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Preparation of $Y(Mn_{1-x}Fe_x)O_3$ and Electrical Properties of the Sintered Bodies

Shin Nishiyama*, Isao Asako, Yasuhiko Iwadate, Takeo Hattori

Graduate School of Engineering, Chiba University, Chiba-Shi, Japan
Email: *shin@faculty.chiba-u.jp

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Abstract

$YMnO_3$ and the Fe doped samples were prepared and the lattice constants, electrical conductivities and Seebeck coefficients were measured. The solubility limit of Fe for Mn of $YMnO_3$ was 25 atomic %, the electrical conductivity increased in the range of 350˚C - 700˚C as Fe increased up to 10%, and the doped samples showed larger Seebeck coefficient than undoped samples.

Keywords

Yittrium Manganite, Iron Doping, Solubility Limit, Electrical Conductivity, Seebeck Coefficient

1. Introduction

$YMnO_3$ is known to crystallize in a hexagonal structure [1] and has both ferroelectric and antiferromagnetic properties [2] [3]. The Curry and the Neel temperatures are 914 and 73 K, respectively. And the crystal transition occurred from the space group of $P6_3cm$ to $P6_3/mcm$ 600 to 990 K [4]. Whereas pure $YMnO_3$ is ferroelectric and insulating, it could be a conducting material with carrier doping. Gutierrez *et al*. substitute Ni for Mn site of $YMnO_3$ and observed hopping conduction behavior up to 700˚C [5].

In this study, sintered bodies of pure $YMnO_3$ were prepared and the electrical conductivity and the thermoelectric power up to 800˚C were measured. The effect of Fe-substitution for Mn was also examined.

2. Experimental

Samples are prepared by ordinary solid state reactions. As starting materials, Y_2O_3 (99.99%), MnO_2 (99.5%), Fe_2O_3 (99.9%) were used. Y_2O_3 were pre-calcined at 600˚C for 10 min for elimination of water. Y_2O_3, Mn_2O_3 and Fe_2O_3 were weighed to prepare $Y(Mn_{1-x}Fe_x)O_3$ (x = 0, 0.05, 0.1. 0.2, 0.225, 0.275, 0.3, 0.4) and mixed with a pastle in a mortar of Al_2O_3 for 1 h. For $YMnO_3$, the mixed powders were calcined in crucibles of Al_2O_3 at

*Corresponding author.

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temperatures among 900˚C and 1300˚C for 2 h. The powders calcined were uniaxially pressed and then isostatically pressed into disks of diameters of about 10 mm or rectangular bar of 4 × 3 × 20 mm. Then, the green bodies were placed in an aluminum-oxide crucible and sintered in air at 1300˚C, 1400˚C or 1500˚C for 4 h.

The phases of the mixed and the calcined powders were analyzed by X-ray diffraction (XRD). The lattice constants of $Y(Mn_{1-x}Fe_x)O_3$ powders were calculated from the precisely measured XRD patterns. The densities of the sintered bodies were measured by Archimedes' method.

The samples prepared were evaluated by electrical properties, electrical conductivity and Seebeck coefficients. Electrical conductivity was measured using the four-probe method with an alternating current of 1 kHz. As the electrodes, four platinum wires were attached using silver paste. The resistivity was measured in air at temperatures between room temperature and 900˚C at increasing and decreasing temperature rates of 10˚C/min using an infrared image furnace.

Thermoelectric power was measured using an apparatus having double heaters to prepare specimens temperature differences of approximately 10˚C. The temperature of both ends of the specimens were measured using CA thermocouples, and the thermoelectric voltage was measured via two platinum wires (0.1 mm *φ*) using a computer-controlled mV-meter (HP 3457A). The Seebeck coefficients were determined using a least-squares analysis of five ΔV vs. ΔT data points, where ΔV was the voltage gradient due to the thermoelectric effect of an induced thermal gradient ΔT. The Seebeck coefficient was measured in air at temperature between 100˚C to 800˚C. The absolute (non-relative) values of the Seebeck coefficient were calculated using the measured values and the absolute ones of platinum, which were measured previously by Cusack *et al*. [6].

3. Results and Discussion

XRD patterns of powders prepared by calcination of mixed powders at temperatures between 900˚C to 1200˚C are shown in **Figure 1**. As for the mixture of Y_2O_3 and Mn_2O_3, only Y_2O_3 was clearly detected with XRD. When calcined at 900˚C, besides Y_2O_3, YMn_2O_5 was detected. Calcination at temperatures higher than or equal 1000˚C caused YMn_2O_5 react with residual Y_2O_3 resulting $YMnO_3$ phase. Finally, the single phase of $YMnO_3$ was prepared to heat at 1100˚C for 2 h.

