



## Impedance spectroscopy, electronic structure and X-ray photoelectron spectroscopy studies of $\text{Pb}(\text{Fe}_{1/2}\text{Nb}_{1/2})\text{O}_3$

Chandrabhas Bharti<sup>a</sup>, Alo Dutta<sup>b,\*</sup>, Santiranjana Shannigrahi<sup>c</sup>, S.N. Choudhary<sup>a</sup>, R.K. Thapa<sup>d</sup>, T.P. Sinha<sup>b</sup>

<sup>a</sup> University Department of Physics, T. M. Bhagalpur University, Bhagalpur 812007, India

<sup>b</sup> Department of Physics, Bose Institute, 93/1, Acharya Prafulla Chandra Road, Kolkata 700009, India

<sup>c</sup> Institute of Materials Research and Engineering (IMRE), 3 Research Link, Singapore 117602, Singapore

<sup>d</sup> Department of Physics, Pachhunga University College, Mizoram University, Aizawl 796001, India

### ARTICLE INFO

#### Article history:

Received 1 August 2008

Received in revised form

14 November 2008

Accepted 3 December 2008

Available online 9 December 2008

#### Keywords:

Ferroelectric ceramics

PFN relaxor

X-ray photoemission spectroscopy

Electronic structure

### ABSTRACT

Impedance spectroscopy is used to study the electrical behaviour of lead iron niobate,  $\text{Pb}(\text{Fe}_{1/2}\text{Nb}_{1/2})\text{O}_3$  (PFN) in the frequency range from 100 Hz to 1 MHz and in the temperature range from 203 to 363 K. The frequency-dependent electrical data are analyzed by impedance and conductivity formalisms. The complex impedance plane plot shows that the relaxation (conduction) mechanism in PFN is purely a bulk effect arising from the semiconductive grains. The relaxation mechanism of the sample in the framework of electric modulus formalism is modelled by Davidson–Cole equation. The scaling behaviour of imaginary electric modulus suggests that the relaxation describes the same mechanism at various temperatures. We have studied the electronic structure of the PFN using X-ray photoemission spectroscopy (XPS). The density of states (DOS) obtained from the first principles full potential linearized augmented plane wave calculation of PFN shows a direct energy gap  $\sim 0.43$  eV. The XPS spectrum is compared with the calculated DOS spectra. It has been observed that the electrical properties of PFN are dominated by the interaction between transition metal and oxygen ions as its valence band consists mainly of the oxygen p-states hybridized with the iron d-states.

© 2008 Elsevier B.V. All rights reserved.

### 1. Introduction

Ferroelectric perovskites have been the subject of extensive studies due to their promising electrical characteristic which has a potential usefulness in fundamental research and technological applications. Investigation of the electrical properties of these materials is desirable to predict their suitability for electronic applications.

Various relaxation processes seem to coexist in complex perovskite ceramics, which contain a number of different energy barriers due to point defects appearing during their fabrication. Therefore, the departure of the response from an ideal Debye model in ceramic samples, resulting from the interaction between dipoles, cannot be disregarded. A method of predicting the relaxation behaviour of a perovskite is through electric modulus theory. The electric modulus spectra, therefore, provide an opportunity to investigate conductivity and its associated relaxation in complex perovskite oxides having general formula  $\text{A}(\text{B}_{1/2}'\text{B}_{1/2}'')\text{O}_3$ .

$\text{Pb}(\text{Fe}_{1/2}\text{Nb}_{1/2})\text{O}_3$  (PFN), is known to be the most intensively investigated 1:1 type relaxor ferroelectric system [1–7]. It is a multiferroic material where the electric and magnetic polarizations are coupled directly or indirectly not only on the macroscopic but apparently also on the local level [8–15]. However, the detail information about the relaxation phenomenon and conductivity process in PFN is still lacking. In this paper, we have tried to explain the relaxation mechanism and conductivity phenomenon of PFN.

