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# Effects of $WO_3$ on the microstructure and optical transmittance of PLZT ferroelectric ceramics

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**Abstract**

The influence of the $WO_3$ addition as sintering aids on the structural, microstructural and optical properties of (Pb,La)(Zr,Ti)$O_3$—PLZT based ceramics was investigated. Ferroelectric $(Pb_{0.9}La_{0.1})(Zr_{0.65}Ti_{0.35})_{0.975}O_3 + x$ wt% $WO_3$ ($x = 0.0$, 0.5, 1.5 and 2.0) ceramics were densified by oxygen assisted uniaxial hot pressing. From the XRD results it was found that the hot pressed samples displayed single pseudocubic perovskite phase. EDS analysis evidenced the presence of $WO_3$ rich phase at the grain boundaries. An inhibition of grain growth and an evolution from transgranular to intergranular fracture behavior was observed, as a consequence of the formation of a PbO–$WO_3$ liquid phase, as the amount of $WO_3$ addition was increased. The optical transmittance in the visible and infrared range was decreased due to the presence of the liquid phase in grain boundaries, for $WO_3$ content lower than 2.0 wt%.


*Keywords:* Hot pressing; Microstructure-final; Dielectric properties; Optical properties; PLZT

## 1. Introduction

Lanthanum-modified lead zirconate titanate solid solution ceramics (PLZT) have been intensively studied for more than 30 years for data storage devices, information displays, and optical shutters because their excellent electro-optical properties which can be tailored in a wide range by various substitutions on A and/or B sites of the (Pb,La)(Zr,Ti)$O_3$ perovskite structure.[1] When well synthesized and processed, these compositions can present high Kerr electro-optical coefficients and high transmittance in the visible and near infrared range.[1]

The sinterability of ceramics is sometimes improved by a liquid phase existing in the sample during the sintering process, because the liquid phase enhances the transportation of materials in the sample through the process of dissolution and deposition. The presence of the liquid phase in sintered bodies, however, is not desirable, since it can form a second phase, which can be deleterious for some physical properties.[2] Especially optical transmittance can be reduced due to scattering contributions of liquid phase clusters distributed inhomogeneously in grain boundaries.

In this work tungsten oxide was investigated as sintering aids to produce transparent PLZT (10/65/35) ceramics. The limit of solubility of $W^{6+}$ was estimated through analysis of its influence on structural, microstructural and optical properties of the samples.

## 2. Experimental procedures

The nominal compositions of the PLZT samples prepared in this work were $Pb_{0,90}La_{0,10}(Zr_{0,65}Ti_{0,35})O_3$ (PLZT 10/65/35) + $x$ wt% $WO_3$, where $x = 0.0$, 0.5, 1.5 and 2.0. The powders were prepared, after ball-mill mixture for 3h, by conventional solid state reaction of PbO (Aldrich, >99.9% purity), $La_2O_3$ (Aldrich, 99.9% purity), $TiO_2$ (Aldrich, >99.9% purity), $ZrO_2$ (TAM, 99.6% purity) and $WO_3$ (Aldrich, >99% purity). After calcination in air for 3 h at 900 °C, the powders were ball-milled for 3 h. Green bodies in the form of disks were cold pressed and then sintered by hot pressing in oxygen atmosphere at 1250 °C for 3 h under a pressure of 6 MPa. Oxygen pressure inside the oven was about 30 KPa. XRD measurements were performed with $2\theta$ varying from 20° to 60° at $2^\circ\,min^{-1}$. A computational method,[3] which uses the diffraction peak position, was utilized for lattice parameter calculation. Archimedes method was employed for apparent

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density measurement. Microstructural and fracture behavior characterizations were realized using a SEM. Average grain diameter was determined with help of an Image software. Optical transmittances were performed with wavelength ranging from 350 to 800 nm.

## 3. Results and discussions

The crystalline phase of the nominal composition of PLZT prepared in this work, i.e., La/Zr/Ti = 10/65/35 ratio, lies near the morphotropic phase boundary,[1] for which is expected a perovskite type pseudo-cubic symmetry. XRD patterns of the PLZT based powders, calcined at 900 °C for 3 h, can be viewed in Fig. 1a. In Fig. 1 are observed peaks of distinct phases. These have been recognized, by JCPDS XRD pattern sheets, as being PLZT phases with orthorhombic (O), pseudocubic (C) and tetragonal (T) symmetries. The presence of these phases indicates a compositional fluctuation, associated to fluctuations on A-site (Pb,La) or on B-site (Zr,Ti) of the perovskite-$ABO_3$ PLZT structure. By XRD analysis, Menegazzo et al.[4] observed distinct phases of the PLZT powder calcined at temperatures lower than 1200 °C, what was related to compositional fluctuation on the A-site and B-site of the perovskite structure.

