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Crystal Structure of High Temperature Phase in Bi_2O_2-layered Perovskites $ABi_2M_2O_9$(A=Pb, Sr, M=Nb, Ta)

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ABSTRACT

Crystal structure of $PbBi_2Nb_2O_9$ and $Sr_{1.2}Bi_{1.8}Ta_2O_9$ were determined by Rietveld refinement method using neutron diffraction data in the temperature range of 300 K~1273 K. Phase transition temperatures were measured from the dielectric permittivitytemperature curve. The $PbBi_2Nb_2O_9$ showed a phase transition at about 810 K. In the Sr-excess compound $Sr_{1.2}Bi_{1.8}Ta_2O_9$ the phase transition was suppressed down to room temperature. Several structural models were tested by the Rietveld refinement. Based on the the 'R' values and the structural parameters, the B2cb model is judged to be the most feasible one for the high temperature phase at above 810 K of the $PbBi_2Nb_2O_9$. The $Sr_{1.2}Bi_{1.8}Ta_2O_9$ sample was refined to show the most reliable results by the Am2m model.

Key words : Paraelectric phase, Neutron diffraction, Crystal structure, SBT, $PbBi_2Ta_2O_9$

1. Introduction

$ABi_2M_2O_9$(A=Pb, Sr, M=Nb, Ta) is a member of the Aurivillius phase $Bi_2A_{n-1}M_nO_{3n+3}$(A=Sr, Ba, Pb, M=Ta, Nb) in which perovskite layers$[AM_2O_7]^{2-}$ are interleaved between the $[Bi_2O_2]^{2+}$ layers.[1,2] The ferroelectric $SrBi_2Ta_2O_9$ (SBT) has been studied as a promising candidate for ferroelectric random access memories (FeRAMs) due to its superior polarization fatigue and low switching coercive field. Crystal structure of SBT has drawn interest in the aspect of the relation with the ferroelectric properties.[3-5] The room temperature crystal structure of the stoichiometric $ABi_2M_2O_9$(A=Pb, Sr, B=Nb, Ta) and the nonstoichiometric $Sr_{0.8}Bi_{2.2}Ta_2O_9$ have been determined recently using neutron powder diffraction data. The calculated polarization P_s from the structural parameter was compared to the measured values of thin films and bulk form of ceramics.

The ferroelectric structure at room temperature is described in the space group $A2_1am$ (a≈5.53 Å, b≈5.54 Å, c≈24.9 Å, z=4) and transforms to a paraelectric phase at high temperature.[6,7] Thomson *et al.*[8] have observed the phase transitions at 583 K and 843 K in SBT. Smolenskii[1] reported a phase transition at 833 K in $PbBi_2Nb_2O_9$ (PBN). Later, Subbaro *et al.*[9] and Srikanth *et al.*[10] reported that the phase transition temperature of PBN was dependent on the cooling rate after sintering and varied from 833 K to 1373 K with the cooling rate.

The previous studies on the paraelectric phase have been lack of sufficient evidences due to the experimental difficulties. Based on the X-ray diffraction analysis, Ismailzade[11] reported that (Pb, Sr) $Bi_2Nb_2O_9$ compounds transforms to tetragonal phase at above 520°C. Thomson *et al.*[12] also suggested that Bi_2TiNbO_9 would become the prototype structure I4/mmm (a=b≈3.9 Å, c=25.1 Å) at above 1223 K. Recently Onodera *et al.*[13] analyzed the high temperature structure of $Sr_{0.85}Bi_{2.1}Ta_2O_9$ using X-ray powder diffraction data. They reported that the ferroelectric $A2_1am$ transforms to the paraelectric structure I4/mmm at above 670 K. On the other hand, Kim *et al.*[14] analyzed the high temperature structure using neutron powder diffraction in the temperature range of 29 K~1273 K for the stoichiometric $SrBi_2Ta_2O_9$. Among several structural models, such as the F2mm, Fmmm, B2cb, $A2_1am$, I4/mm, Bbab, and Abam, the orthorhombic B2cb showed the lowest χ^2 [=$(R_{wp}/R_e)^2$] at above 623 K contrarily to Onodera *et al.*'s result.[14]

