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EXAFS study on the site preference of Mn in perovskite structure of PZT ceramics

B. Cherdhirunkorn [a,*], M.F. Smith [b], S. Limpijumnong [b,c], D.A. Hall [d]

[a] Department of Physics, Faculty of Science and Technology, Thammasart University, Thailand
[b] National Synchrotron Research Center, Nakhon Ratchasima 30000, Thailand
[c] School of Physics, Suranaree University of Technology, Nakhon Ratchasima 30000, Thailand
[d] Manchester Materials Science Centre, University of Manchester, M1 7HS, UK

Abstract

Synchrotron extended X-ray absorption fine structure (EXAFS) measurements at the Mn K edge were performed on Mn-doped PZT ceramics with Mn concentrations of 0.5, 1.0 and 2.0 mol%. The Fourier transforms of EXAFS structures from all samples are similar and agree well with the model of Mn substituting on the Ti/Zr site (i.e. the B site of the perovskite ABO_3 structure). This shows that Mn predominantly substituted for Ti/Zr in the range of concentration under study.

Keywords: D. PZT; EXAFS and defects

1. Introduction

PZT ceramics have been used widely as piezoelectric components in applications such as sensors, actuators, transformers, transducers and ultrasonic motors. The required properties for different applications can be obtained conveniently by the change of the PZT composition (Zr/Ti ratio) and the addition of cation dopants in the structure. Manganese oxide is one of the most effective dopants for hard PZT ceramics. Studies concerning Mn doped PZT ceramics have been reported elsewhere [1–4].

Conventionally, it has been supposed that Mn^{2+} and Mn^{3+} ions substitute for Zr^{4+} and Ti^{4+} ions on the B-site of the ABO_3 perovskite structure, forming acceptor-type defect. Nevertheless, in recent works [3,5–7], it has been observed that at substitution levels below 1 at%, the addition of Mn to PZT ceramics gives rise to unexpected increases in the dielectric and piezoelectric coefficients, and an increase in nonlinearity. In other words, this could be an indicator for donor defects in low Mn level doped PZT ceramics. However, the nature of the donor-type defects is still unclear. Furthermore, the site occupation by Mn is still a matter of controversy.

Synchrotron light is one of the most powerful tools for investigating structure of materials. The extended X-ray absorption fine structure (EXAFS) technique is one of the techniques utilizing the synchrotron light, which allows the local structure of the interesting atoms or ions in the structure of materials to be investigated [8,9]. The local structure around Mn ions within the PZT lattice can be investigated using EXAFS technique.

2. Experimental procedure

PZT samples were prepared according to the formula $Pb(Zr_{0.54}Ti_{0.46})_{1-x-y}Mn_xMg_yO_3$ (with $y = 0$ and 0.01, $x = 0$, 0.005, 0.01 and 0.02) by a conventional mixed oxides method. Magnesium was employed in some of these compositions to provide a well-defined acceptor-type base composition, which could be compensated by any donor-type defects present. The raw materials, PbO (>99.9%, Penarroya Oxide), TiO_2 (>99.9%, Tioxide Group Limited), ZrO_2 (>99.9%, MEL Chemical E101) and dopants; MnO (>99% Aldrich) and MgO (>99.95% Alfa Aesar) were mixed and milled with isopropanol for 20 h, and were then oven dried at 100 °C. The dried mixtures were calcined at 850 °C.

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* Corresponding author. Tel.: +66 2 5644529; fax: +66 2 5644484.
E-mail address: benya@tu.ac.th (B. Cherdhirunkorn).

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The calcined PZT powders were vibrational milled with water for 20 h. At this stage, 0.5 wt% PVA and 0.5 wt% PEG were added in the mixtures. The slurries were freeze dried producing fine uniform powders.

The powders were uniaxially pressed into a 10 mm diameter die with the load of 100 MPa. All samples were sintered in a closed alumina crucible and Pb-rich atmosphere at 1250 °C. Crystal structures of sintered specimens were investigated using X-ray diffractometer (Philips PW 3020).

