Composition-temperature phase diagram for Barium-doped lead zirconate ferroelectric ceramics determined by Raman spectroscopy

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Abstract : The ceramic $(Pb_{1-X}Ba_X)ZrO_3$ composition, hereafter abbreviated PBZ-x, is a ceramic solid solution with perovskite structure. The effect on the antiferro-ferro-paraelectric phase transitions sequence caused by Barium substitution in Pb-sublattice is Raman spectroscopically evidenced and discussed. Furthermore, the basic features of the composition-temperature phase diagram of PBZ-x ($x \leq 0.5$) solid solutions were established.

I. Introduction

The ceramic $(Pb_{1-X}Ba_X)ZrO_3$ derives from lead zirconate ($PbZrO_3$) and barium zirconate ($BaZrO_3$). $PbZrO_3$ undergoes the unique known structural phase transition at 503 K, the antiferroelectric phase of orthorhombic structure A_O (space group given by C_{3v}^8-Pba2) deriving from the paraelectric cubic phase P_C (space group given by O_h^1-Pm3m). On the contrary, $BaZrO_3$ shows no phase transition with temperature since it is stable in the paraelectric cubic structure. It was reported [1, 2] that between antiferroeletric and paraelectric phases occurs an intermediate phase of ferroelectric nature with a rhombohedral structure. Ujma et al [2] have investigated structural, dielectric and pyroelectric properties of the solid solutions with $x \leq 0.25$ and found that certain features permit to include them to the group of ferroelectric relaxors. Indeed, their experiments ascertained the existence of ferroelectric microdomains, which are responsible for the observed relaxation. Furthermore, Li and Haertling [3] have found the relaxor behavior in PBZT ceramics with selected compositions. The relaxor properties are even more distinct in comparison with substitution with lanthanum trivalent cation as for PLZT-8/65/35.

II. Experiments

Polycrystalline samples of PBZ-x with stoichiometric composition series $x \leq 0.5$ were obtained by the technique of thermal synthesis of PbO, $BaCO_3$ and ZrO_2. The ceramics were sintered at 950°C, 1100°C and 1260°C for 3 hours in hermetically sealed double corundum crucibles to avoid PbO sublimation. Samples obtained under these conditions exhibited very good mechanical properties and only slight porosity. Raman spectroscopy experiments, in the right angle scattering geometry arrangement, were carried out in the Stokes region with a Spex 1401 double-grating spectrometer.

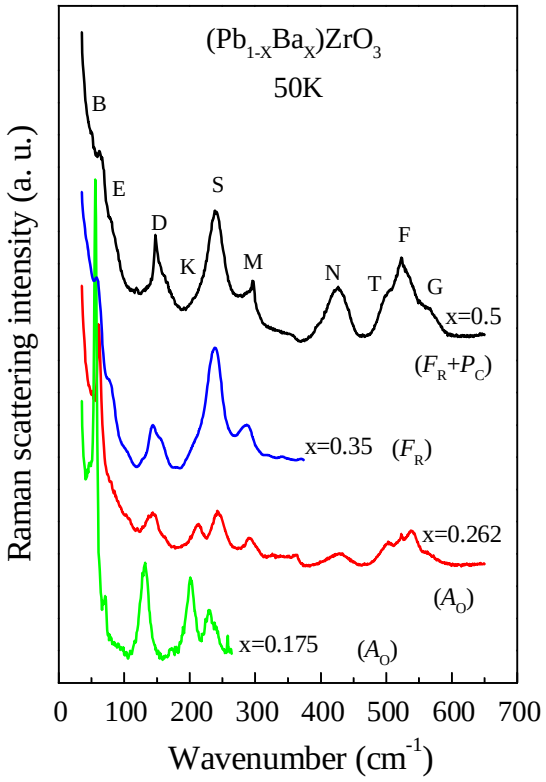

Fig 1: Example of the Raman spectra in $(Pb_{1-X}Ba_X)ZrO_3$ ceramics: Comparison of the spectra recorded at 50 K in the antiferroelectric phase (x=0.175 and x=0.262), ferroelectric phase (x=0.35) and mixed ferro-paraelectric phase (x=0.5).