The phase transitions in the Aurivillius compounds are involved with the rotation mode of oxygen octahedra and ferroelectric displacements.[6,8,12] The oxygen atom has relatively small x-ray scattering factor compared to extremely heavy cations, such as Bi, Pb, and Ta. Hence the x-ray scattering intensity arising from the oxygen polyhedron change are not strong enough for analyzing the structural transition especially at high temperature. On the other hand, neutron scattering length of oxygen(0.58×10^{-14} m) is the same order of value as Bi(0.85×10^{-14} m) or Ta(0.69×10^{-14} m). Hence neutron diffraction is very suitable for the analyzing the displacive mode change of oxygen polyhedrons in Aurivilius compounds.

In this study we analysed the crystal structure of the paraelectric PBN and $Sr_{1.2}Bi_{1.8}Ta_2O_{9-\delta}$ using neutron powder

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diffraction data. In $PbBi_2Nb_2O_9$ structural information for the high temperature phase could be obtained by the high temperature diffraction in the range of 293 K-1273 K. The phase transition temperatures of $Sr_{1\pm x}Bi_{2\pm y}Ta_2O_{9-\delta}$ decreased with the increase of the Sr/Bi ratio.[14] The phase transition of the $Sr_{1.2}Bi_{1.8}Ta_2O_{9-\delta}$ was completely suppressed and the high temperature phase was retained at room temperature as will be discussed.

2. Experimental

Polycrystalline samples of $PbBi_2Nb_2O_9$ and $Sr_{1.2}Bi_{1.8}Ta_2O_{9-\delta}$ were prepared by solid state reaction method from the mixtures of appropriate amounts of $SrCO_3$, PbO, Bi_2O_3, Ta_2O_5, and Nb_2O_5. The raw materials were mixed by ball milling in water for 24 hr and dried. After calcinations at 1153~1323 K, 1.5 wt% PVA was added and pressed into the discs of 10 mm diameter. The pressed specimens were sintered at 1353~1523 K for 3 hr in air and furnace-cooled to 523 K after sintering.

Dielectric permittivity (ε_r) and loss tangent (tan δ) were measured in the LF impedance analyzer (HP4192A) under varying frequency. Neutron diffraction data were obtained in the temperature range of 300 K~1273 K using HRPD diffractometer at HANARO in KAERI (Korea Atomic Energy Research Institute). The neutrons from the HANARO reactor were monochromatized by a vertically focusing composite Ge-monochromator to a wavelength of 0.18348 nm. The neutron diffraction patterns were analysed by the Rietveld profile refinement method using a version 3.2 of the program Fullprof.

3. Results and Discussions

The temperature dependence of dielectric permittivity ε and dielectric loss tan δ of $PbBi_2Nb_2O_9$ are shown in Fig. 1. The positions of maximum values of ε and tan δ slightly change with measuring frequency, suggesting relaxor type behavior. The peak positions decreases from 819 K at 1 MHz to 810 K at 1 kHz similarly to $BaBi_2Nb_2O_9$.[8]

Fig. 2 shows the temperature dependence of dielectric permittivity e of $Sr_{1+x}Bi_{2-x}Ta_2O_{9-\delta}$. The phase transition temperature decreases from 549 K at x=0 to 470 K at x=0.1. The

