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# Electric Spontaneous Polarization in $\text{YbFe}_2\text{O}_4$

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We report the observation of the electric spontaneous polarization in  $\text{YbFe}_2\text{O}_4$ , one candidate “electronic ferroelectric,” where ferroelectricity originates from polar charge order. Though we have proposed that in  $\text{LuFe}_2\text{O}_4$  polar charge ordering of iron ions having different valence states gives rise to ferroelectricity, some reports questioned not only the electronic origin but also the existence of the ferroelectricity itself in this system. In response to this, we show direct macroscopic evidence of the existence of the ferroelectricity by clear  $P$ - $E$  hysteresis loop of  $\text{YbFe}_2\text{O}_4$  belonging to the same system as that of  $\text{LuFe}_2\text{O}_4$ . Although further investigations are required about the electronic origin, we report the direct observation of the macroscopic electric polarization.

Much effort has been made in recent years to design materials exhibiting simultaneous ferromagnetic and ferroelectric properties (termed “multiferroics”). One of the routes is to order the ions having different valence states so as to break the inversion symmetry thereby generating microscopic electric spontaneous polarization. This scenario has led to the concept of “electronic ferroelectricity.”<sup>1</sup> If such ion is a transition metal then the ordering of its spins and the induced electric spontaneous polarization may be strongly coupled. Electronic ferroelectricity has indeed been proposed in References 2-4.

Rare earth ion ferrites  $R\text{Fe}_2\text{O}_4$  ( $R = \text{Y, Dy, Ho, Er, Tm, Yb, Lu, Sc, or In}$ ) are the typical example of electronic ferroelectrics. These materials are composed of doubly stacked iron triangular layers ( $W$ -layer) separated by single rare-earth triangular layer.<sup>8</sup> Equal amounts of  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  exist on triangular lattices and form charge orders due to the Coulombic interaction between iron ions.<sup>9,10</sup> It has been proposed that each  $W$ -layer has microscopic electric spontaneous polarization and the in-phase and out-of-phase stacking of the polar  $W$ -layers generate ferroelectric and antiferroelectric charge orderings respectively.<sup>3,11,12</sup> Thus these materials have been discussed as the prototype of ferroelectric materials where ferroelectricity

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originates from the charge ordering of the iron ions. Recently however, several reports questioned the electronic ferroelectricity in this material from permittivity measurements and bond-valence-sum calculation.<sup>13-17</sup> Furthermore, only banana-like  $P$ - $E$  loops were reported for this material.<sup>16,17</sup> Though ferroelectric-like  $P$ - $E$  loops were reported in Mn-doped  $\text{Lu}_2\text{Fe}_{3-x}\text{Mn}_x\text{O}_7$ ,<sup>5</sup> the possibility of ferroelectricity arising from Mn itself has been pointed out.<sup>18</sup> Also the argument was made that large interface effect between the sample and the electrodes was responsible for the electric measurements.<sup>14-16</sup> Thus not only the electronic origin but also the existence of the ferroelectricity itself are questioned in this system.

In this letter, we show clear  $P$ - $E$  hysteresis loop of pure  $R\text{Fe}_2\text{O}_4$  ( $R = \text{Yb}$ ) single crystal. Extrinsic effects are discarded from impedance analysis. The magnitude of the observed electric remanent polarization was  $1 \text{ nC/cm}^2$ , which is much smaller than the calculated value from charge ordering pattern proposed in Ref. 3. This large difference may arise from the competition of ferroelectric and antiferroelectric charge ordering phases.

High quality single crystal of  $\text{YbFe}_2\text{O}_4$  was grown using floating zone melting method from  $\text{Yb}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$  without any pre-thermal treatment to head off the iron and/or oxygen defects, which change the electric properties strongly.<sup>19,20</sup> The mixture of  $\text{CO}_2/\text{CO}$  gas was flown during the melting. The x-ray diffraction experiments are performed with RIGAKU, Rapid-II VariMax. Impedance analysis and  $P$ - $E$  loop measurements were performed along the  $c$ -axis. Gold was selected as electrodes material to enable Ohmic contacts and the measurement of intrinsic electric properties excluding the interface effect.<sup>20</sup> Impedance analysis was performed with Solartron 1260 and Agilent E4980 and led to the choice of the 20 Hz frequency for the  $P$ - $E$  measurements, thereby excluding contributions not originating from the sample. Furthermore, ferroelectric signal was extracted from conductivity and permittivity signals by double wave method (DWM).<sup>22</sup> In this method, we apply voltage of two positive half waves and two negative half waves in place of one period of wave. The responses of the first half waves (primary loop) is the same as the ordinal  $P$ - $E$  loops and contain all components, that is, ferroelectric, conductivity and permittivity components. On the other hand, the response of the second half waves (secondary loop) contain only conductivity and permittivity signals. Therefore only ferroelectric signal is obtained by subtraction of the second response from the first response (subtracted loop). The set-up was the same as that in Ref. 22. The  $P$ - $E$  loop was obtained at 10 K after the sample was field-cooled under an electric field of  $140 \text{ V/cm}$ .

