THE ELECTRIC PROPERTY OF THE PEROVSKITE COMPOUND $Ca_{1-X}Nd_XMnO_3$

Hoang Van Hai, Nguyen Van Du, Dang Le Minh

Department of Physics, College of Science, VNU

Abstract: The perovskite compounds $Ca_{1-x}Nd_xMnO_3$ (x=0; 0.1; 0.3; 0.5; 0.7; 0.9; 0.95) have been made by the ceramic technology. The crystal structure has been determined and the Rietveld refinement method has been used for the calculation of the structure parameters. The samples have semiconducting behaviour at all temperatures and depending on their composition they can be the n-type or p-type seminconductor.

1. Introduction

Ideal perovskite compound $CaMnO_3$ with the cubic structure is the isolator and antiferromagnetic. Preparing by ceramic method, it must be sintered at high temperature in the air, its composition became non-stochiometry of $CaMnO_{3-\delta}$ and the mix-valence state appeared, it called the seft-doping phenomenon. If a part of Ca is substituted by ion having valence higher than +2, a respective part of Mn^{+4} transfers to Mn^{+3} , the electric and magnetic properties of the compound is changed [1]

In this work, the compounds $Ca_{1-x}Nd_xMnO_3$ (x=0; 0.1; 0.3; 0.5; 0.7; 0.9: 0.95) have been prepared and the influence of the composition and the structure on the electric property was investigated.

2. Experiment

The samples were prepared using the ceramic technique. The materials are $CaCO_3$ (99%) Nd_2O_3 (99.9%) $MnCO_3$ (99.9%). The samples with the rectangular form were sintered at 1300°C for 10hs in air. The phase of the samples were indentified by X-ray powder diffraction. The electric resistivity was measured by two electrods technique in the temperature range of 10K-500K.

3. Results and discussion

The structure refinement was carried out by Rietveld analysis of X-ray powder diffraction data and the structure parameters have shown in the Tab.1. With increasing of Neodium content (x), the Mn^{+3} ions having the radius higher than one of Mn^{+4} are increased and it leads to the increasing of lattice constant, volume and distance of Mn-O [2,3].

Table 1. The structure parameters

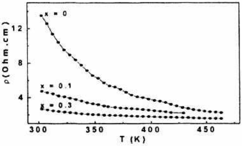
	Samples	*Structure*	a(Å)	b (Å)	c(Å)	V(Å)	*Mn-O distance*	*Mn-O-Mn angle*
1	$CaMnO_3$	*Orthorhombic*	5.259	5.264	7.458	206.5	1.876	165.8
2	$Ca_{0.9}Nd_{0.1}MnO_3$	*Orthorhombic*	5.295	5.294	7.480	209.7	1.893	159.2
3	$Ca_{0.7}Nd_{0.3}MnO_3$	*Orthorhombic*	5.332	5.334	7.547	214.7	1.888	167.0
4	$Ca_{0.5}Nd_{0.5}MnO_3$	*Tetragonal*	3.800	3.800	7.591	219.0	1.903	169.0
5	$Ca_{0.3}Nd_{0.7}MnO_3$	*Orthorhombic*	5.405	5.443	7.640	224.7	1.917	170.0
6	$Ca_{0.1}Nd_{0.9}MnO_3$	*Orthorhombic*	5.426	5.467	7.667	227.4	1.924	175.8

The results of the electrical resistivity measurements are shown in Fig.1. All samples are semiconductors with a negative temperature coefficient of resistivity. There is the metal-insulator transition in the two samples with x = 0.7; 0.9 at 420K and 430 K respectively. Fig.2 shows the dependence of lnρ vs 1/T of the samples. The activation energy calculated from the linear portion of lnρ vs 1/T and the resistivity has been shown in the Tab.2 .

