

# Phase transitions in $\text{PbTi}_x\text{Hf}_{1-x}\text{O}_3$ determined by thermal analysis and impedance spectroscopy

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**Abstract** The objective of this study is to determine the influence of partial substitutions of  $\text{Ti}^{4+}$  by isovalent  $\text{Hf}^{4+}$  in the perovskite-type crystalline structure of  $\text{PbTiO}_3$ . Different samples over the whole composition range ( $0 \leq x \leq 1$ ) in the  $\text{PbTi}_{1-x}\text{Hf}_x\text{O}_3$  family have been prepared. Phase transitions have been determined by thermal analysis (differential scanning calorimeter: DSC) and complex impedance spectroscopy (IS) over a wide temperature range. As a consequence of the cation replacement the changes that take place in the different phase transition temperature are reported. By both techniques, thermal analysis and electrical characterization, it is shown that for all compositions prepared there is only one phase transition in a temperature range between 230 and 460 °C. With these results and the previously known crystalline structure of pure  $\text{PbTiO}_3$  and  $\text{PbHfO}_3$  perovskites, the phase diagram of the  $\text{PbTi}_{1-x}\text{Hf}_x\text{O}_3$  family is presented including a morphotropic phase transition at  $x \sim 0.5$ .

**Keywords**  $\text{PbTiO}_3$  ·  $\text{PbHfO}_3$  · Ferroelectric · Antiferroelectric · Phase transition · Impedance spectroscopy · Differential scanning calorimeter

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## Introduction

Titanates have different interesting properties which make them suitable for many applications in different industrial fields. Zirconium titanate,  $\text{ZrTiO}_4$ , is used as a catalyst and like pigment [1–3]. Nb-doped  $\text{SrTiO}_3$  is widely used in electronic industry due to its high dielectric constant and excellent stability with temperature and voltage [4].  $\text{CaTiO}_3$ ,  $\text{BaTiO}_3$ ,  $\text{PbTiO}_3$  and  $\text{PbZrO}_3$  present various technological uses due to their dielectric, pyroelectric and piezoelectric properties.  $\text{PbTiO}_3$  (PT) at room temperature is tetragonal (relatively large distortion from the ideal cubic perovskite structure,  $c/a = 1.063$ ), belongs to the space group  $P4mm$  and it is ferroelectric [5]. The ferroelectricity is due to correlated displacement in the same direction of the  $\text{Pb}^{2+}$  and  $\text{Ti}^{4+}$  cations with respect to the oxygen octahedron. The shifts occurring along the  $c$  axis are  $\sim 0.48$  Å for Pb and 0.32 Å for Ti [6]. It can be obtained by thermal decomposition of different precursors [7, 8] or by the conventional ceramic route of mixing oxides method.  $\text{PbHfO}_3$  (PHF) is orthorhombic ( $c/a = 0.989$ ) belongs to the space group  $Pbam$  and it is antiferroelectric. With respect to the oxygen octahedron, the Pb and Hf atoms are shifted by 0.24 and 0.17 Å, respectively, along the [100] direction of the orthorhombic cell. In the antiferroelectric phase, the spontaneous polarizations form two sublattices which are antiparallel to each other producing no net macroscopic polarization [6]. The ionic radii of  $\text{Ti}^{4+}$  and  $\text{Hf}^{4+}$  in octahedral coordination are different,  $\text{Ti}^{4+}$ : 0.74 Å and  $\text{Hf}^{4+}$ : 0.84 Å, respectively. With increasing temperature  $\text{PbTiO}_3$  exhibits only one phase transition from ferroelectric to the paraelectric state at 490 °C ( $T_c$ , Curie point) where the crystalline structure changes from tetragonal (space group  $P4mm$ ) to cubic symmetry (space group  $Pm3m$ ). On the other hand,  $\text{PbHfO}_3$  shows two

structural transitions. One is at 160 °C from orthorhombic antiferroelectric to tetragonal antiferroelectric lattice and another one at 215 °C ( $T_c$ ) from this last to the cubic paraelectric phase.

