STUDY OF STRUCTURE AND ELECTRIC PROPERTY OF PEROVSKITES $Ca_{0.85}Pr_{0.15}Mn_{1-x}Ru_xO_3$

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Abstract. We study the perovskite system of composition $Ca_{0.85}Pr_{0.15}Mn_{1-x}Ru_xO_3$ where x = 0.00, 0.03, 0.05 and 0.07 which were prepared by standard ceramic technique. The determination of structures by X-Ray diffraction and Rietveld method showed orthorhombic structures in Pbnm space group with slight distortion. The dependence of resistance on temperature was measured for T from 100 to 500K and the SEM imaging has been involved to identify the particle typology. The effect of the grain boundaries (boundary length, area and space gap) on conductivity of the samples was analyzed by fractal technique and the obtained results show very good correspondence between the two in all studied samples.

1. Introduction

From the branch of the original compound $CaMnO_3$ many doping manganates have been prepared including those doped by ruthenium where the significantly drop of resistivity in the low temperature region and simultaneously induced ferromagnetism of the doped compounds have been reported. For the better understanding of the conduction mechanism in these compounds, the deeper look inside the interplay between the microstructure and the electric properties would be greatly needed. In this paper we are specifically concerned with the boundary effects on the conductivity of the slightly doped ruthenium manganates of the compositions $Ca_{0.85}Pr_{0.15}Mn_{1-x}Ru_xO_3$ (x = 0.00, 0.03, 0.05, 0.07). Their structures were investigated by mean of the X-Ray and SEM method; then the resistance dependence on temperature and frequency was measured. The interdependence between the boundary and the electric properties was studied using the fractal method

2. Experiment

The samples were prepared using the ceramic technique. Powders of $CaCO_3$, $MnCO_3$ (all of 99.9% purity) were weighed in the desired proportions and milled for 10hrs. They were presintered at 1000^{0}C for 10hrs in air. For measuring the resistance the powder was compressed into the rectangular bars of (2 x 2 x 15) mm^3 and then sintered at 1300^{0}C for 10hrs in air.

The phase of the samples were indentified by X-ray powder diffraction with settings: step angle 0.001^0. The structure parameters, including atomic positions, isotropic thermal motions and site occupation factors were then calculated by Rietveld method using WinMProf software [3]. The single crystal size distribution was analyzed by fourier technique with another software, WinFit [4]. The electric resistance was measured by a standard two electrods technique in the temperature range from 100 to 500K. The typology of surfaces was studied by SEM where images with different magnification. This set of images was used in the analysis of the boundary effects on conductivity by fractal technique as discribed in Section 4.

3. Results of measurements

Figure 1 shows the diffraction patterns for all samples; these typical perovskite patterns show good single phase state and the overlapping of dots and lines illustrates the good profile fitting results from the Rietveld analysis.

In Table 1 we list the cell constants, volumes and the important bonding lengths and angles. For all samples the structures exist in the orthorhombic space group Pbnm In general, the unit cell constants and volume increased with Ru content, but this change was mere as the substitution was altered only slightly. There were also the observable increases in the Ca-O and Mn-O distances; the change was seen in the angles Mn-O-Mn too. Table 2 gives the atomic coordinations within the unit cell, their isotropic thermal motion factors (B_{ISO}) and their site occupation factors (s.o.f.) - corresponding to the stoichiometry of compounds. During the refinement of the sum of the s.o.f.s for Mn and Ru was fixed at 1, the s.o.f.s for Ca nad Pr were fixed at 0.85 and 0.15 and the s.o.f.s for the oxygens were refined. A mere deficit was seen in the oxygens s.o.f.s. Concerning the thermal motions, they were largest for the oxygens and smallest for the Mn/Ru; these values, having unit in $Å^2$, are quite good and reasonable.

The model typology shows the statistical image of the physical

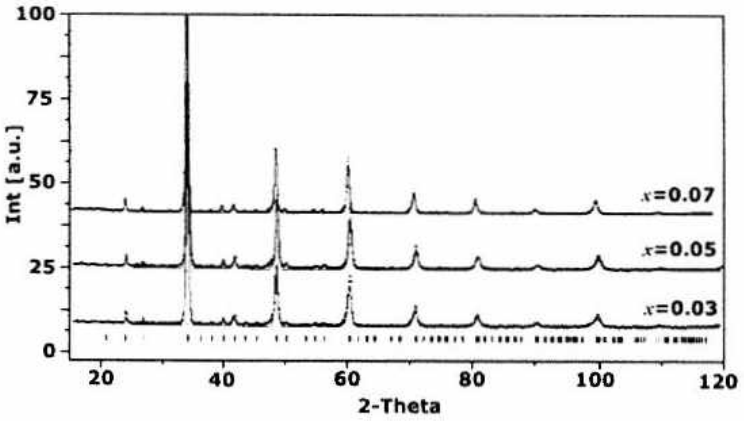

Fig.1. The X-Ray diffraction diagrams for the samples. The dots represent the measured profile points where the lines show the fitted profile function (Pseudo-Voight).

