

Two-steps magnetic phase transition in doped $\text{Lu}_{1-x}\text{A}_x\text{FeO}_3$ (A=Ca, Sr)

Michio Takahashi ^a, Hideaki Takano ^{a,1}, Shigeyuki Murayama ^a

^a Department of Materials Science and Engineering, Muroran Institute of Technology, Muroran, Hokkaido 050-8585, Japan

Abstract

The effect of Ca and Sr substitution for Lu on polycrystalline samples of LuFeO_3 has been studied by means of X-ray diffraction, specific heat and magnetization measurements. $\text{Lu}_{1-x}\text{Ca}_x\text{FeO}_3$ for $x \leq 0.2$ and $\text{Lu}_{1-x}\text{Sr}_x\text{FeO}_3$ for $x \leq 0.1$ crystallize into the same orthorhombic structure as LuFeO_3 . The peak of the specific heat caused by antiferromagnetic transition for $\text{Lu}_{0.9}\text{Ca}_{0.1}\text{FeO}_3$ (LCFO) and $\text{Lu}_{0.9}\text{Sr}_{0.1}\text{FeO}_3$ (LSFO) is seen around 590K and 620K, respectively. Temperature dependence of the magnetization for LCFO and LSFO also show rapid changes around 480K and 605K and 525K and 625K, respectively. $M - H$ measurements indicate that LCFO below 480K and LSFO below 525K are ferromagnetic. These typical changes of the specific heat and the magnetization suggest the existence of the two-steps magnetic phase transition in the doped $\text{Lu}_{1-x}\text{A}_x\text{FeO}_3$ (A=Ca, Sr) system.

Key words: phase transition; carrier doping; $\text{Lu}_{1-x}\text{Ca}_x\text{FeO}_3$; $\text{Lu}_{1-x}\text{Sr}_x\text{FeO}_3$

The rare-earth orthoferrites LaFeO_3 and LuFeO_3 have a common atomic arrangement and crystallize with the orthorhombic distortion of the perovskite structure [1]. Recently, charge ordering phenomena and magnetic transition are observed in $\text{La}_{1-x}\text{Sr}_x\text{FeO}_3$ [2]. Though La atom has no $4f$ electron and Lu atom has a closed $4f$ electron shell, both atoms have a common characteristic in the point that there is no effect of $4f$ electron. Then we have investigated magnetic and electric effects of carrier doping in LuFeO_3 . In this paper we reports two-steps magnetic transition in this carrier doping system.

Starting materials used in this study were Fe_2O_3 , Lu_2O_3 , CaCO_3 and SrCO_3 powder. Mechanical milling was carried out to mix the weighed amount of the powder well and to pre-synthesize for 24h in a vibrating frame using a hardened steel vial and a 50mm diameter steel ball. The mixture, in compressed tablet, was sintered in air at 1200°C for 24h. The tablet was mechanically milled for 12h again, and then the powder

was pressed into a disk. Finally this disk was fired again at 1200°C for 24h in an atmosphere and subsequently cooled to room temperature.

The structures of $\text{Lu}_{1-x}\text{A}_x\text{FeO}_3$ (A=Ca, Sr) were characterized by conventional X-ray powder diffraction with Cu $\text{K}\alpha$ radiation and refined by a Rietveld refinement method. Magnetization measurements were carried out between 10K and 750K in a field of 10kOe by SQUID magnetometer. A light-chopped AC calorimeter was used to measure relative changes of specific heat from 300K to 840K.

Figure 1 shows the X-ray diffraction patterns of LuFeO_3 (LFO), CaFeO_3 (CFO), SrFeO_3 (SFO), $\text{Lu}_{0.9}\text{Ca}_{0.1}\text{FeO}_3$ (LCFO) and $\text{Lu}_{0.9}\text{Sr}_{0.1}\text{FeO}_3$ (LSFO), which are nominal composition. The compounds LFO and CFO are orthorhombic with $a = 5.217\text{\AA}$, $b = 5.554\text{\AA}$, $c = 7.565\text{\AA}$ and $a = 5.594\text{\AA}$, $b = 5.431\text{\AA}$, $c = 14.774\text{\AA}$, respectively, and belong to the space group Pnma. The space group of SFO, which is cubic with $a = 3.863\text{\AA}$, are consistent with $\text{Pm}\bar{3}\text{m}$. We obtained single phases of $\text{Lu}_{1-x}\text{Ca}_x\text{FeO}_3$ for $x \leq 0.1$ and $\text{Lu}_{1-x}\text{Sr}_x\text{FeO}_3$ for $x \leq 0.2$, which crystallized into the same orthorhombic structure as LuFeO_3 . The obvious

¹ Corresponding author. Fax : +81-143-45-5625 E-mail : takano@mmm.muroran-it.ac.jp