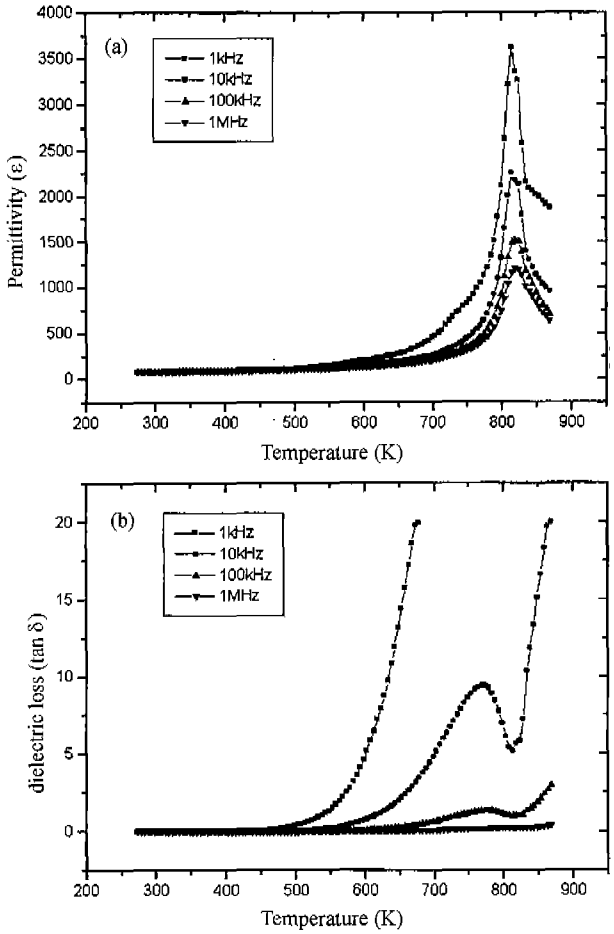

Fig. 1. Dielectric permittivity ε and dielectric loss tan δ of $Pb_1Bi_2Nb_2O_9$ with varying temperature.

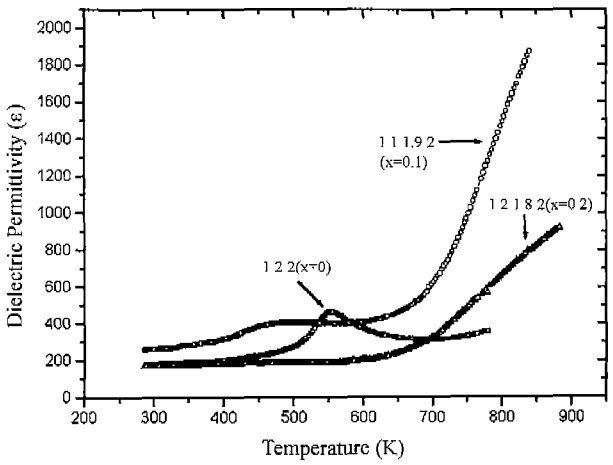

Fig. 2. Dielectric permittivity ε change of $Sr_{1+x}Bi_{2-x}Ta_2O_{9-\delta}$ (x=0, 0.1, 0.2) with temperature.

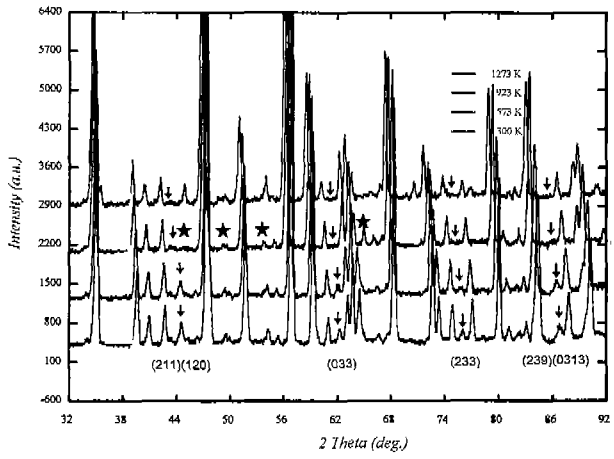

Fig. 3. Neutron diffraction patterns of $Pb_1Bi_2Nb_2O_9$ with temperature.

