

Band Structure of $\text{Sr}_{0.5}\text{Ba}_{0.5}\text{Nb}_2\text{O}_6$ Thin Film Probed by Soft-X-Ray Emission Spectroscopy

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The electronic structure of ferroelectric $\text{Sr}_{0.5}\text{Ba}_{0.5}\text{Nb}_2\text{O}_6$ thin film has been studied by soft-X-ray emission spectroscopy (SXES). In the valence band region, O $2p$ and Nb $4d$ partial densities of states are observed in the O $1s$ and Nb $4p$ SXES spectra. The energy position of the Nb $4d$ state overlaps with that of the O $2p$ state. This finding indicates that the O $2p$ state strongly hybridizes with the Nb $4d$ state in the valence band. [DOI: 10.1143/JJAP.43.7627]

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Ferroelectric $\text{Sr}_{1-x}\text{Ba}_x\text{Nb}_2\text{O}_6$ exhibits a tetragonal tungsten-bronze crystal structure and has a spontaneous polarization along its c -axis.¹⁾ Its ferroelectric properties, such as Curie temperature and dielectric constant, can be adjusted by controlling the Sr/Ba atomic ratio in the range of $0.25 < x < 0.75$. $\text{Sr}_{1-x}\text{Ba}_x\text{Nb}_2\text{O}_6$ is an attractive material for optoelectronic device applications because of its high electrooptic coefficient and strong photorefractive effect. In addition, $\text{Sr}_{1-x}\text{Ba}_x\text{Nb}_2\text{O}_6$ has a large spontaneous polarization that can be used for nonvolatile memory applications. Therefore, $\text{Sr}_{1-x}\text{Ba}_x\text{Nb}_2\text{O}_6$ thin films deposited by several fabrication techniques, such as sol-gel^{2,3)} and pulsed-laser deposition,⁴⁻⁷⁾ have been investigated with respect to their structural properties. We believe that understanding the electronic structure of $\text{Sr}_{1-x}\text{Ba}_x\text{Nb}_2\text{O}_6$ is one of the most important subjects in terms of the science and technology of materials. However, the electronic structure of $\text{Sr}_{1-x}\text{Ba}_x\text{Nb}_2\text{O}_6$ has not been clarified thus far.

In this study, the band structure of a $\text{Sr}_{0.5}\text{Ba}_{0.5}\text{Nb}_2\text{O}_6$ thin film deposited on a MgO substrate was probed by soft-X-ray emission spectroscopy (SXES). SXES can confirm the electronic structure of a film in the bulk state,⁸⁾ because the mean free path of a soft-X-ray is very long compared with that of an electron. The SXES spectra, which have clear selection rules regarding angular momentum due to dipole transitions, reflect the occupied partial densities of states (PDOS).⁸⁾ Thus, we study the band structure of a $\text{Sr}_{0.5}\text{Ba}_{0.5}\text{Nb}_2\text{O}_6$ thin film by measuring O $1s$ and Nb $4p$ SXES measurements.

A $\text{Sr}_{0.5}\text{Ba}_{0.5}\text{Nb}_2\text{O}_6$ thin film was prepared on a (100)-oriented MgO substrate by metalorganic deposition with strontium, barium, and niobium naphthenates, which were supplied by Kanto Kagaku Co., Ltd. The substrate was spin-coated with the mixed solutions at 3000 rpm for 20 s. The spin-coated film was dried at 110°C for 5 min, and subsequently calcined at 600°C for 5 min. This procedure was repeated five times. Then, the thin film was sintered in O₂ atmosphere at 750°C for 60 min. The film thickness was approximately 1 μm. The $\text{Sr}_{0.5}\text{Ba}_{0.5}\text{Nb}_2\text{O}_6$ thin film on the (100) MgO substrate exhibited a strong c -axis orientation. The detailed electrical and structural properties will be published elsewhere.⁹⁾

