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FTIR AND RAMAN SPECTROSCOPIC STUDY OF A COMPLEX PEROVSKITE: $\text{Ca}_{0.91-x}\text{Ce}_{0.09}\text{Rb}_{0.04}\text{Cs}_x[(\text{Zr}_{0.50}\text{Ti}_{0.45})\text{Al}_{0.05}]\text{O}_3$, $x=0.2$ TO 0.4 , DEDICATED FOR RADIOACTIVE WASTE CONFINEMENT

ABSTRACT

Perovskite is able to sequester simultaneously, in its structure, both actinides and alkaline-earth elements. This study is an attempt to synthesize a complex perovskite $\text{Ca}_{0.91-x}\text{Ce}_{0.09}\text{Rb}_{0.04}\text{Cs}_x[(\text{Zr}_{0.50}\text{Ti}_{0.45})\text{Al}_{0.05}]\text{O}_3$ ($0.2 \leq x \leq 0.4$), doped in the same time, with Ce, Cs and Rb. The synthesis is conducted by sintering at 1150°C during 16h. XRD analysis confirms the perovskite formation. SEM observations show a less porous microstructure. FTIR analysis reveals TiO_6 , Ti-O-Ti, Ti-O and Zr-O vibrations. Raman spectroscopy indicates many orthorhombic perovskite active modes, as: Ti-O_6 and Ti-O_3 torsions, ZrO_7 , CaO_8 vibrations, the totally symmetric oxygen, and the O-octahedron cage rotation.

Keywords: perovskite; radioactive waste; XRD; FTIR; Raman

INTRODUCTION

Perovskite is a major mineral of Synroc (Synthetic Rock) material. It is able to confine both alkaline and alkaline-earth elements contained in radioactive waste (RW) [1-6].

Perovskite was first described in 1830 by the Russian mineralogist L.A.V. Perovskite, as calcium titanate mineral, with a cubic structure. Today, the term ‘perovskite’ refers to a mineralogical family [7].

The synthesized perovskites were produced first by Goldschmidt in 1926 at Oslo University [8,9]. This led using the term ‘perovskite’ for the compounds class with the general formula CaTiO_3 [10].

The ABX_3 perovskite structure is able of accommodating a large number of elements, in both A and B sites, since the A^{m+} ion is an alkali metal, alkaline earth metal or a rare earth element, and B^{n+} a transition metal cation [11]. Generally, A is a large monovalent cation which occupies the cubo-octahedral sites in a cubic space, B is a small divalent metal cation occupying the octahedral sites, and X is an anion (halogen, oxygen, carbon, nitrogen). When the O^{2-} anion is used, A and B are usually divalent and tetravalent, respectively [12].

Perovskite can be a simple or complex type structure, depending on A and B cations. When A is: Ce^{4+} , Nd^{3+} , Sm^{4+} , La^{3+} , Yb^{3+} , or Gd^{3+} and B: Al^{3+} , Cr^{3+} , Fe^{3+} or Ga^{3+} , perovskite is

called simple perovskite. It is called complex when it has a mixt structure like: $A_2B'B''O_6$ and $A_3B'B''O_9$ [13].

Perovskite exists in several crystallographic forms, such as tetragonal, monoclinic, triclinic, hexagonal, cubic, rhombohedral and orthorhombic. It can also show some polymorphism [13,14].