EXAFS measurements were performed on the PZT ceramics in order to study the local structure around Mn ions in the PZT perovskite structure. In addition, the effect of Mn concentration on the site occupation of Mn ions in PZT lattice was investigated. The experiments were carried out at the station 7.1 EXAFS beam line of the synchrotron radiation source (SRS), Daresbury, U.K. For EXAFS experiments at station 7.1, X-rays were monochromatized by a Si (1 1 1) double crystal. The EXAFS spectrum was measured at the Mn K edge in the fluorescence mode due to a low concentration of Mn in the samples. The fluorescence detection system consists of an array of nine high-purity germanium diodes mounted in a common cryostat. To do fluorescence measurements, the sample was aligned at 45° to the line of the beam, in order to maximize the solid angle seen by the detector. The data analysis of all EXAFS measurements was carried out using the analysis programs; EXCALIB (the program developed by SRS) and FEFF7 [10].

3. Results and discussion

3.1. Phase investigation for Mn–Mg doped PZT ceramics

XRD patterns of Mn doped PZT and Mn–Mg doped PZT ceramics are shown in Figs. 1 and 2, respectively. The splitting of (1 1 1) and (1 $\bar{1}$ 1) peaks at 38° 2θ, as well as the presence of the $\{0\,2\,0\}_R$ peak at 2θ of 43° indicates the presence of the rhombohedral phase. The production of rhombohedral PZT in this study was done to avoid the effect of Mn on the shift of MPB (morphotopic phase boundary) toward the rhombohedral phase region as reported by Kim and Yoon [2]. In this case, increasing Mn concentration merely stabilizes the rhombohedral phase rather than causing a change in structure from tetragonal to rhombohedral.

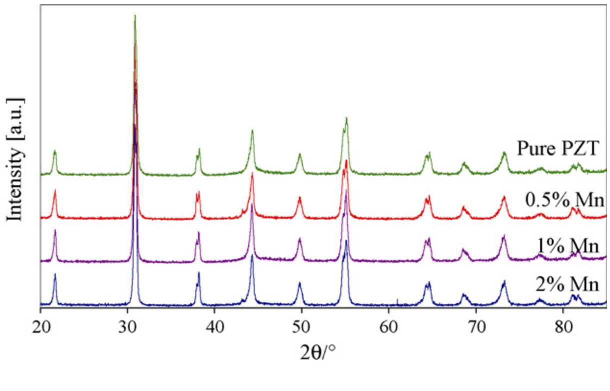

Fig. 1. XRD patterns of Mn doped PZT with the Zr/Ti = 56/44.

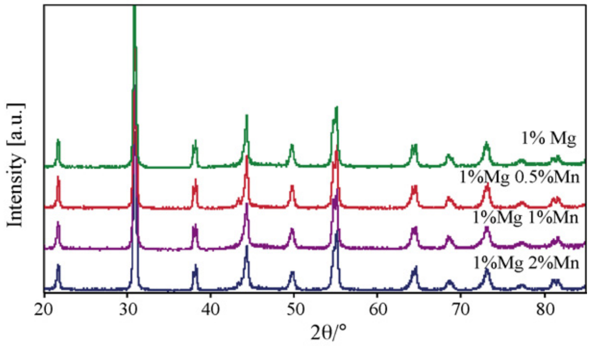

Fig. 2. XRD patterns of Mn–Mg doped PZT with the Zr/Ti = 56/44.

3.2. EXAFS study for Mn–Mg doped PZT ceramics

The data analysis of all EXAFS measurements was carried out using the analysis programs; EXCALIB and FEFF7. Figs. 3 and 4 show the Fourier transform for the EXAFS spectra of various Mn doped PZT samples with and without 1% of Mg.

The Fourier transform is a complex function of distance R, the amplitude of which is denoted by the real function $\rho(R)$. The

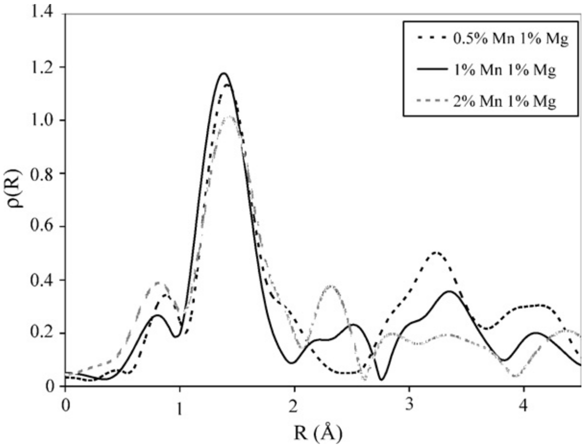

Fig. 3. Fourier transforms of the EXAFS spectra for Mn–Mg doped PZT ceramics.

