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DOI: 10.1017/S1431927607078208

Microsc Microanal 13(Suppl 2), 2007

White lines and electron occupancy for Ti 3*d* states in $BaTiO_3$ by EELS

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The electronic structure plays an important role in the study of phase transformations. Ferroelectric $BaTiO_3$ exists in polymorphs of different crystal symmetries related by simple displacive transformations. Among all posible phase transformations, the most important is the cubic to tetragonal ferroelectric transition, at T_C = 120°C. The permanent electrical dipole is the most important feature in this transformation. The potential applications of these materials are in ultrahigh-density information storage, including dynamic random access memory (DRAM), thermistors, electro-optic devices, varistors, multiplayer capacitors, etc [1].

In this work were studied changes in 3d states electron occupancy during the ferroelectric transition by means of Electron Energy Loss Spectroscopy (EELS), as well as ab initio calculations. EELS spectra were acquired using a Gatan Parallel Electron Energy Loss Spectrometer (PEELS model 766) in diffraction mode with 0.1 eV/ch dispersion, an aperture of 3 mm and a collection semi-angle of about 2.7 mrad. The resolution of the spectra was determined by measuring the full width at half-maximum (FWHM) of the zero loss peak and this was typically close to 1.5 eV, when the TEM was operated at 200 kV. The ferroelectric transition was induced by placing the sample in a heating sample holder and spectra were acquired at 20 and 150 °C temperatures.

In order to isolate L_{23} white lines from a transition 3d metals (Ti), EELS spectra were background subtracted by fitting the pre-edge backgrounds with a power-law function and then Fourier-ratio deconvoluted to remove multiple scattering components. Next a double step function was used to model post-edge backgrounds, as suggested by Pearson et al, who developed a method for quantitatively relate the white lines intensities to the number of 3d holes.

Figures 1 and 2 show Ti L_{23} and O K ionization edges during the ferroelectric transition. Following Pearson's method [2] we calculate the normalized total with lines areas (L_{23}) and the white lines ratio (L_3/L_2). Table 1 resumes the results of these calculations, where it is observed that the Ti total white line intensity increases during the ferroelectric transition. As white lines intensities are related to the number of unoccupied 3d states, we conclude that Ti loses 0.68 electron/atom during the process.

References

[1] S. Piskunov, E. Heifets, R.I. Eglitis , G. Borstel. Bulk properties and electronic structure of $SrTiO_3$, $BaTiO_3$ and $PbTiO_3$ perovskites: an ab initio HF/DFT study. Computational Materiales Science 29 (2004) 165-178

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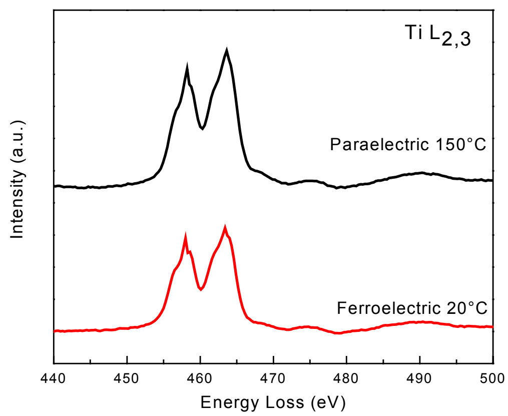

Figure 1 Ti L_{23} during ferroelectric transition

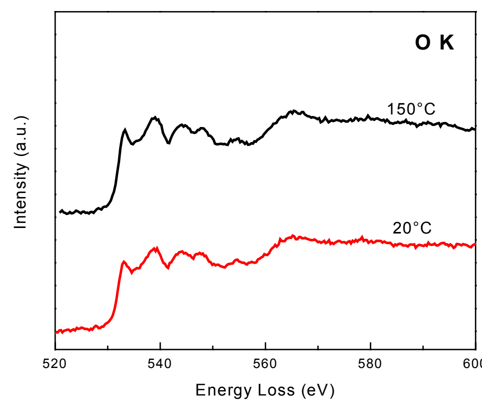

Figure 2. O K edge during ferroelectric transition.

TABLE 1. Normalized total white lines areas L_{23} and white lines ratios L_3/L_2 for Ti during the ferroelectric transition

Temperatura °C	**Ti L_{23}**	L_3/L_2	**n_{3d} electrón/átomo**
0	0.63	0.77	3.14
150	0.75	0.71	2.46