

Magnetism and dielectricity in $\text{Nd}_{1-x}\text{Pr}_x\text{FeO}_{3+\alpha}$

Kiyoshi Horiuchi, Katsuro Oda* and Katsuhisa Nagayama**

Graduate School of Materials Science and Engineering, Shibaura Institute of Technology, Japan

Fax: 81-3-5476-2468, e-mail: m202128@sic.shibaura-it.ac.jp

* Institute of Industrial Science, The University of Tokyo, Japan

Fax: 81-3-5452-6324, e-mail: oda@iis.u-tokyo.ac.jp

** Dept. of Materials Science and Technology, Shibaura Institute of Technology, Japan

Fax: 81-3-5476-2415, e-mail: nagayama@sic.shibaura-it.ac.jp

Magnetic and electric properties of orthoferrite perovskite oxide $\text{Nd}_{1-x}\text{Pr}_x\text{FeO}_{3+\alpha}$ have been investigated. Perovskite oxide have been prepared at different atomic ratios, $x = 0, 0.03, 0.1, 0.3$. A slight decrease in Curie temperature is observed as x increases.

The temperature dependence of magnetization at the low temperature shows a broad transition between 30K and 100K. The transition of sample $x = 0, 0.03$ are attributed to the change in the ferromagnetic to antiferromagnetic order as the temperature is decreased. On the other hand the transition of sample $x = 0.1, 0.3$ are attributed to the change of the antiferromagnetic to ferromagnetic order. In this temperature range, two phase coexistence of ferromagnetic and antiferromagnetic is observed. It is considered that these are closely related to the change in the lattice parameters and the change in the valency by the Pr substitution.

Key words: magnetic phase transitions, two phase coexistence, lattice parameter, valency, dielectricity,

1. INTRODUCTION

The magnetic and structural properties of REFeO_3 (RE : rare earth) have been interestingly studied by many methods. It has been observed that these materials, commonly known as orthoferrites perovskite structure with the space group Pbnm [1], exhibit weak ferromagnetism [2, 3].

Moreover hole doped perovskite-type $\text{RE}_{1/3}\text{AE}_{2/3}\text{FeO}_3$ (AE : alkaline earth metal) is one of systems which undergo a charge ordering transition. In this system, the charge ordering accompanies charge disproportionation of $2\text{Fe}^{4+} \rightarrow \text{Fe}^{3+} + \text{Fe}^{5+}$. A pioneering work with Mössbauer spectroscopy on $\text{La}_{1/3}\text{Sr}_{2/3}\text{FeO}_3$ by Takano et al. revealed that there are two kinds of Fe ions with the ratio of 2:1, and they were attributed to Fe^{3+} and Fe^{5+} [4]. The charge disproportionation of Fe is expected to be occur by substituting the rare earth to realize the non-stoichiometric state.

Valency and dielectric property in Rare-earth-iron mixed oxides have not been studied in detail. Magnetic, crystallographic and dielectric properties of these materials are not only sensitive to the ionic radius and valence state of the constituents, but also to the variation of the metal ion ratio. Furthermore, preparation condition is an important factor. In this study the temperature dependence of magnetization, the lattice parameters by X-ray diffraction, the variation of valence ratio by X ray photoelectron spectroscopy (XPS) and dielectric properties have been investigated for $\text{Nd}_{1-x}\text{Pr}_x\text{FeO}_{3+\alpha}$.

2. EXPERIMENTAL PROCEDURES

$\text{Nd}_{1-x}\text{Pr}_x\text{FeO}_{3+\alpha}$ ($x = 0, 0.03, 0.1, 0.3$) system was prepared by solid-state method. High purity starting

materials, Nd_2O_3 , Pr_6O_{11} and $\alpha\text{-Fe}_2\text{O}_3$ were calcined in oxygen atmosphere at 1553K for 48 h. In the same way, the samples after milled and pressed into pellets (5mm in radius and 1.5mm in thickness) were sintered at 1573K for 24 h. The content of rare earth metals and iron was determined by inductively coupled plasma (ICP) emission spectroscopy. The identification of the phases and the determination of the lattice parameters were carried out by powder X-ray diffraction analysis using $\text{Cu K}\alpha$ radiation by a Rigaku RINT-2000 diffractometer. The lattice parameters were determined by use of silicon powder (Rigaku Standard Reference Powder RSRP-43275G) as an internal standard. Magnetization measurements were carried out with a vibrating sample magnetometer (Model VSM-5SC-5HF, TOEI INDUSTRY CO. LTD) by applying magnetic fields of $-50 - 50$ kOe at the temperature range of 20 K to 800 K. The change of valence for Pr and Fe were obtained by X ray photoelectron spectroscopy (XPS, Quantum 2000, ULVAC-PHI, INC.). Dielectric constant were obtained by 4192A LF impedance analyzer, Hewlett-Packard at 313K-723K for NdFeO_3 . The sample was a disk-shaped capacitor of the radius of 5 mm and the typical thickness of 1.5 mm and a conducting Pt paste was painted.

