Shifts of Core-level Electron Binding Energies for $SrBi_2Ta_2O_9$ Nano-particles

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The electron binding energies of Ta $4d_{5/2}$ and Sr $3p_{3/2}$ levels of $SrBi_2Ta_2O_9$ nano-particles were larger by 1.2 eV than these of bulk $SrBi_2Ta_2O_9$, while the Bi $4d_{5/2}$ electron binding energy was smaller by 1.4 eV than the bulk. Charge distribution in the unit cell of the nano-particles differs from that of the bulk.

Thin film of $SrBi_2Ta_2O_9$ is promising for fabrication of ferroelectric random access memory devices.[1] The crystal structure of $SrBi_2Ta_2O_9$ is anisotropic (a = 5.512, b/a = 1.000, and c = 25.00 Å),[2] and consisted of both Sr–Ta–O perovskite blocks and Bi_2O_2 layers. Size effects are still of great interest in ferroelectrics.[3] In this letter we deliver the first report on changes in the electric states for $SrBi_2Ta_2O_9$ nano-particles due to size reduction.

We used the molecular sieve MCM-41[4] synthesized from a mixture of SiO_2 1.00: *n*-dodecyltrimetylammonium bromide 0.70: NaOH 0.24: H_2O 53.7 in molar ratio. The mixture was stirred at room temperature and then heated at 140 °C for 48 h. After washing at 80 °C for 24 h and thermal dehydration at 80 °C for 24 h, the dried mixture was calcinated at 700 °C for 6 h in flowing oxygen to remove the organic molecules incorporated during the templating process from the mesopores. The 700 °C calcinated molecular sieve was soaked in the precursor solution, prepared by dissolving strontium oxalate monohydrate, bismuth chloride, and tantalum chloride into absolute ethanol, with the concentration of 0.005 mol/L for 24 h. The soaked molecular sieve was dried and then heated in flowing oxygen at 800 °C for 3 h. The bulk sample (powders) was obtained from the solution by drying and calcination at the same conditions.

X-Ray diffraction pattern of the soaked sample, corresponding to $SrBi_2Ta_2O_9$ nano-particles with the molecular sieve, showed no peaks as shown in the inset of Figure 1. High-resolution transmission electron microscopy of the soaked sample was performed with a JEOL JEF-3000F transmission electron microscope operated at 300 kV for an edge of the samples dispersed on a carbon film. The instrument has a filed emission electron source and a resolution of 2 Å. Hexagonal-pore structure of the molecular sieve was highly sensitive to high-energy electron beam irradiation. As shown in Figure 1, the molecular sieve gave the image of amorphous, though we observed periodical lattice images with 50 to 100 Å diameter corresponding to the spacings between Bi–O and Ta–O layers of the $SrBi_2Ta_2O_9$ unit cell.

X-Ray photoelectron spectra were measured in a vacuum of 4×10^{-10} Torr at room temperature using a Surface Science Laboratories Model SSX-100 spectrometer with monochromatized Al Kα source having a diameter of 300 μm spot on the sample surface. The spectrometer was calibrated utilizing the Au $4f_{7/2}$ electrons (83.79 eV) and the full width at half-maximum of the Au $4f_{7/2}$ peak was 1.0_3 eV. Charge shifts were corrected with the C 1*s* electrons (285.0 eV). The experimental uncertainty amounted to $^{+}/_{-}\,0.1_5$ eV.

