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Low temperature magnetic studies on $PbFe_{0.5}Nb_{0.5}O_3$ multiferroic

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ABSTRACT

$PbFe_{0.5}Nb_{0.5}O_3$ (PFN), a well-known $A(B'_{1/2}B''_{1/2})O_3$ type multiferroic, was successfully synthesized in single phase by a single step solid state reaction method. The single phase PFN was characterized through XRD, microstructure through SEM, and magnetic studies were carried out through a temperature dependent vibrating sample magnetometer (VSM) and neutron diffraction (ND) measurements. PFN exhibits a cusp at around 150 K in the temperature dependent magnetic susceptibility corresponding to the Néel temperature (T_{N1}) and another peak around 10 K (T_{N2}) corresponding to spin-glass like transition. In the temperature dependent ND studies, a magnetic Bragg peak appears at $Q=1.35$ Å^{-1} (where $Q=4\pi\sin\theta/\lambda$, is called the scattering vector) below T_N (150 K) implying antiferromagnetic (AFM) ordering in the system. On the basis of Rietveld analysis of the ND data at $T=2$ K, the magnetic structure of PFN could be explained by a G-type antiferromagnetic structure.

1. Introduction

$PbFe_{0.5}Nb_{0.5}O_3$ (PFN) is a well-known $A(B'_{1/2}B''_{1/2})O_3$ type multiferroic [1], which has received considerable attention in recent years due to its potential for technological applications. An intense research is underway on PFN due to the unique magneto-electric (magnetic moment and electric dipole moment) coupling behavior, which makes it very appealing from both the theoretical and the technological points of view [1–3].

Lead based multiferroic systems, $PbFe_{0.5}Nb_{0.5}O_3$ (PFN), $PbFe_{0.5}Ta_{0.5}O_3$ (PFT), and $PbFe_{2/3}W_{1/3}O_3$ (PFW), have attracted attention because in these compounds, the magnetic Fe^{3+} (d^n) ions and nonmagnetic (d^0) Nb^{5+}, Ta^{5+}, and W^{6+} ions share the B^I and B^{II} sites of the $A(B^IB^{II})O_3$ perovskite, respectively. The (d^5) ions in the BO_6 octahedral site lead to ferromagnetic order while the (d^0) ions at the same lattice position provide ferroelectric (FE) order [3–5].

$PbFe_{0.5}Nb_{0.5}O_3$ (PFN) was considered to be ferroelectrically and antiferromagnetically ordered below its Néel temperature ($T_N\sim145$ K) [6]. PFN undergoes transition from paraelectric (PE) to ferroelectric (FE) at Curie temperature of around 385 K [7,8], due to the structural transition from centro-symmetric (cubic) to non-centrosymmetric (monoclinic), which is an indication of existence of ferroelectricity in the system. In addition to ferroelectric and antiferromagnetic features, the magnetoelectric (ME) coupling observed below T_N offers significant interest in PFN for potential applications as well as for fundamental understanding. Though there are few reports on the study of nuclear and magnetic structures in PFN, due to the various different structures reported at different temperature intervals, no conclusive structure model was achieved yet. Lampis et al. [2] through neutron diffraction and X-ray diffraction studies reported that PFN has monoclinic structure (Cm) below 250 K, cubic (Pm3m) above 376 K and in between it is in tetragonal (P4mm) symmetry. Ivanov et al. [9] through neutron diffraction showed rhombohedral structure with R3c symmetry at both 300 K and 10 K. Bonny et al. [10] from their X-ray and synchrotron data on single crystals suggested a small monoclinic distortion away from rhombohedral symmetry at room temperatures, together with the existence of an intermediate phase of tetragonal symmetry at temperature of 355 K and the cubic structure above the ferroelectric Curie point of 376 K. Hence, the structure of PFN is under debate and is a subject of study. Rotaru et al. [11] have studied the magnetic ground state of single crystal PFN with μSR spectroscopy and neutron scattering studies on $Q_N=(0.5, 0.5, \text{and } 0.5)$ magnetic Bragg peak at 5.2 K; however there are no detailed studies on chemical and magnetic structures though Howes et al. [12] have done some magnetic and magneto-electric studies of PFN on PFN single crystals. They have reported only the temperature dependent variation of integrated intensity of magnetic reflection (0.5, 0.5, and 0.5) and the T_N. Their magnetic susceptibility measurements done only up to 250 K show only one anomaly at $T=170$ K corresponding to the T_N.

Single phase formation of the Pb based compounds largely depends upon the synthesis conditions; however, due to magnetic anisotropy or inhomogeneity or competing interactions, a system

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might exhibit phase coexistence. While synthesizing Pb based (such as PFN) compounds, one must consider the loss of lead oxide and has to be careful about the reactivity of each component in the material. That is, two factors play a major role in the synthesis of any lead based complex perovskite viz., (a) high volatility of PbO as its evaporation temperature is around 750 °C and (b) high reactivity of B″ oxide over B′ with PbO in $Pb(B'B'')O_3$. The PbO evaporation results in vacancies at Pb and O sites and also leads to the formation of secondary phases in case of deficiency of lead [13,14]. This result in the formation of $A_2B_2O_7$ is based on pyrochlore phases as parasite secondary phase during the synthesis of PFN. The formation of secondary phases has considerable effect on the physical properties of the resultant material (PFN).

Therefore it is necessary to optimize the synthesis parameters and conditions to produce single phase PFN for better understanding of structure and properties for possible practical applications. In this paper we report the synthesis method for producing single phased PFN by optimizing the synthesis conditions using the modified solid state reaction route. We also present and discuss the low temperature ND and magnetization data of PFN for its structural and magnetic properties.

