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Effect of excess PbO on the structure and piezoelectric properties of Bi-modified $PbTiO_3$ ceramics

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Abstract

Effect of 1–4 wt.% excess PbO, added to the calcined powder, on the structure and dielectric and piezoelectric properties of Bi-doped lead titanate ceramics was investigated. The ceramics containing 4, 6 and 8 mol% Bi were prepared by the usual ceramic technique, using high purity oxides. The calcined powder of each composition was next intimately mixed with 1, 2, 3 and 4 wt.% PbO and then sintered at 1200–1300 °C for 3 h. The dielectric piezoelectric and electromechanical properties were determined as a function of excess PbO. Addition of PbO up to 2 wt.% was found to improve the densification, by the presence of the PbO liquid phase during sintering. For all Bi doping levels, the dielectric constant and the thickness coupling factor reach maxima (representing an increase of 2.5–8% for dielectric constant and 7–8% for thickness coupling factor) at about 2 wt.% PbO addition. The planar coupling factor is very low, less than 0.01, regardless the PbO content. The disipation factor slightly decreases with increasing PbO content and the mechanical quality factor of the thickness mode was about 300. The experimental results were discussed in terms of the mechanisms of densification in the presence of the liquid phase and of lead vacancy concentration.

Keywords: Dielectric properties; PbO; $PbTiO_3$; Piezoelectric properties; Sintering

1. Introduction

Lead titanate ($PbTiO_3$) ceramics are very appropriate for high frequency and high temperature applications, due to their low dielectric constant ($\varepsilon_r \cong 200$), high Curie point ($T_c \cong 490$ °C) and large electromechanical anisotropy (the ratio of the thickness to planar coupling factor $k_t/k_p > 10$).

It is known that pure lead titanate (PT) ceramic is too fragile to be sintered as dense body, since its crystal anisotropy generates high internal stresses, which make it break during cooling.[1–4] However, dense modified PT ceramics were obtained by lead substitution with small amounts of dopants, such as alkaline or rare earth elements, which enhanced their mechanical, dielectric and piezoelectric properties.[1,2,5–7] Other additives, such as Bi and Y, were also successfully used to improve the properties of PT ceramics.[8]

The densification of such materials can also be enhanced by using mineralizer agents, such as: LiF, CaF_2 or MnO_2 (l wt.%), which form a liquid phase at the grain boundaries, thus facilitating the diffusivities of the ions. Lead oxide also forms a liquid phase above its melting point (890 °C), which improves densification, but it also may affect the stoichiometry of the composition, due to its high volatility at the sintering temperatures. Therefore, an excess PbO is usually added to the initial raw materials, in order to prevent the deviation from the stoichiometry by lead loss and also to improve the densification, by forming the liquid phase. It is mostly the case of PT ceramics prepared by wet chemical method.[9,10] On the other hand, a high excess lead oxide could affect the dielectric, piezoelectric and electromechanical properties of the piezoelectric ceramics, as it was reported on lanthanum-modified PT ceramics, prepared by conventional ceramic technique, with up to 10 mol% excess PbO.[11]

A beneficial influence on the piezoelectric properties occurred when small amounts of excess PbO were added to the calcined powders of PZT.[12] Therefore, the aim of this study was to investigate the effect of 1–4 wt.%

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excess PbO, added to the powder after calcination, on the structure and dielectric piezoelectric and electromechanical properties of Bi-doped PT ceramics.