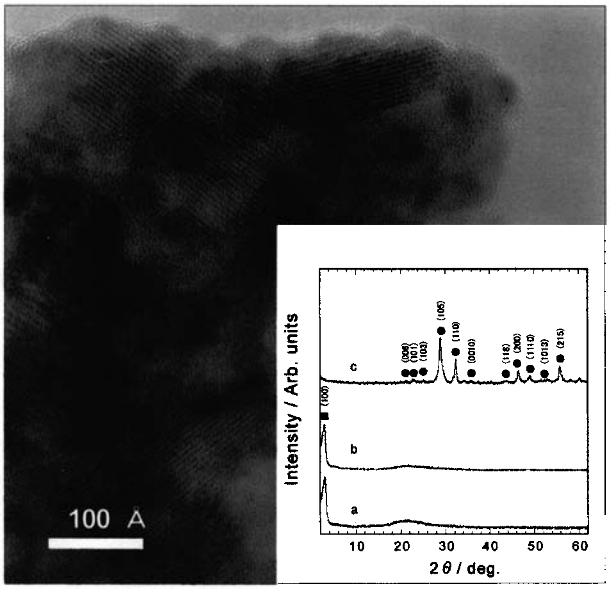

Figure 1. Transmission electron micrograph of the soaked sample. Inset : X-ray diffraction patterns of the molecular sieve sample (a), the soaked sample (b), and the bulk sample (c). Closed circle and square denote the peaks from $SrBi_2Ta_2O_9$ and MCM-41, respectively.

The Ta 4*d*, Sr $3p_{3/2}$, and Bi 4*d* electron spectra of the $SrBi_2Ta_2O_9$ nano-particles and the bulk are shown in Figure 2, and the Ta $4d_{5/2}$, Sr $3p_{3/2}$, and Bi $4d_{5/2}$ electron binding energies are listed in Table 1. The Ta $4d_{5/2}$ and Sr $3p_{3/2}$ electron binding energies of the nano-particles were larger by 1.2 eV, but that of the Bi $4d_{5/2}$ was smaller by 1.4 eV than the bulk. Enlargements of the line width for the $SrBi_2Ta_2O_9$ nano-particles are due to the size reduction which is well known for small clusters.[5] The soaked sample showed the core-level spectra of Sr, Bi, Ta, and O corresponding to $SrBi_2Ta_2O_9$ nano-particles with that of Si from the MCM-41. The intensities of Sr, Bi, Ta, and O spectra were so small, though the chemical state was single as shown in Figure 2. We found no influence of surface contamination on the chemical state of the soaked sample. So, the observed changes in the core-level electron binding energies were due to the quantum size effect.

Tight-binding calculations of $SrBi_2Ta_2O_9$ crystal revealed that the valence band maximum (VBM) at Γ arose from O *p* and

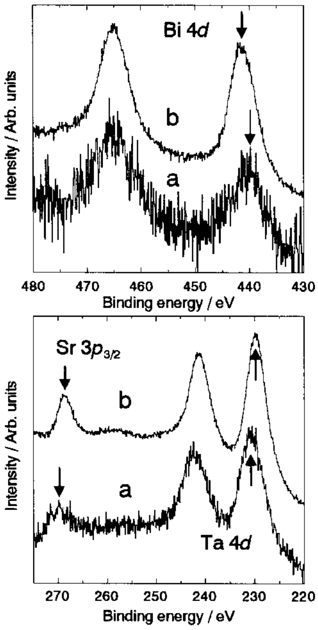

Figure 2. The Ta 4d, Sr 3p, and Bi 4d electron spectra of the soaked sample (a) and the bulk sample (b). The arrows denote the peak positions listed in Table 1.

Table 1. The Ta 4d, Sr 3p, and Bi 4d electron binding energies of the soaked sample and the bulk sample (eV)

Samples	Soaked sample	Bulk sample
Ta 4$d_{5/2}$	230.8	229.6
Sr 3$p_{3/2}$	269.6	268.4
Bi 4$d_{5/2}$	440.0	441.4

The experimental uncertainty amounted to $^{+}/_{-}0.1_5$ eV.

some Bi *s* states, while the conduction band minimum (CBM) at *M* consisted of Bi *p* states.[6] Both the VBM and CBM are the states localized in the Bi_2O_2 layer. The change in the electronic structure for the Bi_2O_2 layer should be resulted from that for the Sr–Ta–O perovskite block of the crystal. Within a unit cell a decrease of effective charge for Sr–Ta–O perovskite blocks results in an increase of that for Bi_2O_2 layers. In one-electron approximation such variation of electron population in the isolated nano-particles brings about the shifts of orbital energy, positive for the Ta 4d and Sr 3p and negative for the Bi 4d.

The charge distribution in a unit cell varied with the size in isolated nano-particles. Smaller electron density in the Sr–Ta–O perovskite blocks should result in a decrease of dipole moments of the nano-particles, and lower the phase transition temperature.

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