The quality of the crystal and formation of the charge order were confirmed by x-ray diffraction experiments. We have found that the significant iron defects ( $> 10 \%$ ) are found in the sample prepared from  $\text{Yb}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$  in 1:2 ratio although the stoichiometry of this system had been discussed only by amount of oxygen.<sup>20</sup> Almost-stoichiometric sample (no more than 3 % of iron vacancy) shows peaks as spots while off-stoichiometric sample shows helical modulation. Figure 1 shows diffraction signal along  $(2/3 \ 2/3 \ l)$  line at room temperature. The signals were observed as spots, indicating no more than 3 %

of iron vacancy and the charge order takes place in the  $ab$ -plane and along the  $c$ -axis. This pattern is similar to that of  $\text{LuFe}_2\text{O}_4$  rather than that of  $\text{YbFe}_2\text{O}_4$  reported in Ref. 23. As the difference between Yb and Lu is only 0.5% in ionic radius and the thickness of  $W$ -layer, it is no wonder that  $\text{YbFe}_2\text{O}_4$  shows essentially the same charge order as that of  $\text{LuFe}_2\text{O}_4$  as mentioned in Ref. 18. The incommensurate signals are observed around  $(n/3, n/3, \text{integer})$  point along  $(\pm\delta, \pm\delta, 0)$  direction with about 0.05 of  $\delta$  at room temperature. However, this incommensurate reflection signal is unlikely to arise from long-period modulation on the charge order. The origin of the incommensurate modulation is associated with magnetic ordering and  $R$ -ion displacement from wide range  $q$ -space observation, magnetization measurements, x-ray magnetic circular dichroism experiments. The details are discussed in another paper.

In order to detect intrinsic electric remanent polarization in the  $P$ - $E$  loop measurement, impedance analysis was performed. Following Ref. 21, the sample intrinsic component gives rise on a Nyquist plot to a circle connected to the origin. On the other hand, if extrinsic effects occur (such as interface, electret etc... effects), they give rise to a second circle, connected to the intrinsic circle at the opposite end from the origin. That is, the quickest responder to the electric field is the sample intrinsic component, and the extrinsic components respond only at lower frequency. Therefore the  $P$ - $E$  loop measurements carried out at high enough frequency to detect the response of the electronic ferroelectric sample only.

Figure 2 shows Nyquist plots at 200 K (a), 150 K (b) and 100 K (c). The data points measured at 20 Hz are indicated by blue arrow. The data points belong to the part of the curve related to the sample itself. Furthermore, the data point at 20 Hz moves toward the origin with decreasing temperature. This tendency should be kept down to 10 K as the permittivity shows no anomaly below 100 K (see Refs. 24 and 25, for example). So only the sample intrinsic properties are detected at 10 K in the electric measurements carried out at 20 Hz.

Figure 3 shows the  $P$ - $E$  loop obtained with a 20 Hz electric field at 10 K. While the primary loops includes all components, the secondary loops includes only permittivity and conductivity components. Therefore the subtracted  $P$ - $E$  loop surely reflects only intrinsic ferroelectric signal as described above. The  $P$ - $E$  loop traces out clear hysteresis loop. From the square shape of the  $P$ - $E$  loop, the coercive field is measured to be  $\sim 1.2$  kV/cm and the remanent polarization is  $\sim 1$  nC/cm<sup>2</sup>. This hysteresis character in the  $P$ - $E$  loop is a direct evidence of the existence of ferroelectricity in  $\text{YbFe}_2\text{O}_4$ . The ferroelectric transition temperature is estimated to 300-350 K from pyroelectric current measurement which will be reported in another paper.