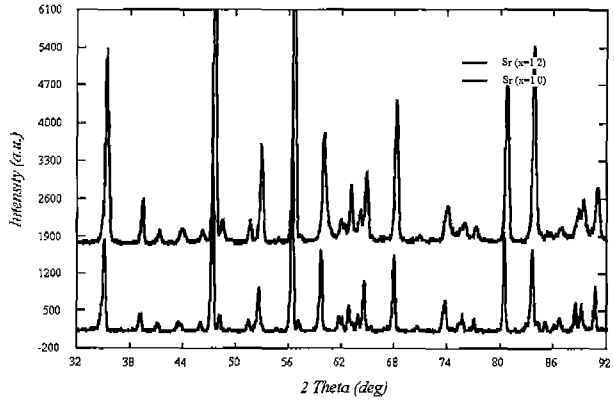

Fig. 4. Neutron diffraction patterns of $Sr_1Bi_2Ta_2O_9$ and $Sr_{1.2}Bi_{1.8}Ta_2O_9$ at room temperature.

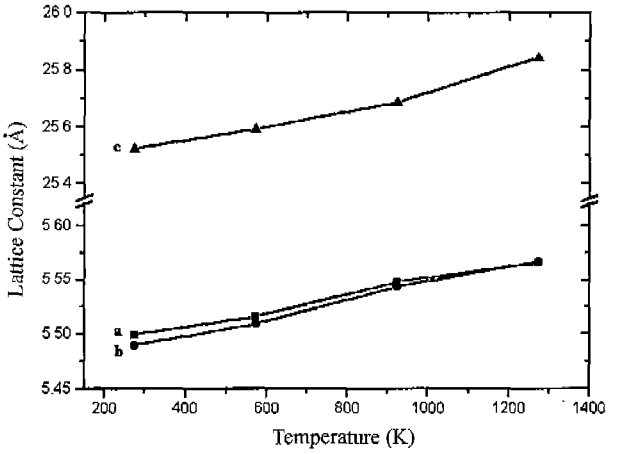

Fig. 5. Lattice parameter change with temperature in the $Pb_1Bi_2Nb_2O_9$.

phase transition peak is very broad at x=0.1, and completely suppressed at x=0.2. The suppression of phase transition at x=0.2 implies that the paraelectric phase is retained at room temperature.

Fig. 3 shows neutron powder diffraction patterns of $PbBi_2Nb_2O_9$ with varying temperature. The arrows indicate the reflections diminishing with increasing temperature, which are indexed based on the $A2_1am$ model and have the reflections with (h+l=odd) in common. Extra diffraction peaks observed at 1273 K is considered to originate from the partial decomposition of the sample.

Fig. 4 shows the patterns of $Sr_{1+x}Bi_{2-x}Ta_2O_{9-\delta}$ (x=0, 0.2). No extra peak was found in $Sr_{1.2}Bi_{1.8}Ta_2O_{9-\delta}$ compared to the stoichiometric sample. The lattice parameters of $PbBi_2Nb_2O_9$ calculated in terms of the $A2_1am$ model are shown in Fig. 5. At 1273 K the aaxis becomes equal to b-axis within the error range: a=5.570±0.009 Å, b=5.568±0.001 Å.

Several structural models considered as the candidates for the high temperature paraelectric phase of PBN were tested. The tested models cover the orthorhombic ($A2_1am$, F2mm, Fmmm, B2cb, Bbab, B2mm, and Am2m) and the teteragonal (I4/mmm and P4/mmm) structures. These candidates were selected based on the (hkl) extinction conditions as shown in Fig. 3 and the previous studies suggesting the symmetry components leading to atomic displacive modes.[6,8,12,14] Especially the two structural models, P4/mmm and Am2m, were additionally included into the space groups which had been previously tested by Kim *et al.* for the high temperature structure analysis of the $Sr_1Bi_2Ta_2O_9$.[14] Fig. 6 shows the χ^2 [=$(R_{wp}/R_e)^2$] values obtained from the Rietveld refinement of PBN.[15,16] The χ^2 values of some of the models fluctuated even at the final stage of refinement at above 500 K. Upto 573 K the $A2_1am$ showed the lowest χ^2 and the others showed too large χ^2 to be considered as a correct model.