3. RESULTS AND DISCUSSION

3.1 Magnetization

Curie-temperatures of each sample is 604K ($x = 0$), 600K ($x = 0.03$), 597K ($x = 0.1$), and 577K ($x = 0.3$), respectively. Here, T_c was determined by the temperature where the slope of magnetization takes maximum.

Figure 1 shows the temperature dependence of

magnetization at the low temperature for $Nd_{1-x}Pr_xFeO_{3+\alpha}$. It shows the existence of broad peaks at temperature range of 30-100K. The peak varies with composition. For samples $x=0$ and $x=0.03$, broad convex peaks were observed. It gradually shifts towards higher temperature range with increase of Pr content.

These transitions are attributed to the change in the direction to antiferromagnetic order from ferromagnetic order as the temperature is decreased [5]. For the other samples $x=0.1$ and $x=0.3$, rather sharp concave peaks were observed at 40-50K. This transition is change to the direction to ferromagnetic order from antiferromagnetic order when decreasing the temperature.

These magnetic transitions were reported to occur around liquid-nitrogen temperature for $NdFeO_3$ (perovskite) prepared by a ceramic method [5-7].

Figure 2 (a) and (b) display the field dependence of magnetization at 50K and 100K. In the samples $x=0.1$ and 0.3, coercive forces are small compared with other samples in all temperature ranges (Fig. 2 (a)). Similarly, at 100K, coercive force for $x=0.03$ is small (Fig. 2 (b)). The temperature range where the coercive forces become small agree to the range where the direction to antiferromagnetic order change to ferromagnetic one for $x=0.1$ and $x=0.3$, as can be seen Fig.1. For $x=0$ and $x=0.03$, this temperature range matches to the range where coercive forces become small. The coexistence of the antiferromagnetic and the ferromagnetic regions at the low temperature has already been reported by the magnetic resonance measurement [8,9]. It is presumed that these two phases antiferromagnetic and ferromagnetic coexistence region exist at the transition of 30-100K.

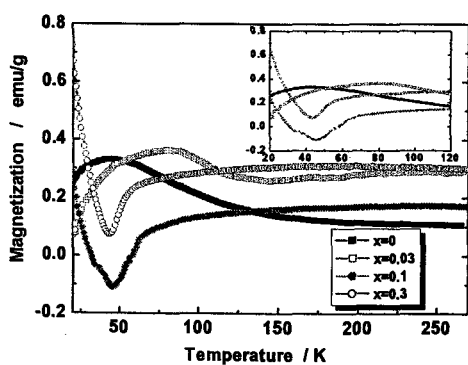


Figure 1 Zero field cooled (ZFC) magnetization as the function of temperature at the field of 0.70Oe for $Nd_{1-x}Pr_xFeO_{3+\alpha}$ ($x=0, 0.03, 0.1, 0.3$)

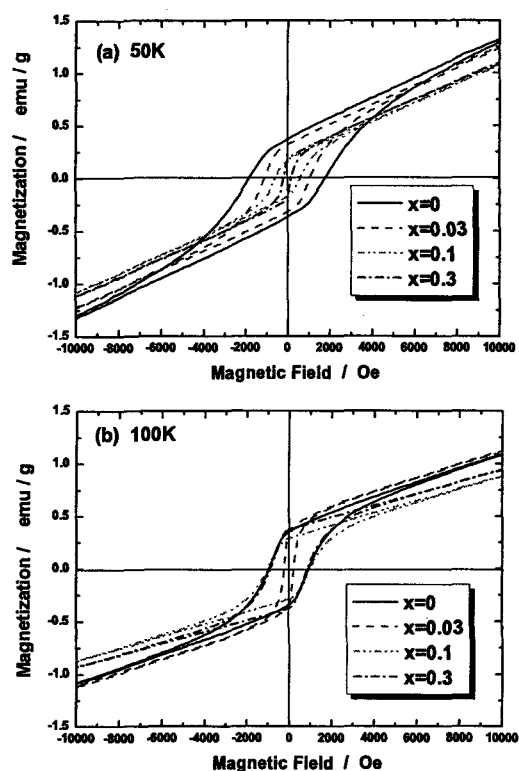


Figure 2 Field dependence of magnetization at 50K (a) and 100K (b) for $Nd_{1-x}Pr_xFeO_{3+\alpha}$ ($x=0, 0.03, 0.1, 0.3$)

3.2 X-ray diffraction

Figure 3 displays the calculated lattice parameters (a, b, and c) of $Nd_{1-x}Pr_xFeO_{3+\alpha}$ from observed X ray powder diffraction data at 20, 50, 80, 100, 200 and 293K. The lattice parameters (a, b and c) decrease with increasing Pr content, which is due to the chemical substitution. Moreover, the lattice parameters increase as temperature is increased.

