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EXAFS Study of Thermal Treatment of Pb-Zr Alkoxide Precursors

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Abstract: The local environment of Zr atoms in amorphous precursors and intermediate products of the thermal treatment leading to perovskite PbZrO_3 ceramic materials is studied by EXAFS. The coordination of Zr depends significantly on the choice of the starting Zr alkoxide. The Zr-O-Zr bond in an amorphous phase persists till the final stage of heating at 800 °C.

The notable ferroelectric properties of $\text{Pb}(\text{Zr,Ti})\text{O}_3$ based ceramics (PZT) in thin film as well as in bulk form are exploited in numerous technological applications. Within research studies on PZT based materials [1] the alkoxide based sol-gel technique has been used to prepare lead zirconate as a model substance for Zr-rich solid solutions. The advantage of the technique as compared to solid state synthesis lies in improved homogeneity of ceramic materials and lower processing temperatures [2].

The amorphous precursors of PbZrO_3 based ceramic powders are prepared by dissolving anhydrous lead acetate and zirconium alkoxide (n-propoxide or n-butoxide) in the parent alcohol. The clear yellow solutions (0.2M) are refluxed, and by-products are removed by distillation. The solutions are hydrolysed at room temperature with 10 moles of water per mole of lead acetate. The resultant suspensions are dried at 150 °C. The final product, a perovskite phase PbZrO_3 , is obtained by heating to 800 °C. Powdered samples of both precursors after drying and after heating to 400 °C, 550 °C and 800 °C for 30 minutes in oxygen, are analysed by XRD and EXAFS.

In spite of similarity of both Zr sources, different reaction paths are observed in XRD of the intermediate phases: in butoxide precursor, the final perovskite phase is reached at 700 °C through a transitory pyrochlore phase formed at 550 °C. In propoxide precursor, on the other hand, metallic lead separates at 400 °C, to be reoxidized to PbO which is present alongside the pyrochlore phase till transition to the pure perovskite phase at 800 °C. Thus, the advantage of the molecular homogeneity in the precursor is apparently lost by Pb separation. The choice of the Zr source seems crucial for preserving the homogeneity of PbZrO_3 upon thermal treatment [3]. On the other side, no information can be gained from XRD on the zirconium dynamics, due to the low long-range order in the amorphous precursor and the pyrochlore phase. Therefore, the local structure around Zr atoms in the precursors is studied by the EXAFS analysis.

Zirconium K edge EXAFS spectra were measured at HASYLAB ROEMO beamline. The unfocused radiation from the storage ring is monochromatized by double crystal Si(311) monochromator with a resolution below 3 eV at 18 keV. Powdered samples were deposited on multiple layers of adhesive tape. Reference spectra were taken on empty tapes.

Table 1: Parameters of the nearest coordination shells around Zr atom in PbZrO_3 propoxide and butoxide precursors after drying at 150 °C and after heating to 400 °C and 550 °C: neighbour species, average number, distance, and Debye-Waller factor. Uncertainty of the last digit is given in parentheses.

Sample temp. [°C]	Zr neighbour	Propoxide			Butoxide		
		N	R (Å)	σ^2 (Å ²)	N	R (Å)	σ^2 (Å ²)
150 (dried)	O	5(1)	2.10(2)	0.005(2)	4.1(6)	2.16(1)	0.005(2)
	O	1.0 (5)	2.71(2)	0.002(1)	/	/	/
	Zr	10 (4)	3.35(2)	0.019(4)	3 (1)	3.44(2)	0.008(4)
400	O	6 (1)	2.11(1)	0.011(2)	6 (1)	2.11(2)	0.009(1)
	Zr	6 (2)	3.36(1)	0.015(4)	4 (1)	3.39(1)	0.010(5)
550	O	4 (2)	2.14(1)	0.009(2)	4.3(6)	2.11(1)	0.005(1)
	Zr	4 (2)	3.52(1)	0.011(4)	4 (1)	3.48(1)	0.011(3)

Spectra were analysed with UW EXAFS program [4] using FEFF6 code for the ab initio calculation of scattering paths. Fourier transforms of k^3 weighted spectra in the interval from 4 Å⁻¹ to 10 Å⁻¹ are shown in Fig. 1. Complete list of best fit

parameters are given in Table 1. The results are characterized by a large correlation between the coordination number and the Debye-Waller factor: thence large estimated errors of these parameters. For samples heated to 800°C, the perovskite lattice model [5] is adopted on the basis of XRD findings: very good agreement with the measured data is obtained for the six oxygen atoms in the first shell. The contribution of more distant shells is obscured by noise.

In all samples, oxygen atoms are found in the first shell, and zirconium atoms in the second shell of neighbors. Further shells are not resolved and the Zr-Pb correlation cannot be established. Even within this close neighborhood, significant differences are found between the two alkoxide precursors in all stages. In both cases, however, final product at 800°C shows the same local structure around Zr, corresponding to the perovskite structure identified by XRD.

In the dried samples, the propoxide precursor exhibits a richer neighborhood, both in O and Zr atoms. At 400°C six oxygens are identified for both precursors, indicating a possible octahedral coordination around Zr atoms. Number of Zr neighbours, however, remains significantly higher in the propoxide sample: also the Zr-Zr distances are consistently shorter. The results for 550°C samples are not in agreement with a presumed pyrochlore phase identified in XRD: the number of the first shell oxygen neighbours is too low. Additionally, the Zr-Zr distance remains close to that in previous heating stages, while in pyrochlore phase Pb atoms should be the closest metal neighbors, with Zr neighbors removed further out. Existence of additional, probably amorphous ZrO_2 phase is thus indicated.

Figure 1. Comparison of Fourier transform magnitudes for propoxide (solid line) and butoxide (dashed line) precursor samples: dried at 150 °C (a), heated to 400 °C (b), 550 °C (c) and 800 °C (d).

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