PROC. JSSF-2, KYOTO, 1980
J. PHYS. SOC. JPN. 49 (1980) SUPPL. B, pp. 95–97.

Electron Microscopic and Diffraction Studies of $Sr_2Nb_2O_7$, $Sr_2Ta_2O_7$ and Their Solid Solutions

Naoki YAMAMOTO, Masatoshi NAKAMURA, Katsumichi YAGI and Kikuo OHI†

Department of Physics, Tokyo Institute of Technology, Oh-okayama, Meguro-ku, Tokyo, 152
†Department of Physics, Waseda University, Shinjuku-ku Tokyo, 160

The structures of the incommensurate phase of $Sr_2Nb_2O_7$ and its solid solutions $Sr_2(Ta_{1-x}Nb_x)_2O_7$ with $Sr_2Ta_2O_7$ were studied by electron diffraction and microscopy. The high resolution electron microscope directly revealed the sinusoidal modulation in the incommensurate phase. In solid solutions it was found that the superlattice structure of $Sr_2Ta_2O_7$ changed into the incommensurate structure of $Sr_2Nb_2O_7$ through the intermediate structure which shows the diffuse streaks along the extra diffraction spots with varying composition.

$Sr_2Nb_2O_7$ (abbreviated here after by **SN**) and $Sr_2Ta_2O_7$ (**ST**) are ferroelectric $A_2B_2O_7$ type oxide compounds with the Curie temperatures of 1342°C and −107°C, respectively. Their structures are composed of perovskite type slabs with distorted octahedra. Solid solution of them was reported to be ferroelectric whose transition temperature varies continuously from 1342°C to −107°C with composition.[1] Recently, new phases of **SN** (phase III) with an incommensurate structure and **ST** (phase II) with a superlattice structure were found by electron microscopy,[2] as shown in Fig. 1. The incommensurate phase (***INC*** phase) of **SN** gives the irrational satellite spots at the positions apart from the fundamental diffraction spots of the high temperature phase (phase II) by $\boldsymbol{q} = \pm(1/2-\delta)\boldsymbol{a}^*$ (see Fig. 2b)). The value of δ is temperature dependent and is in the range of $0.008 \sim 0.022$. At the normal–***INC*** phase transition temperature of 215°C, the elastic and dielectric anomalies were also reported by Ohi *et al.*[3] The superlattice structure phase (phase II) of **ST** is monoclinic below 170°C, the *a* lattice parameter being two times of that of the phase I.

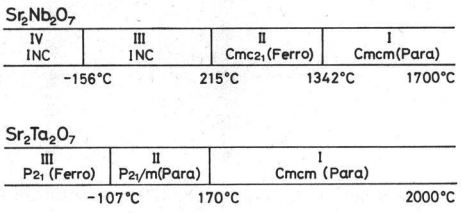

Fig. 1. Phases of $Sr_2Nb_2O_7$ and $Sr_2Ta_2O_7$.

Present paper briefly describes the structural investigations of the ***INC*** phase of **SN** and of the solid solutions $Sr_2(Ta_{1-x}Nb_x)_2O_7$.

(1) Structure of the incommensurate phase of $Sr_2Nb_2O_7$

The irrational diffraction spots in the ***INC*** phase have systematic absences of $(h\pm q, k, l)$ for $h+k$ odd, $k\neq 0$, and $(h\pm q, 0, l)$ for l even, and there is no higher order satellite spot. From above extinction rules, following two points are concluded for atomic displacements in the ***INC*** phase. First, displacements of the four atoms at the 4*a* sites of the space group $Cmc2_1$ of the high temperature phase (phase II) are equal but with a special phase relation. The displacements may be due to the rotation of NbO_6 octahedra about the *b* axis, since in the phase II of **SN**, NbO_6 octahedra were reported to rotate slightly about the *a* axis[4] from the high symmetrical positions in the phase I. Second, the displacements are sinusoidally modulated in the [100] direction. The calculation showed that a spatially discontinuous one such as an array of antiphase boundaries could hardly explain the intensity distributions of the satellite spots in the diffraction pattern. The latter conclusion was directly observed by using a high resolution electron microscope of 200CX. Fig. 2 a) reproduces the electron micrograph of a **SN** crystal taken with an incident electron beam parallel to the [011] direction. The reflections inside a circle in the corresponding diffraction pattern of b) were allowed to pass through the

