Local structures around Co and Mn ions in ZnO-based varistors

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Local structures around Co and Mn ions in $ZnO:M_L$, Co, Mn (M_L=Bi and La) varistors were analyzed by fluorescent XAFS. It was found that Co ions are occluded in the ZnO matrix, taking a divalent state. As for Mn ions, they considered to take a trivalent state and a 6-fold coordination in the Bi-system. In the La-system, they would exist as a form of $LaMnO_{3+x}$ and the Mn-O distances varied with the content of Mn^{4+} ions. We could estimate the content of Mn^{4+} ion in $LaMnO_{3+x}$ from the distances obtained, and about 35% Mn^{4+} ions may exist in the as-fired ZnO:La, Co, Mn varistor.

1. Introduction

Zinc oxide ceramics containing 1-3mol% of Bi_2O_3, La_2O_3, CoO and MnO etc. to Zn exhibit highly nonlinear current-voltage (I-V) characteristics and are thereby widely used as varistors for surge absorption in various electric devices. The nonlinear I-V characteristics have been explained on the basis of the formation of a double Schottky-type potential barrier at the grain boundaries (Gupta, 1990). It is known that the additives Bi_2O_3 and La_2O_3 have a decisive influence on the barrier formation and the other additives such as CoO and MnO improve the electrical properties of the varistor (Matsuoka, 1971). The chemical state of grain boundaries in Bi_2O_3-doped ZnO varistor was investigated by Auger electron spectroscopy, and it was found that the additive Bi was segregated into grain boundaries 2 to 3 nm thick, where oxygen deficiency occurred (Tanaka *et al.*, 1993). However, it is not clarified whether Co and Mn ion in varistors may exist in the ZnO matrix or in the grain boundaries.

In this study, local structures around Co and Mn ions in $ZnO:M_L$, Co, Mn (M_L=Bi and La) varistors were analyzed by fluorescent XAFS.

2. Experimental

Samples were prepared by a solid-state reaction among the constituent metal oxide powders. The amount of additives was fixed to be 1mol% to Zn. Weighted amounts of the dried powders were ground together with a mortar and a pestle. The mixed powder was pressed into pellets (13mmϕ) and then fired at 1200°C for 1h. The as-fired pellets were divided into three groups. One was annealed in air, another was oxidized in an O_2 flow, and the other was reduced in an Ar flow. Each treatment was performed at 500°C for 1h.

The Co and Mn K-XAFS spectra were measured at BL-7C branch line with Si(111) double-crystal monochromator in the Photon Factory, KEK, Japan. Measurements were carried out in a fluorescence mode by using a Lytle-type detector (Lytle *et al.*, 1984) at room temperature. The X-rays were focused on the pellet sample by means of saggital focusing of the second monochromator. As the fluorescent X-rays from the sample were relatively weak, the signals were accumulated for 3 seconds per point. The peak position at the midpoint of the Cu K-edge jump for Cu foil was calibrated to be 24.9391°.

Using the program library "XANADU" (Sakane *et al.*, 1993), the EXAFS data analyses were performed. Background was calculated by a least-squares fitting of the pre-edge region with Victoreen's formula. The energy of the midpoint of the edge jump was used as the value of the threshold energy (E_0). At the Fourier transform calculation of EXAFS, Hanning window function was used to reduce ripples in the transform. The phase shift and the backscattering amplitude functions used were the theoretical values tabulated by Teo and Lee (Teo & Lee, 1979) or McKale *et al.* (McKale *et al.*, 1988) combined with interpolation using the natural cubic spline function. The same k-ranges (35nm$^{-1} \leq k \leq$ 135nm^{-1} for Co K-edge and 35nm$^{-1} \leq k \leq$ 125nm^{-1} for Mn K-edge) were used for the transform. In Fourier filtering, the smooth window functions were used. The values of r_{min}, r^s_{min}, r^s_{max} and r_{max} were 0.145-0.147nm, 0.159-0.162nm, 0.237-0.239nm and 0.249-0.251nm for Co oscillations and 0.149-0.150nm, 0.159-0.162nm, 0.236-0.239nm and 0.247nm for Mn ones, respectively. Here the r_{min} and the r_{max} are the limits in the r-space for the transform and the r^s_{min} and the r^s_{max} are the square window limit. In order to determine structural parameters, a curve-fitting technique was applied to the Fourier-filtered experimental EXAFS spectrum. In the curve-fitting, each coordination shell has its own scattering atom (oxygen), interatomic distance r, amplitude factor B, k-dependent mean-free path of photoelectron η ($\eta=k/\lambda$), Debye-Waller factor σ and energetic difference ΔE_0 between the experimentally determined E_0 and the theoretical one. The cubic $SrCoO_3$ (CN=6, r=0.1920nm) and the cubic $SrMnO_3$ (CN=6, r=0.1904nm) (Yoshiasa *et al.*, 1990) were used for reference of amplitude factor B, which is converted into coordination number CN. The same k-range (45nm$^{-1} \leq k \leq$ 125nm^{-1} for Co K-edge and 45nm$^{-1} \leq k \leq$ 115nm^{-1} for Mn K-edge) were used for the fitting. The errors estimated can be as small as $\leq$0.001nm in distance and $\leq$1 in CN, according to the method suggested at the "International Workshop on Standards and Criteria in X-ray Absorption Spectroscopy 1988" (Lytle *et al.*, 1989).