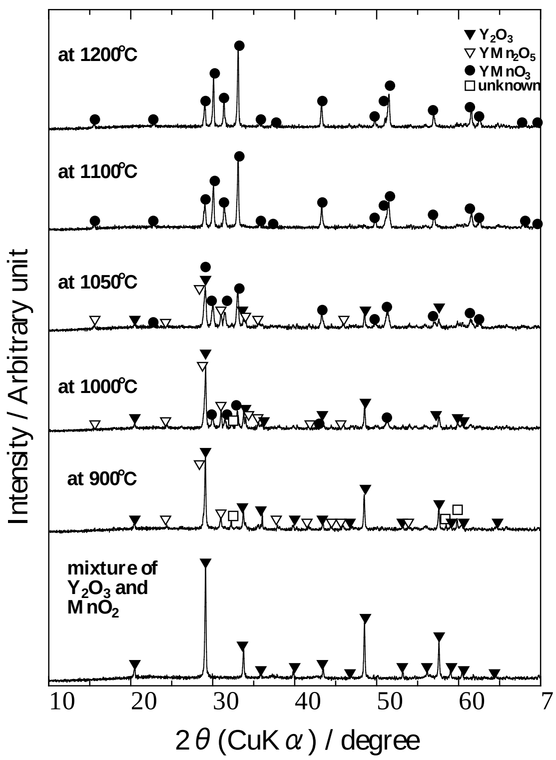

Figure 1. XRD patterns of powders prepared by calcination of mixed powders at temperatures between 900˚C to 1200˚C.

The relative densities of the sintered bodies fired at 1300˚C, 1400˚C or 1500˚C as a function of calcining temperature of powder preparation are shown in **Figure 2**. This result indicates that densification of this material needs temperature up to 1500˚C and the best calcining temperature is 1100˚C - 1200˚C. When fired at 1500˚C, color of the bottom of the crucibles changed slightly brown. This shows that firing over that temperature make Mn volatile and the stoichiometry not maintained. In case sintered up to 1500˚C, all the resulting bodies were single phase of $YMnO_3$.

Figure 3 shows XRD patterns of calcined powders composition of which were $Y(Mn_{1-x}Fe_x)O_3$ (x = 0, 0.1, 0.2, 0.225, 0.25 and 0.3). When x reached 0.3, the peak reflected from $YFeO_3$ phase was detected. **Figure 4** shows the lattice constants *a* and *c* of the Fe doped samples. From these results, the limit of Fe doping for solid solution was said to be 0.25. The relative densities of all of the Fe-doped and single phased samples were around 90%, which showed Fe did not affect to sintering conditions.

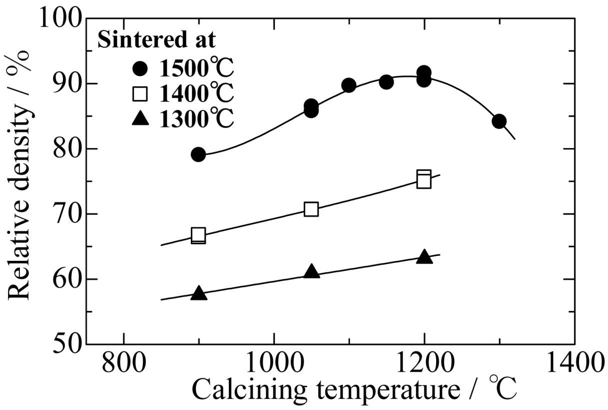

Figure 2. The relative densities of the sintered bodies fired at 1300˚C, 1400˚C or 1500˚C as a function of calcining temperature of powder preparation.

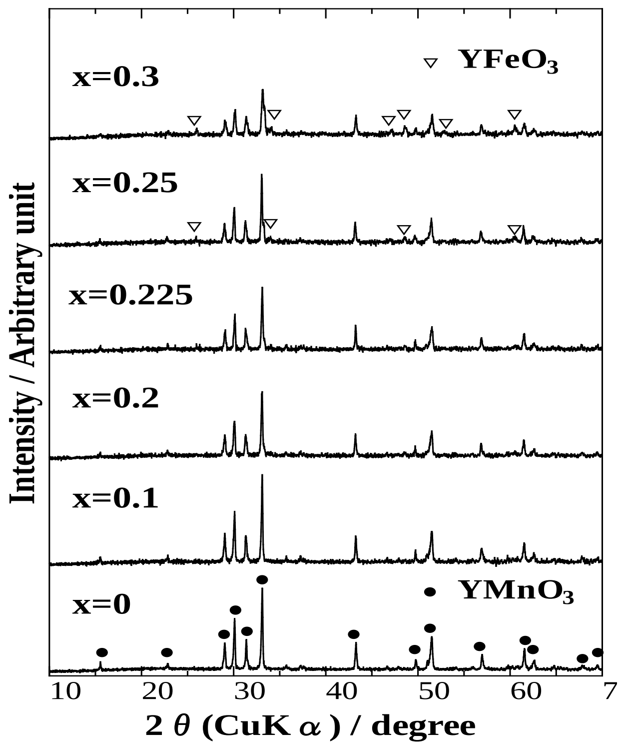

Figure 3. XRD patterns of calcined powders composition of which were $Y(Mn_{1-x}Fe_x)O_3$ (x = 0. 0.1, 0.2, 0.225, 0.25 and 0.3).