The magnitude of the observed electric remanent polarization was  $\sim 1$  nC/cm<sup>2</sup>. It is much smaller than 4.5  $\mu\text{C}/\text{cm}^2$ , which is the value calculated from the charge ordering pattern proposed in Ref 3, where the charge ordering pattern only give rise to ferroelectricity. The observed small polarization value may be explained if two kinds of charge ordering phases coexist and

generate ferroelectricity as well as antiferroelectricity as proposed in Refs. 3, 11 and 12. They proposed that ( $n/3$   $n/3$  integer) and ( $n/3$   $n/3$  half integer) reflections are consistent with ferroelectric and antiferroelectric phases where  $n$  is integer. Their charge ordering patterns are shown in left part of Figure 4. Actually, we have observed the coexistence of two kinds of super lattice reflections, ( $n/3$   $n/3$  half integer) and ( $n/3$   $n/3$  integer). The integrated intensity of the latter was 10 to 100 times smaller than that of the former, which is agreement with the smallness of the observed electric remanent polarization.

On the other hand, non-polar charge ordering pattern was proposed recently from bond-valence-sum (BVS) method.<sup>13</sup> In that model, the charge neutral rule is lost in each domain and called “charged  $W$ -layer.” The charge ordering patterns with charged  $W$ -layers are shown in right part in Figure 4. As the ratio of  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$  is 2:1 or 1:2 in each charged  $W$ -layer, the net valence of  $\text{YbFe}_2\text{O}_4$  is  $+1/3$  or  $-1/3$  with charged  $W$ -layer, while it is zero with polar  $W$ -layer. From our diffraction experiments, the in-plane and out-of-plane domain sizes corresponding to the ( $n/3$   $n/3$  integer) signal are estimated to 100 nm and 30 nm respectively from diffraction peak profile. It might be unstable for the charged  $W$ -layer to form such large domains. Our experimental observation suggests the possible  $W$ -layer model is not only the charged  $W$ -layer but also the polar  $W$ -layer.

In conclusion, we observed clear intrinsic ferroelectric  $P$ - $E$  loop in  $\text{YbFe}_2\text{O}_4$ . Though further investigations are required to ascertain the electronic origin of the ferroelectricity, our experimental results prove that  $\text{YbFe}_2\text{O}_4$  is ferroelectric.

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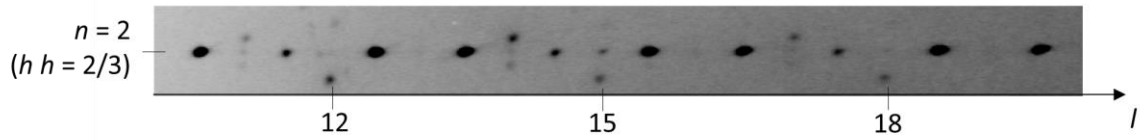


FIG. 1. Superlattice diffraction spots along  $(2/3 \ 2/3 \ l)$  line.

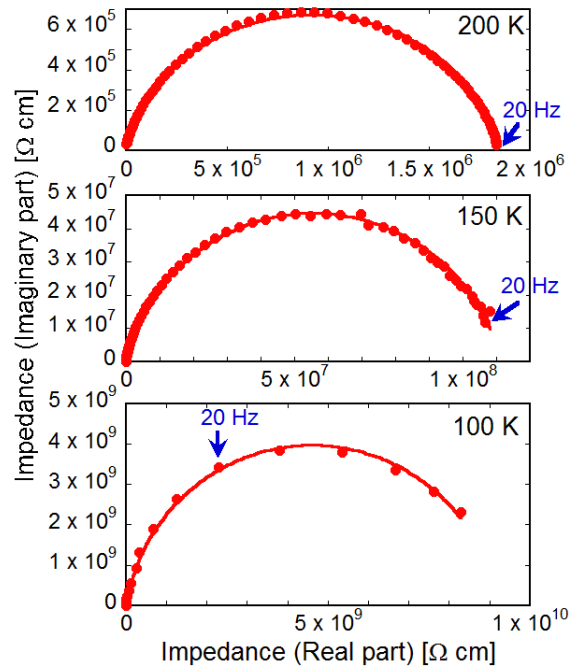


FIG. 2. Nyquist plots at 200 K (a), 150 K (b) and 100 K (c). Blue arrows indicate the data points measured at 20 Hz. Only the response from the sample is observed, free of secondary extrinsic contribution such as electrodes or electrets.

