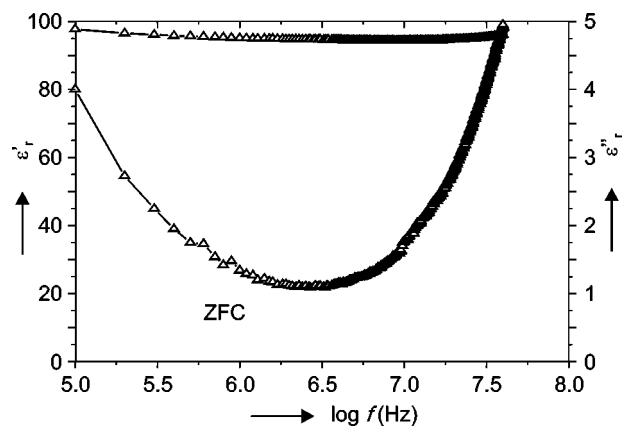

Figure 2. ε'$_r$ and ε"$_r$ versus frequency for Ca(Ti$_{0.95}$Li$_{0.05}$)O$_{2.85}$F$_{0.15}$ at room temperature.

The variation of ε'_r and ε''_r with frequency at room temperature display the same behavior for all the samples and therefore, the curves of $Ca(Ti_{0.95}Li_{0.05})O_{2.85}F_{0.15}$ are only depicted in figure 2. The real part of the permittivity is stable over a large frequency range with a value of ~100. In the opposite, a broad minimum is shown in the imaginary component around 3MHz.

CONCLUSIONS

Ceramics of $CaTiO_3$ modified with 5 mol.% of MF_2+LiF (M = Ca, Sr, Pb) were sintered in air at low temperature (950°C). The orthorhombic symmetry of calcium titanate at room temperature is not affected by the chemical substitutions Ca–M, Ti–Li and O–F whereas the phase transitions seem to be strongly influenced by the incorporation of the fluoride mixture MF_2+LiF into the host lattice. Three phase transitions are detected by DSC in the range 190-550°C. Between room temperature and 200°C, the dielectric permittivity and losses of $Ca_{0.95}M_{0.05}(Ti_{0.95}Li_{0.05})O_{2.85}F_{0.15}$ (M = Ca, Sr, Pb) are practically independent of frequency and slightly dependent of temperature. At room temperature, $?'_r$ is stable over a large frequency range with $\tan\delta < 1\%$. The oxyfluorides $Ca_{0.95}M_{0.05}(Ti_{0.95}Li_{0.05})O_{2.85}F_{0.15}$ (M = Ca, Sr, Pb) are promising materials to manufacture type I capacitors and resonators.

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MATERIÁLY ODVOZENÉ OD CaTiO3 PRO REZONÁTORY

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Keramické materiály $Ca_{0.95}M_{0.05}(Ti_{0.95}Li_{0.05})O_{2.85}F_{0.15}$ (M = = Ca, Sr, Ba) byly připraveny ze směsí práškového $CaTiO_3$, MF_2 a LiF čtyřhodinovým sintrováním při 950°C na vzduchu. Vzorky byly zkoumány rtg difrakcí, řádkovací elektronovou mikroskopií, diferenciální skenovací kalorimetrií a dielektrickým měřením. Fázové transformace čistého $CaTiO_3$ jsou silně ovlivněny vstupem fluoridové směsi MF_2 a LiF do jeho mřížky ale orthorhombická symetrie při pokojové teplotě není vůbec ovlivněna chemickou substitucí Ca–M, Ti–Li a O–F. Dielektrická permitivita ε'_r a ztráty $\tan\delta$ jsou mírně závislé na teplotě mezi 20 a 200°C. Při pokojové teplotě je ε'_r stálá v širokém rozsahu frekvencí s $\tan\delta < 1\%$. Oxifluoridy $Ca_{0.95}M_{0.05}(Ti_{0.95}Li_{0.05})O_{2.85}F_{0.15}$ (M = Ca, Sr, Ba) jsou slibné materiály pro výrobu rezonátorů.