Kwapulinski et al. shows a possible displacive-type phase transition close to 400 °C by means investigations in  $\text{PbHfO}_3$  single crystals of the amplitude of the thermal vibrations for Pb ions in the high temperature  $\text{Pm}3\text{m}$  paraelectric phase [9].  $\text{PbBO}_3$  (B = Ti, Zr and Hf), in the paraelectric phase have been considered isomorphous. Kuroiwa et al. [10] points to that  $\text{PbZrO}_3$  and  $\text{PbHfO}_3$  with AFE phase transition are different to  $\text{PbTiO}_3$  in the cubic structure respect to the charge density distribution. In  $\text{PbHfO}_3$ , a new phase at higher temperature is induced by the application of pressure and this phase is also antiferroelectric. The temperature range stability of this new phase increases with pressure. Sani et al. by means synchrotron X-ray powder diffraction at different temperatures under applied pressure point to that the FE–PE phase transition takes place at RT with 11.6 GPa. The phase transition loses its first-order character and gradually becomes a second-order phase transition [11]. In the perovskites, with decreasing T, transitions to ferroelectric (FE) phases are accompanied by increases in unit cell volume, whereas transitions to AFE phases are accompanied by decreases in volume. Therefore, pressure lowers ferroelectric transition temperatures and raises antiferroelectric transition temperatures. The application of pressure increases the temperature of the phase transitions and takes place a sharp reduction in the dielectric constant  $\epsilon$  anomaly at the AFE–PE transition [12, 13].

The interest of these ceramics  $\text{PbHf}_x\text{Ti}_{1-x}\text{O}_3$  (PHT) solid solutions which exhibits strong ferroelectric properties as occurred with the isostructural family  $\text{PbZr}_x\text{Ti}_{1-x}\text{O}_3$  (PZT) is due to its possible industrial applications in the field of microelectronics and micromechanical systems (MEMS). Although the phase diagram of the PHT family has been less studied than PZT, there are some studies about different compositions in the  $\text{PbTiO}_3$ – $\text{PbHfO}_3$  system. Jaffe et al. studied various compositions, determined the Curie temperatures and in accordance with the results they proposed a first approximation of the solid state phase diagram. These authors stand out that these solid solutions are structurally very similar to those in the PZT system. In the same way Jaffe points out that the rhombohedral Hf-rich phase is also separated from the tetragonal Ti-rich phase by a diffuse morphotropic phase boundary (MPB), which is observed somewhere between 47.5 and 50 mole%  $\text{PbHfO}_3$  [14]. An abrupt change in the structure of a solid solution with variation in composition is known as morphotropic transformation. These morphotropic transformations occur because of free energy differences between two or more alternative

crystallographic modifications of a given basic structure type exist. As one ion replaces another in a solid solution, the energies of the different structures change, and the crystal assumes the structure having the minimum free energy. In this region for which  $x$  is close to 0.5, the coexistence of a rhombohedral and a tetragonal phase enhances the dielectric and mechanical properties. Increasing the content of  $\text{PbHfO}_3$ , as it replaces  $\text{PbTiO}_3$  lowers the Curie temperature and at room temperature decreases the tetragonal  $c/a$  ratio. The equimolar composition was predominantly rhombohedral with a small content of the tetragonal phase. Solid solutions richer than this in  $\text{PbHfO}_3$  were rhombohedral. As the composition approaches the MPB ( $x$  close to 0.5), the coexistence of the rhombohedral and tetragonal phases enhances the dielectric and mechanical properties. At room temperature the dielectric constant and the radial coupling coefficient  $k_t$  become maximums [14]. There are not much works in this system and the great majority of the works correspond to studies by neutron powder diffraction with temperature of the Ti-rich region such as Frantti et al. [15] who investigates the crystal symmetries of  $\text{PbHf}_x\text{Ti}_{1-x}\text{O}_3$  with  $10 \leq x \leq 50$  or Muller et al. [16, 17] who determined FE–PE phase transition in  $\text{PbHf}_{0.2}\text{Ti}_{0.8}\text{O}_3$  and  $\text{PbHf}_{0.4}\text{Ti}_{0.6}\text{O}_3$ . Regarding to Hf-rich region, only Sicron et al. [18] studied the structure of rhombohedral ferroelectric perovskite  $\text{PbHf}_{0.9}\text{Ti}_{0.1}\text{O}_3$  by X-ray absorption fine structure (XAFS).