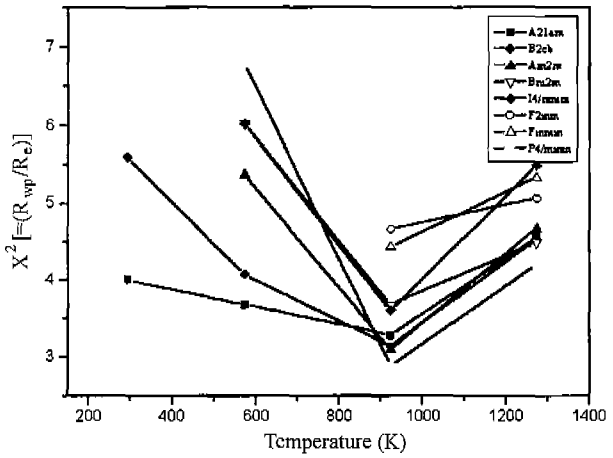

Fig. 6. χ^2 [=$(R_{wp}/R_e)^2$] values of the various structural models of $Pb_1Bi_2Nb_2O_9$ at 923 K.

At 923 K the B2cb, Am2m, and P4/mmm models show improved χ^2, R_f, and R_b values than the $A2_1am$(χ^2≈3.28). The P4/mmm shows the lowest χ^2 values of 2.88 and 4.2 at 923 K and 1273 K, respectively. At 1273 K the other models, i.e. the B2cb, Bm2m, $A2_1am$, and Am2m, also showed similar χ^2 values (≈4.5). If only the discrepancy factors, such as χ^2, R_{wp}, R_b, and R_f are considered, both the P4/mmm and B2cb can be assigned to the high temperature structure at 923 K and 1273 K. The structural parameters of the PBN at 923 K by the P4/mmm and the B2cb models are shown in Tables 1 and 2. The Pb and Bi-sites are partially displaced each other similarly to the room temperature analysis by Srikanth *et al.*[10] Some of the oxygen atoms show abnormally large thermal parameters in the P4/mmm model, while those in the B2cb are reasonable level. The unreasonably large and/or negative thermal parameters in the P4/mmm model as shown in Table 1 lead to choice of the B2cb model instead of the P4/mmm model for the high temperature phase of the of $PbBi_2Nb_2O_9$.

The refinement results for the $Sr_{1.2}Bi_{1.8}Ta_2O_{9-\delta}$ are summarized in Table 3. The $A2_1am$, B2cb, Am2m, I4/mmm, P4/mmm, and Fmmm models were tested. The P4/mmm model showed the lowest χ^2. The Am2m produced the next smallest χ^2 to the P4/mmm. The B2cb showed similar χ^2 to the $A2_1am$.

Table 1. Refined Structural Parameters of $Pb_1Bi_2Nb_2O_9$ at 923 K for the P4/mmm Model

