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Phase Development in Sol-Gel Derived Lead Titanate: A XAS Study

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Abstract. PbTiO_3 powders have been obtained by the sol-gel method using different precursors and catalysts. The whole gelation and crystallisation process was studied by means of XAS spectroscopy at the Ti K-edge and at the Pb L_{III}-edge. The XANES spectra on the Ti K-edge indicate a marked change of the local environment at 500 °C. The local structure around the Ti atoms determined by EXAFS is similar to that observed in the pyrochlore phase for annealing temperatures below 500 °C. At this temperature both Ti and Pb environments show the occurrence of the Pb-O-Ti bonds indicating the onset of the transformation to the perovskite phase.

1. INTRODUCTION

Lead titanate PbTiO_3 (PT) is a perovskite type ferroelectric material with interesting dielectric, pyroelectric and piezoelectric properties and is used for many technological applications. To obtain the expected properties, the development of a pure perovskite phase is required. The sol-gel process is well suited to produce PT powders and thin films, and is based on the preparation of a solution from organic oxides and salts, which is hydrolysed and polymerises to give metal-oxygen-metal linkages. The resulting gel is further heat treated to remove the organic residues to obtain the crystalline phases. Sol-gel derived PT powders often crystallise directly into the perovskite structure [1] but sometimes form first into the cubic paraelectric pyrochlore $\text{Pb}_2\text{Ti}_2\text{O}_6$ phase [2] and subsequently transform to perovskite at higher (500-700 °C) temperatures.

The understanding of the interaction between lead and titanium compounds during the gel formation and the following crystallisation is of great importance to control the whole process.

2. EXPERIMENTAL DETAILS

Three different preparation methods, A, B and C, were used.

(A) PbTiO_3 gel was obtained by mixing the solutions of lead(II) acetate trihydrate $\text{Pb}(\text{CH}_3\text{COO})_2 \cdot 3\text{H}_2\text{O}$ (LAT) in methoxyethanol (MOE) and of titanium isopropylalkoxide $\text{Ti}[(\text{CH}_3)_2\text{CHO}]_4$ (TPOT) in MOE.

(B) TPOT was distilled in MOE substituting the isopropyl group with the methoxyethoxy group in the titanium precursor, obtaining the tetramethoxyethoxytitanium (TMET). The distillation was performed in order to obtain more homogeneous gelation and condensation processes, because TMET has a lower reactivity than TPOT, which is hydrolysed very quickly with respect to LAT. The difference in the hydrolysis rate between LAT and TPOT may originate some precipitates or phase separation.

(C) The starting materials and the solvent were the same as in the A method, but a little amount of HCl (0.14 %) as catalyst was added to the solution to favour the hydrolysis process and then the polycondensation.

The obtained gels were dried in air at 125 °C for 1 hour, then powdered and heat treated from room temperature to 700 °C at an heating rate of 100 °C/h. For the Pb edge the solid samples were ground to fine powders, dispersed in boron nitride and pressed to obtain pellets suitable for transmission. At the Ti edge the absorption length of PbTiO_3 is only 2 µm and, to avoid thickness effects, pellets for fluorescence were obtained by pressing the pure samples. For liquids and gels an ad-hoc cell was used. The data were collected at room temperature on D32 IF CRG beamline at ESRF in Grenoble, France, using a Si(111) double crystal monochromator. The beam was sagittally focused and at the Ti edge a double mirror was installed to avoid the contribution from the harmonics. EXAFS measurements were performed on A, B, C samples from the starting solutions to final PbTiO_3 heat treated samples. XANES spectra were collected at the Ti edge on the B samples, starting from gels. Ti and Pb foils, TiO_2 anatase, $\text{Pb}_2\text{Ti}_2\text{O}_6$ pyrochlore were used as reference compounds.

The EXAFS signal was extracted from the experimental absorption coefficient using the background removal technique AUTOBK [3] whereas, for the determination of the structural parameters, the FEFFIT (UWXAFA package [4]), which uses theoretical phase functions and amplitudes from FEFF6 software [3], was used.

3. RESULTS AND DISCUSSION

In Fig. 1 are reported the near edge spectra at the Ti K-edge of the B samples. The XANES region shows characteristic features related to the Ti symmetry; the $1s \rightarrow 3d$ bound state transitions are the origin of the pre-edge peaks and are related

to the octahedral crystal field. There is no difference between the spectra up to the 400 °C annealed samples and the cubic Fd3m pyrochlore reference, while a marked change is observed for the samples treated at higher temperatures, corresponding

Figure 1: XANES at the Ti K-edge of the samples of B preparation.

Figure 2: EXAFS Radial Distribution Function (RDF) for the samples of B preparation.

Figure 3: EXAFS RDF for the samples of A preparation

to the transformation into P4mm perovskite PbTiO_3 .

The spectra above 500 °C remain unchanged up to the higher treatment temperatures; this fact indicates that the Ti environment undergoes a sharp transformation into a stable phase during the heating in the range 400 °C to 500 °C.

In Fig. 2 (B samples) and in Fig. 3 (A samples) the magnitude of the Fourier transform at the Ti and Pb edges is shown, respectively. The EXAFS RDF around the Ti atoms shows only a peak corresponding to the first oxygen shell with six atoms at 1.94 Å, like in the pyrochlore reference sample, up to 400 °C; this is an indication of the favoured occurrence of a pyrochlore phase instead of the more stable perovskite. A clear change in the RDF is observed for the powders treated at $T > 500$ °C where the main peak shifts to larger R value and higher coordination shells become discernible. At the Pb edge, the EXAFS RDF shows an analogous evolution for all the preparations A-B-C. The first Pb-O coordination shell dominates the spectrum up to the samples treated at 400 °C, while a second Pb-Ti peak is clearly observable for higher annealing temperatures. This suggests that the homocondensation is favoured during the gelation leading to Pb-O-Pb and Ti-O-Ti linkages instead of the heterometallic Pb-O-Ti bonds. A model of the Ti-Pb linkage through bidentate acetate bridging has been recently proposed [2]. At both Ti and Pb edges a fitting of the EXAFS data of the 700 °C A and C samples gives results in full agreement with the crystallographic data of tetragonal PbTiO_3 . For the samples obtained according to the preparation B, the EXAFS data are compatible with a perovskite phase with the coexistence of lead trititanate PbTi_3O_7 as evidenced by Raman measurements [2]. The EXAFS signals at the Pb edge of A and C gels are similar with that of LAT in MOE up to the annealing at 300 °C. In the B samples (distilled) the data give no evidence of the presence of the LAT precursor, even in the gel. This can be due to the more homogeneous hydrolysis process obtainable using TMET instead of TPOT, that involves the lead precursor in a larger amount.

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