It is known that the nature of the B cation plays an important role in the resulting crystalline structure of these oxides. In these series of compounds it should be expected that the competition between Ti–O and Hf–O bonds exists, due to that both the ionic radius of  $\text{Ti}^{4+}$  and  $\text{Hf}^{4+}$  and the covalence grade of the bonds are different. In fact, as it was mentioned above,  $\text{PbTiO}_3$  and  $\text{PbHfO}_3$  have different phase diagrams and as the partial substitution of Ti by Hf takes place, the formation of a series of new compounds with different crystalline structures depending on the level of substitution occurs.

The aim of this work is to study the phase stability of the  $\text{PbTi}_x\text{Hf}_{1-x}\text{O}_3$  family of compounds as a function of the temperature at normal atmosphere conditions. The perovskite structure at room temperature (RT) depending on composition was determined by X-ray diffraction (XRD). Samples with compositions over the whole  $x$  concentration range were analyzed by impedance spectroscopy (IS) and differential scanning calorimeter (DSC), in order to study the phase transitions in these materials by means of two, in principle independent physical properties (dielectric constant and specific heat), as a function of temperature and composition. Phase transitions are accompanied by anomalies in the dielectric constant and changes in the specific heat.

## Experimental

Different compositions of  $\text{PbHf}_x\text{Ti}_{1-x}\text{O}_3$  with  $0 \leq x \leq 1$  were prepared by conventional ceramic route of mixing oxide method. Powder raw materials (98% purity) of  $\text{PbO}$ ,  $\text{HfO}_2$  (2%  $\text{ZrO}_2$ ) and  $>99\%$   $\text{TiO}_2$ , were mixed thoroughly in a high speed mill for 10 min in ethanol with  $\text{ZrO}_2$  balls. The powders were dried at  $60^\circ\text{C}$  and sieved at  $63\ \mu\text{m}$ , followed by calcination at  $850^\circ\text{C}$  for 4 h where the material is synthesized. After that, the compositions were milled again in the same conditions and after drying, a binder was added. Pellets of 1 mm in thickness and 10 mm in diameter were uniaxially pressed at 80 MPa followed by binder burnout at  $600^\circ\text{C}$  for 1 h. Finally the samples were sintered at  $1250^\circ\text{C}$  for 4 h with a heating rate of  $3^\circ\text{C}/\text{min}$ . The difficulty in the preparation of  $\text{PbTi}_{1-x}\text{Hf}_x\text{O}_3$  ceramics arises from the high volatility of  $\text{PbO}$  during sintering. In order to minimize the  $\text{PbO}$  volatilization, the pellets were sintered in a Pb-rich atmosphere by carrying out the sintering in a closed system by means a double alumina crucible setup where the pellets were placed on platinum sheet with a buffer powder of  $\text{PbZrO}_3$  and  $\text{ZrO}_2$  that was 5% of the total weight of the samples. The joint between alumina crucibles is sealed with  $\text{ZrO}_2$  powder. The weight change of the samples was less than 2%. To eliminate layers on top and bottom where the Pb loss is more noticeable, the pellets were polished with a SiC sandpaper. After that, the surfaces were tan in colour and XRD of the surfaces showed only the perovskite phase. Even with the Pb evaporation, all the samples show a very high density,  $>95\%$  of the theoretical density, determined by Arquímedes dipping method. With this procedure all the samples showed even higher densities after the elimination of the Pb-poor surfaces. In the surface the presence of  $\text{HfO}_2$  and  $\text{TiO}_2$  should be proportional to the Pb-loss, but the pellets used to the electrical and thermal characterization do not show either of these oxides in the X-ray characterization of the polished surface.