2. Experimental details

2.1. Single-step method (modified solid state reaction method)

AR grades of $Pb(NO_3)_2$, Fe_2O_3 and Nb_2O_5 were taken in stoichiometric quantities and ground in a pestle and a mortar using ethanol medium for 2 h. The resultant powder was subjected to calcination at 650 °C for 2 h. After calcination, the powder was ground again with polyvinyl alcohol (PVA) as binder. The dried powder was then cold-pressed uni-axially at 50 kN pressure and then sintered at 1050 °C for 1 h in a closed Pb rich environment to minimize the PbO evaporation [15,16].

The sintered samples were characterized by X-ray diffraction (XRD; *Phillips* 1070) using Cu-Kα radiation (wavelength, λ= 1.5406 Å), for phase purity. Scanning Electron Microscopy (SEM) was used for the study of microstructure and morphology. Magnetization studies were carried out on a vibrating sample magnetometer (VSM) attached to a physical property measurement system (*Quantum Design* PPMS). Neutron diffraction measurements were carried out on a focusing crystal based powder diffractometer, available at UGC–DAE CSR beam line in Dhruva reactor, BARC. Neutrons at a wavelength of 1.48 Å were used for the present study. Rietveld analysis was carried out on powder XRD and ND data using the *Fullprof* suite programs for crystallographic as well as for magnetic structural studies [17].

3. Results and discussions

3.1. Phase and microstructural analysis

Fig. 1 shows XRD pattern of PFN obtained by a single step solid state reaction method. Using the structural model given in Ref. [3], the XRD data was refined using the Rietveld method. The analysis confirms that the sample prepared, using the method described above, is in single phase and has no secondary parasite phases like $Pb_2Nb_2O_7$ or $Pb_2Nb_4O_{13}$.

The low temperature calcination and sintering proved to be effective in achieving the single phase without secondary phases. Good agreement is found between observed and calculated profiles for XRD data. The SEM micrograph of PFN is shown in Fig. 2. From the micrograph, average grain size is found to be 2 μm.

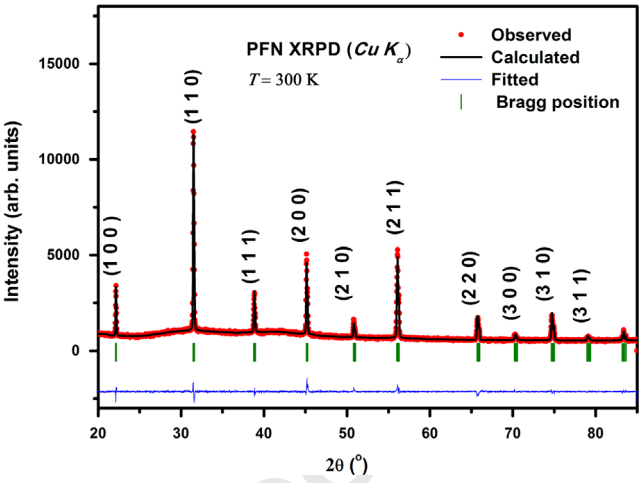

Fig. 1. Room temperature X-ray powder diffraction data of PFN. The Rietveld analysis was carried out assuming a monoclinic structure.

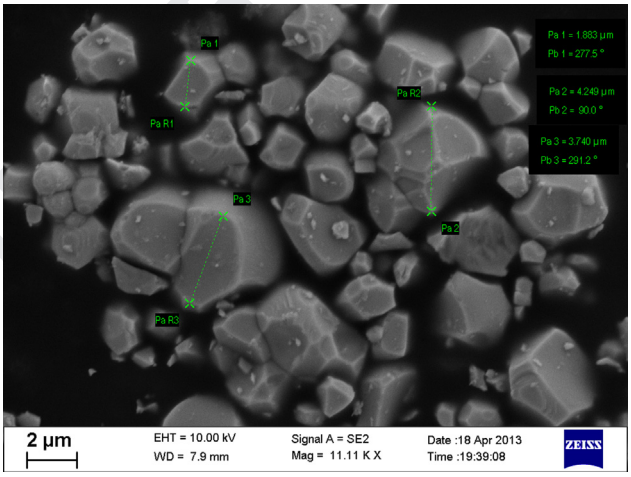

Fig. 2. SEM micrograph of PFN sintered at 1150 °C for 1 h exhibiting surface microstructure.

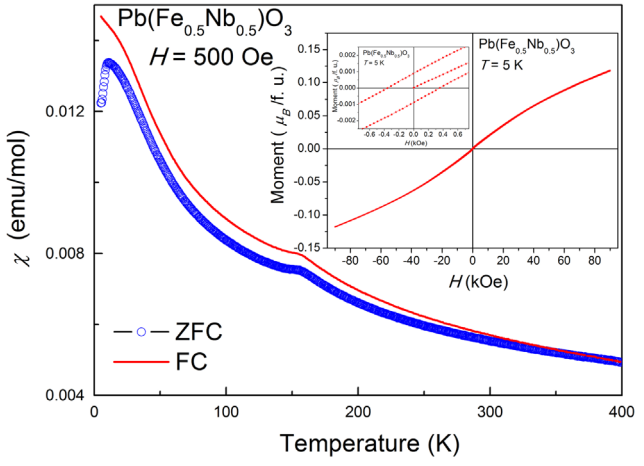

Fig. 3. Temperature dependent molar susceptibility (ZFC and FC) for PFN at 500 Oe. Inset shows the *M*–*H* curve at 5 K for PFN.

3.2. Magnetization studies

Magnetic susceptibility (χ=M/H) of PFN measured in both zero field cooled (ZFC) and field cooled (FC) in a field of 500 Oe is shown in Fig. 3. The ZFC curve increases monotonically on