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Structural and electromagnetic characteristics of perovskites in $La_{1-c-x}Sr_{c+x}Mn_{1-x}Me^{4+}{}_{x}O_3$ systems (Me=Ge, Ti)

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Abstract. Experimental data are shown for the influence of substituting quadrivalent ions on the concentration phase transitions “rhombohedral-orthorhombic structure” and “semiconductor-metal” in ceramic manganites of specifically designed system $La^{3+}{}_{1-c-x}Sr^{2+}{}_{c+x}Mn^{3+}{}_{1-c-x}Mn^{4+}{}_{c}Me^{4+}{}_{x}O_3$ (c=0.15, 0.17, 0.19; $0.025 \le x \le 0.125$). Regularities in the concentration dependences of unit cell volume, saturation magnetization, Curie point, and resistivity were established. Ge-substituted manganites had essentially higher values of magnetization and Curie temperature than analogous compositions with Ti. The approach to the interpretation of experimental results is discussed in terms of electron configurations and ionic radii of substituents taking into account oxygen nonstoichiometry and cation vacancies.

1 Introduction

Colossal magnetoresistance (CMR) in manganites is generally agreed to be a result of the competition between certain phases with different electronic, magnetic and structural orders, and is mainly concerning with double exchange and Jahn-Teller effect of Mn^{3+} ions [1-2]. Despite the large number of papers devoted to the study of Mn site doping on the structure and characteristics of manganites, some mechanisms of phase and properties formation in these materials are not yet fully understood, taking into account heterovalent ions, their localization and radii, electron exchange, occurrence of vacancies in various sublattices, and thermodynamics of solid-atmosphere interaction [2-6]. Modifying the bonds between $Mn^{3+}$and Mn^{4+} ions, the doping by small amount of substituting cations and defects can lead to drastic changes in the main properties of manganites [2,5-7].

The effect of substituting divalent and trivalent ions on the phase composition, magnetic and electrical properties of La-based manganites with substitution of Mn by Mg, Zn, Ni, Ga and, simultaneously, of La by Sr has already been investigated in the works [6, 8-10].

It was found that divalent substituting ions in the system of chemical compositions $La_{1-c+x}Sr_{c-x}Mn_{1-x}Me^{2+}{}_{x}O_3$ shifted phase boundary “rhombohedral-orthorhombic structure” to higher values of “c” [8] in comparison with classical phase diagram for $La_{1-c}Sr_{c}MnO_3$ system [7], while Ga^{3+} in $La_{1-c}Sr_{c}Mn_{1-x}Me^{3+}{}_{x}O_3$ compositions shifted them in opposite direction [9]. Excess of oxygen content (γ>0) over stoichiometric one promotes the existence of rhombohedral phase.

Simultaneously, concentration transition “semiconductor-metal” displaced in the region of higher “c” independently of substituting ion [8,9]. Moreover, for divalent ions the displacement of this transition is greater than the displacement of the boundary “rhombohedral-orthorhombic structure”. As a result, manganites with rhombohedral structure can exhibit semiconducting type of temperature dependence of conductivity, even at high value of “c”, when the charge carrier concentration is high enough [8,9].

The effect of Ge substitution for Mn on the properties of La-Ca manganites, in partular, on the metal-insulator transition, has been investigated in [11-13].

Here, we present the experimental investigations on the influence of substituting quadrivalent ions (Ge^{4+}, Ti^{4+}) on the concentration phase transitions “rhombohedral-orthorhombic structure” and “semiconductor-metal” in manganites of specifically designed systems $La^{3+}{}_{1-c-x}Sr^{2+}{}_{c+x}Mn^{3+}{}_{1-c-x}Mn^{4+}{}_{c}Me^{4+}{}_{x}O_3$ in the connection with their structural and electromagnetic characteristics. Under the condition that concentration of oxygen is stoichiometric, the content of Mn^{4+} (f.u.) is equal to “c”, and is independent of x in these systems. In fact, here Me^{4+} substitute for Mn^{3+} ions, that results in diamagnetic dilution and decreasing of Jahn-Teller ions concentration.

The values of “c” are chosen near the boundary between orthorhombic and rhombohedral phases (c =0.175) established earlier for $La_{1-c}Sr_{c}MnO_3$ system [7].