Table 1

Results of curve-fitting analysis for ZnO:M$_L$, Co, Mn varistors.

		Co-O						Mn-O					
		r /nm	CN	$\eta/$ 10^2nm^{-2}	$\sigma/$ 10^{-2}nm^{-1}	ΔE_0/eV	$R/\%$	r /nm	CN	$\eta/$ 10^2nm^{-2}	$\sigma/$ 10^{-1}nm^{-1}	ΔE_0/eV	$R/\%$
M$_L$=Bi	reduced	0.198	4.2	3.24	9.52	5.99	3.70	0.197	5.8	2.94	13.12	5.50	4.10
	as-fired	0.198	3.9	3.35	9.29	6.57	2.51	0.198	6.3	3.08	10.72	5.52	4.43
	oxidized	0.198	4.3	3.62	8.94	4.17	3.82	0.197	6.3	3.04	8.08	4.01	4.50
M$_L$=La	reduced	0.197	3.7	3.77	10.04	4.44	2.49	0.197	6.3	3.24	7.39	6.24	10.08
	as-fired	0.198	4.3	3.85	9.07	6.46	4.70	0.195	5.6	3.41	9.15	5.30	11.40
	oxidized	0.197	4.0	3.69	9.36	4.52	3.66	0.193	5.9	3.06	9.88	4.57	12.07

3. Results and Discussion

Table 1 shows the Co-O and Mn-O distances and the coordination shell parameters obtained by curve-fitting analyses for ZnO:M$_L$, Co, Mn varistors, and Fig. 1 shows the quality of the curve-fitting for Co K-edge of the as-fired ZnO:Bi, Co, Mn varistor. In all the systems, the distance was calculated to be 0.196-0.197nm and did not change even after oxidized and reduced treatments. If the Co ions take a divalent state and are coordinated tetrahedrally by oxide ions, the distance would be 0.196nm, which can be calculated from their effective ionic radius (Shannon, 1976). These results suggest that Co^{2+} ions are occluded in the wurtzite-type ZnO matrix in the varistors.

Our X-ray diffraction studies have indicated that Mn ions in ZnO:Bi, Co, Mn varistor exist as a form of Mn$_2$O$_3$ and those in the ZnO:La, Co, Mn one exist as a form of LaMnO$_{3+x}$. These results imply that the Mn in the varistors is not incorporated into the ZnO matrix. The difference of chemical states appeared in the shape of the respective Mn K-XANES spectrum, as shown in Fig. 2.

The Mn-O distance in the ZnO:Bi, Co, Mn varistors was calculated to be 0.197nm and did not change after the treatments (Table 1). In the ZnO:Bi, Co, Mn varistors, Mn
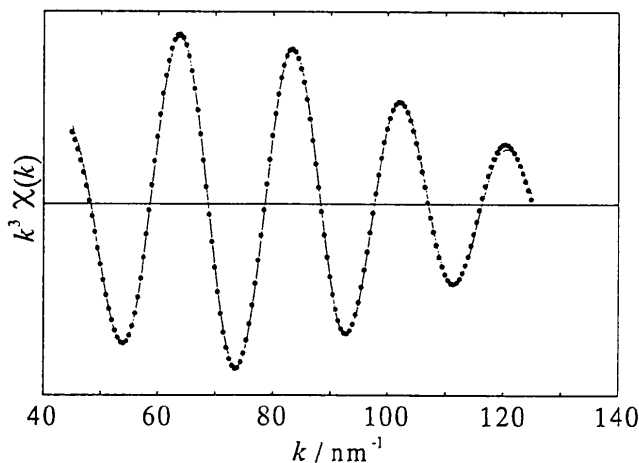
ions are also confirmed to take a trivalent state and a 6-fold coordination by XAFS, from the analogy to the crystal structure of Mn$_2$O$_3$. Whereas it is of interest that the Mn-O distance in the ZnO:La, Co, Mn varistors varied with the oxidized/reduced treatments. Here, the reliability factors for the Mn-O distance in the ZnO:La, Co, Mn varistors were not good because the La L1-edge EXAFS oscillation interferes the Mn K-edge one. As the distance was considered to vary with the oxygen contents of LaMnO$_{3+x}$, we estimated the content of Mn^{4+} ion in LaMnO$_{3+x}$ from the distance obtained. In the Fig. 3, the value of r(Mn-O)=0.199nm at 0% Mn^{4+} is a sum of effective ionic radii of the 6-coordinated Mn^{3+} and O^{2-} ions (Shannon, 1976). The value of r(Mn-O)=0.188nm at 100% Mn^{4+} is a sum of those of the 6-coordinated Mn^{4+} and O^{2-} ions. A straight line can be drawn between the two values by assuming that the

