Low-temperature neutron diffraction and magnetic studies on the magnetoelectric multiferroic $\text{Pb}(\text{Fe}_{0.534}\text{Nb}_{0.4}\text{W}_{0.066})\text{O}_3$

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Received: 21 March 2017

Accepted: 30 May 2017

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ABSTRACT

We report detailed low-temperature magnetic and neutron diffraction studies on $0.8 \text{ Pb}(\text{Fe}_{0.5}\text{Nb}_{0.5})\text{O}_3$ – $0.2 \text{ Pb}(\text{Fe}_{0.67}\text{W}_{0.33})\text{O}_3$ which is written as $\text{Pb}(\text{Fe}_{0.534}\text{Nb}_{0.4}\text{W}_{0.066})\text{O}_3$ (PFWN) in the general form. Magnetic susceptibility measurement data show that PFN exhibits antiferromagnetic to paramagnetic transition (T_N) around 155 K (Matteppanavar et al. in J Mater Sci 50:4980–4993. doi:10.1007/s10853-015-9046-5, 2015). In the present solid solution, the magnetic susceptibility (χ) shows Néel temperature enhanced up to around 187 K. Temperature-dependent neutron diffraction studies well support the tuning up of T_N from 155 to 187 K. On decreasing the temperature, for $T < T_N$ ($T_N = 187$ K), an extra peak grows at scattering vector $Q = 1.35 \text{ \AA}^{-1}$, which indicates the onset of antiferromagnetic ordering. The observed magnetic structure is G-type antiferromagnetic with the propagation vector, $k = [0.25, 0.5, 0.5]$. The refined *monoclinic* lattice parameters (a , b and c), angle (β), unit cell volume, derivative of unit cell volume, magnetic moments and integrated intensity of magnetic peak (111) show anomaly around the T_N , which is a manifestation of spin–lattice coupling. Also, the lattice parameters (a , b and c) and unit cell volume exhibit negative thermal expansion below T_N and a large thermal expansion above T_N .

Introduction

The simultaneous display of ferroelectric and magnetic (ferromagnetic or antiferromagnetic) ordering in single-phase material increased intense research activities since last few years [1]. Understanding the

fundamental coupling mechanism between electric and magnetic order parameters has been the hottest topic of research in the present scenario [2, 3]. Recently, $A(B'B'')\text{O}_3$ -type complex perovskite-structured oxides with different solid solutions have been reported as room temperature (RT) or near RT

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magnetoelectric multiferroics. Among the complex-structured solid solutions, $\text{Pb}(\text{Fe}_{1/2}\text{Nb}_{1/2})\text{O}_3$ (PFN), $\text{Pb}(\text{Fe}_{2/3}\text{W}_{1/3})\text{O}_3$ (PFW) and $\text{Pb}(\text{Fe}_{1/2}\text{Ta}_{1/2})\text{O}_3$ (PFT) are the promising candidates and exhibit extraordinary dielectric constant with diffuse kind of ferroelectric phase transition [4, 5].

