1204 CD
DOI: 10.1017/S1431927606067353
Microsc Microanal 12(Supp 2), 2006

Study of the ferroelectric transition in $BaTiO_3$ by low-loss electron energy loss spectroscopy

V. Gallegos-Orozco, A. Santos-Beltrán, R. Martínez-Sánchez, F. Espinosa-Magaña

Centro de Investigación en Materiales Avanzados (CIMAV), Miguel de Cervantes No.120, C.P. 31109, Chihuahua, Chih., México.

During the last decades very important advances have been achieved in the description of the electronic structure in crystalline solids and recent developments with regard to ferroelectric materials have put on the agenda the urgent need for studying their electronic structure because of their potential use in numerous devices, including dynamic random access memory (DRAM), thermistors, electro-optic devices, varistors, multiplayer capacitors, etc.

In this work, we studied the changes in electronic structure and optical properties of the perovskite $BaTiO_3$ during the ferroelectric transition from cubic (paraelectric) to tetragonal (ferroelectric) phases by Electron Energy Loss Spectroscopy (EELS). We have also performed ab initio calculations in Density Functional Theory (DFT) and comparisons between experimental and theoretical results are made.

Electron energy loss spectra were obtained using a Gatan Parallel Electron Energy Loss Spectrometer (PEELS model 766) attached to a transmission electron microscope (TEM). Spectra were acquired 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.

The numerical calculations presented in this work were performed within the local density approximation for the exchange-correlation functional in density functional theory, using the pseudopotential method. We used CASTEP implementation of the method. The lattice parameters for cubic and tetragonal structures were a = b = c = 4.000 Å and a = b = 3.994 y c = 4.038 Å respectively.

As shown in Figs. 1(a), 1(b), an acceptable similarity is observed for both the numeric calculations (continuous line) and the experimental results (dashed line), for the energy loss function $Im(-1/\varepsilon)$, and imaginary part of dielectric function ε_2 for ferroelectric $BaTiO_3$. In Fig. 1(a) the dominant peak at 27 eV is the volume plasmon that represents the energy of collective excitation of the electronic charge density in the crystal. The plasmon shows more structure, that can be associated to interband transitions. These transitions can be observed in Fig. 1(b). The energy loss function $Im(-1/\varepsilon)$ and imaginary part of dielectric function ε_2 of paraelectric $BaTiO_3$ are shown in Figs.1(c), 1(d), where it is observed that plasmon position presents a small displacement towards the left in 26.7 eV, due to a decrease in the number of electrons that participate in the collective oscillations. Also, an interband transition is observed in 6.9 eV for the paraelectric $BaTiO_3$ which is not observed in Im(-1/e) for the ferroelectric $BaTiO_3$, this difference might be of great utility in the identification of the two phases. Our calculations are in good agreement with the experiment in shape as well as energy position. The numeric calculations are then, of great help in the EELS spectra interpretation.

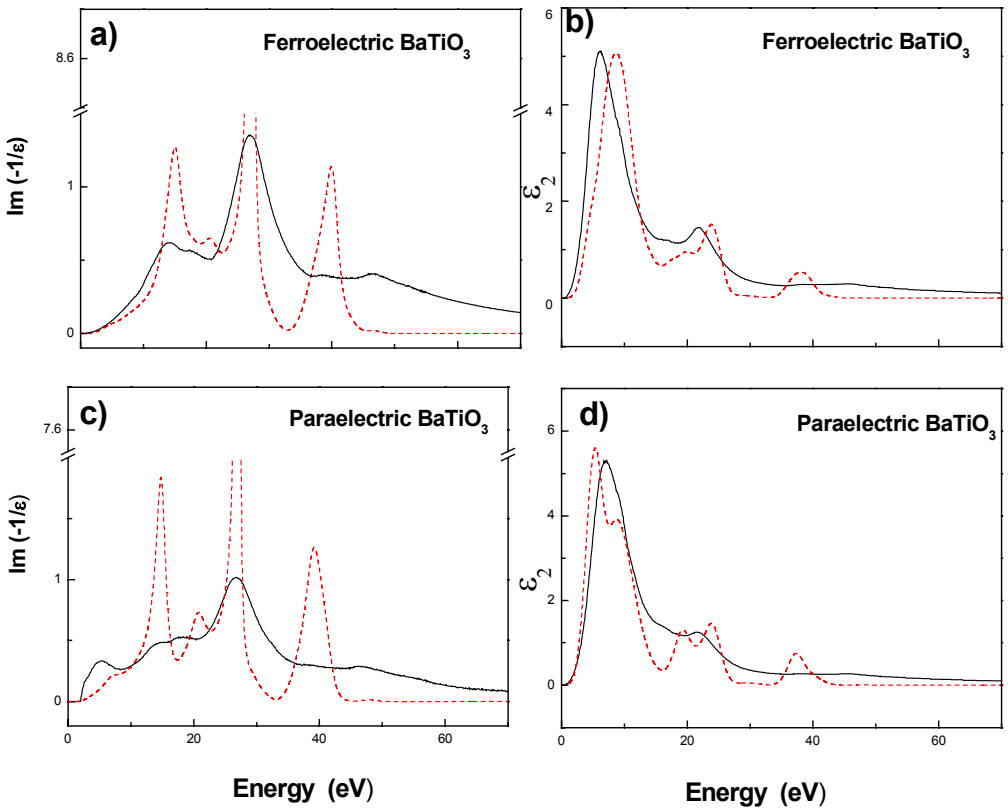

Figure 1. EELS Spectrum of $BaTiO_3$, experimental results (continuous line) and theoretical (dashed line). (a) Im(-1/ε), ferroelectric phase, (b) ε_2, ferroelectric phase , (c) Im(-1/ε), paraelectric phase and (d) ε_2, paraelectric phase

https://doi.org/10.1017/S1431927606067353 Published online by Cambridge University Press