



Original Article

Ferroelectricity and high tunability in novel strontium and tantalum based layered perovskite materials



Florent Marlec^a, Claire Le Paven^{a,*}, François Cheviré^b, Laurent Le Gendre^a, Ratiba Benzerga^a, Benoît Guiffard^c, Thibaut Dufay^c, Franck Tessier^b, Bachir Messaid^a, Ala Sharaiha^a

^a Univ Rennes, CNRS, IETR (Institut d'Electronique et des Télécommunications de Rennes)-UMR6164, F-22000 Saint Brieuc, France

^b Univ Rennes, CNRS, ISCR (Institut des Sciences Chimiques de Rennes)-UMR6226, F-35000 Rennes, France

^c Univ Nantes, CNRS, IETR (Institut d'Electronique et des Télécommunications de Rennes)-UMR6164, F-44000 Nantes, France

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ABSTRACT

The present study reveals the ferroelectric nature of the novel (Sr₂Ta₂O₇)_{100-x}(La₂Ti₂O₇)_x layered perovskite materials and highlights a large variation of their permittivity under electric fields associated with very low dielectric loss in the radio-frequency range. More precisely, an ideal solid solution has been evidenced within the composition range $0 \leq x \leq 5$ with lattice parameters and cell volume varying linearly with x . The relative permittivity also depends on the composition and reaches a maximum value (365 @10 kHz, RT), associated with a high tunability (17.6% @0.38 kV/mm) with very low dielectric loss lower than 2.10^{-3} . Variation of the relative permittivity as a function of the temperature is also demonstrated, with the existence of a temperature maximum, increasing with the composition. Polarization-electric field (P-E) measurements feature hysteresis loops for compositions $x \geq 1.85$, in conjunction with current peaks in the I-E curves originating from ferroelectric domains switching.

1. Introduction

Designing and/or combining new functions in nomad and communicating objects constitute a multi-disciplinary work and a source of major innovations. The present article deals with this theme through the research of new functional materials for the development of agile telecommunication devices, in particular antennas. In this case, frequency agility can be achieved by replacing the multiband frequency antennas in the communicating system by a single one which is reconfigurable in frequency. The material route consists in associating the radiating element with a tunable material, one of whose properties can be controlled by an external excitation (electric field, magnetic field, temperature, mechanical strain, etc). Ferroelectric materials are then attractive candidates as their permittivity is tunable under DC electric field E [1]. In the form of dense ceramics, requirements for their integration in reconfigurable devices involve a moderate relative permittivity value ($\kappa = 50$ –500) in order to achieve devices with industrially compatible dimensions, very low dielectric losses ($\tan \delta < 1\%$) in order to limit the insertion losses of the device and a tunability higher than 10% for a field of 2 kV/mm [2] (the tunability is defined as $Tun.(\%) = (|\kappa(E) - \kappa(E=0)| / \kappa(E=0) \times 100)$). Various ferroelectric systems have been studied and, in recent years, work has

been focused on the reduction of the dielectric loss of the materials, especially by combining, within a composite compound, the ferroelectric with a low-loss dielectric material [3,4].

The current study concerns a new family of lead-free perovskite-based ferroelectric materials, with the formulation (Sr₂Ta₂O₇)_{100-x}(La₂Ti₂O₇)_x (hereafter referred as STL_T). Our work refers to undoped materials, not combined with a dielectric compound, and our objective is to highlight the dielectric and ferroelectric potential of these original materials in the radio-frequency range. It is the statement of a more complete study in the microwave range in view of integrating the materials in telecommunicating agile devices.

The STL_T system combines two $n = 4$ members of the layered perovskite $A_nB_nX_{3n+2}$ series [5]: Sr₂Ta₂O₇ (ST) and La₂Ti₂O₇ (LT). Cross-substitution of La³⁺ for Sr²⁺ and Ti⁴⁺ for Ta⁵⁺ enables the charge compensation between cations and ensures the electroneutrality of the compounds. ST and LT are ferroelectric, with dissimilar Curie temperatures (T_C), respectively -105°C and 1461°C [6,7]. All these conditions met the requirements for the formation of a solid solution between ST and LT, thus offering the possibility of controlling the properties of the synthesized materials. A long time ago, Nanamatsu et al. demonstrated the variation of the Curie temperature of (Sr₂Ta₂O₇)_{100-x}(La₂Ti₂O₇)_x compounds with the chemical composition x

* Corresponding author.