2. Experimental

2.1. Material preparation

Bi-doped PT ceramics, with general formula $(Pb_{1-3x/2}Bi_x)(Ti_{0.98}Mn_{0.02})O_3$, with $x=0.04$, 0.06, 0.08, were prepared by conventional ceramic technique, using p.a. purity raw materials. The starting oxides were wet (in methanol) mixed in a planetary ball mill, in agate vessels, for 2 h. After drying, the mixture was triple calcined at 900, 925 and 950 °C, respectively, for 2 h, with intermediate millings and a final milling of 5 h. Portions of the calcined powders of each composition were mixed with 1, 2, 3 and 4 wt.% PbO, respectively, and separately wet milled for 2 h, in order to get the best intimately mixed powders. The resulting powders were pressed, at about 75 MPa, in a steel die, into disks of 16 mm diameter and 2 mm thickness. The disks were sintered for 3 h, in air, at temperatures between 1200 and 1300 °C. All the samples were mechanically processed on a lapping machine to about 0.6 mm thickness and silver electroded. Poling was done under a d.c. field of about 70 kV/cm, in silicon oil, at 150 °C for 10 min.

2.2. Measurements

Dielectric, piezoelectric and electromechanical properties of sintered ceramics were determined 24 h after poling, using a HP 4194A Impedance/Gain-Phase Analyser.

The capacitance C_p and the dissipation factor D were measured at 1 kHz and dielectric constant K_{33}^T was calculated from the relationship $K_{33}^T = C_p t/\varepsilon_0 A$, where t is the sample thickness and A the electroded area.

Planar and thickness coupling factors were determined by resonance antiresonance method.[13] The planar coupling factor k_p, was evaluated according to IEEE Standard,[13] after Poisson's ratio σ was calculated by fitting the data given in Table 10 of IEEE Standard. to a polynomial.[14] The thickness coupling factor k_t was determined either by a polynomial fit[15] based on Onoe's method,[16] or from IEEE Std.[13] by the relationship $K_t^2 = \frac{\pi}{2}\frac{f_s}{f_p} ctg\left(\frac{\pi}{2}\frac{f_s}{f_p}\right)$, using the fundamental series and parallel resonance frequencies of the thickness mode, when series resonance frequencies and its overtones could not be accurately measured. The mechanical quality factor Q_{mg} of the thickness mode was estimated, according to IEEE Std.[10] from the relationship $Q_{mg} = (L_1/C_1)^{1/2}/R_1$, using the values of the equivalent circuit elements of the thickness mode resonance.

The densities were estimated both by Archimedes and geometrical methods. The microstructure was investigated by scanning electron microscopy (SEM), energy dispersive X-ray analysis (EDX) and X-ray diffraction (XRD), using a CuK_α radiation.

3. Results and discussion

Bismuth additions to the basic compound has a beneficial effect on the properties of modified compound. First of all, it helps the compound to stabilize against cracking. This is obvious from the fact that the sintered ceramic bodies become compact and dense, without traces of cracking or microcracking, and can be easily poled in reasonable moderate fields (70 kV/cm). The densities as a function of Bi addition, for an optimum sintering temperature of 1250 °C are shown in Fig. 1. One can see that the density increases nearly linearly with increasing Bi content at a rate of 0.025 g/cm^3 for each Bi percent. At the same time, the tetragonality decreases with increasing Bi content as can be seen from the same figure. This clearly indicates that bismuth ions enter the lattice on A positions replacing Pb ions and thus creating lead vacancies which allow an easy alignment of the dipoles during poling. As concerns the densification, we believe that a short discussion about the density would be worthwhile. According to the 1995 JCPDS International Centre for Diffraction Data, the theoretical density of pure PT compound should be 7970 kg/m^3. This reference value can be taken as theoretical density for pure PT only, but not for any modified PT samples, since the elementary cells of modified compounds are different from that of pure PT, because their lattice constants a and c are different. Consequently, in order to estimate the degree of densification for a certain compound, one needs to calculate the theoretical density for that specific compound, taking the real values of its elementary cell from the experimental X-ray data. In our case we calculated the theoretical densities for each Bi doped compound, taking the values of the lattice constants a and c as given by X-ray measurements. Thus, for example, for the compound with 8 mol% Bi, having a tetragonality of 1.060 and $a = 3.904\times10^{-10}$ m and $c = 4.139\times10^{-10}$ m, we estimated an X-ray density of 7766 kg/m^3 as theoretical density for it. Thus the experimental value of 7585 kg/m^3 represents a densification degree of 98% and not 95.3% as compared with the theoretical density of pure PT. Our experimental value is similar to that reported by Damjanovic et al.[17] on sintered Sm modified PT ceramic, prepared by hot isostatic pressing. Therefore, one may say that Bi doping enhances the densification and stabilizes the sintered compounds to a high degree. The densification process can be even further enhanced by small additions of PbO to the calcined product. In this

