



Experiment title: Structural investigation of the ferroelectric perovskites in the BaTiO₃-CaTiO₃-BaZrO₃ system and phase sequence of PbFe_{0.5}Ta_{0.5}O₃ and PbFe_{0.5}Nb_{0.5}O₃

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Report:

Most of the complex perovskites A(B_{1-x}B'_x)O₃ with relaxor behavior, related –as well accepted– to the presence of more than one ionic species in the octahedral sublattice, contains lead as A-type cation. Well known examples are PbMg_{1/3}Nb_{2/3}O₃, PbSc_{1/2}Nb_{1/2}O₃ and PbSc_{1/2}Ta_{1/2}O₃. Relaxors have strong potential applications as components in electronics (dielectrics for capacitors, actuators...) and lead-free compositions would be of great interest for environmental protection. Studies were performed in particular on ceramics with composition derived from BaTiO₃. Dielectric measurements showed that the relaxor behaviors is observed in zone III of the BaTiO₃-BaZrO₃-CaTiO₃ ternary diagram (Fig. 1). In addition, compositions belonging to region A (Fig. 1) show a relaxor behaviour of the dielectric constants followed, at lower temperature, by a further anomaly which seems to correspond to a true ferroelectric transition. X-ray measurements performed on a high resolution prototype goniometer, using a rotating anode generator, have shown that the symmetry at low temperature are rhombohedral. Unfortunately, the resolution of such experiments was not enough to follow the rhombohedral distortion as a function of temperature.

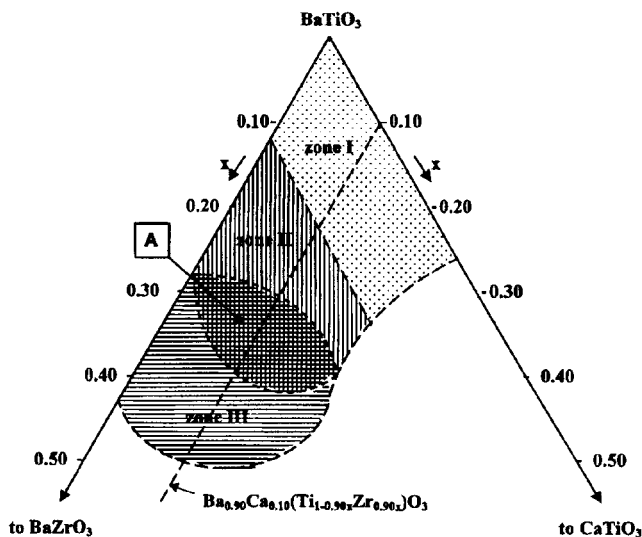


Fig.1 BaTiO₃-BaZrO₃-CaTiO₃ ternary diagram

Our study has allowed to clarify the phase diagram of this ternary system. We have analyzed the behaviour in temperature of the following compositions : $\text{BaTi}_{0.8}\text{Zr}_{0.2}\text{O}_3$ (zone II), $\text{BaTi}_{0.65}\text{Zr}_{0.35}\text{O}_3$ (zone III) and $\text{Ba}_{0.92}\text{Ca}_{0.08}\text{Ti}_{0.75}\text{Zr}_{0.25}\text{O}_3$ (region A).

$\text{BaTi}_{0.8}\text{Zr}_{0.2}\text{O}_3$ has a normal ferroelectric phase transition at about 350 K. Below this temperature the symmetry is clearly rhombohedral. $\text{BaTi}_{0.65}\text{Zr}_{0.35}\text{O}_3$ presents a typical relaxor behaviour and no apparent symmetry change below T_m (200 K at 1kHz). The evolution vs temperature of the cell parameter a is shown in Fig. 2. No anomaly is found near T_m , while a significant slope change is observed at about 150 K. This temperature is in rather good agreement with the Vogel-Fulcher temperature determined from dielectric measurement and Raman freezing temperature. As known, in $\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3$ the relaxor behavior is assigned to the non homogeneous distribution of the Mg^{2+} and Nb^{5+} cations over the B site of the perovskite structure. The difference of charge of the two cations is supposed to create space-charges and hence, electric field fluctuations on an atomic length scale. The quenched local random fields prevent further increasing of the polar domain size. The application of an external field eliminates the influence of the random fields, allowing a macro-ferroelectric state to be induced. In $\text{BaTi}_{0.65}\text{Zr}_{0.35}\text{O}_3$, the two cations (Ti^{4+} and Zr^{4+}) on the B site have the same charge and cannot induce strong random fields even if their distribution is irregular. Nevertheless, an inhomogeneous distribution should be at the origin of relaxor behavior. It can be supposed that the regions rich in Ti^{4+} have the behaviour of BaTiO_3 and become polar, whereas the regions rich in Zr^{4+} tend to remain paraelectric (BaZrO_3 is paraelectric at all temperatures). The fact that the solid solution $\text{Ba}(\text{Ti}_{1-x}\text{Zr}_x)\text{O}_3$ does not exist for $x > 0.42$ (Fig.1) supports a description in terms of a segregation of Zr^{4+} ions.