SXES was carried out at the revolver undulator beamline BL-19B at the Photon Factory (PF) of the High Energy Accelerator Organization (KEK), in Tsukuba, Japan. High brightness and high resolution were realized using a varied-

line-spacing plane grating monochromator. The SXES spectra were measured by a soft-X-ray emission spectrometer. The spectrometer used the Rowland circle geometry that consisted of a grating with a groove density of 300 lines/mm and a Cs-coated multichannel detector. The total resolution of the SXES spectrometer was approximately 0.4 eV at $h\nu = 450$ eV. The incidence angle of the soft-X-ray was set at approximately 75° against to the surface in order to avoid the surface effect.

Figure 1(a) shows the O $1s$ X-ray absorption (XAS) spectrum of the $\text{Sr}_{0.5}\text{Ba}_{0.5}\text{Nb}_2\text{O}_6$ thin film. From the dipole selection rules, it is understood that the O $1s$ XAS spectrum of the $4d$ transition metal oxide corresponds to the transition from O $1s$ state to O $2p$ state hybridized with the unoccupied metal $4d$ state. The broad band at approximately 535 eV is attributed to the Sr $4d$ and Ba $5d$ bands that are mixed with the unoccupied O $2p$ state. The peak at approximately 530 eV corresponds to the t_{2g} -subband of the Nb $4d$ state: the e_g -subband is considered to be obscured by the Sr $4d$ or Ba

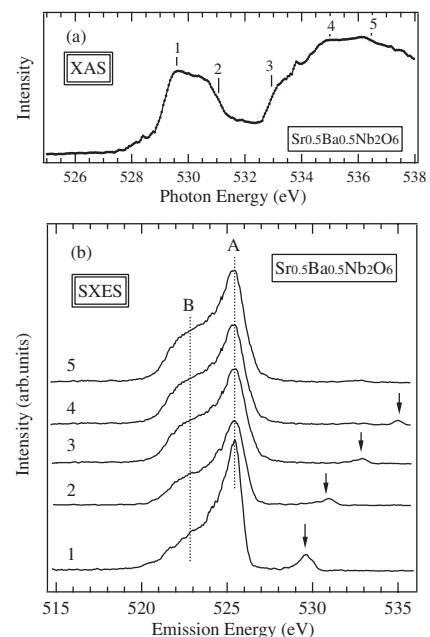


Fig. 1. (a) O $1s$ XAS spectrum of $\text{Sr}_{0.5}\text{Ba}_{0.5}\text{Nb}_2\text{O}_6$ thin film. The numbers indicate the photon energies at which the resonant-SXES spectra were measured. (b) O $1s$ SXES spectra of $\text{Sr}_{0.5}\text{Ba}_{0.5}\text{Nb}_2\text{O}_6$ thin film excited at various photon energies indicated in (a). Arrows show the excitation photon energies.

5d band. The vertical bars, which are labeled from 1 to 5, indicate the selected photon energies from the resonant SXES measurements.

Figure 1(b) shows the O 1s resonant-SXES spectra of the Sr_{0.5}Ba_{0.5}Nb₂O₆ thin film. The clear selection rule of SXES is caused mainly within the same atomic species, because the core holes are strongly localized. For this reason, the O 1s SXES spectra reflect the O 2p PDOS. The obtained O 2p PDOS corresponds to the band structure in the valence band region, since the valence band of Sr_{0.5}Ba_{0.5}Nb₂O₆ is mainly composed of the O 2p state. An arrow shown on each spectrum indicates the elastic scattering of an excitation photon. Two features, denoted by A and B, are observed at ~525.5 eV and ~522.7 eV, respectively. Except for spectrum 1, the intensities of features A and B increase slightly with increasing excitation photon energy in all spectra, since the numbers of electrons excited to the conduction band from the O 1s core level increase with excitation photon energy, as shown in Fig. 1(a). On the other hand, the intensity of the feature A of spectrum 1 is stronger than those of other spectra. This indicates that the O 1s → 2p resonance effect occurs at the t_{2g}-absorption peak, as shown in Fig. 1(a). However, the O 1s resonant-SXES spectra reflect the O 2p fluorescence component in the valence band region. This is because soft-X-ray Raman scattering and a new structure formed by excitation photons, which are often observed in resonant-SXES spectra excited at transition metal sites, are not observed in these spectra. Therefore, the hybridization effect between the Nb 4d and O 2p states in the valence band region can be discussed quantitatively on the basis of the SXES spectra.