In fact, both Fourier Transform Infra-red (FTIR) and Raman spectroscopies are useful tools to study such crystalline networks. The characteristic perovskite Raman active modes of a given crystalline form can confirm the position, and thus the valence of doping cations (A and B). As an example, in $CaTiO_3$, when doping the molecule in Ca position by a lanthanide, the number of Raman modes in the region $150-700\text{ cm}^{-1}$ varies, as a consequence of the metal-oxygen bond length variation, and thus the nature of the vibrations (stretching, bending or torsional), which indicates the polarizability of the cations also appearing in FTIR spectra [15,16]. In a complex perovskite, the appearance or disappearance of both active and inactive modes shows the competitiveness of two cations in a given position (as B). A good example is that of Co and Fe in $Ce_{0.6}Sr_{0.4}Fe_{0.8}Co_{0.2}O_{3-\delta}$ perovskite. The nature of A cation involves oxygen's vacancies due to the presence of redox couples (more than one valence), influencing the cations charges in the B position. All these phenomena are traduced by the bands shifts in FTIR and the observed Raman modes. The enhanced performance is attributed to the presence of lanthanides with a positive effect in the electrochemical activity for oxygen reduction reaction due to their redox couples like $Ce^{3+} \leftrightarrow Ce^{4+}$. This perovskite system contains a lanthanide (Ce) which possesses high reaction rates due to the catalytic redox couple of Ce (Ce^{4+} or Ce^{3+}). Consequently, the oxygen reduction steps are enhanced. Since there are more oxygen vacancies, the oxidation state of the B-site cations changes ($Co^{2+} \rightarrow Co^{3+} \rightarrow Co^{4+}$, $Fe^{2+} \rightarrow Fe^{3+} \rightarrow Fe^{4+}$) [17,18].

The existence and stability of $CaTiO_3$ perovskite structure, for a wide range of ionic radii, is assessed by steric considerations [19]. V.M. Goldschmidt [8] stated a stability condition, by introducing the Goldschmidt's t tolerance factor, which allows linking the oxygen radii (r_O) with both A (r_A) and B (r_B) cations radii by the mathematical relation (1). This relation is valid only if oxygen stoichiometry is respected.

$$t = \frac{r_A + r_O}{\sqrt{2}(r_B + r_O)} \quad (1)$$

The t factor provides information on the structure distortion such as: deformation, rotation, octahedral tilting or deformation of the A coordination' polyhedron. In the ideal case: $t=1$ and the structure is cubic. When moving away from this value, the lattice size undergoes distortions, which are summarized in Table 1.

The interest in ABO_3 perovskites results in the ease of changing the nature of cations A and B, leading to a change in the intrinsic materials properties, such as: ferroelectricity, antiferro electricity, magnetism, ferromagnetism, antiferromagnetism, superconductivity, and RW confinement [7,11-14,19,20].

Perovskite belongs to Synrocs B, C, D and E [21-24].

The Synroc B is mainly constituted by titanates phases : perovskite ($CaTiO_3$), zirconolite ($CaZrTi_2O_7$), hollandite ($BaAl_2Ti_6O_{16}$) and rutile (TiO_2) [25].

The Synroc C is constituted by hollandite ($BaAl_2Ti_6O_{16}$), zirconolite ($CaZrTi_2O_7$) and perovskite ($CaTiO_3$), where hollandite mainly immobilizes cesium (Cs), potassium (K), rubidium (Rb) and baryum (Ba). Both zirconolite and perovskite are hosting actinides radionuclides. In this structure, perovskite can also accommodate strontium (Sr) and baryum (Ba). The Synroc C can load till 30 wt.% of high-level radioactive waste [26-29].

The Synroc D is composed by nepheline - $(\text{Na,K})\text{AlSiO}_4$ instead of hollandite, as a host phase for Cs, Rb and Ba. The Synroc D can solve issues arising from non-radioactive elements, belonging to radioactive waste' solutions, during the material processing [30-34].

Finally, the Synroc E structure is based on a micro-encapsulation in a synthetic rutile. It can accommodate over 7 wt.% of high-level waste. It is constituted by hollandite, zirconolite, perovskite, pyrochlore and metallic alloys (about 20 wt.%) in a well-densified rutile matrice [35].

CaTiO_3 perovskite is a key feature for the immobilization of light rare-earth elements (La,Ce), actinides, ^{90}Sr and its decay products [36]. It can be synthesized by sintering or by sol-gel/Pechini methods [37-40].