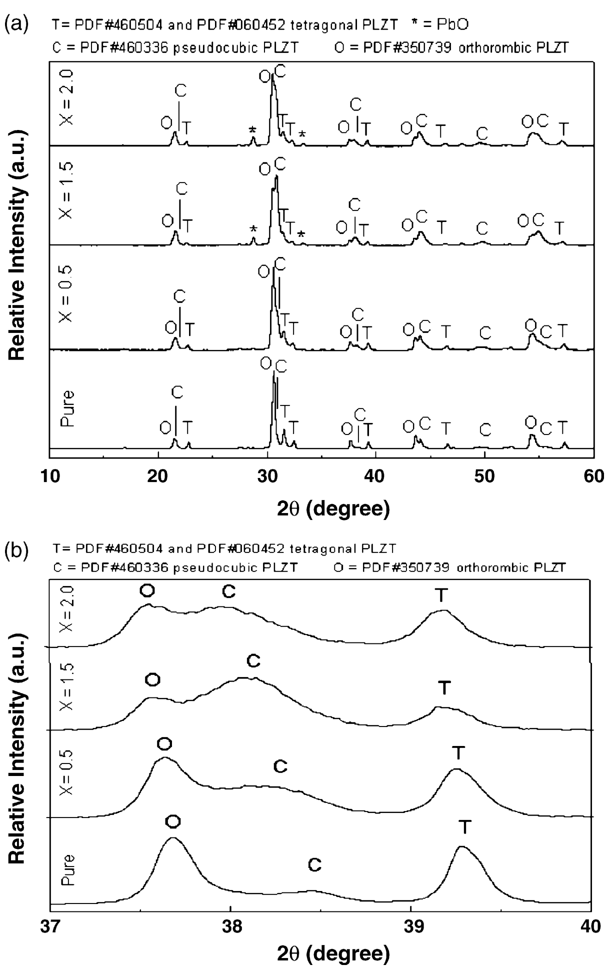


Fig. 1. (a) XRD patterns for the PLZT + $x$ wt% $WO_3$ powders, calcined at 900 °C for 3 h. (b) The same as (a) for $2\theta$ ranging from 37° to 40°.

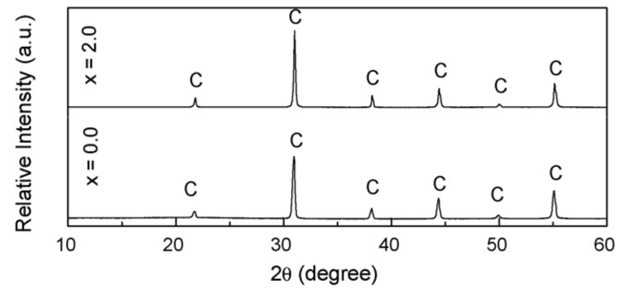


Fig. 2. XRD of the hot-pressed PLZT + $x$ wt% $WO_3$. The results of the PLZT + $x$ wt% $WO_3$ ($x$ = 0.5 and 1.5) were omitted because are similar to the others.

In this work $WO_3$ additive was chosen viewing the formation, when combined with PbO, of a eutectic liquid-phase at temperatures around 730 °C,[5] i e, well below the traditional sintering temperature of PLZT ceramics. A liquid phase can speed up the densification processes by rearrangement of the particles and enhances material transport that might contribute to better chemical homogenization.[6,7] In Fig. 1b is shown that the $WO_3$ enhanced the intensity of the peaks related to the pseudocubic symmetry, although no single perovskite phase was obtained. The presence of any PbO–$WO_3$ phase could not observed in the XRD pattern.

After sintering at 1250 °C, XRD patterns presented only one PLZT phase with the expected pseudocubic symmetry, as can be observed in Fig. 2. Here the results for the PLZT + 0.5 wt% $WO_3$ and PLZT + 1.5 wt% $WO_3$ were omitted, because presented similar results. The densities of the pellets were around 99% of the theoretical PLZT density, assuming a $W^{6+}$ incorporation in the B site of the perovskite structure.