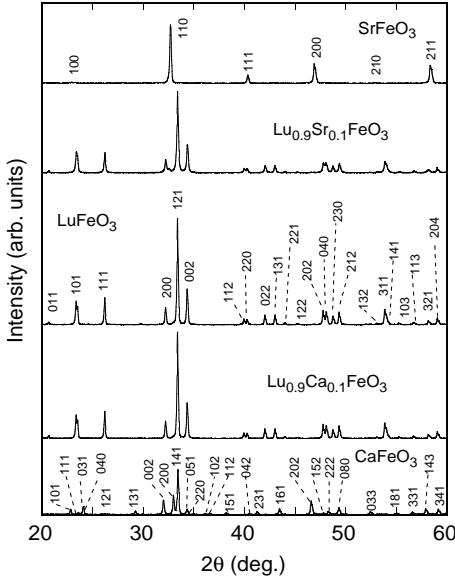


Fig. 1. X-ray-diffraction patterns of $\text{Lu}_{1-x}\text{Ca}_x\text{FeO}_3$ and $\text{Lu}_{1-x}\text{Sr}_x\text{FeO}_3$ recorded with Cu K α radiation.

difference of lattice constants among LFO, LCFO and LSFO could not be confirmed from Rietveld refinement. It seems that a chemical pressure effect is very small in these doped LFO system at least for $x \leq 0.1$.

Figure 2 shows the temperature dependence of magnetization $M(T)$ with decreasing temperature for these five samples. The inset shows $M(T)$ of CFO and SFO. The increase of $M(T)$ upon cooling of LFO, LCFO, LSFO and CFO are seen at about 625K, 605K, 625K and 710K, respectively. In SFO the peak of the magnetization is shown at 630K. (These temperatures are denoted by T_N .) Figure 3 shows the specific heat $C_p(T)$ of these five samples between 300K and 750K. The peak of $C_p(T)$ of all samples is seen around T_N . These anomalies of $M(T)$ and $C_p(T)$ indicates the existence of a magnetic phase transition at T_N . Treves [1] and White [3] reported that LuFeO₃ was a canted antiferromagnets with $T_C = 625\text{K}$. Then we conclude this magnetic phase transition at T_N is a canted antiferromagnetic or an antiferromagnetic transition. Another abrupt increase of $M(T)$ at about 480K and 525K (T_C) upon cooling with no anomaly in $C_p(T)$ is observed for LCFO and LSFO, respectively. Arrott plots obtained from $M - H$ measurements at various temperatures indicate the existence of the spontaneous magnetization only below T_C for LCFO and LSFO. Then we conclude that the secondary increase of $M(T)$ for LCFO and LSFO suggest the existence of a ferromagnetic or a ferrimagnetic transition induced by carrier doping.

In summary we could obtain the single-phase $\text{Lu}_{1-x}\text{A}_x\text{FeO}_3$ ($\text{A}=\text{Ca}, \text{Sr}$) for $x \leq 0.1$, which are similar orthorhombic as LuFeO₃. In $\text{Lu}_{0.9}\text{A}_{0.1}\text{FeO}_3$,

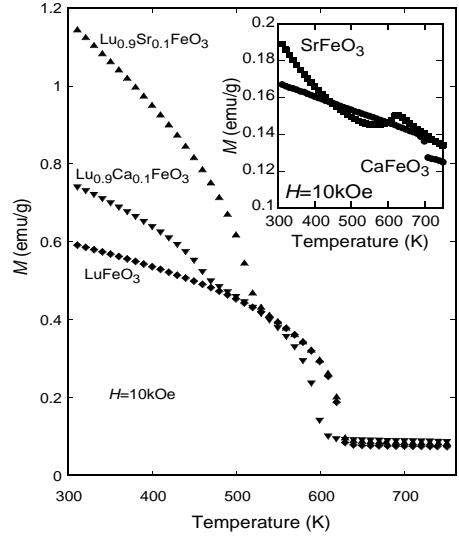


Fig. 2. DC magnetization upon cooling in a 10kOe magnetic field for $\text{Lu}_{1-x}\text{C}_x\text{FeO}_3$ and $\text{Lu}_{1-x}\text{Sr}_x\text{FeO}_3$. The inset shows $M(T)$ curves of CaFeO₃ and SrFeO₃ in a same field.

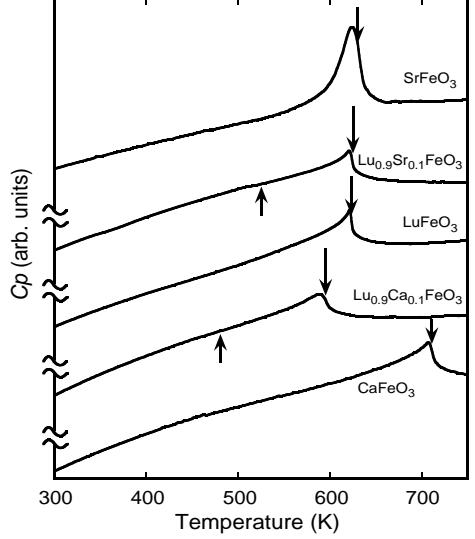


Fig. 3. Specific heat of $\text{Lu}_{1-x}\text{C}_x\text{FeO}_3$ and $\text{Lu}_{1-x}\text{Sr}_x\text{FeO}_3$. The arrow shows the temperature at which $M(T)$ shows rapid increase or peak.

two-steps magnetic phase transition was observed.

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