The effect of Sr decay products - yttrium and zirconium - on the material has not been examined in great detail [36], especially on the CaTiO_3 lattice. A multi-doping of the perovskite will play an important role in assessing the sustainability of the material at the different stages of wastes disposal process, knowing that secondary phases constitute an issue in the distortion of the crystalline cell, and thus will affect its stability [36]. It is interesting to anticipate the synthesis feasibility of a perovskite doped by Ce, Rb and Cs in A position. Moreover, Zr is an element belonging to radioactive waste. And doping the material with such an element (in B position), will make perovskite a multi-element confinement material. [41].

So, a complex perovskite structure is interesting for multi-elements immobilization, such as Ce (actinide/fission products simulator), Cs, Rb and Zr.

In this study, we attempt doping of a complex perovskite $\text{Ca}_{0.91-x}\text{Ce}_{0.09}\text{Rb}_{0.04}\text{Cs}_x[(\text{Zr}_{0.50}\text{Ti}_{0.45})\text{Al}_{0.05}]\text{O}_3$, $x=0.2$ to 0.4 , both with Ce, an actinide surrogate, and cold isotopes of Cs and Rb, which are present in some radioactive wastes. The synthesis is conducted by sintering at 1150°C for 16 h. Phase identification is performed by X-ray diffraction (XRD) analysis. A microstructural study is performed by both FTIR and Raman spectroscopies.

Table 1. Crystallographic forms of perovskite as a function of Goldschmidt t tolerance factor

$t < 0.75$ [42,43]		$0.75 < t < 1.13$ [42,43]	
$t < 0.75$ Hexagonal	$0.75 < t < 0.90$ Orthorhombic	$0.90 < t < 1.00$ Cubic	$1.00 < t < 1.13$ Hexagonal
$t < 0.77$ [44] Ilmenite	$0.77 < t < 1.05$ [44] Perovskite		$t > 1.05$ [44]
$t < 0.77$ Hexagonal	$0.77 < t < 0.99$ Orthorhombic	$0.99 < t < 1.05$ Cubic	$t > 1.05$ Hexagonal

METHODOLOGY

Goldschmidt tolerance factor (t) is calculated using the mathematical relation (1) [8], for three chemical compositions $\text{Ca}_{0.91-x}\text{Ce}_{0.09}\text{Rb}_{0.04}\text{Cs}_x[(\text{Zr}_{0.50}\text{Ti}_{0.45})\text{Al}_{0.05}]\text{O}_3$, $x=0.2$ to 0.4 . The calculated tolerance factors are given in Table 2. The charge stability calculations are given in Table 3.

Table 2. Goldschmidt *t* tolerance factor for $\text{Ca}_{0.91-x}\text{Ce}_{0.09}\text{Rb}_{0.04}\text{Cs}_x[(\text{Zr}_{0.50}\text{Ti}_{0.45})\text{Al}_{0.05}]\text{O}_3$, $x=0.2$ to 0.4 perovskite

Chemical composition	<i>T</i>	Distortion	Ionic radii (Å) [45]
$\text{Ca}_{0.67}\text{Ce}_{0.09}\text{Rb}_{0.04}\text{Cs}_{0.2}[(\text{Zr}_{0.5}\text{Ti}_{0.45})\text{Al}_{0.05}]\text{O}_3$	0.80	Orthorhombic $0.75 < t < 0.96$	$r_{\text{Ca}^{2+}} = 1.34$
$\text{Ca}_{0.57}\text{Ce}_{0.09}\text{Rb}_{0.04}\text{Cs}_{0.3}[(\text{Zr}_{0.5}\text{Ti}_{0.45})\text{Al}_{0.05}]\text{O}_3$	0.86		$r_{\text{Ce}^{3+}} = 1.102$
$\text{Ca}_{0.47}\text{Ce}_{0.09}\text{Rb}_{0.04}\text{Cs}_{0.4}[(\text{Zr}_{0.5}\text{Ti}_{0.45})\text{Al}_{0.05}]\text{O}_3$	0.81		$r_{\text{Rb}^{+}} = 1.49$ $r_{\text{Cs}^{2+}} = 1.74$ $r_{\text{Zr}^{4+}} = 0.84$ $r_{\text{Ti}^{4+}} = 0.7$ $r_{\text{Al}^{3+}} = 0.54$ $r_{\text{O}^{2-}} = 1.4$