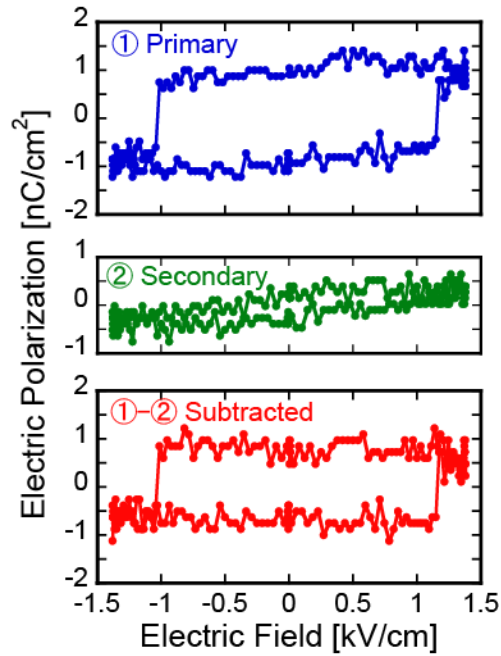


FIG. 3.  $P$ - $E$  loop obtained with a 20 Hz electric field by DWM. As the Primary loop contains all components and Secondary loops contain only extrinsic components such as conductivity, Subtracted loop contains only intrinsic ferroelectric component. Hysteresis character was observed in the Subtracted  $P$ - $E$  loops.

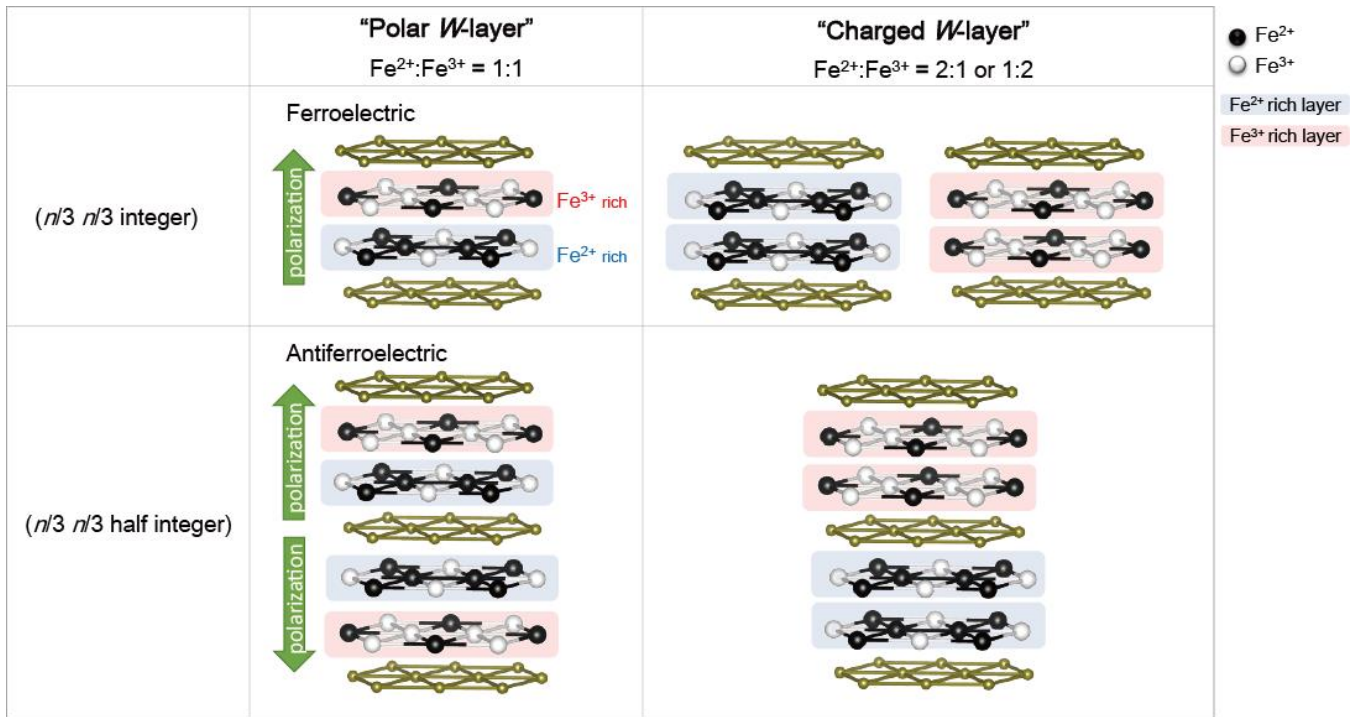


FIG. 4. Schematic view of polar and charged  $W$ -layers generating  $(n/3 \ n/3 \text{ integer})$  and  $(n/3 \ n/3 \text{ half integer})$  diffraction signals, where  $n$  is integer.  $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$  and  $R^{3+}$  are indicated by black, white and yellow balls, respectively. Red and Blue shadowed layers indicate  $\text{Fe}^{3+}$  and  $\text{Fe}^{2+}$  rich layers, *i.e.*, positive and negative charged layers, respectively. Two kinds of charged  $W$ -layers are proposed to satisfy the charge neutral rule.

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