J. Synchrotron Rad. (1999). **6**, 535–536

EXAFS study of Zr environment in amorphous precursors of $Pb(Zr,Ti)O_3$

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Homogeneity of the amorphous sol-gel precursors of $Pb(Zr,Ti)O_3$ ferroelectric ceramics is studied at various Zr/Ti ratios. From Zr K-edge EXAFS spectra the immediate vicinity of Zr atoms is determined. A distorted octahedron of O atoms with all the bonds continued in Zr-O-Zr links is observed down to Zr/Ti ratio of 1:1, indicating the prevalent homocondensation of Zr. In the precursor with Zr/Ti ratio of 25/75 a smaller distortion of O octahedra is observed and heterometallic bonding Zr-O-Ti is found. Mixing of the two metals (Zr, Ti) at molecular level is thus established at low Zr/Ti ratios.

Keywords: $Pb(Zr,Ti)O_3$ ferroelectric ceramics, sol-gel precursor, Zr EXAFS

Improved homogeneity is expected from the sol-gel processing of ferroelectric ceramics based on lead zirconate titanate solid solution $Pb(Zr,Ti)O_3$ (PZT) (Chandler *et al.*, 1993). At the molecular level, homo- or heterocondensation is deduced from EXAFS-determined local environments of constituent metal atoms in PZT liquid and as-dried precursors. In $PbZrO_3$ and $Pb(Zr_{0.53}Ti_{0.47})O_3$ thin films prepared by 2-methoxyethanol sol-gel route zirconium atoms were found to be octahedrally coordinated by oxygen atoms at nonequal distances and by zirconium atoms in the second shell (Arčon *et al.*, 1998). EXAFS study of butoxide derived $PbZrO_3$ amorphous precursor revealed only Zr-O-Zr linkages; Zr-Pb correlation could not be determined (Arčon *et al.*, 1997). Sangupta *et al.* (1995) found Zr-O-Zr linkages in amorphous precursors of $Pb(Zr_{0.53}Ti_{0.47})O_3$ and $PbZrO_3$ and evidence of additional Zr-O-Pb correlation only in the latter. Predominance of Zr-O-Zr correlations in various heterometallic precursors indicates heterogeneity at the molecular level. The aim of the present contribution is to study how local environment of zirconium atoms in amorphous PZT solid solution precursors is influenced by varying Zr/Ti ratio.

Amorphous precursors of stoichiometric $Pb(Zr,Ti)O_3$ solid solutions (PZT) with Zr/Ti ratios 75/25, 50/50 and 25/75 are prepared by dissolving anhydrous lead acetate (II) in transition metal n-butoxides in n-butanol. The 0.2M solutions are refluxed and by-products are distilled-off. The solutions are cooled to room temperature and hydrolysed with 10 moles of deionised water per mole of lead acetate. The resultant suspensions are dried at 150°C to constant weight.

Powdered samples of the precursors were prepared on multiple layers of adhesive tape with the total absorption thickness of μd ~2 above the Zr K-edge. EXAFS spectra were measured at the ROEMO 2 station at the HASYLAB synchrotron facility at DESY (Hamburg, Germany), which is equipped with a Si(311) double-crystal monochromator with 3 eV resolution at 18 keV. Detuning the monochromator crystal using a stabilization feedback control on both beamlines effectively eliminated harmonics. Reference spectra without the samples were taken under identical conditions.

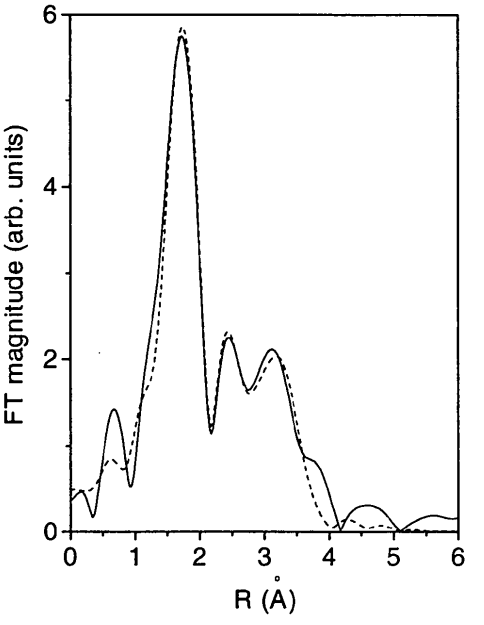

Figure 1
The k^2 weighted Fourier transform of the EXAFS spectrum ($k = 5 .. 11.5$ Å^{-1}) of PZT precursor with Zr/Ti molar ratio of 75/25: (solid line)- experiment, (dotted line) - fit.