Table 3. Charge stability calculation for $\text{Ca}_{0.91-x}\text{Ce}_{0.09}\text{Rb}_{0.04}\text{Cs}_x[(\text{Zr}_{0.50}\text{Ti}_{0.45})\text{Al}_{0.05}]\text{O}_3$, $x=0.2$ to 0.4 perovskite

Chemical composition	Charge calculation
$\text{Ca}_{0.67}\text{Ce}_{0.09}\text{Rb}_{0.04}\text{Cs}_{0.2}[(\text{Zr}_{0.5}\text{Ti}_{0.45})\text{Al}_{0.05}]\text{O}_3$	$+2(0.67)+3(0.09)+(0.04)+2(0.2)+0.5(4)+0.45(4)+0.05(3)-3(2)$ $= (1.34+0.27+0.04+0.4+2.0+1.8+0.15)-6=0$
$\text{Ca}_{0.57}\text{Ce}_{0.09}\text{Rb}_{0.04}\text{Cs}_{0.3}[(\text{Zr}_{0.5}\text{Ti}_{0.45})\text{Al}_{0.05}]\text{O}_3$	$+2(0.57)+4(0.09)+(0.04)+2(0.3)+0.5(4)+0.45(4)+0.05(3)-3(2)$ $= (1.14+0.27+0.04+0.6+2.0+1.8+0.15)-6=0$
$\text{Ca}_{0.47}\text{Ce}_{0.09}\text{Rb}_{0.04}\text{Cs}_{0.4}[(\text{Zr}_{0.5}\text{Ti}_{0.45})\text{Al}_{0.05}]\text{O}_3$	$+2(0.47)+4(0.09)+(0.04)+2(0.4)+0.5(4)+0.45(4)+0.05(3)-3(2)$ $= (0.94+0.27+0.04+0.8+2.0+1.8+0.15)-6=0$

The following starting reagents are used in the synthesis: $\text{ZrO}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ (Aldrich), CaO (Merck), TiO_2 (Merck), Al_2O_3 (FlukaAG. Puriss), Rb_2CO_3 (Merck), CsNO_3 (Biochem), and CeO_2 (Aldrich). To get oxides, Zr nitrate is calcined at 923K for 4h; and both Rb_2CO_3 and CsNO_3 at 623K for 5h.

The reagents are manually crushed in an agate mortar. They are mixed according to the stoichiometric ratio of the starting chemical formulae. The powder mixtures are homogenized for 8h in an adapted D403 Controls homogenizer. They are pelletized in 13 mm diameter cylindrical pellets at 13t. The pellets are sintered under air at 1150°C for 16h in a BLF1800 Carbolite furnace, with a heating step of 6°/min. This last has been optimized in order to obtain compact pellets. Each synthesis has been conducted twice.

The green (d_g) and sintered (d_s) geometrical densities of the materials are measured. Phase identification is performed by XRD analysis using a Philips X'Pert Pro diffractometer, equipped with an X-ray tube and a copper anticathode ($\lambda_{\text{K}\alpha 1} = 0.15406$ nm). The experimental parameters are: $V = 45\text{kV}$, $I = 40$ mA, 2θ ranging from 10 to 110°, with a step of 0.02°. Both phase identification and perovskite lattice parameters' calculations are performed using Philips X'Pert High Score Plus version 4.1 software [46].

The materials microstructure is observed on a polished cross-section of the pellets using a Gemini 300 Zeiss SEM microscope in SE mode.

The FTIR analysis is conducted using a 380 NICOLET spectrometer on KBr films at room temperature. The spectral range is from 4000 to 300 cm^{-1} . Spectral processing is performed using OMNIC software [47].

