MLF Experimental Report	提出日 Date of Report 1 July 2011
課題番号 Project No. 2009A0004 実験課題名 Title of experiment To understand the multiferroic mechanism of $Pb(Fe_{0.5}Nb_{0.5})O_3$ 実験責任者名 Name of principal investigator Je-Geun Park 所属 Affiliation Department of Physics and Astronomy, Seoul National University	装置責任者 Name of responsible person T . Kamiyama 装置名 Name of Instrument/（BL No.） BL-08 実施日 Date of Experiment 2010. 05. 16 – 0.5 18.

試料、実験方法、利用の結果得られた主なデータ、考察、結論等を、記述して下さい。（適宜、図表添付のこと）
Please report your samples, experimental method and results, discussion and conclusions. Please add figures and tables for better explanation.

1. 試料 Name of sample(s) and chemical formula, or compositions including physical form.

Pb(Fe0.5Nb0.5)O3 powder sample 5g

2. 実験方法及び結果（実験がうまくいかなかった場合、その理由を記述してください。）
Experimental method and results. If you failed to conduct experiment as planned, please describe reasons.

Lead iron niobate $PbFe_{0.5}Nb_{0.5}O_3$(PFN) is an interesting multiferroics compound with T_N~143 K [1] and T_c= 356 and 376 K [2], exhibiting anomalous behavior in the frequency dependence of dielectric constant at T_N [3]. It is also noticeable that it has a very large dielectric constant of about 10000 with potential applications for capacitors and electronic devices.

However, it is still unclear about the room temperature structure. So far, two models have been put forward, R 3 m and C m. And recently Singh *et al*. [4] reported that it forms in the Cm space group with very unusual negative thermal expansion behavior below T_N from their synchrotron experiments. Although the results themselves appear to be interesting, they failed to offer any reasonable explanation for their findings.

In order to understand this negative thermal expansion, in general, and multiferroic mechanism through structural change, in particular, we have carried out high resolution neutron powder diffraction at S-HRPD from 10 to 300 K, with 10 different temperatures.

2. 実験方法及び結果（つづき） Experimental method and results (continued)

As a starting model, we used the Cm structure proposed by Singh *et al.*[4], and subsequently found that although unreported in Ref. 4 it produces unusual charge valences according to our bond-valence-sum analysis (see Table. 1). As comparison, we have tried the R3m space group. As shown in Figure. 1, both models show similar level of agreements with the experimental data although both fail to produce perfect description of the peak profiles. It is noticeable that the R3m model now gives more reasonable values of charge valences as shown in Table. 1. We have then carried the analysis throughout the whole temperature range using the R3m space group. The summary of our refinement results is summarized for three representative temperatures in Table. 1.

Our results show a clear difference from the reported results in Ref. 4. Most important of all, our data did not show any anomalous negative thermal expansion behavior at all. As shown in Fig. 2, all the temperature dependence of both lattice constants and unit cell volume are conventional although the temperature dependence of the unit cell volume seems to deviate from the theoretical predictions of Debye-Gruneissen model. This discrepancy asides, there is nothing unusual about the temperature dependence in stark contrast with the claim of Ref. 4, which is already a important step forward in our work.

Instead, by carefully examining the results we noticed that our refinement gives very large values of thermal motion for Pb, much larger than O. This large value of thermal motion of Pb may explain the discrepancy between our refinement and the experimental results in Fig. 1. We think that this large thermal motion also means some kind of disorder at Pb site. In order to check this possibility, we plan to carry out further experiments using X-ray. It will also be interesting to measure the diffraction patterns above 330 K, at which it is reported to have a structural transition.

[1] A F Garcia-Flores *et al.*, J. Phys.: Condens. Matter 23 015401 (2011)

[2] A. Kania *et al.*, Ferroelectrics, 391, 114-121 (2009)

[3] Y. Yang *et al.*, Phys. Rev. B **70**, 132101 (2004)

[4] S. P. Singh *et al.*, Appl. Phys. Lett. **90**, 242915 (2007)

	Cm 300K	R3m 300K
Num. of paramter	14	13
Rp	5.79	5.71
Rwp	7.20	7.46
Rexp	3.64	3.77
chi2	3.91	3.92
Pb^{2+} Charge	4.206(21)	2.102(3)
Fe^{3+} Charge	6.117(63)	3.060(11)
Nb^{5+} Charge	9.224(96)	4.614(16)
$O1,O2^{2-}$ Charge	-3.852/-4.012	-1.980(6)

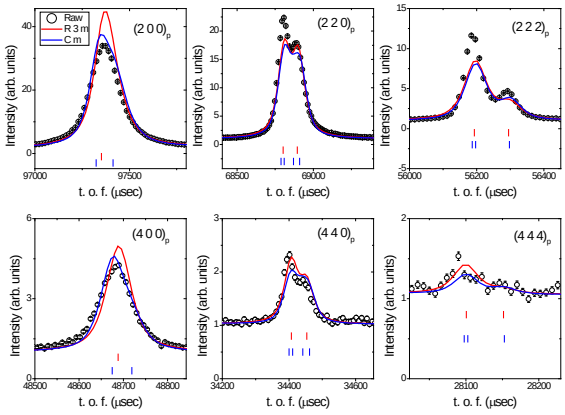

Figure 1. Comparison of Cm and R3m structures for a selection of Bragg peaks..

Table 1. Comparison of both Cm and R3m structures using data taken at 300 K.

2. 実験方法及び結果（つづき） Experimental method and results (continued)

	300 K	150 K	10 K
a (Å)	5.67253(3)	5.66732(3)	5.66491(3)
c (Å)	6.96155(6)	6.96822(6)	6.97068(6)
V ($Å^3$)	193.995(2)	193.824(2)	193.727(2)
Pb 2a (0,0,0)			
x	0	0	0
y	0	0	0
z	0	0	0
Biso(Equiv.)	2.6603	2.1232	1.8620
β11	0.018896(462)	0.017888(370)	0.016389(378)
β22	0.018896(462)	0.017888(370)	0.016389(378)
β33	0.009804(789)	0.003217(330)	0.001686(276)
β12	-0.009448(231)	-0.008939(185)	-0.008184(189)
β13	0	0	0
β23	0	0	0
Fe/Nb 2a (0,0,z)			
x	0	0	0
y	0	0	0
z	0.47934(50)	0.47455(29)	0.47328(28)
Biso	0.229(10)	0.227(12)	0.167(12)
O 4b (x,-x,z)			
x	0.16301(29)	0.16279(23)	0.16235(22)
y	-0.16301(29)	-0.16279(23)	-0.16235(22)
z	0.29451(49)	0.28582(33)	0.28266(33)
Biso	0.668(22)	0.453(14)	0.335(14)

Table 2. Summary of refinement results using R3m space group for three temperatures.

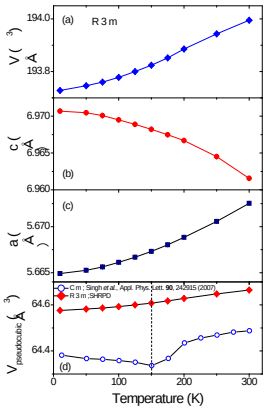

Figure 2. Temperature dependence of Lattice constants and unit cell volume. We also compared our results with the data reported in Ref. 4.