The PFN and PFW are the potential candidates for various applications, such as multilayer ceramic capacitors and memory devices [2, 6]. The PFN, PFW and their solid solutions are the centre of attention in recent years, due to their unique origin of magnetoelectric coupling which has not been understood fully [6–10]. The PFN exhibits ferroelectric phase transition (Curie temperature, T_C) at ~ 350 K, and its antiferromagnetic (AFM) ordering, Néel temperature, is at $T_N \sim 155$ K [1, 2, 11]. For PFW, the Curie temperature (T_C) is at ~ 150 to 200 K and AFM ordering below its Néel temperature of $T_N \sim 350$ K [2, 6]. Also, PFN exhibits unique magnetoelectric coupling around its Néel temperature ($T_N \sim 155$ K). Magnetoelectric coupling of PFN can be bettered by tuning its magnetic-order temperature (T_N) by making a solid solution with PFW; however, the microscopic origin of this influence is still unclear. Recently, few efforts have been made to understand the magnetoelectric coupling in PFN [12–14]. However, due to its T_N being far below room temperature, its practical applications in devices are limited. In this study, we concentrate on enhancing T_N making a solid solution of PFN–PFW for near room temperature magnetoelectric applications [15, 16]. Recently, many researchers have tried to tune the T_N of PFN with various solid solutions, synthesis method and annealing parameters [17]. Gusev et al. succeeded to tune the T_N of PFN, PFT and $\text{Ba}(\text{Fe}_{1/2}\text{Nb}_{1/2})\text{O}_3$ (BFN) through the mechanical activation technique and the T_N increased by 40–50 K in both lead-containing and lead-free ternary perovskites $\text{A}(\text{Fe}_{1/2}\text{B}_{1/2})\text{O}_3$ (A–Pb, Ba; B–Nb, Ta) [17].

Peng et al. [18] reported enhanced Néel temperature at 200 K of epitaxial PFN 200-nm film and ascribed this increase of T_N to the increase in disorder in the Fe and Nb arrangement due to mechanical activation and misfit strain inherent to epitaxial nanofilms [17, 18]. Yuzyuk et al. [19] also mentioned T_N of the PFN (PFN) nanofilm on SrTiO_3 substrate was reported to be about 50 K higher than that in the bulk samples.

In the present work, solid solution of PFWN was synthesized and characterized with temperature and

magnetic field-dependent magnetization measurements and neutron diffraction experiments. Since PFN is highly controversial with regard to the crystallographic structure at room temperature, the structural properties were studied using X-ray, neutron and electron diffraction techniques in the form of XRD, ND and selected area electron diffraction (SAED) from transmission electron microscopy (TEM). The temperature-dependent ND studies compliment the magnetization properties and exhibit spin–lattice coupling around the T_N . In the solid solution of PFN and PFW, the T_N increases from 155 K (for PFN only) to 187 K for (80% PFN + 20% PFW). Such an enhancement of T_N makes this a potential material for magnetoelectric applications and also generates fundamental knowledge for developing new mechanism for tuning magnetic and electrical properties through tailor-made solid solutions.

Experimental

Sample preparation and characterization

The single-step solid-state reaction method optimized for the single phase through low-temperature sintering technique (>850 °C) is implemented to

Figure 1 Room temperature Rietveld refined **a** X-ray diffraction and **b** neutron diffraction data of $\text{Pb}(\text{Fe}_{0.534}\text{Nb}_{0.4}\text{W}_{0.066})\text{O}_3$.

synthesize high-quality polycrystalline PFWN [20, 21]. High-purity (all with stated purity better than 99.9%) starting materials such as PbO, Fe₂O₃, WO₃ and Nb₂O₅ (Sigma–Aldrich) were taken in an appropriate stoichiometry. The detailed synthesis method and optimization of single phase was explained elsewhere [1, 20, 21].

Structural properties of polycrystalline PFWN were studied using X-ray diffraction (Phillips 1070 model, CuK α radiation; $\lambda = 1.5406$ Å). The vibrating sample magnetometer (VSM) attached to a 9 T physical property measurement system (Quantum

Design PPMS) at UGC-DAE-CSR, Mumbai Centre, was used to study the magnetic properties. The neutron diffraction (ND) experiments were carried out at Dhruva reactor, Trombay, India, using a PSD-based powder diffractometer, PD3 [20] using neutrons at a wavelength of 1.48 Å. The particle size and morphology of the powders were studied using the transmission electron microscopy (TEM) Model JEM-2010, JEOL, Japan. Powder diffraction data, both X-ray and neutron, were refined by Rietveld refinement method using the *Fullprof* suite programs [21].

Figure 2 SAED pattern and TEM image of highly sintered Pb(Fe_{0.534}Nb_{0.4}W_{0.066})O₃ powder.