E-mail address: claire.lepaven@univ-rennes1.fr (C. Le Paven).

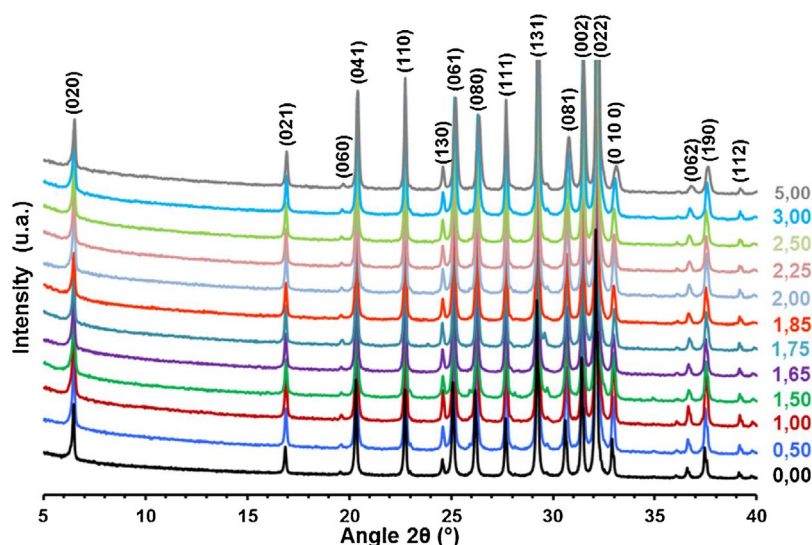


Fig. 1. $\theta-2\theta$ X-ray diagrams of the $(\text{Sr}_2\text{Ta}_2\text{O}_7)_{100-x}(\text{La}_2\text{Ti}_2\text{O}_7)_x$ powders with $0 \leq x \leq 5$, synthesized by solid state route. Diffraction peaks are indexed according to an isotype of the paraelectric $\text{Sr}_2\text{Ta}_2\text{O}_7$ compound (JCPDS File No. 70-0248).

in the range 0–100 [8]. The ferroelectric behavior of the two end members, $\text{Sr}_2\text{Ta}_2\text{O}_7$ and $\text{La}_2\text{Ti}_2\text{O}_7$, was proved by hysteresis loops of the polarization versus electric field (P-E curves), but no data were given for the solid solution compositions. To our knowledge, no further studies have been reported on the STLT system.

The present study aims to reexamine the $(\text{Sr}_2\text{Ta}_2\text{O}_7)_{100-x}(\text{La}_2\text{Ti}_2\text{O}_7)_x$ ceramic system, by performing a complete dielectric and ferroelectric characterization in the radio-frequency range, including, for the first time, κ -E (permittivity-electric field) measurements. We are dealing with STLT ceramics with composition x ranging from 0 to 5; our goal is to determine which compositions (x) lead to a value of T_C close to RT, in order to benefit from a maximum tunability. We will compare our results to those obtained on standard ferroelectrics, for example $\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$ [3,4], as well as isotype layered perovskite systems such as $(\text{Sr},\text{La})_2(\text{Ta},\text{Nb})_2\text{O}_7$ ceramics [9] and $\text{Sr}_2(\text{Ta}_{1-x}\text{Nb}_x)_2\text{O}_7$ as single-crystals [10,11] and thin films [12–14]. The present work relies also on our previous studies concerning $\text{La}_2\text{Ti}_2\text{O}_7$ in the form of ceramics [15] and thin films [16] and our first attempt to produce directly STLT films [17].