Table 2. Resistivity ρ (Ωcm) (T_{room}) & Activation energy E (eV)

	Samples	*ρ (Ωcm) at T_{room}*	*E (eV)*
1	$CaMnO_3$	14	0.261
2	$Ca_{0.9}Nd_{0.1}MnO_3$	5	0.135
3	$Ca_{0.7}Nd_{0.3}MnO_3$	3	0.083
4	$Ca_{0.5}Nd_{0.5}MnO_3$	2	0.079
5	$Ca_{0.3}Nd_{0.7}MnO_3$	12	0.215
6	$Ca_{0.1}Nd_{0.9}MnO_3$	18	0.221

In the range of 0≤x≤0.5 the value of ρ (Ωcm) and E (eV) were decreased and increased in the range of 0.5≤x≤0.9. It can be explained by the influence of the ratio Mn^{+3}/Mn^{+4} and the distance Mn-O as well as the angle of Mn-O-Mn.



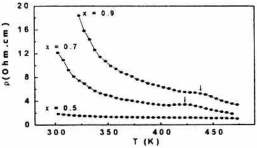


Fig 1. The resistivity temperature dependence curvers of the samples

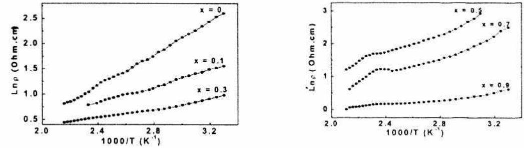


Fig.2. The curvers lnρ - 1000/T of the samples

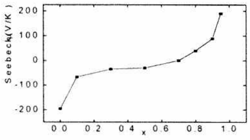


Fig.3. The Seebeck coefficient of the samples at the room temperature

The measuring result of the Seebeck coefficient at room temperature (Fig.3) shown that, depending on Nd concentration, the materials were the semiconductor of n-type (x=0÷0.5) and semiconductor of p-type (x=0.7÷0.95)

4. Conclusion

The samples of $Ca_{1-x}Nd_xMnO_3$ (x=0; 0.1; 0.3; 0.7; 0.9) are the orthorhombic perovskite type structure . The sample $Ca_{0.5}Nd_{0.5}MnO_3$ is tetragonal. With increasing of Nd content the resistivity of the sample has a minimum at x=0.5. At high temperature, the metal-insulator transistion occurs in the composition range of $0.7 \leq x \leq 0.9$, it is like the case of [3,4]. Depending on Nd concentration, the materials were the semiconductor of n-type (x=0÷0.5) or semiconductor of p-type (x=0.7÷0.95).

References

1. Dang Le Minh, Bach Thanh Cong, Hoang Nam Nhat, Phung Quoc Thanh Structure and Magnetic property of the compound $Ca_{1-x}Nd_xMnO_3$ (x=0; 0.1 ; 0.9) & $Ca_{0.9}Nd_{0.1}Mn_{1-y}Fe_yO_3$ (y=0.1; 0.3) National Conference on *The Solid State Physics, Nui Coc - Thai Nguyen-Vietnam* from 5-7/11/2003.

2. H. Taguchi and M.Shimada Metal-Insulator Transistion in the System ($Ca_{1-x}La_x$) $MnO_{2.97}$ ($0.05 \leq x \leq 0.4$), *Jounal of solid state chemistry* **63**(1986), 290-294.

3. T.Kobayashi, H. Takizawa, T.Endo, T.Sato and M.Shimada. Metal-Insulator Transition and Themoelectric Properties in the System $(R_{1-x}Ca_x)MnO_{3-\delta}$ (R: Tb, Ho, Y) *Journal of solid state chemistry,* **92**(1991), 116-129.

4. H.Taguchi, M.Nagao and M.Shimada Mechanism of Metal-Insulator Transistion in Systems $(Ln_{1-x}Ca_x)$ $MnO_{3-\delta}$ (Ln: La,Nd, and Gd) and $(Nd_{0.1}Ca_{0.9-y}Sr_y)MnO_{2.97}$. *Jounal of solid state chemistry*, **97**(1992), 476-480.