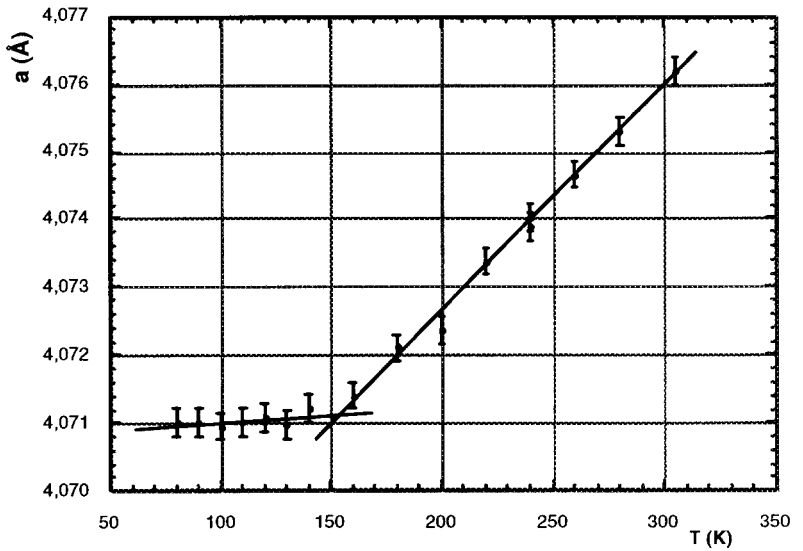


Fig. 2 cubic cell parameter v.s. temperature

The behaviour of $\text{Ba}_{0.92}\text{Ca}_{0.08}\text{Ti}_{0.75}\text{Zr}_{0.25}\text{O}_3$ is similar to that of $\text{PbSc}_{1/2}\text{Nb}_{1/2}\text{O}_3$. The rhombohedral distortion is of the same order. It has been possible to follow the rhomboedral distortion vs. temperature and to determine the spontaneous deformation. The transition temperature of 208 K, found by the fitting of the spontaneous deformation, agrees with the dielectric and pyroelectric measurements. The critical exponent are in the typical range of the values derived from the Wilson's theory for 3D systems. The composition $\text{BaTi}_{0.75}\text{Zr}_{0.25}\text{O}_3$ belong to the zone II of the ternary diagram (Fig. 1). No dispersion is observed around the dielectric anomaly. The proportion of Zr is not high enough to give rise to a relaxor phase. The appearance of the relaxor behaviour before the onset of long-range polar order, when Ca^{2+} is substituted for Ba^{2+} , should be due to a supplementary local polarization resulting from the Ca^{2+} displacement in the structure. Such a local effect would break the long range cationic correlation. Indeed the strong polarisability and the fact that Ca^{2+} (1.36 Å) is smaller than Ba^{2+} (1.61 Å), when twelfefold-coordinated, leads to a displacement of Ca^{2+} from its crystallographic site.

The study vs. temperature on the ferroelectric perovskite $\text{PbFe}_{0.5}\text{Ta}_{0.5}\text{O}_3$ has confirmed the results of the latest measurements at the ESRF (line BM16) and has allowed to follow the evolution of the very small structural distortion with the temperature. The study of the similar compound $\text{PbFe}_{0.5}\text{Nb}_{0.5}\text{O}_3$ was not performed because of lack of time.

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