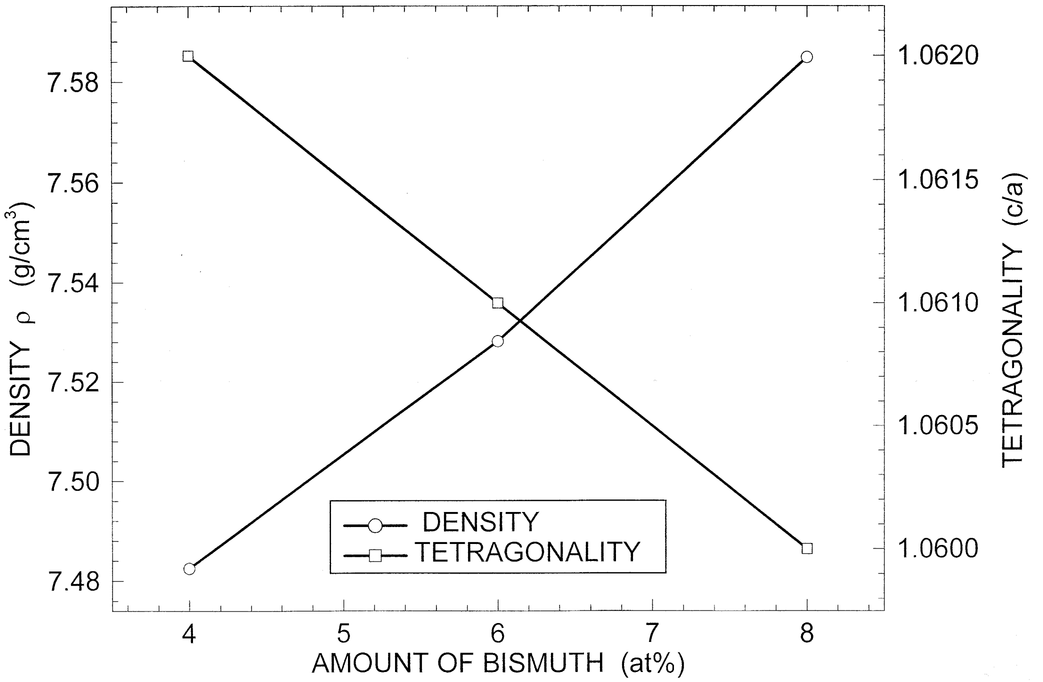


Fig. 1. The behavior of density and tetragonality as a function of Bi content for PT modified samples sintered at 1250 °C/3 h.

respect, Fig. 2 illustrates the effect of excess PbO on the bulk density of 4, 6 and 8 mol% Bi modified PT samples, sintered at 1250 °C, for 3 h. One can see that the density increases with increasing amount of PbO until 2 wt.%, then slightly decreases, for all samples. Though the increase is not significantly high (it is around 1%), it exists and shows that the general trend is towards enhancing the density when excess lead oxide is added to the calcined powder.

A similar trend shows the dielectric constant, as well as the thickness coupling factor, as can be seen in Figs. 3 and 4, respectively. The highest values of K_{33}^{T} and k_t were 130 and 0.43, respectively, which means an increase with 2.5–8% and 7–8%, respectively, for samples containing 2 wt.% PbO. It is obvious that the addition of PbO improved the dielectric and piezoelectric properties of Bi-doped PT ceramics, except the planar coupling factor k_p which still remained extremely low (less than 0.01) for all samples with or without excess PbO.

The behavior of the dissipation factor as a function of PbO content is shown in Fig. 5. It slightly decreases with increasing amount of PbO. Higher D corresponds to higher Bi doping level. The mechanical quality factor of the thickness mode is about 300, with slightly higher values at higher PbO and lower Bi contents.