Figure 3 Temperature-dependent ZFC and FC studies of Pb(Fe_{0.534}Nb_{0.4}W_{0.066})O₃.

Figure 4 Inverse susceptibility with temperature at 20 kOe (recorded in FC mode) and linear fitted Curie–Weiss law of Pb(Fe_{0.534}Nb_{0.4}W_{0.066})O₃ and inset shows derivative of inverse susceptibility.

Results and discussion

Structure using X-ray and neutron diffraction

Synthesis of single-phase lead-based perovskite compounds such as PFN or PFW through the solid-state reaction is always endangered by the formation of secondary pyrochlore or other phases such as $\text{Pb}_2\text{Nb}_2\text{O}_7$, Pb_2WO_4 and $\text{PbFe}_{12}\text{O}_{19}$ due to low boiling

point of lead oxide [22–24]. The presence of $\text{PbFe}_{12}\text{O}_{19}$ admixtures was supposed as a possible reason of room temperature magnetic hysteresis loops observed for some PFN- and PFT-based solid solutions [17, 22–24]. To overcome this problem, samples were prepared using the single-step method in a Pb-rich environment, reported in detail elsewhere [1, 13, 14].

To understand the modification of the structure of PFN with substitution of PFW, structural studies were carried out using X-ray, neutron diffraction and electron diffraction (SAED). Figure 1a shows the Rietveld refined RT XRD pattern of PFWN. The crystal structure of PFWN shows *monoclinic* structure (space group Cm) and it is similar to the PFN structure reported by Matteppanavar et al., Ivanov et al., Kleeman et al. and Singh et al. [1, 6, 8, 9].

Figure 1b shows the neutron diffraction pattern refined with the *monoclinic* structure (space group Cm). The PFWN structure is consistent with the previously reported structure of $\text{Pb}(\text{Fe}_{1/2}\text{Nb}_{1/2})\text{O}_3$ (PFN) [1, 9, 25, 26]. The refined lattice parameters $a = 5.6664$ (5) Å, $b = 5.6563$ (3) Å, $c = 4.0122$ (2) Å and $\beta = 89.9988^\circ(1)$ are near to the reported values of PFN [1]. Figure 2 shows the TEM micrographs of PFWN showing crystalline and irregular-shaped (non-spherical) particles. The average particle size from TEM studies was found to be around 100 nm. The d -values computed from the XRD and the

Figure 5 Isothermal magnetization (M) data of $\text{Pb}(\text{Fe}_{0.534}\text{Nb}_{0.4}\text{W}_{0.066})\text{O}_3$ at temperatures from 300 to 5 K above and below the T_N . The *inset* shows the zoomed view of M – H loops from 300 to 5 K.

Figure 6 $\text{Pb}(\text{Fe}_{0.534}\text{Nb}_{0.4}\text{W}_{0.066})\text{O}_3$ neutron diffraction patterns recorded at different temperatures across the T_N to show the evolution of the magnetic peak around the Q value of 18.36° .

selected area electron diffraction (SAED) (Fig. 2) patterns match well with the standard d -values of PFN with *monoclinic* structure with Cm space group.