This is due to the thermal expansion, and each thermal expansion coefficient of unit cell volume ($10.809 \times 10^{-6}/K$ ($x=0$), $12.375 \times 10^{-6}/K$ ($x=0.03$), $10.907 \times 10^{-6}/K$ ($x=0.1$), $9.0511 \times 10^{-6}/K$ ($x=0.3$)) agrees to the general ceramic thermal expansion coefficient of about $5-11 \times 10^{-6}/K$.

A decrease in lattice parameters (particularly a and b) at the vicinity of the liquid-nitrogen temperature range is observed. This temperature range where the lattice parameters decrease agree to the temperature of magnetic transition in Fig. 1. It is expected that once the magnetic transition occurs, the lattice distorts and lattice parameter reduces contrary to thermal expansion. Therefore, magnetic transition is closely related to the change of lattice parameters.

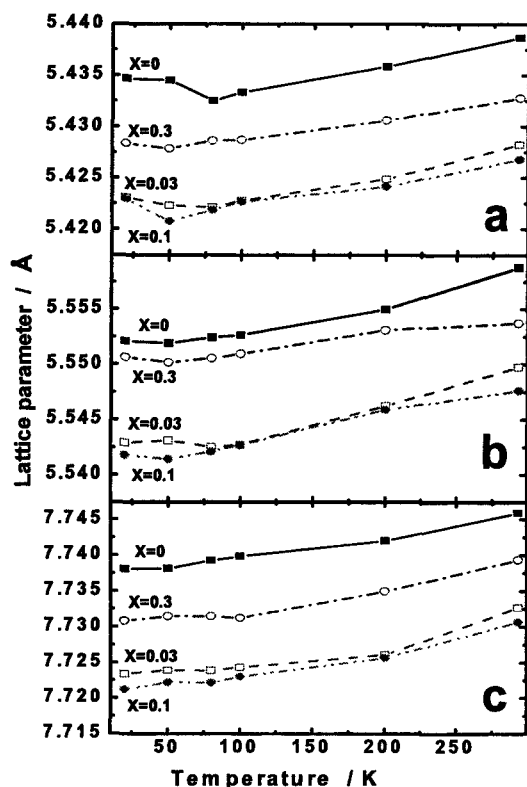


Figure 3 Lattice parameters (a, b, and c) as a function of temperature (20K-293K) T for $Nd_{1-x} Pr_x FeO_{3+\alpha}$ ($x=0, 0.03, 0.1, 0.3$)

3.3 X ray photoelectron spectroscopy

Pr 3d and Fe 2p XPS spectra for $Nd_{1-x} Pr_x FeO_{3+\alpha}$ ($x=0, 0.03, 0.1, 0.3$) are shown in Figure 4 (a:Pr3d) and (b:Fe2p). The background due to inelastic scattering of electrons was calculated and subtracted from the measured spectra using Tougaard formalism. As can be seen Fig.4 (a), the Pr 3d $5/2$ peak shifts to low binding energy side (933.82eV ($x=0.03$), 933.58eV ($x=0.1$), 933.14eV ($x=0.3$)) as the content of Pr increases. Similarly the Fe 2p $3/2$ peak similarly shifts to low binding energy side (710.49eV ($x=0$), 710.72eV ($x=0.03$), 710.84eV ($x=0.1$), 710.40eV ($x=0.3$)) in fig. 4 (b).

Comparison with the spectra reported in literature [9-14] shows that the spectra of Pr 3d $5/2$ of the sample, $x=0.3$ is typically characteristic for Pr^{3+} . For $x=0.03$ and 0.1 the peaks are sifted toward Pr^{4+} than that for $x=0.3$. On the other hand the spectra of Fe 2p $3/2$ of all sample shows characteristic of Fe^{3+} cations. The change in the valence of Fe^{3+} by Pr substitution was not observed.