Fig. 6 shows the X-ray diffraction pattern for 8 mol% Bi doped sample with 2 wt.% excess PbO, corresponding to a unique tetragonal phase, with a tetragonality $c/a = 1.060$. corresponding to an elementary cell with $a = 3.904 \times 10^{-10}$ m and $c = 4.139 \times 10^{-10}$ m. Similar X-ray patterns were obtained for all investigated Bi- and -PbO doped samples.

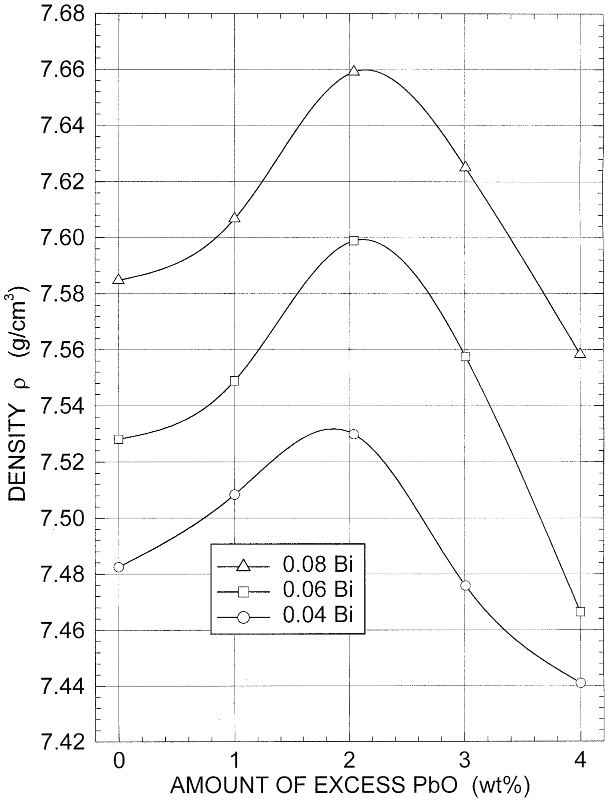


Fig. 2. Density as a function of the amount of PbO addition for PT ceramics doped with 4, 6 and 8 mol% Bi.

Fig. 7 shows SEM micrographs of the fracture surfaces of 8 mol% Bi doped samples without PbO addition (a), with 2 wt.% PbO addition (b) and with 4 wt.%

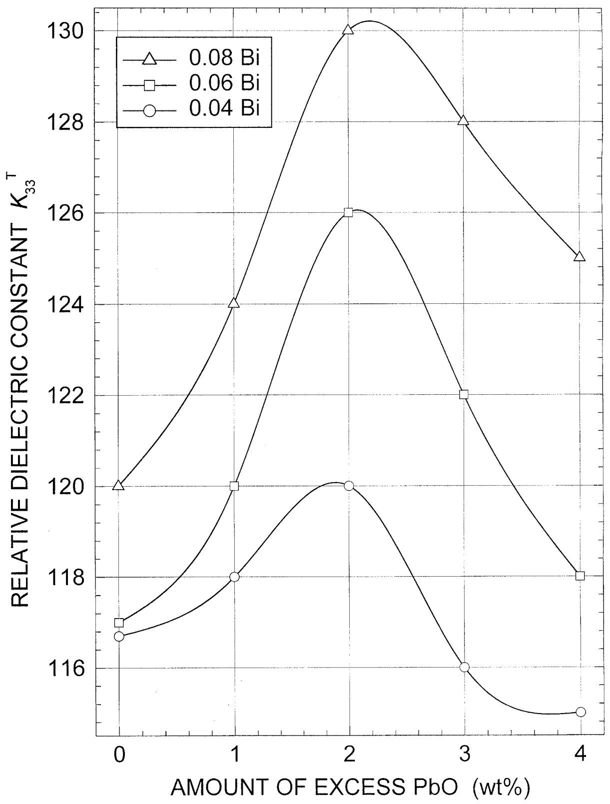


Fig. 3. Dielectric constant as a function of the amount of PbO addition for PT ceramics doped with 4, 6 and 8 mol% Bi.