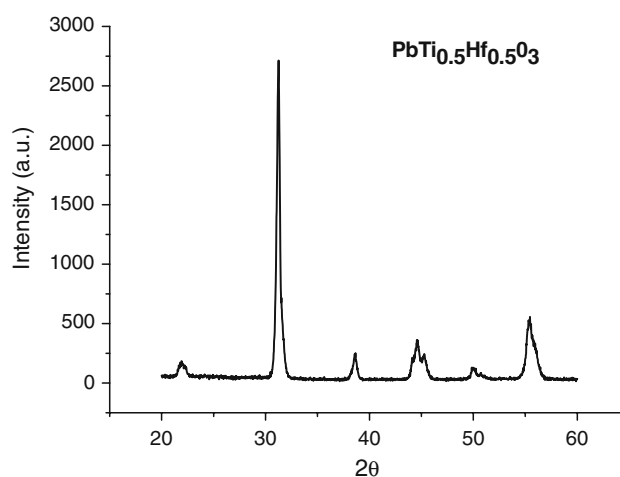
The samples selected for dielectric characterization by impedance spectroscopy were coated on both sides with evaporated platinum film. These measures were carried out in a Solartron 1260 impedance/gain-phase analyzer between 100 Hz and 10 MHz with an oscillation level of 3 V. Thermal measurements are carried out in a Shimadzu DSC 50 calorimeter in  $\text{N}_2$  atmosphere with a heating rate of  $10^\circ\text{C}/\text{min}$ . The structural characterization is carried out by D-5000 Siemens XRD equipment between  $2\theta = 20\text{--}60$ .

## Results and discussion

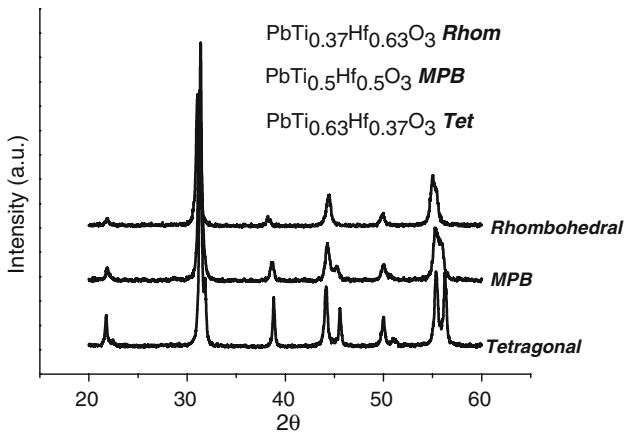
Figure 1 corresponds to XRD analysis of composition  $\text{PbTi}_{0.5}\text{Hf}_{0.5}\text{O}_3$  treated at  $850^\circ\text{C}$  for 4 h (powder) which

corroborates that at this temperature the perovskite phase is formed and there is not presence of the starting oxide. In Fig. 2 the diffractograms of  $\text{PbHf}_x\text{Ti}_{1-x}\text{O}_3$  at RT for the compositions  $x = 0.37, 0.5$  and  $0.63$  sintered at  $1250^\circ\text{C}$  for 4 h (pellets) are shown. All of them were fitted according to different crystallographic structures which appear in this kind of perovskites in agreement with literature [19, 20]. For  $x = 0.37$  (i.e. Ti-rich composition) the tetragonal structure, for  $x = 0.5$  point out that this composition is sited in the MPB coexist the tetragonal and the rhombohedral structures and finally  $x = 0.63$  (the Hf-rich composition) corresponds to the rhombohedral structure. Therefore with the substitution of Ti by Hf a new phase with rhombohedral symmetry is stabilized which neither exist in  $\text{PbTiO}_3$  nor in  $\text{PbHfO}_3$ . This results shows the existence of a narrow region in composition, close to the equimolar composition of Ti and Hf, i.e. the MPB, where coexists both ferroelectric phases; the tetragonal and the rhombohedral structures. Similarly as in PZT series, the coexistence of both phases would enhance the dielectric and mechanical properties and it must be interesting carry out a piezoelectric and mechanical characterization of the samples with  $\text{PbTi}_{0.5}\text{Hf}_{0.5}\text{O}_3$  composition.