In Fig. 3, the lattice parameters of the PLZT ceramics, for a pseudocubic structure, are shown as a function of the $WO_3$ content. Pure PLZT ceramic presented the higher value of lattice parameter, while the $WO_3$ containing PLZT ceramics showed smaller lattice parameters. The reduction of the lattice parameter values due to the $W^{6+}$ incorporation can be associated with the cell volume reduction, caused by ionic radii differences and by vacancies generation due to valence difference, between substituted and incorporated ions. This same hypothesis is currently utilized in the literature to justify the decrease of the lattice

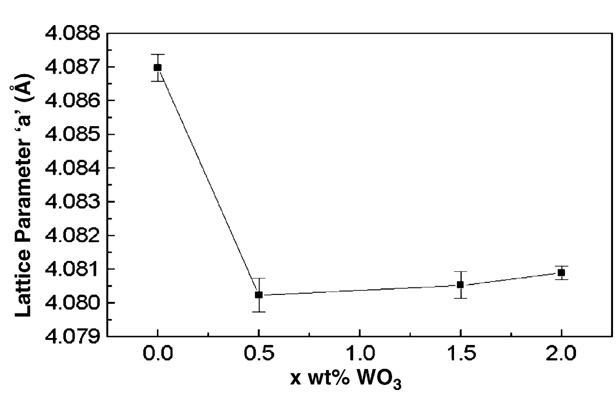


Fig. 3. Lattice parameters of the hot-pressed PLZT + $x$ wt% $WO_3$. Computational calculations were made considering a pseudocubic symmetry for all samples.

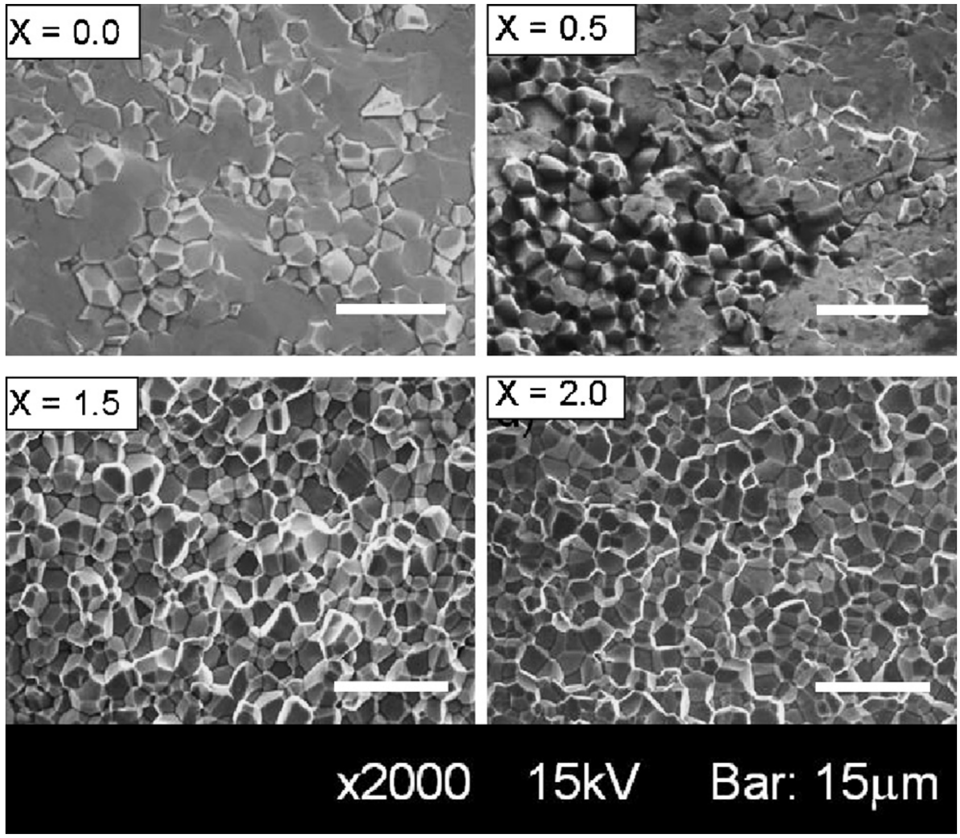


Fig. 4. Micrographs of the fractured sample showing the fracture behavior for PLZT + $x$ wt% of $WO_3$.

parameter when the sample is doped with alliovalent ions.[8–11] Similar results were obtained by Shannigrahi and Yao[8] who observed dramatic structural changes from tetragonal to cubic symmetry of PLZT 3/52/48 thin films when small amounts of $WO_3$ was incorporated.