Magnetic studies

The zero field-cooled (ZFC) and field-cooled (FC) magnetic susceptibility (χ) data of PFWN measured under a field of 500 Oe are shown in Fig. 3. The ZFC curve increases on decreasing temperature from 400 K and displays a clear visible hump around 187 K (T_{N1}), indicating the transition from antiferromagnetic to paramagnetic ordering. This is due to the magnetic interactions (T_{N1}) through $\text{Fe}^{3+}\text{--O--Fe}^{3+}$ superexchange paths, which is similar to the mechanism observed in case of PFN, PFW and other Pb-based multiferroics [1, 9]. The 20% substitution of PFW in PFN has increased the Néel temperature from 155 to 187 K. Another hump was observed around 10 K (T_{N2}) in ZFC, not seen in FC, and is due to the spin glassy nature (T_g) of magnetic moments as T approaches 5 K. Also noticed was that there is small bifurcation in ZFC and FC curves below 187 K (i.e. T_N), which indicates existence of magnetic anisotropy well below T_N . The bifurcation of ZFC–FC and hump in ZFC below 10 K, similar to $\text{Pb}(\text{Fe}_{0.5}\text{Nb}_{0.5})\text{O}_3$ (PFN) [1], may be due to the local clustering of the spins or anti/ferromagnetic domain growth [27–29]. Also, the magnetic origin for this 10 K hump is not understood clearly. Kumar et al., and Laguta et al., have mentioned the contribution of many different parameters for this low-temperature magnetic order [30, 31]. ^{93}Nb NMR studies have shown the occurrence of Fe-rich–Nb-poor region as well as Fe-poor–Nb-rich region in PFN [31–34]. Inverse susceptibility (χ^{-1}) also shows similar anomalies at 187 K and around 10 K (Fig. 4). The Curie–Weiss law was used to estimate the paramagnetic Curie temperature (θ_p) and the effective Bohr magneton number (μ_{eff}) from the linear fitting

$$\chi = \frac{C}{T - \theta_p}$$

where C is Curie constant, θ_p is paramagnetic Curie temperature. Laguta et al. reported for PFN that to estimate the magnetic moment per Fe^{3+} , extrapolate the derivative $d(1/\chi_{\text{FC}})/dT$ towards higher temperatures (from 389 to 500 K), where it approaches a constant value [Fig. 4 (inset curve)] [35]. The values of θ_p and μ_{eff} obtained using that approach is

–185.09 K and $3.82 \mu_B/\text{f.u.}$, respectively. The negative sign of θ_p shows predominant antiferromagnetic correlations in PFWN.

The isothermal magnetization data measured at different temperatures are shown in Fig. 5. The 200 K data show very small opening with coercive field of 2.1 Oe. However, the 5 K hysteresis loop shows clear opening of the loop with enhanced coercive field (135.0 Oe) and the remnant magnetization ($2.5382 \times 10^{-4} \mu_B/\text{f. u.}$), suggesting the presence of a possible canting in the coupled magnetic moments.

Figure 7 Observed (I_{obs}) (circles) and calculated (I_{cal}) (line) difference profile = $I_{\text{obs}} - I_{\text{cal}}$ (blue line) and Bragg peak positions (vertical green line) neutron diffraction patterns of $\text{Pb}(\text{Fe}_{0.534}\text{Nb}_{0.4}\text{W}_{0.066})\text{O}_3$ at different temperatures. Highlighted region shows the origin of AFM ordering (T_N) at 18.36° ($Q = 1.35 \text{ \AA}^{-1}$).

Similar results were reported for PFN by Mathepanavar et al. and Laguta et al. [1, 35], where the considerable remnant magnetization observed at around 5 K decreases with increase in temperature.

Temperature-dependent neutron diffraction studies

Figure 6 shows the temperature-dependent ND raw data of PFWN in the temperature range 2–300 K, showing the structural evolution across the Néel temperature (180 K). It can be seen from the figure that, with decrease in temperature from 300 K, an additional peak starts to grow below 180 K at scattering vector, $Q = 1.35 \text{ \AA}^{-1}$ (18.36° in 2θ) ($^\circ$), which

corresponds to a paramagnetic to antiferromagnetic transition. The additional magnetic Bragg peak below 180 K was indexed with a propagation vector $k = (0.125, 0.5, 0.5)$ corresponding to space group Cm. This magnetic transition at 180 K clearly indicates PFWN shows enhanced Néel temperature compared to that of PFN. Recently, low-temperature neutron diffraction studies on PFN with the magnetic transition around 155 K were reported [1]. After formation of the solid solution of PFN with PFW (20%), the magnetic Néel temperature was increased. All the raw data were analysed by using Rietveld technique (Fig. 7).