Figures 3 and 4 show the curves  $Z$  versus temperature for different frequencies, previously specified, in samples prepared over the composition range  $\text{PbHf}_x\text{Ti}_{1-x}\text{O}_3$ , with  $0 < x < 1$ . Figure 3 corresponds to Ti-rich region and Fig. 4 to the Hf-rich one. In Fig. 5 the DSC analysis for all the compositions is shown. For Ti-rich compositions in the impedance curves versus temperature show one anomaly or change for the higher frequencies, corresponding to the existence of a phase transition which represents the structural change from the ferroelectric tetragonal phase to the



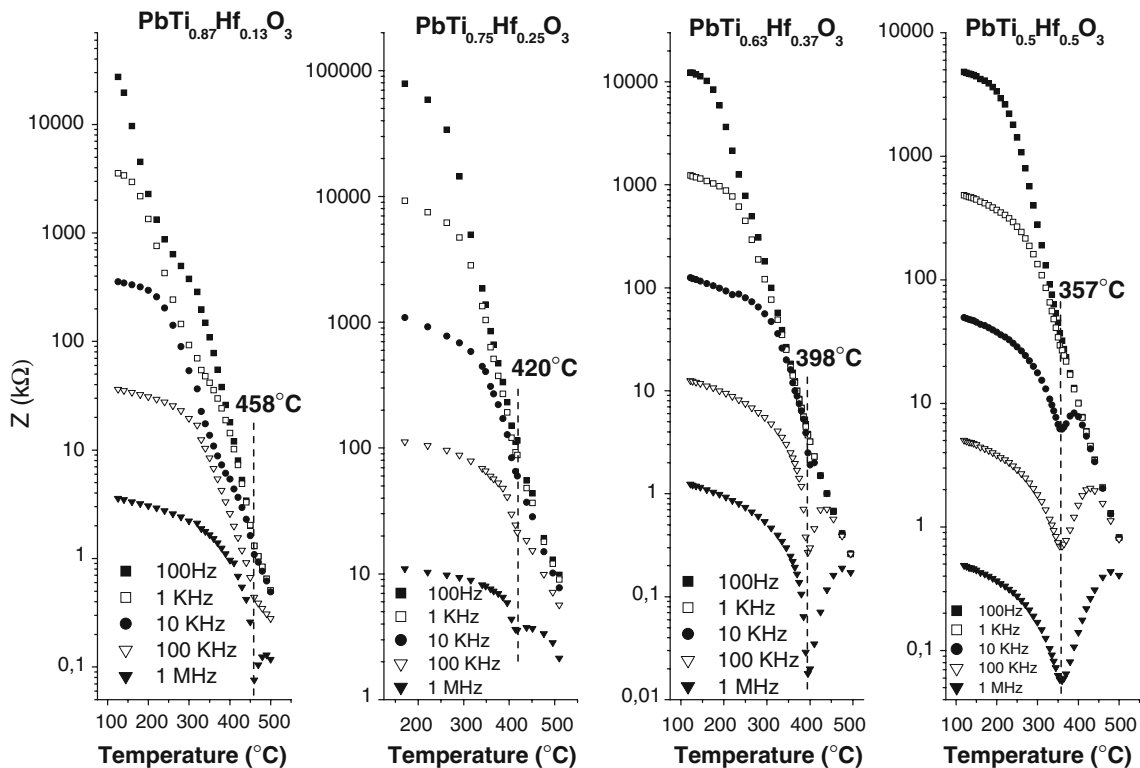
**Fig. 1** XRD for  $\text{PbTi}_{0.5}\text{Hf}_{0.5}\text{O}_3$  powder synthesized at  $850^\circ\text{C}$  for 4 h