From these XPS results, as the Pr substitution increases the peak of 3d $5/2$ shifts to higher binding energy region. Therefore the valence of Pr gradually and slightly shifts from Pr^{4+} like to Pr^{3+} like as Pr substitution increase. The lattice parameters of $Nd_{1-x} Pr_x FeO_{3+\alpha}$ decrease ($x=0.03, 0.1$) with increasing Pr content as shown in Fig. 3 (a) and (b), which is due to the chemical substitution of the smaller Pr^{4+} ions (0.85 Å)

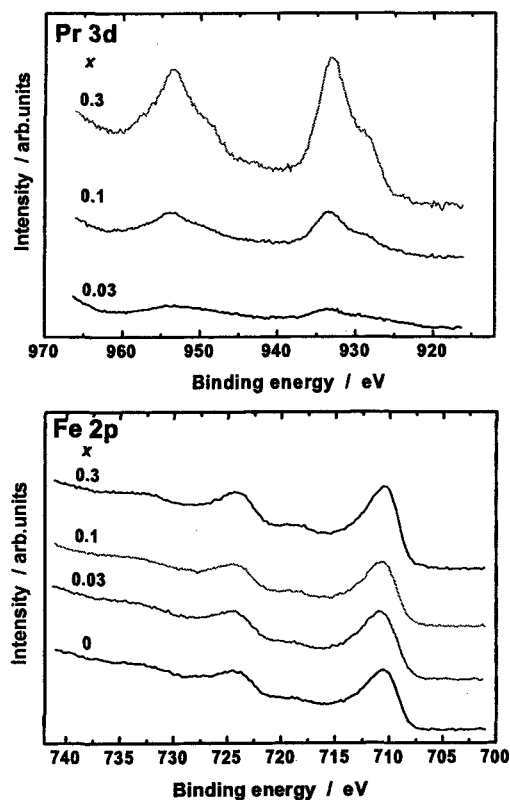


Figure 4 Pr 3d and Fe 2p XPS spectra for $Nd_{1-x} Pr_x FeO_{3+\alpha}$ ($x=0, 0.03, 0.1, 0.3$), (a) Pr3d, (b) Fe2p

into the bigger Nd^{3+} ionic (0.98 Å) sites. In addition, as the amount of Pr substitution increases, lattice parameters increase by the change of valence of Pr from Pr^{4+} (0.85 Å) to Pr^{3+} (0.99 Å). And it thought that the difference of broad convex peak ($x=0.03$) and sharp concave peak ($x=0.3$) is due to amount of Pr^{4+} and Nd^{3+} by Pr substitution.

3.4 Dielectricity

Figure 5 shows the temperature dependence of dielectric constant at the high temperature for $NdFeO_{3+\alpha}$.

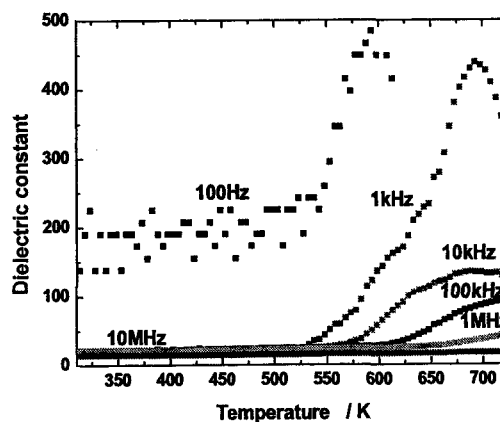


Figure 5 Temperature dependence of dielectric constant for $NdFeO_{3+\alpha}$

It shows that peaks exist which indicates ferroelectric to paraelectric transition. Furthermore, the temperature the peak appears depends on frequency. The temperature the peak appears shifts high temperature range as the frequency increase. This characteristic is typical behavior seen in relaxor ferroelectric. Therefore, $NdFeO_{3+\alpha}$ in this study have the characteristic like relaxor ferroelectric. But dielectric constant is extremely small compared with general ferroelectrics.

4. CONCLUSIONS

The magnetic transition at temperature range of 30-100K is observed for $Nd_{1-x}Pr_xFeO_3$. The transitions for $x=0$ and $x=0.03$ are attributed to the change in the direction to antiferromagnetic order from ferromagnetic order as the temperature is decreased. The transition for samples with higher Pr concentration is due to the change of the direction to order from antiferromagnetic to ferromagnetic order when decreasing the temperature.

The temperature range where the coercive forces become small agree to the range where the direction to antiferromagnetic order change to ferromagnetic order. This is presumed to be due to the coexistence of antiferromagnetic and ferromagnetic regions.

Also a decrease in lattice parameter is observed at the same temperature region.

As Pr substitution increases the valence of characteristic shifts toward Pr^{3+} from Pr^{4+} for the samples $x=0.03$ and 0.1 , and change to typical Pr^{3+} for $x=0.3$. Therefore, the lattice parameters decrease for $x=0.03$ and 0.1 . Furthermore, the amount of Pr substitution reached to $x=0.3$, lattice parameters largely increases. And it thought that the difference of broad convex peak ($x=0.03$) and sharp concave peak ($x=0.3$) attribute to amount of Pr^{4+} and Nd^{3+} by Pr substitution.

The shift of dielectric constant peaks depends on frequency. $NdFeO_{3+\alpha}$ shows the behavior to realize the characteristic of relaxor ferroelectric.

Acknowledgements

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