Raman spectroscopy is performed at ambient temperature by using a LabRAM HR Evolution spectrometer equipped with a Peltier cooled CCD detector. A red laser is used

(633nm) as the excitation source. Entrance slit is of 40 μm . The spectral range is: 2000–100 cm^{-1} . The acquisition zone is splited into three consecutive windows, each with 05 acquisitions. Both peak positions and widths are assessed with the PeakPt software (JANDEL) using Lorentzian-shaped functions.

RESULTS AND DISCUSSIONS

Material density

The geometrical densities of perovskite for the three chemical compositions before (d_g) and after sintering (d_s) are given in Table 4. The d_s ($\approx 3700 \text{ kg/m}^3$) values are lower than d_g values (about 5100-5200 kg/m^3). The compacted materials exhibit some porosity which decreases the final density. In fact, in the published studies, perovskite is in a powder form [48-50].

Table 4. Green and sintered density of $\text{Ca}_{0.91-x}\text{Ce}_{0.09}\text{Rb}_{0.04}\text{Cs}_x[(\text{Zr}_{0.50}\text{Ti}_{0.45})\text{Al}_{0.05}]\text{O}_3$, $x=0.2$ to 0.4 perovskite

Chemical composition	d_g (kg/m^3)	d_s (kg/m^3)
$\text{Ca}_{0.67}\text{Ce}_{0.09}\text{Rb}_{0.04}\text{Cs}_{0.2}[(\text{Zr}_{0.5}\text{Ti}_{0.45})\text{Al}_{0.05}]\text{O}_3$	5152	3621
$\text{Ca}_{0.57}\text{Ce}_{0.09}\text{Rb}_{0.04}\text{Cs}_{0.3}[(\text{Zr}_{0.5}\text{Ti}_{0.45})\text{Al}_{0.05}]\text{O}_3$	5128	3734
$\text{Ca}_{0.47}\text{Ce}_{0.09}\text{Rb}_{0.04}\text{Cs}_{0.4}[(\text{Zr}_{0.5}\text{Ti}_{0.45})\text{Al}_{0.05}]\text{O}_3$	5291	3682

O.P. Shrivastava et al. [48] have synthesized a $\text{Pr}_{0.1}\text{Ca}_{0.9}\text{TiO}_3$ perovskite by sintering at 1050°C during 72 h. They found a higher density (4200 kg/m^3) compared with our results, probably due to the Pr high atomic mass, jointly with the operating conditions (grinding-pelletizing-sintering repeated steps) which favor a good material shrinkage.

O.P. Shrivastava and R. Srivastava [49] published comparable results (4350 kg/m^3) for an orthorhombic perovskite, $\text{Ca}_{1-x}\text{Sr}_x\text{TiO}_3$ ($0.02 < x < 0.2$), obtained by sintering at 1150°C during 6h. R. Zhang et al. [50] reported a 4200 kg/m^3 density for a perovskite titanate Synroc, synthesized by the self-propagating high-temperature method with a SrO content over 35 wt.%.

Phase identification

The perovskite DRX analysis gives the diffractograms depicted on Fig. 1. Both phase's identification and perovskite lattice parameters are given in Table 5. An orthorhombic perovskite is identified as the main crystalline phase for the three chemical compositions. The semi-quantitative phases' analyzes, performed by High-Score Plus software [46], allow estimating this phase from 51 to 83%, for a Cs content ranging from 0.2 to 0.4 at.%. The aim of perovskite formation as the material main phase is achieved.

Fig. 1. Diffractograms of $\text{Ca}_{0.91-x}\text{Ce}_{0.09}\text{Rb}_{0.04}\text{Cs}_x[(\text{Zr}_{0.50}\text{Ti}_{0.45})\text{Al}_{0.05}]\text{O}_3$ ($x=0.2$ to 0.4) perovskite

Table 5. $\text{Ca}_{0.91-x}\text{Ce}_{0.09}\text{Rb}_{0.04}\text{Cs}_x[(\text{Zr}_{0.50}\text{Ti}_{0.45})\text{Al}_{0.05}]\text{O}_3$ ($x=0.2$ to 0.4) perovskite phases' identification [46]

