

THE ELECTRIC AND MAGNETIC PROPERTIES OF THE PEROVSKITE COMPOUND SYSTEM

$\text{Ca}_{1-x}\text{Fe}_x\text{MnO}_3$ ($x = 0; 0.01; 0.03; 0.05$)

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Abstract. The samples of $\text{Ca}_{1-x}\text{Fe}_x\text{MnO}_3$ ($x = 0; 0.01; 0.03; 0.05$) have been made by ceramic and sol-gel technologies. The crystalline structure was analysed by X-ray diffractometer and the Rietveld method was used for determination of the structure parameters. The electric and magnetic properties, including the temperature dependence of resistivity, conducting mechanism and activation energy of conducting process, Seebeck coefficient at room temperature, the temperature dependence of susceptibility ($\chi - T$) have been determined. It is suggested that the studied compounds have the hopping conductivity and are weak ferromagnetic with the magnetic ordering of antiferromagnetic and uncompensated antiferromagnetic (ferrimagnetic).

1. Introduction

In recent years, the perovskite ABO_3 has attracted scientists in the world and in Vietnam because of their interesting physical properties and wide application. One of them is perovskite with high temperature thermoelectric property. It can be used for the power generator because of their high thermal stability, oxidation resistance, and weak-toxicity [1]. Thermoelectric power generation utilizes the Seebeck effect in solid materials to convert thermal energy directly to electrical energy. Three fundamental physical parameters related to the electrical and thermal transport properties of solids, as the electrical conductivity, the Seebeck coefficient and the thermal conductivity, govern the conversion efficiency of thermoelectric devices [2,3,4].

The perovskite compound system $\text{Ca}_{1-x}\text{Fe}_x\text{MnO}_3$ ($x = 0; 0.01; 0.03; 0.05$) have been made in order to investigate the thermoelectric properties (Seebeck coefficient, electrical conductivity, thermal conductivity ...) and the influence of the magnetic ions (Fe, Mn ions) on their electric and magnetic properties.

2. Experiment methods

1 - Preparation of the samples:

CaMnO_3 made by two technology: ceramic and sol-gel [5]

The system of $\text{Ca}_{1-x}\text{Fe}_x\text{MnO}_3$ ($x=0; 0.01; 0.03; 0.05$) have been prepared by ceramic technology.

2 - Study the structure and properties:

2.1 Powder X-ray diffraction:

The phase of the samples were identified by powder X-ray diffraction using X-ray diffractometer D 5005 Bruker - Germany. The structure refinement was carried out by Rietveld analysis of the powder X-ray diffraction data [6]

2.2 Resistivity measurements :

Electrical resistivity of the samples was measured between $30^{\circ}\text{C} \div 400^{\circ}\text{C}$ in air using two contacts technique.

2.3 Magnetic measurements

The measurements of the χ , χ'' , $1/\chi$ vs temperature were performed in the Lab. of Institute for Materials Science -NCST

3. Results and discussion

The structure analysis of the samples by X-ray diffractometer has shown that all samples are single phase (Fig.1).

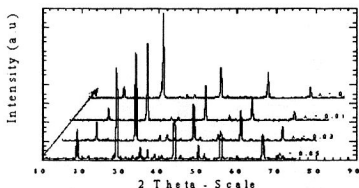


Figure 1. The X-ray diffraction of the samples

The sample 1 is cubic with $a = 3.724 \text{ \AA}$; $\alpha = 90^{\circ}$.

The samples 2,3,4 are orthorhombic with $\alpha \neq 90^{\circ}$

All samples are oxygen deficient $\delta \neq 0$

Table 1. The structure parameters

Samples	$\delta(0)$	$a(\text{\AA})$	$\alpha(^{\circ})$	Ca - O(\AA)	Mn - O(\AA)
1	0.23	3.724	90.00	2.633	1.862
2	0.22	3.725	90.05	2.634	1.863
3	0.21	3.725	90.10	2.634	1.863
4	0.20	3.726	90.15	2.635	1.863

Fe^{3+} ions are smaller than Ca^{2+} ($r \text{Fe}^{3+} = 0.67 \text{ \AA}$; $r \text{Ca}^{2+} = 1.04 \text{ \AA}$), when some Ca^{2+} is substituted by Fe^{3+} ions, the lattice constant is almost not change, but with the appearance of the mixed valence state $\text{Mn}^{3+}/\text{Mn}^{4+}$ and weak Jahn-Teller distortion, the

cubic structure transfers to orthorhombic with $\alpha \neq 90^\circ$. It was the mixed valence state that leads to change the conducting behavior, as well as the magnetic ordering and magnetic interaction in the samples.

Fig.2 shown the temperature dependence of resistivity of the samples. They are like the semiconductor. The resistivity decreased with increasing of temperature. From room temperature to around 500 K, the plot $\log \rho$ vs T^{-1} is linear (Fig.3) and the activation energy of the conducting process is provided in the Table 2.