Figure 2 shows the Nb 4p and O 1s SXES spectra in the valence band region of the Sr_{0.5}Ba_{0.5}Nb₂O₆ thin film. The intensity of each spectrum is normalized to beam current and measurement time. The O 1s SXES spectrum, which reflects the O 2p-PDOS, corresponds to spectrum 2 in Fig. 1, and exhibits nonresonance because spectrum 1, which also corresponds to nonresonance, does not reflect the true DOS. The Nb 4p SXES spectrum measured at $h\nu = 65$ eV reflects the Nb 4d-PDOS in the valence band region. The contributions of the Sr 4d and Ba 5d bands were not observed in the valence band region. Thus, the sum of the O 2p PDOS and Nb 4d PDOS is the total DOS in the valence band of the Sr_{0.5}Ba_{0.5}Nb₂O₆ thin film.

The Nb 4d PDOS has a broad distribution on the left side of feature B. The Nb 4d PDOS contribution is more significant at high binding energies (feature B), where the O 2p state has a larger admixture with the Nb 4d state. That is, the valence states originating from the O 2p state are hybridized with the Nb 4d state. From the distributions of the Nb 4d PDOS and O 2p PDOS, we consider that feature A corresponds to the nonbonding state and feature B corresponds to the bonding state that is well mixed with the Nb 4d state. The hybridization effect between the Nb 4d and O 2p states in Nb oxide has not been reported to date. However, a similar hybridization effect has been observed in 4d⁰ metal transition oxides, such as ZrO₂ and CaZrO₃.^{10,11} In perovskite-type oxide CaZrO₃, it was reported that the contribution of Zr 4d PDOS is more significant at high

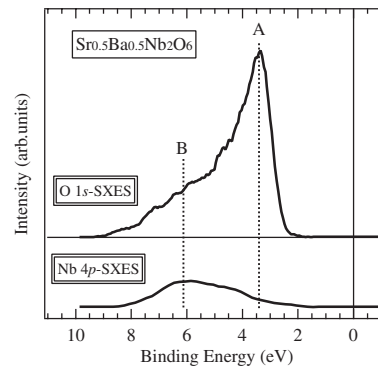


Fig. 2. Comparison of O 1s and Nb 4p SXES spectra in the valence band region of Sr_{0.5}Ba_{0.5}Nb₂O₆ thin film. The O 1s SXES spectrum corresponds to spectrum 2 in Fig. 1(b).

binding energies in the valence band region, where the bonding O 2p state has a larger admixture with the Zr 4d state. The contribution of the Zr 4d PDOS to the total DOS has been reported to be approximately 25% in the valence band.¹⁰ For the Sr_{0.5}Ba_{0.5}Nb₂O₆ thin film, the contribution of the Nb 4d PDOS, which was estimated from the total DOS, was approximately 20% in the valence band.

In conclusion, we have studied the band structure of a Sr_{0.5}Ba_{0.5}Nb₂O₆ thin film using SXES. The O 1s and Nb 4p SXES spectra exhibited the O 2p PDOS and Nb 4d PDOS, respectively, in the valence band. The energy position of the O 2p state overlaps with that of the Nb 4d state, indicating that the O 2p state hybridizes with the Nb 4d state in the valence band. The contribution of the Nb 4d PDOS to the total DOS was estimated to be approximately 20% in the valence band.

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