**Fig. 2** XRD for different compositions ( $x = 0.37, 0.5$  and  $0.63$ ) in  $\text{PbHf}_x\text{Ti}_{1-x}\text{O}_3$  system sintered at  $1250^\circ\text{C}$  for 4 h

paraelectric cubic one (Curie temperature). In the case of Hf-rich compositions, the variation in  $Z$  versus temperature shows only one phase transition again but for all frequencies, corresponding to the ferroelectric rhombohedral to paraelectric cubic phase transition. DSC analysis, according with IS, shows only one phase transition for all the compositions corresponding to the ferroelectric–paraelectric phase transition. Figure 6 shows the good agreement for the temperatures of the phase transitions as determined

by these two very different techniques. The greater differences between both temperatures are of the order of  $10^\circ\text{C}$  for intermediate compositions ( $x = 0.37, 0.5$  and  $0.63$ ) in the  $\text{PbHf}_x\text{Ti}_{1-x}\text{O}_3$  system. The meaningful difference between DSC and IS is the intensity of the peak corresponding to the only phase transition that take place for all the composition range. In DSC, for Ti-rich compositions, the peak is more intense than for the Hf-rich compositions and unlike IS where the change in  $Z$  is very significant for all the frequencies in Hf-rich compositions. Point to that Curie temperature increases with Ti-content. Thus, it can be said that both techniques complement each other. As far as we know after an extensive literature search on the mixtures of the  $\text{PbTiO}_3$  and  $\text{PbHfO}_3$  perovskite-type compounds, Fig. 6 shows for the first time the complete phase diagram of the  $\text{PbHf}_x\text{Ti}_{1-x}\text{O}_3$  family. It can be observed the variation of the phase transition temperature (Curie temperature,  $T_c$ ) from the rhombohedral–tetragonal ferroelectric phase to the paraelectric cubic phase can be adjusted almost with a line. In this figure the phase transition temperature corresponds to the averaged temperature between those obtained by IS and DSC. It can be said that the stability of the tetragonal and rhombohedral structures decreases continuously with temperature as Ti is substituted with Hf or in the same way, the stability of the cubic structure also increases with the Hf substitution. These



**Fig. 3** Impedance module  $Z$  versus temperature at different frequencies for Ti-rich compositions in the  $\text{PbHf}_x\text{Ti}_{1-x}\text{O}_3$  system