Figure 1

Co K-edge experimental (solid line) and calculated (dotted line) k^3-weighted filtered EXAFS signals for the as-fired ZnO:Bi, Co, Mn varistor.
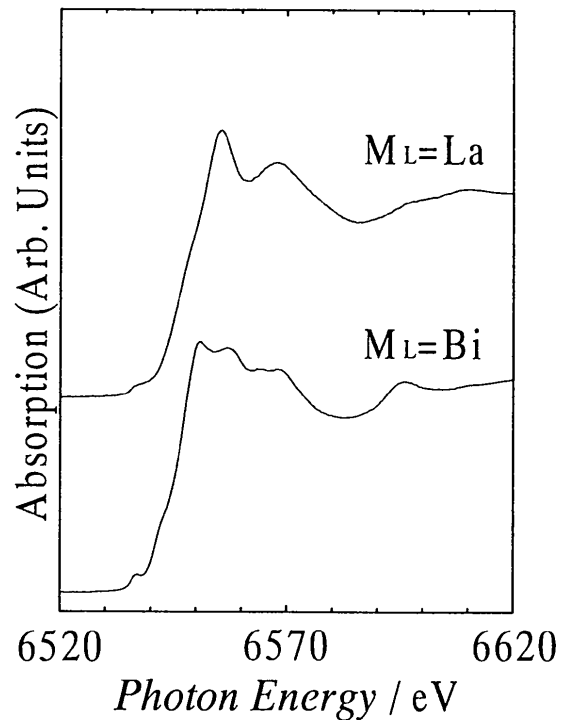

Figure 2

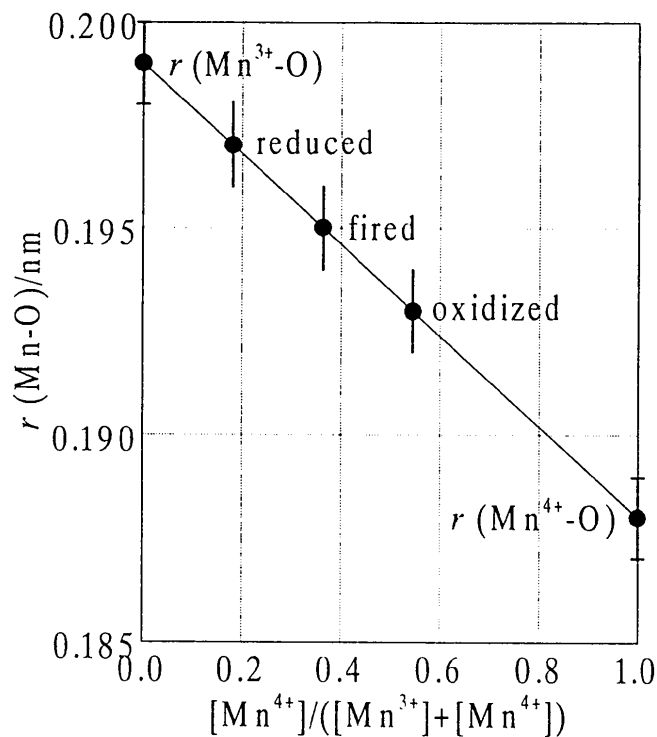Mn K-XANES spectra for the as-fired ZnO:Bi, Co, Mn and ZnO:La, Co, Mn varistors.

Figure 3
Ratio of Mn^{4+} ions in ZnO:La, Co, Mn varistor.

mixed valence states follow Vegard's law. The Mn-O distances determined by XAFS can be plotted on the line defined by Vegard's law. From the figure, about 20% Mn^{4+}

ions may exist in the reduced specimen, about 35% Mn^{4+} ions in the as-fired one and about 55% Mn^{4+} ions in the oxidized one, respectively. It is well-known that Mn ions in $LaMnO_{3+x}$ easily take mixed valence states in bulk samples. Using the fluorescence XAFS, we can detect the variation of Mn-O distance in the ZnO:La, Co, Mn varistors.

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