Perovskite	0.2 at.% Cs	0.3 at.% Cs	0.4 at.% Cs
Crystalline phases	CaTiO_3 (79%) JCPDS:00-022-0153	$\text{Ca}(\text{TiO}_3)$ (83%) JCPDS:01-088-0790	CaTiO_3 (51%) JCPDS:01-076-2400
	$(\text{ZrTi})\text{O}_4$ (12%) JCPDS:01-080-1783	$(\text{La}_{0.1}\text{Zr}_{0.9})\text{O}_{1.95}$ (12%) JCPDS:01-082-1011	$\text{Ca}_2\text{Zr}_5\text{Ti}_2\text{O}_{16}$ (11%) JCPDS:01-075-2282
	CaZrO_3 (9%) JCPDS01-076-2401.	$\text{Ca}_2\text{Zr}_5\text{Ti}_2\text{O}_{16}$ (5%) JCPDS:01-088-0881.	CaZr_4O_9 (37%) JCPDS:01-080-1342.
Theoretical Lattice parameters	$a=5.44\text{\AA}$	$a=5.44\text{\AA}$	$a=5.38(2)\text{\AA}$
	$b=7.64(3)\text{\AA}$	$b=7.64(3)\text{\AA}$	$b=7.64(5)\text{\AA}$
	$c=5.38(1)\text{\AA}$	$c=5.38(1)\text{\AA}$	$c=5.44(5)\text{\AA}$
	$\alpha=90^\circ$	$\alpha=90^\circ$	$\alpha=90^\circ$
	$\beta=90^\circ$	$\beta=90^\circ$	$\beta=90^\circ$
	$\gamma=90^\circ$	$\gamma=90^\circ$	$\gamma=90^\circ$
	$V=223.78\text{\AA}^3$	$V=223.78\text{\AA}^3$	$V=224.12\text{\AA}^3$
Experimental Lattice parameters	$a=5.457(8)\text{\AA}$	$a=5.43(1)\text{\AA}$	$a=5.379(9)\text{\AA}$
	$b=7.65(1)\text{\AA}$	$b=7.67(2)\text{\AA}$	$b=7.65(1)\text{\AA}$
	$c=5.389(8)\text{\AA}$	$c=5.34(2)\text{\AA}$	$c=5.460(9)\text{\AA}$
	$\alpha=90^\circ$	$\alpha=90^\circ$	$\alpha=90^\circ$
	$\beta=90^\circ$	$\beta=90^\circ$	$\beta=90^\circ$
	$\gamma=90^\circ$	$\gamma=90^\circ$	$\gamma=90^\circ$
	$V=224.99\text{\AA}^3$	$V=222.45\text{\AA}^3$	$V=224.57\text{\AA}^3$

In CaTiO_3 , tilting of the octahedrons, provoked by ions size variations, change the cubic system to an orthorhombic symmetry. Many authors report that Sr incorporation is particularly easy in CaTiO_3 due both to the similar ionic radii and properties of Ca and Sr elements, which belong to group 2' alkaline earth [51-60]. A solid solution between CaTiO_3 and SrTiO_3 exists, demonstrating the ability of Sr to be incorporated in perovskite skeleton [41].

Moreover, there are no residues of Cs and Rb, identified by XRD analysis. These elements seem to be confined in the perovskite structure.

Secondary phases of calzirtite, Ca-Zr and Zr-Ti oxides appear, showing that the synthesis process is not achieved after 16h of sintering. However, calzirtite and Zr-Ti oxides are durable against radiation damages in RW confinement materials, and will constitute a second barrier, embedding the material.

The a,b,c calculated lattice parameters are in accordance with the theoretical ones, except b values which are slightly higher compared to the theoretical values. Consequently, the lattice volume increases very slightly for the materials with $x=0.2$ and 0.4 at.%, highlighting a good accommodation of both Rb and Cs in perovskite unit cell.

SEM microstructure observation

The SEM micrographs, taken on polished cross-sections of the three perovskite samples, show a less porous structure with a uniform grains' distribution (Fig. 2).