The formation of single perovskite phase of PFN has been the subject of debate [10,12,15,16]. Recently, Majumder et al. [12] have also discussed the inability of the formation of single perovskite phase of PFN by using sol–gel method. Although, many methods such as co-precipitation, molten-salt, sol–gel or hydrothermal, hot-pressed, etc. have been introduced from time to time [17–21] to synthesize the single perovskite phase of PFN, the mixed oxide synthetic route which includes (a) two-stage calcinations, (b) using higher purity and finer precursor powders, (c) carrying out repeated calcinations and milling cycles and (d) employing longer heat treatment, reducing the firing temperature and adjusting the cooling rate, reported by Fu and Chen [22], Lejeune and Boilet [23] and Chiu and Desu [24] and later confirmed by Ananta and Thomas [16,21] and Lee et al. [17] has demonstrated the possibility of obtaining single phase PFN powder.

\* Corresponding author. Tel.: +91 33 23031189; fax: +91 33 23506790.  
E-mail address: [alo.dutta@yahoo.com](mailto:alo.dutta@yahoo.com) (A. Dutta).

The electronic structure of the perovskite oxides consisting of 4f and 3d orbitals has been studied widely [25–31]. The electronic structure of niobates attracts attention due to their intense ferroelectric and relaxor properties. The electrical properties of these oxides are dominated by the interaction between the transition metal cation and oxygen anion. Thus, to get proper information about the transport properties, the study of electronic structure of these materials is required.

In the present work, we have performed the electronic structure of PFN by first principles calculation. The electrical properties of PFN are studied by the impedance spectroscopy. The X-ray photoemission spectra (XPS) of this material have been used to get the information about the spectral density function. The density of states (DOS) are obtained by full potential linearized augmented plane wave (FLAPW) method based on density functional theory (DFT) [32] under the generalized gradient approximation (GGA) [33] as implemented in Wien 2k code [34]. The experimental XPS results are compared with the calculated electronic structure.

It is to be noted that the XPS is the method to obtain the information about valence states and environment of ions in a compound. In XPS, the excitation by low energies gives direct access to the band structure of the compounds. The ability of XPS method to distinguish the different oxidation states allows an efficient study of the change of binding state of atoms in chemical compounds and the change of surface chemistry in the materials. Most of such studies are concerned with the core levels.

## 2. Experiment

The polycrystalline sample of PFN is synthesized by Coulombite precursor method using high purity oxides  $\text{Fe}_2\text{O}_3$  (~99.99% pure, Alfa aesar)  $\text{Nb}_2\text{O}_5$  (~99.9% pure, Loba chemie) and  $\text{PbO}$  (~99% pure, Loba chemie) taken in stoichiometric ratio. First, the finely mixed powder of  $\text{Fe}_2\text{O}_3$  and  $\text{Nb}_2\text{O}_5$  is calcined at  $1000^\circ\text{C}$  for 6 h. The calcined powder then grinded and mixed with  $\text{PbO}$  for 6 h. At this stage of mixing 4 wt% of extra  $\text{PbO}$  is taken for compensating the lead loss during calcination and sintering. The finely mixed powder is calcined at  $950^\circ\text{C}$  for 6 h. The calcined powder is regrinded and used to make pellet of diameter 9.87 mm and thickness 1.65 mm using polyvinyl alcohol as binder. The pellet is sintered at  $1000^\circ\text{C}$  for 2 h and then brought to room temperature under controlled cooling. To measure the electrical properties, gold electrodes are formed on both surfaces of sintered disk. The frequency dependence of the capacitance and conductance is measured using an LCR meter in the temperature range from 203 to 363 K and in the frequency range from 100 Hz to 1 MHz. The complex electric modulus  $M^*$  ( $=1/\epsilon^*$ ) and the ac electrical conductivity  $\sigma$  ( $=\omega\epsilon_0\epsilon''$ ) were obtained from the temperature dependence of the real ( $\epsilon'$ ) and imaginary ( $\epsilon''$ ) components of the complex dielectric constant  $\epsilon^*$  ( $=\epsilon' - j\epsilon''$ ).

The X-ray photoemission spectrum of PFN is taken by X-ray photoemission spectroscopy (XPS) (VG ESCALAB 2201-XL Imaging System, England). XPS profiles of the samples were obtained using  $\text{Al-K}_\alpha$  source (1486.6 eV). The C 1s peak was used as the reference standard.