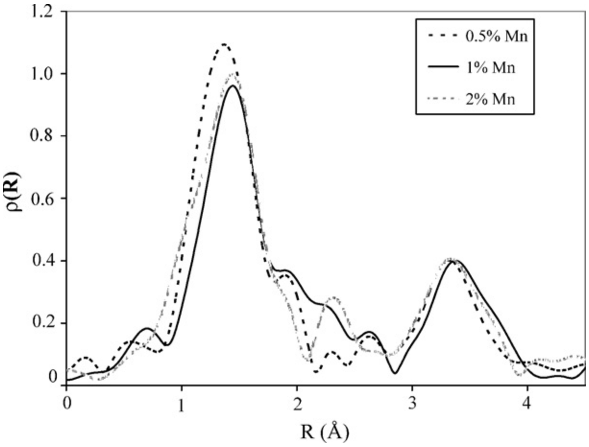

Fig. 4. Fourier transforms of the EXAFS spectra for Mn doped PZT ceramics.

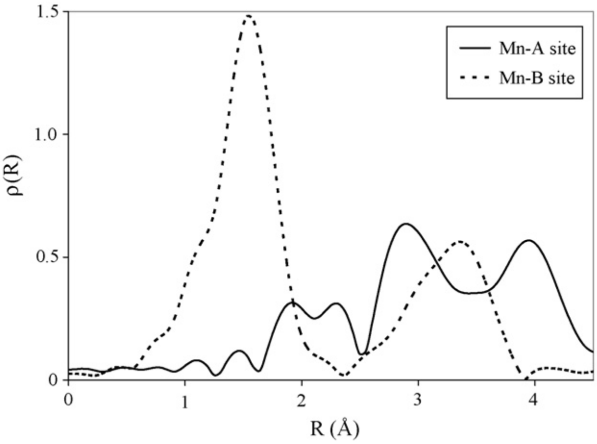

Fig. 5. Simulated EXAFS for rhombohe-dral PZT with Mn impurity in A(Pb)-site and B(Ti/Zr)-site.

position of peaks in $\rho(R)$ is related to bond distances between the Mn ion and neighbouring ions while the height of each peak is proportional to the number of neighbours. However, the bond lengths and coordination numbers cannot be read directly from $\rho(R)$. In order to determine the bond lengths and coordination numbers, the k-dependent amplitude and phase corrections must be made to the EXAFS signal. For instance, prior to the phase correction, the peaks in $\rho(R)$ are normally smaller than the corresponding bond lengths by 0.5 Å. However, the location of Mn within PZT unit cell can be resolved without making phase and amplitude corrections. By simply comparing the raw Fourier transform, $\rho(R)$, for different Mn concentrations, as shown in Figs. 3 and 4, there is no observable change in peak positions, particularly for the first main peak, with Mn concentration over the range of 0.5–2% for either the samples with or without Mg doping. Since the peak position indicates the bond distance between Mn and its neighbours or the location of Mn within the PZT unit cell, the coincidence of the main peaks as seen in Figs. 3 and 4 is evidence that no change in the location of the majority of Mn ions occurs with increasing Mn concentration. Furthermore, the location of Mn appears to be unaffected by the presence of 1% Mg.

In order to determine the preferred site occupation of Mn ions in PZT unit cell, the Fourier transform of EXAFS spectra for rhombohedral PZT with Mn ion occupying A(Pb) and B(Ti/Zr) sites were simulated, as shown in Fig. 5.

For the B-site curve, the first main peak occurring at roughly 1.5 Å is due to the six nearest oxygen atoms, while the second peak at 3.5 Å is attributed to the nearest Pb atoms. There is no significant feature at 1.5 Å for the A-site spectrum. This is the obvious distinction between A-site and B-site EXAFS. Comparing the results shown in Figs. 3 and 4, it is evident that the peaks are clearly incompatible with a simulation of EXAFS when Mn occupies the A(Pb)-site but are in good qualitative agreement with a simulation that assumes Mn occupies the B(Ti/Zr)-site. However, the minority A-site occupation cannot be ruled out.

4. Conclusions

The X-ray diffraction measurements for all PZT samples indicated the presence of rhombohedral phase.

EXAFS measurements and analysis indicated that Mn ions seemed to be a B-site favoured dopant in the PZT lattice, since the position of the highest peak of the Fourier transform of EXAFS spectra for all Mn–Mg doped PZT samples occurred in the region of 1.5 Å, corresponding to the simulated EXAFS for B-site substitution. The evidence for the A-site substitution was not obviously observed.

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