The ceramics were exited using the 514.5 nm line of an argon-ion laser. For measurements with temperature, the Raman spectra was obtained first by heating the samples in a cooled cryogenic RCAC 31034 PMT and then the samples were mounded on a furnace for measurements above the room temperature. The uncertainty in the measurements of the temperature was 5 K for the low temperatures and 5 °C for the high temperatures. The spectra were reproducible within about 1 cm^{-1} under the same

experimental conditions. An accurate analysis of the lattice modes was performed with the help of non linear algorithm with the structure profiles taken as Lorentzian shapes.

III. Results and discussion

With progressive increasing temperature and/or barium content the several Raman modes initially well resolved broaden and their intensities decrease. The Fig. 1 shows example of Raman spectra recorded at 50 K for four values of barium content. The spectra are typical of different electric phases. We have built a composition-temperature phase diagram of the $(Pb_{1-x}Ba_x)ZrO_3$ system. Experimentally, this task was performed using the Raman spectroscopy as a tool in an attempt to correlate between antiferro-ferro-paraelectric (A_O-F_R-P_C) phase transitions sequence and the lattice vibrational modes which are characteristic of different electric phases. After this method based on the identification of various phases, with the help of characteristic transition anomalies exhibited by some analyzed modes and the relaxor strength, the basic features of the phase diagram of PBZ-x ($x \leq 0.5$) solid solutions were established (Fig. 2).

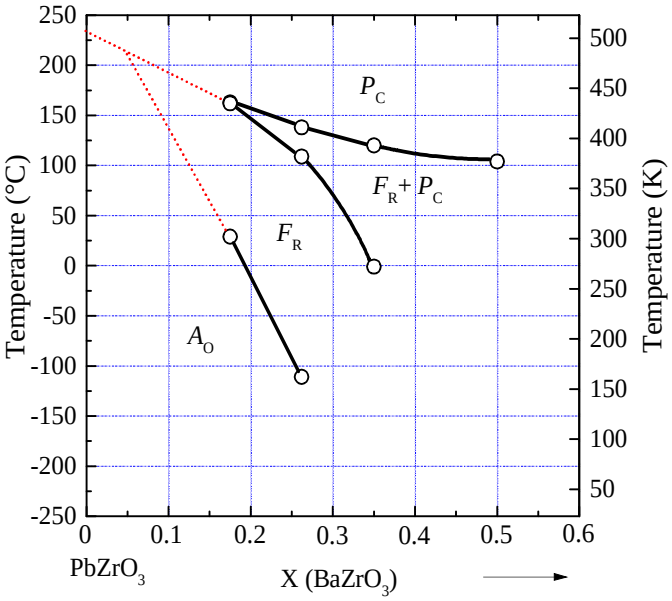

Fig. 2: Composition-temperature phase diagram for barium-doped lead zirconate ceramics. The open circle symbols indicate phase transition temperatures from Raman investigation performed in this work.

In comparison with the initial temperature-composition phase diagram [1], built from the dielectric measurements, the newly measured and additive compositions from Raman measurements confirm the tendency in the antiferro-ferroelectric phase boundary. However, the points initially reported as a phase boundary between pure ferroelecric and pure paraelectric phases are found to limit the pure ferroelectric phase and a mixed intermediate phase (F_R+P). The antiferro-ferroelectric (A_O–F_R) and ferro-paraelectric (F_R–P_C) phase transitions in these ceramics generally show a diffuse character. The presence of the mixed phase (F_R+P_C) reflects the coexistence of both phases due the compositional and polarization fluctuations [4, 5].

As conclusion the principal feature of the phase diagram is the following: increase of barium content in lead zirconate $PbZrO_3$ progressively alters the electrical properties from antiferro- to ferro- then to paraelectric state with presence of mixed electric phases.

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IV. References

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