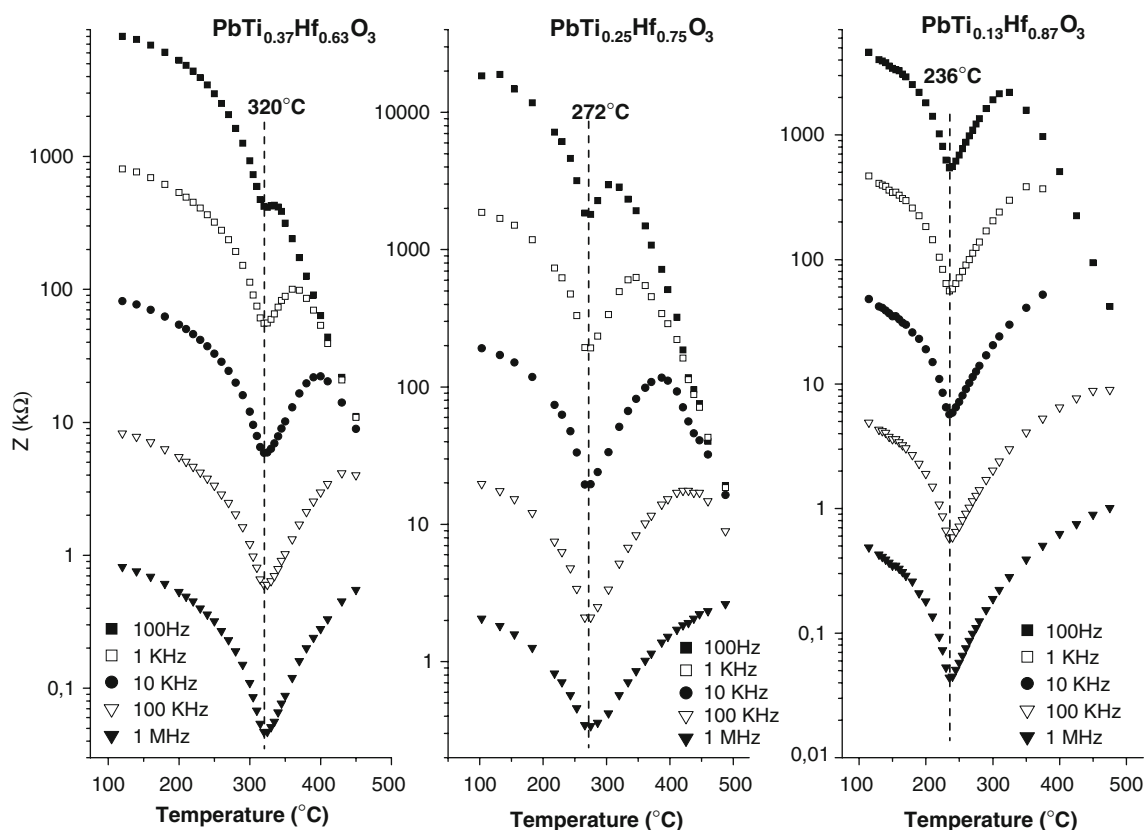


Fig. 4 Impedance module  $Z$  versus temperature at different frequencies for Hf-rich compositions in the  $\text{PbHf}_x\text{Ti}_{1-x}\text{O}_3$  system

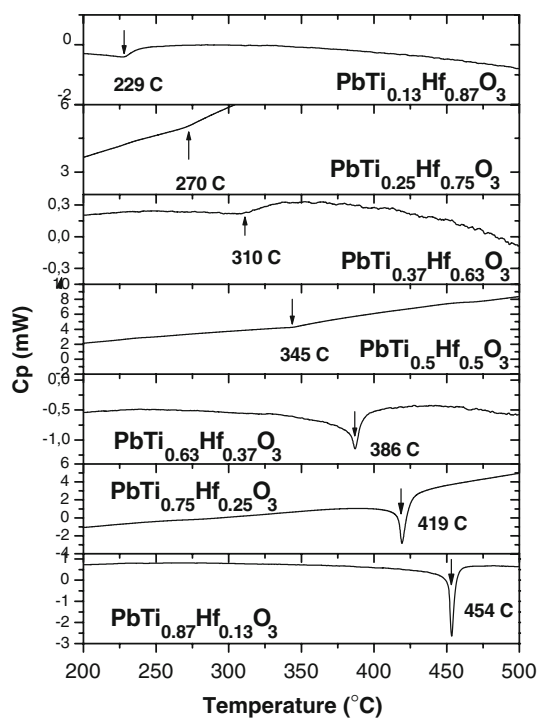


Fig. 5 DSC measurements for all the compositions prepared in the  $\text{PbHf}_x\text{Ti}_{1-x}\text{O}_3$  system