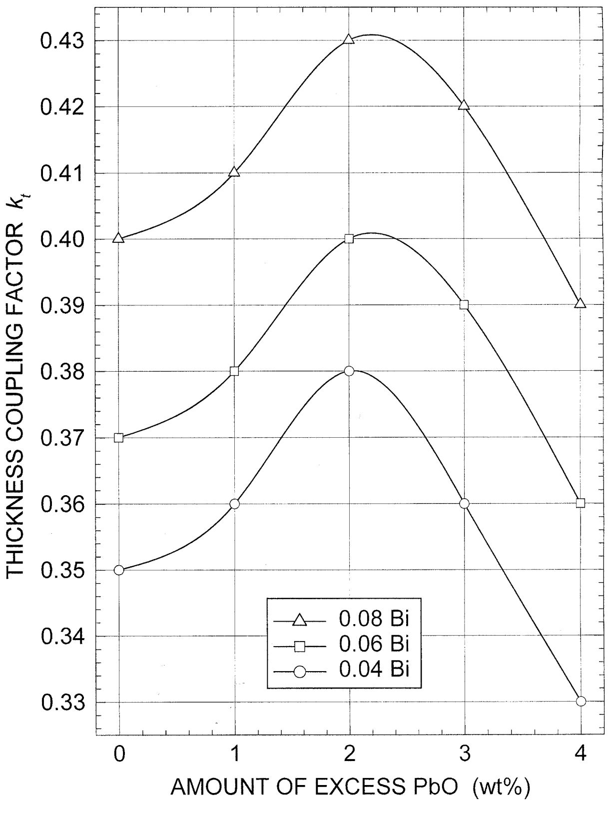


Fig. 4. Thickness coupling factor as a function of the amount of PbO addition for PT ceramics doped with 4, 6 and 8 mol% Bi.

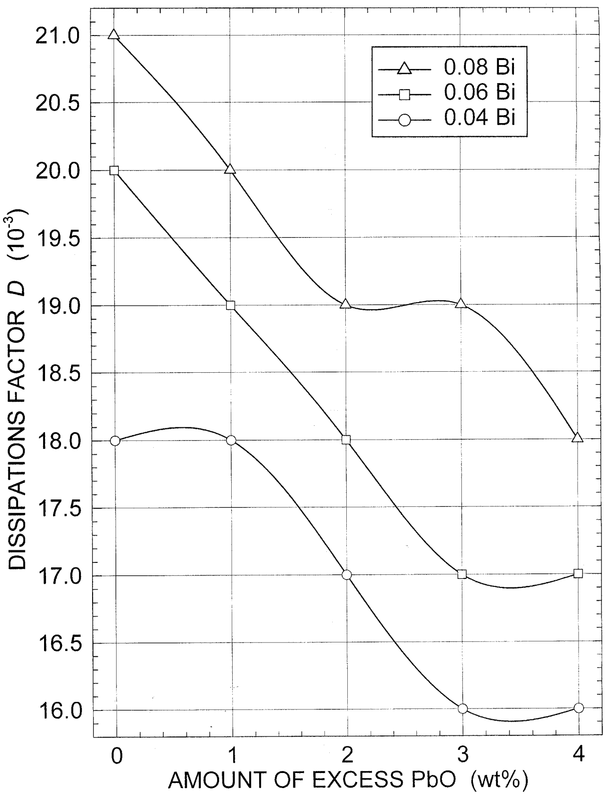


Fig. 5. Dissipation factor as a function of the amount of PbO addition for PT ceramics doped with 4, 6 and 8 mol% Bi.

PbO addition (c), respectively. The highest degree of densification, with more evidenced grains boundaries is clearly seen on the sample with 2 wt.% PbO addition.