The mechanism of the conducting process is hopping of electrons between $Mn^{+3}-Mn^{+4}$ [2]. When substituting some Ca^{+2} by Fe^{+3} ions the resistivity of samples is increased with increasing of Fe ions content and the activation energy is increased too (Tab.2). The Fe ions do not take part in the conducting process. It was suggested that there are only Fe^{+3} ions when substituting for Ca^{+2} [5] and the resistivity is increased because of the scattering of charge carriers [2,7] on the strong magnetic impurity

Table 2. The activation energy (E) of the system $Ca_{1-x}Fe_xMnO_3$

Samples	E(eV)
x=0	0.63
x=0.01	0.92
x=0.03	1.08
x=0.05	1.17

The Seebeck coefficients of the samples measured in the Lab. of the Solid State Department, Faculty of Physics, college of Sciences, at room temperature have shown in the Table 3.

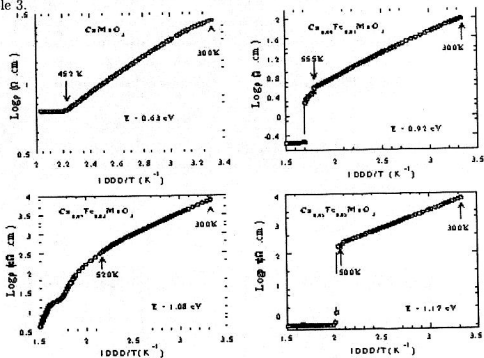


Fig 2. The plots of $\text{Log} \rho$ vs temperature

Especially, when $x = 0.05$ the sample is p-type semiconductor ($S > 0$) while with $x = 0; 0.01; 0.03$ the samples are n - type one ($S < 0$)

Table. 3 Seebeck coefficient (S) at room temperature of the system $\text{Ca}_{1-x}\text{Fe}_x\text{MnO}_3$

Samples	$S(\mu\text{V}/\text{K})$	Type
$x=0$	-280	n-type
$x=0.01$	-360	n-type
$x=0.03$	-55	n-type
* $x=0.05$	+360	*p-type

The Fig.4 shown the plot of Seebeck coefficient vs temperature up to 1000°C of the sample CaMnO_3 made by ceramic method in Vietnam, was measured in the Lab. of JAIST, Japan. The maximum value of S at 500°C is around $-265 \mu\text{V}/\text{K}$. It is comparably high in comparison with the results of the other authors in Japan[10,11].

As mentioned in our work [5], the magnetic ions Fe^{+3} and Mn^{+3} - Mn^{+4} present in the samples. The magnetic ordering and interaction between them decided the magnetic properties of the samples. Fig. 4 and Fig. 5 pointed out the plots of χ , $1/\chi$ vs temperature

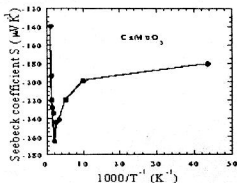


Fig. 3 The temperature dependence of Seebeck coefficient (from room temperature up to 1000°C) of CaMnO_3 measured in JAIST.

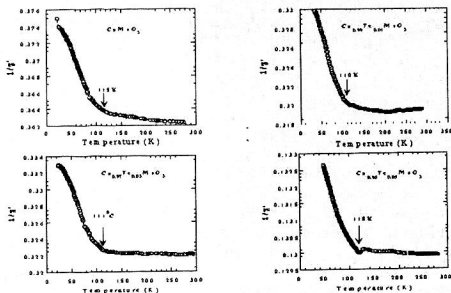


Fig. 4. The temperature dependence of $1/\chi$

It is suggested that the interaction between the magnetic ions in the samples is superexchange and the interaction between Fe^{+3} - Fe^{+3} that is in the center of the cubic (substituting for Ca^{+2}) is antiferromagnetic while the interaction between Mn^{+3} - Mn^{+4} that is in octahedral site is uncompensated antiferromagnetic ($\text{Mn}^{+4} = 3 \mu\text{B}$; $\text{Mn}^{+3} = 4 \mu\text{B}$). It resulted in the weak ferromagnetic property of the samples.

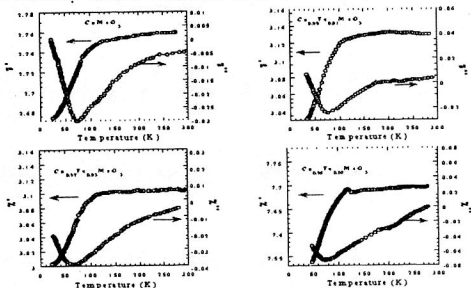


Fig.5. The temperature dependence of χ' and χ'' .

4. Conclusions

- The samples of system $\text{Ca}_{1-x}\text{Fe}_x\text{MnO}_3$ ($x=0; 0.01; 0.03; 0.05$) are the magnetic semiconductor with hopping electron conducting mechanism.
- The samples have the rather high Seebeck coefficient at room and high temperature.
- The samples are weak ferromagnetic with the co-existence of two magnetic orderings that are antiferromagnetic and uncompensated antiferromagnetic like ferrimagnetic.

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