Fig. 2. SEM micrographs of $\text{Ca}_{0.91-x}\text{Ce}_{0.09}\text{Rb}_{0.04}\text{Cs}_x[(\text{Zr}_{0.50}\text{Ti}_{0.45})\text{Al}_{0.05}]\text{O}_3$ ($x=0.2$ to 0.4) perovskite

FTIR analysis

On the perovskite FTIR spectra (Fig. 3), the bands at 710 , 570 , 527 , 460 and 415 cm^{-1} traduce the vibrations of TiO_6 octahedrons lattice. This vibration is strongly attenuated in complex perovskites due to the presence of a second cation in Ti position (Zr in the present study) which interferes with TiO_6 movements. This is highlighted by the absence of TiO_6 group's vibration band around 710 cm^{-1} .

The $\delta(\text{Ti-O-Ti})$ bending active mode, which is characteristic of alkaline titanates, appears at 460 , 457 and 463 cm^{-1} , for Cs contents of 0.2 , 0.3 and 0.4 at.% respectively [61]. This band can shift from 460 cm^{-1} to lower values when Ca content increases in CaTiO_3 lattice, demonstrating the steric effect of Ca on TiO_6 octahedrons vibrations [15]. The stretching

mode around 521, 524 and 526 cm^{-1} , for Cs contents of 0.2, 0.3 and 0.4 at.%, respectively, is due either to Ti-O or Zr-O vibrations [62].

The Ca-O bonds' vibration in CaTiO_3 cuboids is evidenced at 563 and 558 cm^{-1} for Cs contents of 0.2 and 0.3 at.%. It is nonexistent for 0.4 at.% Cs (the lowest Ca content), indicating the Ca-O vibration energy attenuation [61]. The TiO_3^{2-} groups' asymmetric Ti-O stretching appears at 425, 425 and 420 cm^{-1} , for Cs contents of 0.2, 0.3, and 0.4 at%, respectively [63].

The -OH water stretching is identified by the bands between 2900–3700 cm^{-1} and at 3552 cm^{-1} [64,65].

Fig. 3. FTIR spectra of $\text{Ca}_{0.91-x}\text{Ce}_{0.09}\text{Rb}_{0.04}\text{Cs}_x[(\text{Zr}_{0.50}\text{Ti}_{0.45})\text{Al}_{0.05}]\text{O}_3$ ($x=0.2$ to 0.4) perovskite

Raman analysis

Materials Raman spectra show 7 of the 24 expected Raman-active modes of an orthorhombic-structured perovskite, with Pnma space group [66,67]. All the bands can be assigned to a first order Raman scattering, and are probably due to both internal TiO_6 stretching and bending vibrations, and to external modes [66]. The $\text{E}(2\text{LO})$ vibration (P_7 mode) at 466, 468 and 469 cm^{-1} , for $x=0.4$, 0.3 and 0.2, respectively, is assigned to Ti-O_6 bending, internal oxygen cage vibration, and to Ti-O_3 torsions [54,67]. This band, which can shift till 471 cm^{-1} traduces the Ti-O bond distance, which is strongly dependent on the cation in A position (Ca, Sr, etc.), which affects the A-O distance. The totally symmetric oxygen breathing mode vibration $\text{A}_1(2\text{TO})$ (350 cm^{-1} [68]) and the $\text{E}(2\text{TO})$ mode (210 cm^{-1} [68]) are absent. I.M. Penatti et al. [69] attribute the absence of some perovskite modes to their low polarizabilities. The $\text{B}_1+\text{E}(\text{P}_5)$ mode (280 cm^{-1} [68]) shifts to 278 cm^{-1} .

The P_2 to P_6 perovskite modes are strongly depend on the metal-oxygen distances, and their bands vary as a function of the dopants in both A and B positions, these last, in turn, affect the modes polarizabilities [69-71]. The bands at 181 cm^{-1} , and 224, 246, 278, 339 cm^{-1} are assigned to O-Ti-O bending (P_2 to P_6 modes, respectively) [71]. Penatti I.M. et al. [69] report these bands, in a comparative table, at 172, 219, 237, 280 and 333 cm^{-1} . A morphotropic phase boundary, which is mainly associated to the $\text{A}_g(\text{P}_2)$ band (181 cm^{-1}) indicates an orthorhombic phase [67,71].