In Fig. 3 can be also observed that the lattice parameters of the ceramics show a tendency to increase for $WO_3$ content higher than 0.5%. The incorporation of $W^{6+}$ on PLZT structure is related to the Goldschmidt tolerance factor $t$, for stable perovskite structure $0.8 \leq t \leq 1.1$. Shannigrahi and Yao[8] calculated a value of $t = 0.761$ and 0.860 for A and B sites, respectively, indicating that $W^{6+}$ ions were incorporated in B site of the perovskite structure with solubility limit about ≤1 at%. Higher $WO_3$ addition should be segregated and spread at the grain boundaries.

Fig. 4 shows the microstructure and respective average grain size dependence with the $WO_3$ content. Pure PLZT presented quite normal distribution, centred at about 5 μm. When doped with tungsten oxide, the mean grain size is shifted to smaller values. This indicates that tungsten oxide inhibited grain growth during sintering. The inhibition of the grain growth was attributed to a thin layer of PbO–$WO_3$ liquid phase. It is well known that segregated phases tend to diminish the mechanical resistance of the grain boundaries. If a thin layer of liquid phase exists on the grain boundaries intergranular fracture behaviour is generally observed.[12] In Fig. 4 are shown

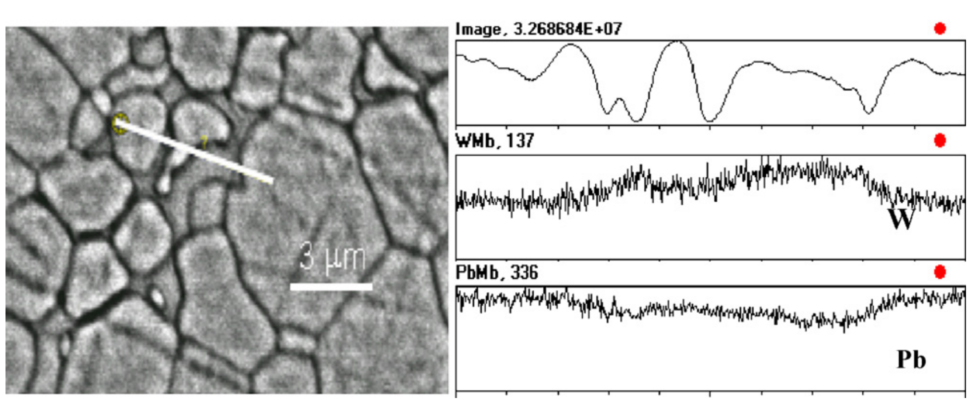


Fig. 5. Micrograph of the PLZT + 1.5 wt% $WO_3$ ceramic and EDS analysis, for Pb and W, evidencing a $WO_3$ rich region at the grain boundaries.

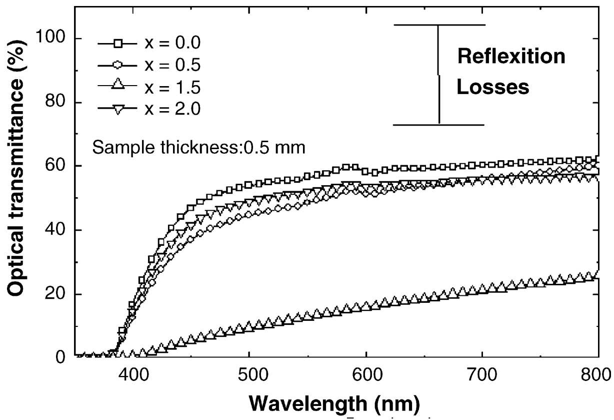


Fig. 6. Optical transmittance of the PLZT + $x$ wt% $WO_3$ as a function of the radiation wavelength.

the mechanical fracture behaviour for the investigated PLZT samples. It can be observed that "pure" PLZT presented preferentially transgranular fracture behaviour, while PLZT + 0.5 wt% $WO_3$ presented both, trans- and intergranular, PLZT + 1.5 wt% $WO_3$ and PLZT + 2.0 wt% $WO_3$ samples presented intergranular fracture behaviour. These changes in fracture behaviour are an indication of the presence of a liquid phase in grain boundaries. By EDS microprobe analysis (Fig. 5) was evidenced an increase of W content in grain boundary region of the PLZT + 1.5 wt% $WO_3$ sample. Fig. 6 shows the optical transmittance of the PLZT ceramics for the different contents of $WO_3$. The samples with $x$ = 0.0, 0.5 and 2.0 presented maximal optical transmittance of about 60% for wavelengths higher than 600 nm. The lower transmittance of the doped samples is attributed to the presence of the liquid phase in grain boundaries. As the amount of $WO_3$ increases from 0.5 to 1.5 wt% the amount of liquid phase is not enough to form a homogenous thin layer around the grains, so that it segregates, as observed in Fig. 5, diminishing the transmittance. For the samples containing 2.0 wt% of $WO_3$ the amount of the PbO–$WO_3$ the amount of liquid phase is enough to form a thin layer around the grains, with a thickness smaller than the investigated wavelengths, resulting in an increase the optical transmittance.