The electrical properties of the nominal pure $YMnO_3$ were those of canonical extrinsic semiconductors. **Figure 5** shows electrical conductivity of pure and Fe-doped $YMnO_3$ sintered bodies. The electrical conductivity of the pure $YMnO_3$ increased with increasing temperature. However, the plateau was observed from 450˚C to 750˚C, which seems the region of saturation of carriers. **Figure 6** shows Seebeck coefficients of the samples. From this graph, it is shown that every sample showed positive Seebeck coefficients, so that the carrier of $YMnO_3$ was holes. As temperature increased above 700˚C, the Seebeck coefficients of pure $YMnO_3$ decreased, which

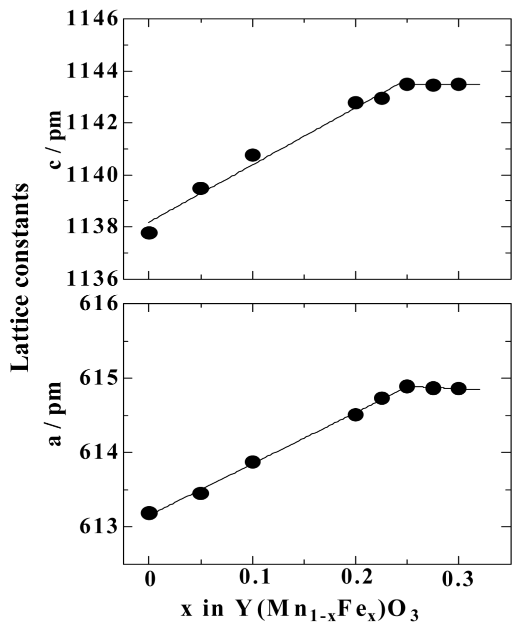

Figure 4. The lattice constants *a* and *c* of pure and Fe-doped $YMnO_3$ samples.

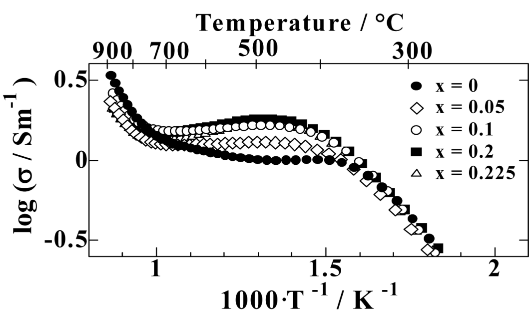

Figure 5. Electrical conductivity (σ) of pure and Fe-doped $YMnO_3$ sintered bodies.

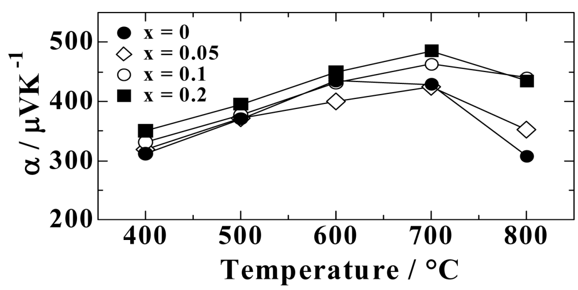

Figure 6. Seebeck coefficients (α) of pure and Fe-doped $YMnO_3$ sintered bodies.

means that the tendency of the intrinsic conduction was detected in this temperature range. This also explained the increase of electrical conductivity above 750˚C.

As Fe substituted for Mn, electrical conductivity around 500˚C increased, and Seebeck coefficient over 700˚C also increased, up to x = 0.1. This showed that Fe substitution made the hole concentration rise and the extrinsic behavior of the conduction became conspicuous. Although Fe can substitute up to x = 0.25, which is concluded from the crystal data, the effect of substitution on the electrical properties was limited up to x = 0.1.

4. Conclusion

The single phase of $YMnO_3$ was prepared to heat at 1100˚C for 2 h and densification of this material needs temperature up to 1500˚C and the best calcining temperature was 1100˚C - 1200˚C. The plateau of the electrical conductivity was observed from 350˚C to 750˚C. The limit of Fe doping for solid solution was said to be 0.25 and the effect of substitution on the electrical properties was limited up to x = 0.1.

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