2. Material and methods

2.1. Material synthesis

$(\text{Sr}_2\text{Ta}_2\text{O}_7)_{100-x}(\text{La}_2\text{Ti}_2\text{O}_7)_x$ powders with composition (x) ranging from 0 to 5 (see details in Supporting information Table S1) were prepared by solid state reaction using a two-step process. First, for each composition (x), stoichiometric amounts of high purity powders of SrCO_3 , Ta_2O_5 , La_2O_3 and TiO_2 were homogenized in isopropanol for 1 h in an agate mortar and dried in an oven at 110 °C. The obtained powder was pressed into a pellet using an uniaxial press, then calcined in air for 15 h at 1000 °C, milled and calcined again at 1400 °C for 15 h. The final product was checked by X-ray diffraction (XRD) for phase identification. Then, the powder was mixed with a rhodoviol solution (5 wt.%) as a binder, pressed at 220 MPa to form a pellet (12 or 18 mm in diameter and 0.5 mm thick) and subsequently sintered at 1500 °C for 2 h, by burying it or not in $\text{Sr}_2\text{Ta}_2\text{O}_7$ powder placed in an alumina crucible.

2.2. Structural characterization

The phase structure of calcined powders and sintered ceramics was analyzed by XRD technique using, respectively, a Panalytical X'pert Pro diffractometer (Cu K-L2,3 radiation) and a Seifert 3003 PTS diffractometer (Cu K-L3 radiation). Lattice parameters for the different powder samples were estimated from Le Bail-type profile fit carried out

with the Fullprof program [18] and considering the Cmc m space group; the Pseudo-Voigt profile function was used and the background was approximated by linear interpolation between a set of background points. Energy Dispersive Spectrometry (EDS) was used to investigate the cations chemical composition of the STLT ceramics; analysis was performed using the Aztek OXFORD software through a JEOL JSM IT-100 scanning electron microscope (SEM) operating at 10 kV. The surface and fracture morphologies of ceramics were examined using the previous JEOL equipment.

2.3. Dielectric and ferroelectric characterization

For electrical properties measurements, gold electrodes were deposited through a rigid mask by dc sputtering on both faces of the pellets. The frequency and temperature dielectric spectra were measured using a LCR meter (LCR-819 GWInstek) in the 1 Hz–100 kHz frequency range and temperature interval from 20 °C to 300 °C. External DC voltages (0–max 200 V, Keithley 2400) were applied through a Keysight 16065A voltage bias fixture to point out a variation of the relative permittivity (i.e. Tunability). Ferroelectric hysteresis P–E were characterized at room temperature ($f = 50$ Hz) using a Sawyer-Tower circuit with a 68 nF serial capacitor; a high voltage amplifier (Trek 609E-6, 0–5000 V) was used to tune the amplitude of the applied electric field. I–E loops were also recorded; values of current were calculated from the polarization using the relation $I = A \, dP/dt$, where A is the electrode area.

3. Results

3.1. Synthesis of powders

Fig. 1 shows the XRD patterns of the calcined $(\text{Sr}_2\text{Ta}_2\text{O}_7)_{100-x}(\text{La}_2\text{Ti}_2\text{O}_7)_x$ powders for x ranging from 0 to 5. Given the small content of $\text{La}_2\text{Ti}_2\text{O}_7$ in the synthesized STLT powders, diffraction peaks of all the samples were found to match either those of the JCPDS File No. 70-0248 (space group Cmc m) or the No. 72-0921 (space group Cmc 2_1) of $\text{Sr}_2\text{Ta}_2\text{O}_7$. These two space groups are associated to the paraelectric state and ferroelectric state of $\text{Sr}_2\text{Ta}_2\text{O}_7$ respectively and are nearly indiscernible, as discussed later.

To further evaluate the variation of the crystal structure, lattice parameters and cell volume were calculated (data are gathered in Table S1) and plotted as a function of the composition (x) in Fig. 2. Both parameters a (Fig. 2a) and c (Fig. 2c) slightly vary with x whereas b (Fig. 2b) significantly decreases. The resulting cell volume (Fig. 2d) decreases. These evolutions are due to the ionic radii difference on the

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