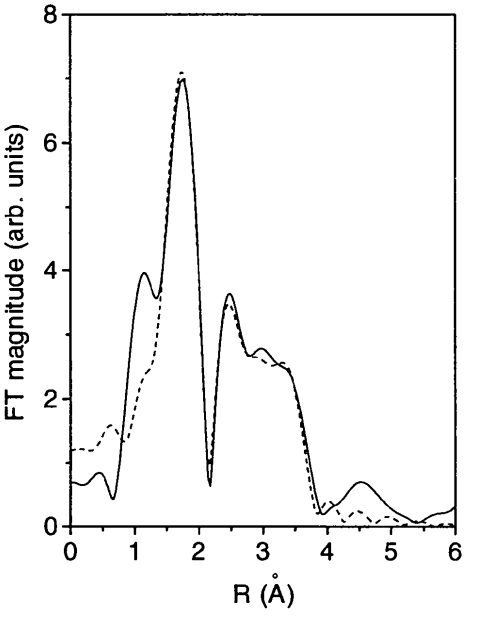

Figure 2
The k^2 weighted Fourier transform of the EXAFS spectrum ($k = 5 .. 11.5$ Å^{-1}) of PZT precursor with Zr/Ti molar ratio of 50/50: (solid line)- experiment, (dotted line) - fit.

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Table 1
Parameters of the nearest coordination shells around zirconium and titanium atoms in PZT precursors with different Zr/Ti molar ratios: type of the neighbour atom, average number N, distance R, and Debye-Waller factors σ^2. Uncertainty of the last digit is given in parentheses.

Sample	Zr/Ti = 75/25			Zr/Ti = 50/50			Zr/Ti = 25/75		
Zr neigh.	N	R (Å)	σ^2 (Å^2)	N	R (Å)	σ^2 (Å^2)	N	R (Å)	σ^2 (Å^2)
O	4.1(4)	2.18(2)	0.004(1)	4.6(6)	2.19(3)	0.003(1)	4.6(6)	2.16(3)	0.003(1)
O	1.7(5)	2.78(3)	0.004(1)	2.4(5)	2.82(3)	0.003(1)	2.3(6)	2.31(3)	0.003(1)
Ti	/	/	/	/	/	/	1.9(6)	3.27(2)	0.006(3)
Zr	6(2)	3.48	0.014(2)	6.6(9)	3.49(1)	0.011(3)	/	/	/

EXAFS spectra were analysed with the University of Washington analysis programs using FEFF6 code for ab initio calculation of scattering paths (Stern *et al.*, 1995, Rehr *et al.*, 1992). Fourier transforms are shown in Figs. 1 to 3 together with best-fit FEFF models. The parameters of the models are given in Table I. The rather large uncertainty intervals of N and σ^2 result from large correlation of the two parameters in a shell. Between parameters of different neighbor shells, however, the correlation is negligible. No significant differences in the local Zr environment are found for samples with the Zr/Ti molar ratio 75/25 and 50/50. In both, Zr atom is located in the distorted octahedron of oxygen atoms, with four oxygens at 2.18 Å and two at 2.78 Å. There are approximately six Zr atoms in the second coordination shell at 3.48 Å.

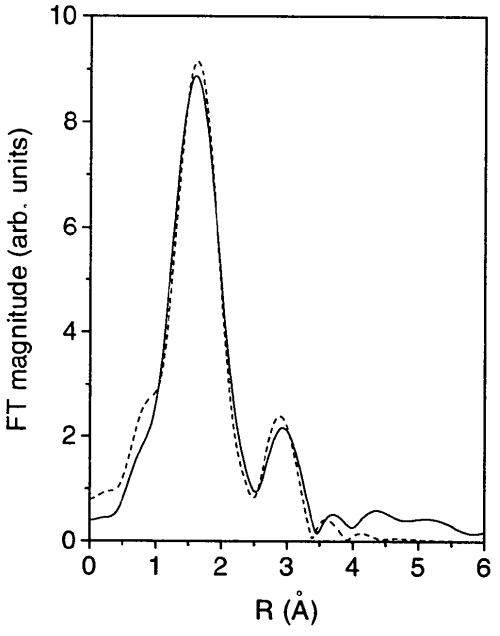

Figure 3
The k^2 weighted Fourier transform of the EXAFS spectrum (k = 4 .. 10 Å^{-1}) of PZT precursor with Zr/Ti molar ratio of 25/75: (solid line)- experiment, (dotted line) - fit.

In the low-Zr sample (Zr/Ti = 25/75) significant structural changes are observed in the second coordination shell, where two Ti atoms located at 3.27 Å are found instead of the six Zr. As a consequence the six O atoms of the first shell are drawn closer to the central Zr and the distortion of the octahedron is diminished.

It is evident from these results that Zr-O-Zr linkages are the dominant structural feature in amorphous PZT precursors for Zr/Ti ratios down to 1:1, in accord with the known tendency of zirconium atoms for homocondensation. In the precursor with low Zr content (Zr/Ti = 25/75) heterometallic bonding Zr-O-Ti is found. Mixing of the two metals (Zr, Ti) at molecular level is thus established at low Zr/Ti ratios.

Support by the Ministry of Science and Technology of the Republic of Slovenia, and Internationales Büro(Germany) is acknowledged. M. Tischer and L. Troeger of HASYLAB provided expert advice on beamline operation.

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(Received 10 August 1998; accepted 1 December 1998)