## 3. Results and discussion

### 3.1. Impedance spectroscopy

Fig. 1 shows the complex plane impedance plots for PFN at the temperatures 313 and 343 K. The values of resistance  $R$  and capacitance  $C$  can be obtained by an equivalent circuit of one parallel resistance–capacitance (RC) element. This RC element gives rise to one semicircular arc on the complex plane plot, representing the

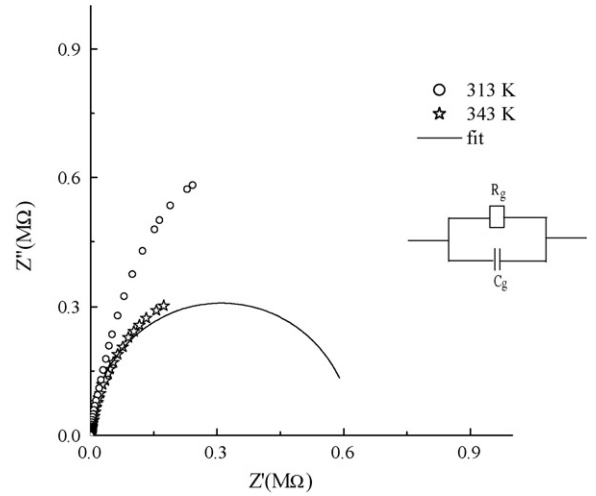


Fig. 1. Complex plane impedance plots at 313 and 343 K (solid line is the fitting to the data by the RC equivalent circuit at 343 K).

grain effect. The equivalent electrical equation for grain is

$$Z^* = Z' - jZ'' = \frac{1}{R_g^{-1} + j\omega C_g}; \quad Z' = \frac{R_g}{1 + (\omega R_g C_g)^2} \quad (1)$$

$$Z'' = R_g \left[ \frac{\omega R_g C_g}{1 + (\omega R_g C_g)^2} \right] \quad (2)$$

where  $C_g$  and  $R_g$  are the grain capacitance and grain resistance, respectively. We have fitted the experimental data using these expressions and the best fit of the data at 343 K is shown by solid line in Fig. 1 with  $R_g = 6.2 \times 10^5 \Omega$  and  $C_g = 1.1 \times 10^{-9} \text{ F}$ .

The angular frequency ( $\omega = 2\pi\nu$ ) dependence of the real part ( $\epsilon'$ ) of dielectric constant, real part ( $\sigma_{ac}$ ) of ac conductivity and imaginary part ( $M''$ ) of electric modulus of PFN are shown in Fig. 2 at various temperatures. The nature of the dielectric permittivity as shown in Fig. 2(a) can be explained by considering that the free dipoles oscillate in an alternating field. At very low frequencies ( $\omega \ll 1/\tau$ ,  $\tau$  = relaxation time), dipoles follow the field and we have  $\epsilon' = \epsilon_s$  (value of the dielectric constant at quasistatic field). With the increase of frequency ( $\omega \ll 1/\tau$ ), dipoles begin to lag behind the field and  $\epsilon'$  slightly decreases. When the applied frequency reaches the characteristic frequency of the material (i.e.  $\omega = 1/\tau$ ), the dielectric constant drops and indicates the relaxation. At very high frequencies ( $\omega \gg 1/\tau$ ), dipoles can no longer follow the field and  $\epsilon' \approx \epsilon_\infty$  (high frequency value of  $\epsilon'$ ). Qualitatively, this behaviour has been observed in Fig. 2(a).

The frequency-dependent conductivity plots of PFN at various temperatures as shown in Fig. 2(b) possess a characteristic dispersion. The frequency spectra in Fig. 2(b) display the typical shape found for electronically conducting system. The conductivity spectra have the tendency to merge at higher frequencies with the increase in temperature. At a particular temperature, the conductivity decreases with decreasing frequency and becomes independent of frequency after certain value. The extrapolation of this part towards lower frequency gives  $\sigma_{dc}$  which is attributed to the long range translational motion of the charge carriers. The basic fact about ac conductivity ( $\sigma_{ac}$ ) in PFN is that  $\sigma_{ac}$  is an increasing function of frequency (any hopping model has this feature) and thus the real part of conductivity spectra can be explained by the power law defined as [35–37]:

$$\sigma_{ac} = \sigma_{dc} \left[ 1 + \left( \frac{\omega}{\omega_H} \right)^n \right] \quad (3)$$

Download English Version:

<https://daneshyari.com/en/article/5396791>

Download Persian Version:

<https://daneshyari.com/article/5396791>

[Daneshyari.com](https://daneshyari.com)