Atoms	x	y	z	Biso	Occup.
Pb 1	0.0000(0)	0.0000(0)	0.0000(0)	5.53(84)	1.0
Pb 2	0.5000(0)	0.5000(0)	0.0000(0)	1.10(35)	1.0
Pb 3	0.0000(0)	0.5000(0)	0.5000(0)	5.81(45)	1.0
Bi 1	0.0000(0)	0.0000(0)	0.2037(7)	1.90(37)	1.0
Bi 2	0.5000(0)	0.5000(0)	0.2008(7)	3.15(39)	1.0
Bi 3	0.0000(0)	0.5000(0)	0.3002(3)	2.28(21)	1.0
Nb 1	0.0000(0)	0.0000(0)	0.4125(6)	0.09(27)	1.0
Nb 2	0.5000(0)	0.5000(0)	0.4139(6)	1.11(34)	1.0
Nb 3	0.0000(0)	0.5000(0)	0.9109(3)	0.72(19)	1.0
O1	0.0000(0)	0.0000(0)	0.5000(0)	0.80(48)	1.0
02	0.0000(0)	0.5000(0)	0.0000(0)	8.80(86)	1.0
O3	0.5001(0)	0.5001(0)	0.5000(0)	0.07(67)	1.0
O4	0.0000(0)	0.0000(0)	0.3431(11)	9.37(91)	1.0
O5	0.5000(0)	0.5000(0)	0.3439(9)	1.75(68)	1.0
O6	0.0000(0)	0.5000(0)	0.8427(5)	3.20(39)	1.0
O7	0.2402(12)	0.2402(12)	0.2516(4)	1.38(9)	1.0
O8	0.2769(11)	0.2769(11)	0.0832(3)	2.82(22)	1.0
O9	0.7545(16)	0.7545(16)	0.4268(2)	1.85(16)	1.0

Space group : P4/mmm a=b=5.5453(2)Å, c=25.6867(11)Å
R_p=4.70, R_{wp}=6.18, R_e=3.51, R_f=11.5, R_b=10.0, χ^2=3.10

Table 2. Refined Structural Parameters of $Pb_1Bi_2Nb_2O_9$ at 923 K for the B2cb Model

Atoms	x	y	z	Biso	Occup.
Pb/Bi	0.0000(0)	0.0000(0)	0.0000(0)	3.72(14)	0.82/0.18
Bi	1.5178(28)	0.5029(23)	0.2009(1)	2.26(11)	0.87/0.13
Nb	0.5077(35)	0.5047(25)	0.4117(1)	0.48(8)	1.0
O1	0.4760(33)	0.0000(0)	0.0000(0)	2.60(17)	1.0
O2	0.4593(35)	0.5088(35)	0.3419(1)	1.26(15)	1.0
O3	0.7487(36)	0.7461(25)	0.2477(4)	1.05(11)	1.0
O4	0.2318(39)	0.7790(30)	0.0822(4)	4.00(35)	1.0
O5	0.7733(34)	1.2594(20)	0.5745(2)	1.13(16)	1.0

Space group : B2cb a=5.5496(5), b=5.5457(4)Å, c=25.6975(10)Å
R_p=4.76, R_{wp}=6.09, R_e=3.49, R_f=11.4, R_b=9.72, χ^2=3.05

Table 4 shows the refined parameters of $Sr_{1.2}Bi_{1.8}Ta_2O_{9-\delta}$ by the Am2m model. The Sr- and Bi- sites are partially displaced with each other. In terms of the discrepancy 'R' values, both the B2cb and Am2m in addition to the P4/mmm can be equally assigned to the structure of $Sr_{1.2}Bi_{1.8}Ta_2O_9$. The former two space groups are crystallographically ferroelectric, while the P4/mmm is paraelectric. The phase transition behaviors in Figs. 1-2 indicate the $Sr_{1.2}Bi_{1.8}Ta_2O_9$ at room temperature and PBN at above 820 K are non-ferroelectric. However, similarly to the case of the of $PbBi_2Nb_2O_9$, the thermal parameters of the P4/mmm model showed the

Table 4. Refined Structural Parameters of $Sr_{1.2}Bi_{1.8}Ta_2O_9$ at 923 K for the Am2m Model