Table 1. Cell papameters, some important mean bond lengths and bond angles for $Ca_{0.85}Pr_{0.15}Mn_{1-x}Ru_xO_3$ (the standard deviations are given in the parenthesis)

Sample	*a* [Å]	*b* [Å]	*c* [Å]	*V* [$Å^3$]	Ca-O [Å]	*Mn-O* [Å]	*Mn-O-Mn* [°]
x =0.03	5.321(5)	5.311(4)	7.540(5)	213.1(3)	2.661	1.882	166.8
x =0.05	5.317(3)	5.318(3)	7.541(1)	213.2(3)	2.662	1.883	167.0
x =0.07	5.319(1)	5.321(1)	7.545(0)	213.5(2)	2.663	1.884	167.5

Table 2. Atomic positions, isotropic thermal motion B_{ISO} and site occupation factor for $Ca_{0.85}Pr_{0.15}Mn_{1-x}Ru_xO_3$

Sample	*Atom*	*x*	*y*	*z*	B_{ISO} [$Å^2$]	*s.o.f.*
x=0.03	Ca	0.002	0.002	0.25	0.42	0.85
	Pr	0.002	0.002	0.25	0.40	0.15
	Mn	0.5	0	0	0.32	0.97
	Ru	0.5	0	0	0.43	0.03
	Op	0.250	0.249	-0.008	0.68	0.98
	Oa	-0.005	0.494	0.25	0.76	1.01
x=0.05	Ca	0.001	0.002	0.25	0.48	0.85
	Pr	0.001	0.002	0.25	0.52	0.15
	Mn	0.5	0	0	0.41	0.95
	Ru	0.5	0	0	0.54	0.05
	Op	0.249	0.247	-0.004	0.76	1.00
	Oa	-0.003	0.499	0.25	0.77	0.98
x=0.07	Ca	0.002	0.0	0.25	0.37	0.85
	Pr	0.002	0.0	0.25	0.45	0.15
	Mn	0.5	0	0	0.34	0.93
	Ru	0.5	0	0	0.34	0.07
	Op	0.248	0.251	0.002	0.56	0.99
	Oa	0.002	0.497	0.25	0.56	0.98

orientation of the crystal preferred axis and offer the chance to estimate the averages of the grain isotropies, of the measures of grain inheritance of crystal anisotropic properties.

The microstructures of the samples were analyzed by SEM. Fig.2 shows four images for the samples with x = 0.00, 0.03, 0.05 and 0.07 consequently; these pictures were taken at the magnification of 10μm scale. There was another set of images at 2μm, 5μm and 10μm scale, taken at different surface positions. They all were used in the fractal analysis of boundary characteristics but not shown here for clarity. These photographs allowed us to estimate the grain average size, thus the average number of the single crystal pieces within one grain; the lengths, the areas and the gaps associated with the grain boundary.

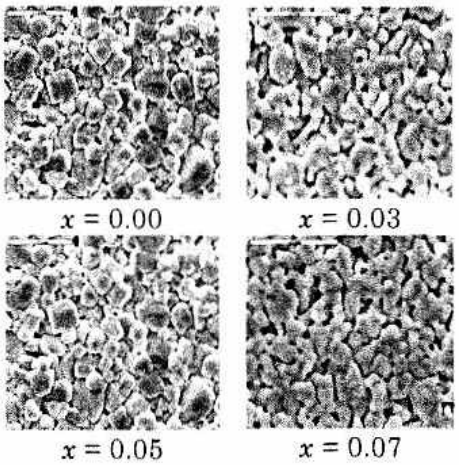

Fig.2. SEM images of the surface for samples at the 10μm scale.

To study the dependence of conductivity of samples on temperature we measured their resistance from 100 to 500K and the results are summarized in Fig.3, where one may easily recognize the sharp drop of resistivity due to the substitution of Ru. At the room temperature the resistivity of the samples has practically reduced to several ohms.

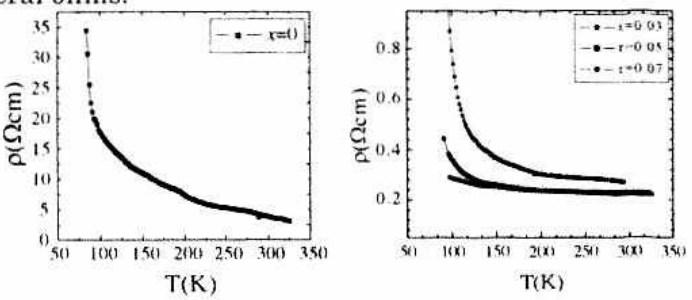

Fig.3. The development of resistivity from low temperature region to room temperature. A sharp fall of ρ due to substitution may be easily recognized

4. Conclusion

The small doping of Ru was accompanied by the mere enlargement in the cell constants and volume but the cell symmetry remained orthorhombic. The single crystal size distribution showed to be standard for perovskites where the average sizes moved around 25nm. The grains were radically larger and contained 40 single crystal pieces by average. The resistivity of samples was measured by standard two electrode technique from 100 to 500K. The fast drop of the resistivity of all samples to the low several ohms in the room temperature region was observed as the content of Ru substitution increased. The calculation of the single crystal domain average isotropic conductance resulted in the value near 1/2 of the maximal anisotropic conductance.

References

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