The obtained lattice parameters, cell volume, β (monoclinic angle), derivative of cell volume,

Figure 8 Schematic evolution of the **a** lattice parameters **b** β -angle ($^\circ$) **c** cell volume (left side) and derivative of cell volume (right side) and **d** magnetic moment (left side) and integrated intensity of (111) peak (right side) as a function of temperature of $\text{Pb}(\text{Fe}_{0.534}\text{Nb}_{0.4}\text{W}_{0.066})\text{O}_3$.

Figure 9 G-type magnetic structure, indicating a monoclinic unit cell with doubled axes of $\text{Pb}(\text{Fe}_{0.534}\text{Nb}_{0.4}\text{W}_{0.066})\text{O}_3$. Here the arrows indicate the moment and direction of the magnetic ion, that is, the Fe spin.

magnetic moments of Fe and integrated intensity of magnetic (111) peak are plotted as function of temperature to understand the spin–lattice coupling (Fig. 8a). The monoclinic lattice parameters (a , b and c) show anomalies around 180 K, which is close to the magnetic transition temperature (T_N). Figure 8b shows with the increase in temperature from 2 to 150 K, monoclinic angle (β) increases sharply and after that it drops down and again increases. Recently, Raevski et al. [36] observed similar anomaly for PFT monoclinic angle (β). Slight negative thermal expansion behaviour is observed below T_N and above T_N there is a sudden expansion. This thermal expansion behaviour was similar to that of PFN as reported by Mattepanavar et al. and Singh et al. [1, 9]. The observed anomaly of lattice parameters across T_N is an indication of direct spin–lattice coupling in PFWN multiferroic. The unit cell volume and derivative of unit cell volume (Fig. 8c) show large anomaly around the T_N and this also indicates the existence of magnetoelastic coupling. Figure 8d shows the magnetic moments obtained from the refinement of ND data and the integrated intensity of (111) magnetic peak.

The PFWN shows the G-type antiferromagnetic structure (Fig. 9) similar to that of PFN [1, 9]. The magnetic moment for the Fe cations at 5 K is $1.606 \mu_B$, which is smaller than that of Fe^{3+} ($\mu_{\text{eff}} = 2\sqrt{S(S+1)} = 5.9 \mu_B$). This large difference in magnetic moment is due to the simple antiferromagnetic model used and also may be due to the disordered nature of $\text{Fe}^{3+}\text{--Nb}^{5+}\text{--W}^{6+}$ at B sites. This is similar to the behaviour of magnetic moments of Fe in other Pb-based systems [1, 37–40].

Conclusion

In the present work, PFWN multiferroic was synthesized through the single-step solid-state reaction method at relatively lower calcination and sintering temperatures. From the room temperature XRD, ND and SAED data, it confirms that PFWN is in the *monoclinic* structure with Cm space group. Interestingly, PFWN structure was not changed even after formation of the solid solution of PFN with PFW (20%), it remains *monoclinic* structure only. Temperature-dependent magnetization ZFC–FC susceptibility, inverse FC susceptibility, M–H loops and ND studies clearly showed the enhanced magnetic Néel temperature in PFWN with respect to PFN. Our present study thus provides convincing explanation for the enhanced magnetic ordering in PFN by the solid solution of 20% of PFW. The PFWN system also exhibit spin–lattice coupling and classifying it is a potential multiferroic material.

Acknowledgements

The authors (SM and BA) are grateful for the support from UGC-DAE-CSR, Mumbai, for providing experimental facilities and financial support through the project CRS-M-159 and 200. Also, the authors are thankful to the DST-FIST for providing XRD facilities at the Department of Physics, Bangalore University, Bangalore. Authors thank Prof. S M Shivaprasad, ICMS & CPMU JNCASR Bangalore, for providing TEM facility.

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