## 4. Conclusions

Microstructural and optical properties of PLZT 10/65/35 ceramics were investigated after using $WO_3$, from 0.5 to 2.0 wt%, as an improving element for liquid phase sintering. Tungsten ion solubility limit on the crystalline structure of the PLZT was around 0.5 wt%. The presence of a liquid phase was detected by fracture behaviour and evidenced by EDS analysis in the microstructures. In general, the samples were transparent at visible and near infrared radiation. The transmittance was diminished by the presence and form of distribution of the liquid phase in grain boundaries. The optical transmittance in the visible and infrared range was decreased due to the presence of the liquid phase in grain boundaries, for $WO_3$ content lower than 2.0 wt%, but for $WO_3$ content higher than 1.5 wt % a homogeneous thin liquid phase layer was formed, which enhanced the optical transmittance of the doped samples.

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## References

1. Haertling, G. H., Ferroelectric ceramics: history and technology. *J. Am. Ceram. Soc.*, 1999, **82**(4), 797–818.
2. Zhou, L., Zimmermann, A., Zeng, Y.-P. and Aldinger, F., Effects of PbO content on the sintering behaviour, microstructure, and properties of La-doped PZST antiferroelectric ceramics. *J. Mater. Sci.*, 2004, **15**, 145–151.
3. Pinheiro, J. M. V. and Mascarenhas, Y. P., Dois programas computacionais úteis em difratometria de raios-x por amostras policristalinas. In *Anais of the 37th annual meeting of the SBPC, Vol. 37*, 1985, p. 294 (in Portuguese).
4. Menegazzo, B. A., Garcia, D. and Eiras, J. A., Structural analysis of PLZT powders prepared by conventional and precipitation methods. *Solid State Ionics*, 1993, **63–65**, 692–695.
5. Chang, L. L. Y., Phase relations in system PbO–$WO_3$. *J. Am. Ceram. Soc.*, 1971, **54**(7), 357–358.
6. Yuan, G. L., Or, S. W., Wang, Y. P., Liu, Z. G. and Liu, J. M., Preparation and mult-properties of insulated single-phase $BiFeO_3$ ceramics. *Solid State Commun.*, 2006, **138**, 76–81.
7. Yokoi, A. and Ogawa, H., Crystal structure and ferroelectric properties of mixed bismuth layer-structured $Bi_7Ti_{4+x/2}Nb_{1-x}W_{x/2}O_{21}$ ceramics. *Mater. Sci. Eng. B*, 2006, **129**, 80–85.
8. Shannigrahi, S. and Yao, K., Effects of $WO_3$ dopant on the structure and electrical properties of $Pb_{0.97}La_{0.03}(Zr_{0.52}Ti_{0.48})O_3$ thin films. *J. Appl. Phys.*, 2005, **86**, 092901.
9. Arillo, M. A., Gómez, J., López, M. L., Pico, C. and Veiga, M. L., Structural and electrical characterization of new materials with perovskite structure. *Solid State Ionics*, 1997, **95**, 241–248.
10. Kasl, C. and Hoch, M. J. R., Preparation and properties of the trivalent-ion doped tungsten bronze $La_xWO_3$. *J. Appl. Phys.*, 2006, **99**, 063711.
11. Zhang, S., Xia, R. and Shrout, T. R., Low temperature sintering and properties of piezoelectric ceramics PSNT-Mn with $LiBiO_2$ addition. *Mater. Sci. Eng. B*, 2006, **129**, 131–134.
12. Winter, M. R., Pilgrim, S. M. and Lejeune, M., Study on the effects of lanthanum doping on the microsture and dielectric properties 0.9Pb(Mg1/3Nb2/3)$O_3$–0.1Pb$TiO_3$. *J. Am. Ceram. Soc.*, 2001, **84**(2), 314–320.