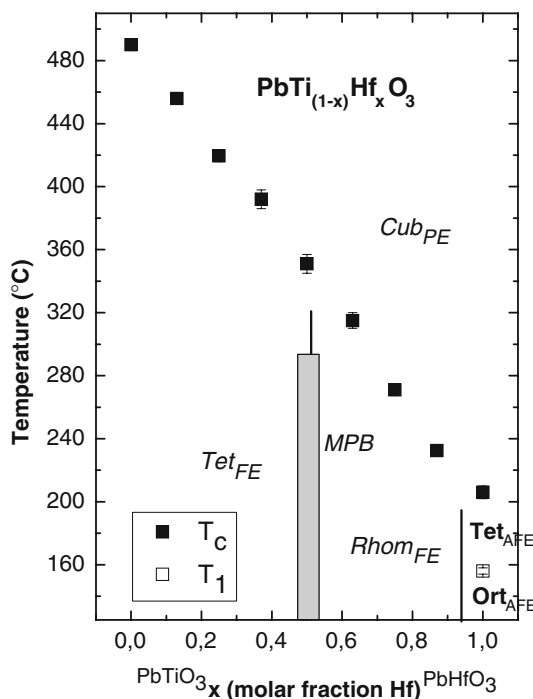


Fig. 6 Average phase transition ( $T_c$ ) obtained by impedance spectroscopy (IS) and differential scanning calorimeter (DSC) for  $\text{PbHf}_x\text{Ti}_{1-x}\text{O}_3$  system



results are in agreement with the assertion that Ti and Hf are slightly chemically different although both are isovalent,  $Ti^{4+}$  and  $Hf^{4+}$ . This assertion is based on the electronic structure, the electronegativity and the ionic radius of  $Ti^{4+}$  and  $Hf^{4+}$  (0.74 and 0.84 Å), respectively. The electronic structures of Ti ( $[Ar]3d^25s^2$ ) and Hf ( $[Xe]4f^{14}5d^26s^2$ ) show two main differences: one is that Hf has f-electrons, but the f levels in Hf are full occupied in a sharp and deep level with respect to the Fermi energy that prevents these electrons to any hybridization with O electrons. The other is the different number of nodes and the shape of the shell and mean radius of the 3d and 5d electrons. Titanium electronegativity is slightly higher than hafnium, 1.54 versus 1.3. In a recent work [20] it has been determined the grade of covalence of the Hf d-electrons in  $HfO_2$  and, contrary with a pure ionic scheme, it can be seen that the Hf-d shell is not completely empty, showing a big but completely ionic behaviour. Similar results analyzing the covalence grade were obtained for others compounds as ionic as NaCl. Thus, the changes in the phase stabilities when Ti is substituted with Hf may due to tiny differences in the electronic structure related with the mainly empty d shells of Ti and Hf. Moreover, Pb must play a role that amplifies this effect. In Fig. 6 it can be also observed that if one stands at some point in the tetragonal or rhombohedral phase near the transition temperature to the cubic phase, one can go to the cubic phase both by moving horizontally by adding Hf, or by moving vertically by heating. This effect was previously observed in other perovskite-type families of compounds [20], and can be of great interest in the design of new materials. One phonon mode goes soft to lead to a phase transition by two apparently unconnected different ways. The increase in mass by means of the  $Ti \rightarrow Hf$  substitution has the same effect than the increase in the amplitude of the vibration modes.

## Conclusions

In this study we have determined the complete phase diagram of the  $PbHf_xTi_{1-x}O_3$  (PHT) family by means of impedance spectroscopy and differential scanning calorimetry. In the mixed perovskites  $PbHf_xTi_{1-x}O_3$ , with  $0.13 < x < 0.87$ , the substitution of the central cation in the oxygen octahedron,  $Ti^{4+}$ , by another isovalent cation with a different ionic radius and electronic structure  $Hf^{4+}$ , results in the stabilization of a new rhombohedral phase that does not exist neither in pure  $PbTiO_3$  or  $PbHfO_3$ . Moreover,  $Ti \rightarrow Hf$  substitution produces the same effect that the change in temperature for a fixed composition, that it is possible to change from one phase to other changing the temperature or the composition. We obtained a good agreement between the temperature of phase transitions

determined by two characterization techniques as different in nature as IS and DSC are.

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