The band at 246 cm^{-1} , reported in the literature at 244 cm^{-1} , is overlapping the hard mode $\text{B}_{1g}(\text{P}_4)$ assigned to the oxygen octahedron cage rotation [69,71]. The symmetrical stretching ($\cong 794 \text{ cm}^{-1}$) derived from A_{1g} vibrations of TiO_6 octahedrons movement does not appear [72], due to steric considerations and to B site cations' nature (Ti^{3+} , Zr^{4+}), these last inhibiting TiO_6

stretching. The absence of peaks at 495 cm^{-1} , and 537 cm^{-1} assigned to a distortion due to Ti octahedrons clusters tilts indicates that the structure is not distorted [71]. This is confirmed by the absence of the Ti–O stretching band ($639\text{--}669\text{ cm}^{-1}$) related to A_g modes of TiO_6 distortion modes [72,73]. The $A_1(3\text{TO})$ mode ($\cong 625\text{ cm}^{-1}$) is weak for 0.2 at.% Cs. It is highly attenuated for 0.3 and 0.4 at.% Cs in the perovskite [68]. This indicates an increase in the long-range order (LRO).

Fig. 4. Raman spectra of $\text{Ca}_{0.91-x}\text{Ce}_{0.09}\text{Rb}_{0.04}\text{Cs}_x[(\text{Zr}_{0.50}\text{Ti}_{0.45})\text{Al}_{0.05}]\text{O}_3$ ($x=0.2$ to 0.4) perovskite

CONCLUSIONS

In this study, a complex perovskite for multi-elements immobilization, $\text{Ca}_{0.91-x}\text{Ce}_{0.09}\text{Rb}_{0.04}\text{Cs}_x[(\text{Zr}_{0.50}\text{Ti}_{0.45})\text{Al}_{0.05}]\text{O}_3$, $x=0.2$ to 0.4 , doped in the same time with Ce, Cs and Rb has been synthesized by sintering at 1150°C during 16h. A multi-doping of the perovskite will play an important role of assessing the sustainability of the material at different stages of the waste disposal process. The material density values are about 3700 kg/m^3 . A main orthorhombic perovskite phase has been identified by XRD, with no residues of Cs and Rb. The perovskite lattice parameters are similar to those of the theoretical phase. One can conclude that Cs, Rb and Ce elements are well inserted in the perovskite unit cell, and don't distort it.

The material SEM observation shows a less porous structure. The FTIR analysis reveals the vibrations of TiO_6 octahedrons, Ti-O, Zr-O, Ca-O, and Ti-O-Ti vibrations.

The Raman spectroscopy analysis shows 7 of the 24 expected Raman-active modes of an orthorhombic-structured perovskite, with Pnma space group. All the bands, assigned to first order Raman scattering, are probably due to both internal TiO_6 stretching and bending vibrations, and also to external modes: $E(2\text{LO})$, $A_1(3\text{TO})$, B_1+E , A_g , B_{1g} , P_3 and P_6 . The $E(2\text{LO})$ vibration (P_7 mode) shifts traduces the Ti-O bond distance, which is strongly dependent on the cation in A position (Ca, Sr, etc.), which affects the A-O distance, especially for complex perovskite forms. The P_2 to P_6 perovskite modes are strongly depend on the

metal-oxygen distances, and their bands also vary as a function of the dopants in both A and B positions, these last affecting the modes polarizabilities. For the whole of materials, the inactive modes are E(3LO), A₁(1TO), E(1LO) and E(1TO). The Raman analysis confirms that the perovskite unit cell isn't distorted. Moreover, with changes in elements contents, some bands are more sensitive to the unit cell volume, or to the tolerance factor, and others to the cations site' ordering.

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