Atoms	x	y	z	Biso	Occup
Sr	0.0000(0)	0.0000(0)	0.0000(0)	2.42(52)	1.0
Sr/Bi	0.5000(0)	0.5023(55)	0.0000(0)	1.45(37)	0.93/0.07
Bi	0.0000(0)	-0.0093(67)	0.1933(5)	2.35(35)	0.94
Bi	0.5000(0)	0.0111(62)	0.7055(4)	3.00(31)	1.0
Ta	0.0000(0)	0.0017(62)	0.4174(4)	-0.88(19)	1.0
Ta	0.5000(0)	0.0029(72)	0.9101(5)	1.16(35)	1.0
O1	0.0000(0)	0.4501(65)	0.0000(0)	-1.39(36)	1.0
O2	0.5000(0)	-0.0318(81)	0.0000(0)	1.86(37)	0.80
O3	0.0000(0)	0.0428(73)	0.3447(6)	0.92(31)	1.0
O4	0.5000(0)	-0.0678(74)	0.8392(6)	0.795(33)	1.0
O5	0.2402(25)	0.2441(71)	0.2480(4)	0.23(11)	1.0
O6	0.2515(35)	0.2332(69)	0.0829(3)	1.09(20)	1.0
O7	0.7481(31)	0.2423(64)	0.5718(3)	1.52(24)	1.0

Space group : Am2m a=5.5270(6)Å,
b=5.5244(7)Å, c=24.9935(18)Å
R_p=8.77, R_{wp}=11.5, R_e=4.20, R_f=8.42, R_b=10.6, χ^2=7.45

unreasonably large and/or negative thermal parameters. Therefore, the Am2m model was considered to be more plausible than the P4/mmm model of the $Sr_{1.2}Bi_{1.8}Ta_2O_{9-\delta}$.

The I4/mmm and F2mmm models claimed to be the paraelectric structure in the previous literatures showed higher χ^2 values than the P4/mmm, B2cb, and Am2m at both 923 K and 1273 K. The star-marked reflections in the Fig. 3 are absent by the extinction rule in the I4/mmm, while present in the P4/mmm, B2cb, and Am2m structures.

As discussed by Rae *et al.* the major displacive modes of Aurivillius phases $Bi_2O_2A_{n-1}B_nO_{3n+1}$ (n=1~3) are the ferroelectric displacive along a-axis, alternating rotations of octahedral about a-axis, and rotation of octahedron about c-axis. In the B2cb the last mode is precluded. The restoring of the octahedron rotations can accompany the phase transition of PBN at 820 K or the $Sr_{1.2}Bi_{1.8}Ta_2O_9$. These modifications cannot be correctly detected by x-ray diffraction due to the relatively small atomic scattering factor of oxygen compared to the other heavy cations.

4. Conclusion

The PBN showed a phase transition at about 810 K. The crystal structure of PBN was analysed to change from the $A2_1am$ to the B2cb(a, b≒5.52 Å, c≒24.98 Å) at above 820 K by the Rietveld refinement analysis. The Curie temperature Tc of $Sr_{1-x}Bi_{2-x}Ta_2O_9$ decreased with increasing Sr/Bi ratio

Table 3. Summary of the Refinement Results of $Sr_{1.2}Bi_{1.8}Ta_2O_9$ for the Various Structural Models

Space group	χ^2	R_b	R_f	R_{wp}	a	b	c
$A2_1am$	10.5	12.5	9.34	13.4	5.5213(6)	5.5297(7)	24.9908(12)
B2cb	11.4	15.4	12.8	14.1	5.5274(9)	5.5231(10)	24.9884(23)
Am2m	7.91	11.0	8.52	11.8	5.5268(6)	5.5252(7)	24.9951(19)
I4/mmm	13.0	16.1	12.0	14.9	3.9044(3)	3.9044(3)	24.9742(22)
P4/mmm	7.25	10.5	9.27	11.3	5.5231(3)	5.5231(3)	24.9819(17)
Fmmm	13.1	15.2	12.1	15.0	5.5204(-)	5.5273(-)	24.9869(-)

and the phase transition was suppressed in $Sr_{1.2}Bi_{1.8}Ta_2O_9$ down to room temperature. The most reliable refinement result was obtained from the Am2m model in the $Sr_{1.2}Bi_{1.8}Ta_2O_9$. The P4/mmm model showed the lowest 'R' values. But the refined structural thermal parameters showed abnormally large and/or negative thermal parameters.

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