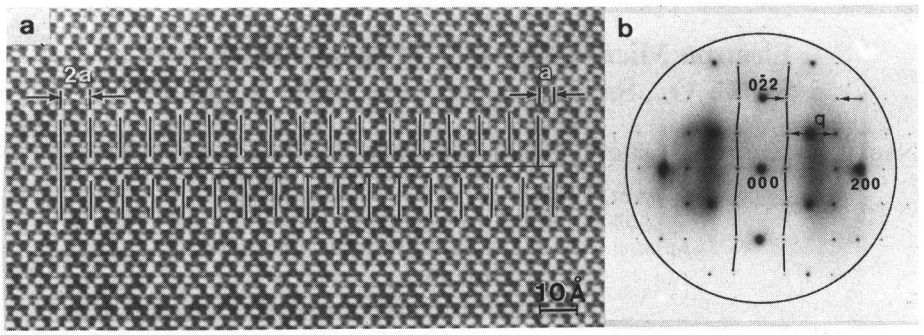

Fig. 2. a) High resolution electron micrograph of $Sr_2Nb_2O_7$ with an (011) crystal showing sinusoidal modulation of the incommensurate structure and b) the corresponding diffraction pattern.

objective aperture and contributed to the image formation. Small black and white spot images with an interval of the a parameter in the [100] direction show the basic structure of the phase II. In the upper part of the micrograph equal lattice points are marked with short vertical lines with an interval of $2a$. With narrow eyes there are also seen faint and broad vertical fringes at the positions marked by lower short vertical lines. The spacing of them is slightly larger than $2a$, which clearly indicates that the fringes are characteristic to the ***INC*** phase. The fact that the lower lines make a shift sinusoidally with respect to the upper lines, clearly indicates the spatially continuous lattice modulation in the ***INC*** phase. Image simulation and the details of the comparison will be reported elsewhere.[5)]

(2) Structures of the solid solutions $Sr_2(Ta_{1-x}Nb_x)_2O_7$

The sample crystals of the solid solutions $Sr_2(Ta_{1-x}Nb_x)_2O_7$ ($x=0.1, 0.2, \ldots, 0.9$) were grown by heating pressed rods of mixed powders of $SrCO_3$, Ta_2O_5 and Nb_2O_5 with proper ratios. The samples obtained were polycrystalline with crystal sizes smaller than $(0.5\ \mathrm{mm})^3$. They were crushed to fine fragments for electron microscope observations. Bulk crystals ($x=0.2$, 0.8) grown by the floating zone technique[1)] were also used for the observations.

The extra diffraction spots appearing in the phase II of **ST** and the phase III of **SN** are in the different positions in the diffraction pattern; the superlattice spots of **ST** have the positions of $h=$ half integer and $k=\pm 1/2, \pm 3/2, \pm 5/2, \ldots$ (**ST** type spots) of indexed with respect to the high temperature phase, while the position of the ***INC*** spots of **SN** are close to the positions of $h=$ half integer and $k=0, \pm 1, \pm 2, \ldots$ (**SN** type spots). This made it easy to identify the structures of the sample crystals. The two types of the extra spots are seen in Fig. 3; the diffraction pattern of a) from the crystal with $x=0.2$ shows the **ST** type spots and the diffraction pattern of c) from the crystal with $x=0.7$ shows the **SN** type spots. The value of δ measured from the **SN** type spot positions decreases as the composition x decreases. In the diffraction patterns from many crystals with the compositions of $x=0.4$, 0.5 and 0.6, the extra

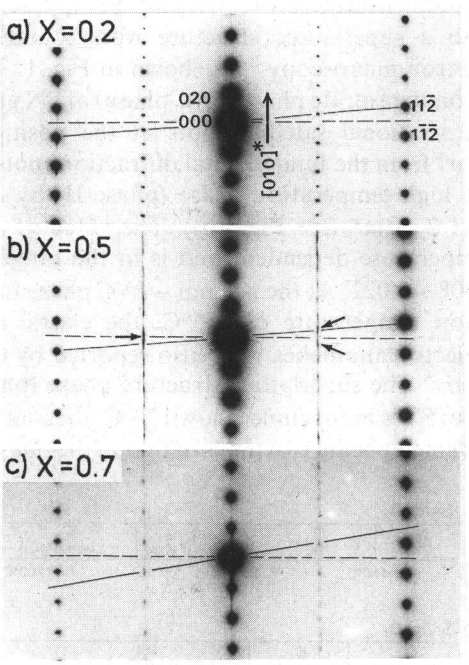

Fig. 3. Diffraction patterns in the (201) orientation from the crystals with the composition of a) $x=0.2$, b) $x=0.5$ and c) $x=0.7$.