The improvement of the dielectric and piezoelectric properties of Bi modified PT ceramics, after adding small amounts of PbO to the calcined powder, is mainly due to the mechanisms of densification, during sintering, enhanced by the presence of PbO liquid phase. For our PbO doped samples, the mechanisms of densification by rearrangement, dissolution-reprecipitation and coalescence,[18] play probably the most important role. Each mechanism becomes preponderent depending on temperature and time of sintering, on material composition and particle shape, but mostly on the amount of liquid PbO.

The rearrangement of the particles begins most probably at the melting temperature of PbO (890 °C) and takes place rapidly, in minutes.[19] This process becomes more intense if sufficient liquid phase is present to allow an easy rearrangement of the grains. Consequently, the densification should be proportional to the amount of liquid PbO. In our case, though the amount of liquid PbO is obviously not enough to fill in the pores of the sample, it undoubtedly helps the densification. So does the solution–reprecipitation mechanism, by capilar forces which enhances dissolution of the grains at the contact points, followed by reprecipitation on the free surfaces of the grains, thus allowing a better packing.[18]

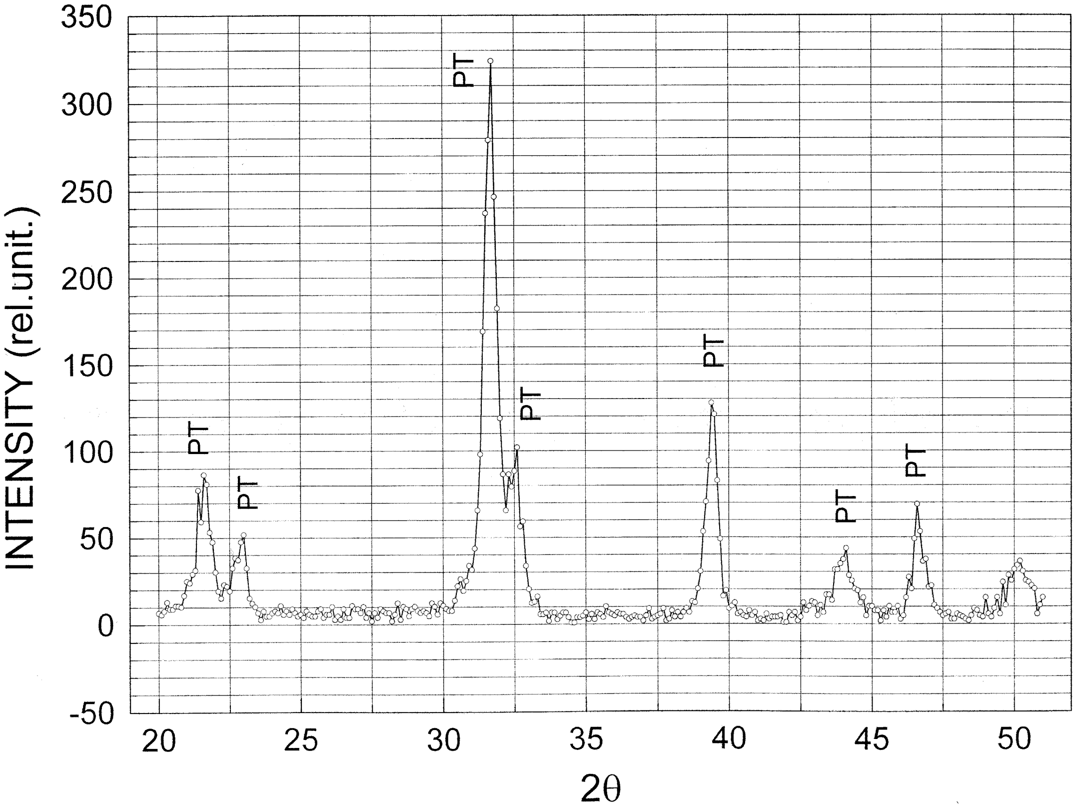


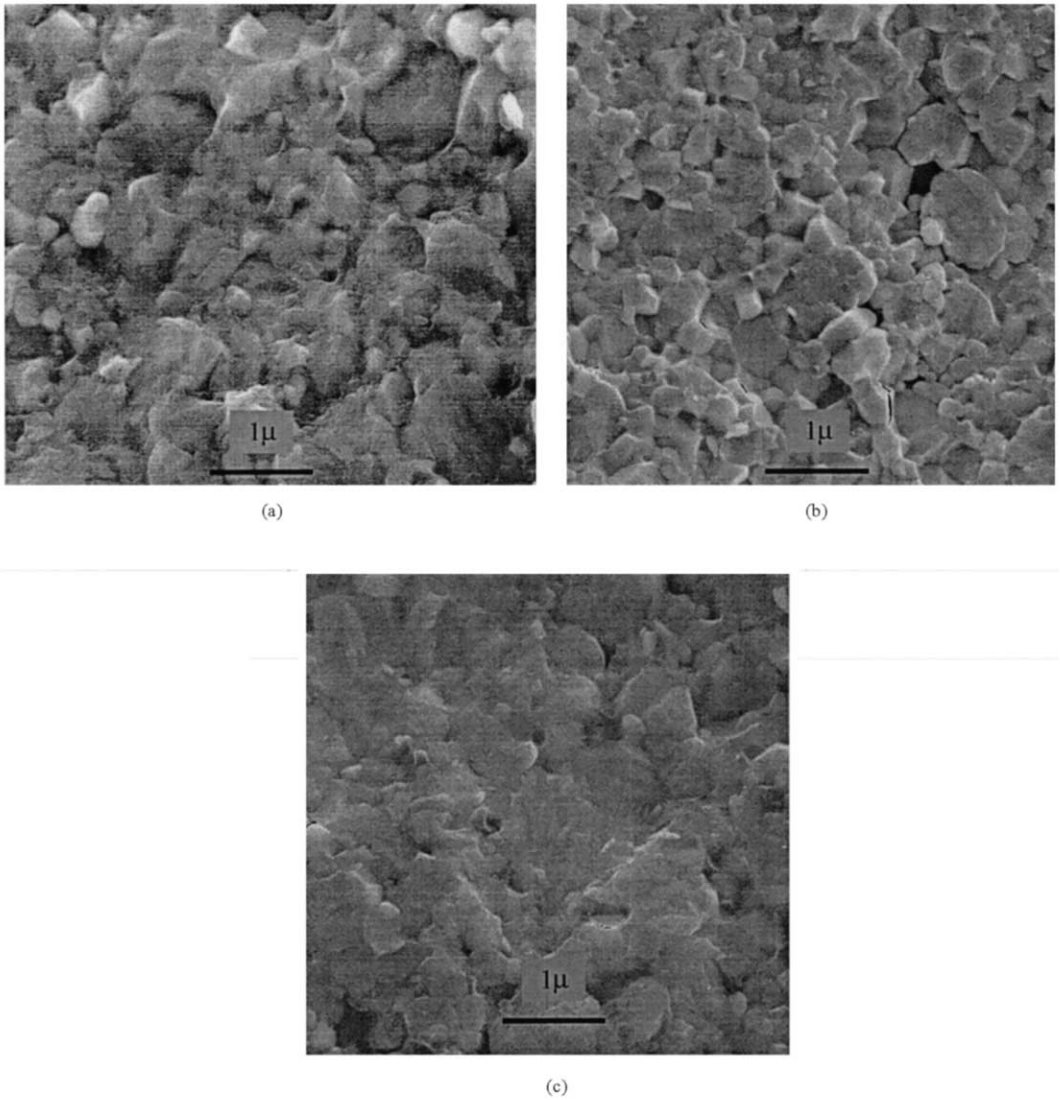
Fig. 6. XRD pattern of 8 mol% Bi doped PT ceramic with 2 wt% PbO addition.

This makes possible a better shape accommodation and a release of the available liquid into remaining pores. followed by a new rearrangement and solution–reprecipitation. As a consequence of this process, the solid–liquid interfacial area decreases along with the interfacial energy, since the large grains increase at the expense of small grains, more soluble in the liquid [Fig.7(c)], but the increase of large grains over a certain limit, at higher amounts of liquid phase, decreases the ceramic density. It appears that maximum densification would be expected, for an optimum amount of liquid phase, when an equilibrium between these mechanisms would be attained. In our case this optimum seems to be at 2 wt.% PbO excess.

Another effect of excess PbO addition, that must be taken into account, is the decrease of lead vacancies. It was assumed that vacancies in lead position reduce the local stress in domains and thus increase the domain walls mobility and the associated losses and also facilitate domain switching under electrical or mechanical drive.[4]

Lead ions from PbO liquid phase will certainly occupy some lead vacancies at the grain surface and therefore it seems naturally to assume that a thin layer of the grain boundaries would be richer in lead, than the grain core. Consequently, this lead excess will reduce the domain walls mobility and thus the poling degree, by decreasing lead vacancies. This will affect the material constants by decreasing the dielectric constant, the dissipation factor and the thickness coupling factor and increasing the mechanical quality factor of the thickness mode. This was experimentally observed, as one can see in Figs. 3–5.

Lead vacancy concentration of 2, 3 and 4 mol% was estimated for the initial compositions doped with 4, 6 and 8 mol% Bi, respectively. But due to the lead loss during sintering, these figures must be higher. If we assume a lead loss of only 1–2 mol%, according to EDX results, then the vacancy concentration would probably be 3–4 mol% for 4 mol% Bi, 4–5 mol% for 6 mol% Bi and 5–6 mol% for 8 mol% Bi. It means that lower concentrations of lead vacancies correspond to lower amounts of bismuth and consequently, for an excess PbO of 1–4 wt.% (1–5 mol%), the remaining lead vacancies will be less than for higher bismuth doping levels. Therefore, the effect of excess PbO on decreasing K_{33}^{T}, k_t and D will be more pronounced for lower amounts of Bi, as it is illustrated in Figs. 3–5, where lower values of material constants correspond to lower Bi doping levels. It appears that, for small amounts of 2 wt.% excess PbO, the effect of decreasing lead vacancy concentration is compensated by higher densification, which increases the dielectric constant, the degree of poling and thus the thickness coupling factor. This might explain the maxima of K_{33}^{T} and k_{t}, for all amounts of Bi doping, shown in Figs. 3 and 4, respectively.



(a) (b) (c)

Fig. 7. Scanning electron micrographs of the fracture surfaces of 8 mol% Bi doped PT ceramic: (a) without PbO addition, (b) with 2 wt.% PbO addition and (c) with 4 wt.% PbO addition.

4. Conclusions

Dense and stable PT ceramics, doped with 4–8 mol% Bi, were prepared by the usual ceramic technique, after addition of 1–4 wt.% PbO to the calcined powder of each composition. Samples without PbO addition were also prepared.

The densification of the sintered samples reached 98% of the theoretical density, calculated using the X-ray data for the lattice constants of the doped compounds. The densification process was enhanced by the presence of the PbO liquid phase by rearrangement, dissolution–reprecipitation and coalescence mechanisms.

The dielectric piezoelectric and electromechanical properties were determined as a function of Bi and excess PbO content. It was found that, for all Bi doping levels, the dielectric constant and thickness coupling factor have optimum values, for about 2 wt.% PbO addition, which means an increase of 2.5–8% for K_{33}^{T} and 7–8% for k_t. The excess PbO also improved the large electromechanical anisotropy to over 40, since the planar coupling factor remains very low, less than 0.01, while the thickness coupling factor increases to about 0.43. The dissipation factor slightly decreases with increasing PbO content and the mechanical quality factor of the thickness mode is about 300.

Higher amounts of PbO deteriorate these properties, probably by decreasing the density and Pb vacancy concentration.

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