spots were seen to be accompanied by diffuse streaks along the [010] direction. Especially for the crystals with $x=0.5$, the diffuse streaks are strong and continuous as seen in Fig. 3 b), in which the two types of the extra spots were hardly recognized. However, the diffuse streaks do not appear around the fundamental diffraction spots, which indicates that the basic structure of the phase II is not disordered. The intensity of the diffuse streaks changes from crystal to crystal even from the same sample. One reason for this may be due to the inhomogeneity of the composition of the sample crystal.

In this way many crystals from the samples of each composition could be roughly classified into three groups, which show the diffraction pattern containing the extra spots of **ST** type, diffuse type and **SN** type. The phase boundary between the two low temperature phases may be nearly at the composition of around $x=0.5$. When the crystals were heated in an electron microscope, the extra spots and diffuse streaks disappeared. It was found that the transition temperatures are at around 200°C for the crystals of any compositions, i.e., the transition temperature continuously changes from that of **ST** at 170°C to that of **SN** at 215°C with varying composition in the solid solution system. From these observations the phase diagram shown in Fig. 4 was obtained.

The dark field images of the extra spots were also taken for the crystals of various compositions under the condition that the incident beam was nearly perpendicular to the *b* axis. The domain structure in the **ST** crystal and domain-like textures in the **SN** crystal corresponding to those observed under the condition of the [010] incidence[2] were seen in the images. The images from the solid solutions showed the change of textures along the *b* axis with varying composition. This is closely related to the change of the crystal symmetry from **ST**

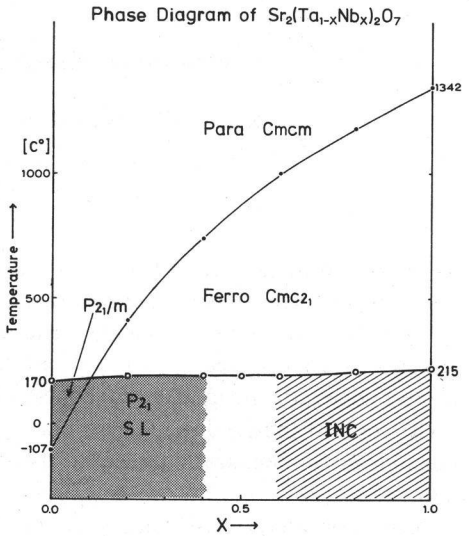

Fig. 4. Proposed phase diagram for the solid solution $Sr_2(Ta_{1-x}Nb_x)_2O_7$.

to **SN** structure and of the diffuse streaks along the extra spots with composition. The details of the observations and discussions will be given elsewhere.[6] No appreciable changes in the images and diffraction patterns were noticed at the ferroelectric phase transitions of samples with $x=0$ and 0.2 (Fig. 4). Studies on the crystal symmetry of the solid solutions by the convergent beam electron diffraction method are in progress by Tanaka *et al.*[7]

References

1) S. Nanamatsu, M. Kimura, K. Doi and M. Takahashi: J. Phys. Soc. Jpn. **30** (1971) 300.
2) N. Yamamoto, K. Yagi, G. Honjo, M. Kimura and T. Kawamura: J. Phys. Soc. Jpn. **48** (1980) 185.
3) K. Ohi, M. Kimura, H. Ishida and H. Kakinuma: J. Phys. Soc. Jpn. **46** (1979) 1965.
4) N. Ishizawa, F. Marumo, T. Kawamura and M. Kimura: Acta Crystallogr. **B31** (1975) 1912.
5) N. Yamamoto: in preparation.
6) M. Nakamura, N. Yamamoto and K. Yagi: in preparation.
7) M. Tanaka: private communication (1980).