2 Experimental

The experiments were performed on polycrystalline samples synthesized by traditional ceramic processing. The starting components (dried La_2O_3, $SrCO_3$, MnO_2, GeO_2, TiO_2 powders) were mixed in stoichiometric proportions and ground in a ball mill with addition of alcohol. Pellets compacted of the obtained charge mixture were then preliminarily burned at 1273 K for 4 h. This operation was followed by grinding, introducing a binder (an aqueous solution of polyvinyl alcohol), pressing the samples, and burning out the binder. The final sintering step was performed at 1473 K for 10 h, and the samples were cooled together with the furnace. Then, in order to provide stoichiometric oxygen content, the samples were annealed at 1223 K and partial pressure of oxygen $P_{O2}=10^{-1}$ Pa for 96 h. The choice of annealing conditions was based on the results of the work [3], which demonstrate the achievement of stoichiometry at above-mentioned temperature and P_{O2} almost independently of composition in the systems $La_{1-c}Sr_cMnO_3$.

Phase composition and cell parameters were determined by powder X-ray diffraction at room temperature (diffractometer Shimadzu XRD-7000, CuK_α radiation). The magnetization (per mass unit, σ) was determined by measuring the variation of the magnetic flux, which run through the measuring coil placed in the interpolar space of a permanent magnet, upon pulling a capsule with the powder sample out of it. The magnetic field strength in the interpolar space was 5600 Oe. Measurements of dc electrical characteristics were made using copper electrodes sputter-deposited onto opposite planes of pellets (thickness of about 4 mm). The temperature dependence of magnetic permeability (μ(T)) was measured by the induction method at a frequency of 15 kHz using a thermocryostat. The Curie point (T_c) was determined as the temperature corresponding to the maximum of $|d\mu/dT|$.

3 Results and discussion

All Ge-contained manganites were rhombohedral, while some of Ti-substituted samples (with c=0.15, x≤0.05) had orthorhombic structure, that gives some evidence for more significant effect of Ge on the shift of phase boundary.

Table 1 summarizes the structural parameters and magnetization of initial (sintered) samples for the sets of rhombohedral phase composition.

The unit cell volume (v) of Ge-substituted manganites decreases as a function of “x” at fixed “c”, and as a function of “c” at x=0.075 despite of Sr concentration rise. However, compositions with Ti exhibit the increase of v when ‘x” grows (excluding the point c=0.19, x=0.125). These dependencies can be explained taking into account that ionic radius of Ge^{4+} (0.53 Å) is much smaller than Mn^{3+} (0.645 Å), the radii of Ti^{4+} (0.605 Å) and Mn^{3+} differ slightly. Tolerance factor of Ge-substituted manganites is greater and rises more sharply as a function of x than tolerance factor of Ti-substituted manganites.

Besides that, the dilution of Mn sublattice by Ti (such as increase of Sr concentration) reduces the oxygen content [3,14], that results in reduction of cation vacancies concentration (radius of 0.888 Å); but on the other hand, the number of Mn^{3+} ions increases simultaneously with the decrease of oxygen content. On the contrary, it is possible that addition of Ge rises the excess of oxygen content (γ) over stoichiometric one in sintered samples. After annealing in vacuum, the unit cell volume of manganites increases irregularly, that can be due to competitive influence of Sr and Ge additions on the value of γ.

It was found that magnetization at 80 K and T_c in most cases rise with “c” increasing at each fixed value of “x”, and decrease as a functions of “x” at fixed “c” (Table 1, Figure 1).

These regularities are related to the rising of Mn^{4+} concentration when “c” increases, to dilution and destabilization of Mn sublattice by diamagnetic ions. Ge-substituted manganites had essentially higher values of magnetization and Curie temperature than analogous compositions with Ti. Upon substitution, T_c of Ti-contained manganites shows more sharp decrease as a function of “x” than Ge-substituted compositions (Figure 1). Such different concentration dependencies of Curie temperature are attributed to the differentiations of interionic spacings in Ge^{4+}- and Ti^{4+}-doped manganites, electron orbitals of these ions (configurations $3d^{10}$ and $3p^6$, respectively), and their effect on oxygen nonstoichiometry.

It is interesting that dependencies of magnetization at 300 K on Ge and Ti concentration differ radically: σ(x) is decreasing function for Ge-contained manganites, but

Table 1. Unit cell volume/formula unit (v), and magnetization (σ, at 80 and 300 K) of sintered samples

c	x	Me=Ge			Me=Ti		
		v, Å^3	σ, emu/g		v, Å^3	σ, emu/g	
			80 K	300 K		80 K	300 K
0.15	0.075	58.772	80.6	2.4	59.123	65.4	1.3
0.17	0.075	58.713	80.9	2.8	58.904	64.6	1.6
0.19	0.025	58.785	85.4	9.3	58.747	75.7	3.0
	0.050	58.727	78.2	4.8	58.933	71.6	2.5
	0.075	58.639	81.5	4.5	58.945	70.7	3.7
	0.100	58.533	78.3	4.2	59.104	59.5	6.1
	0.125	58.413	75.0	4.6	58.926	49.9	7.1

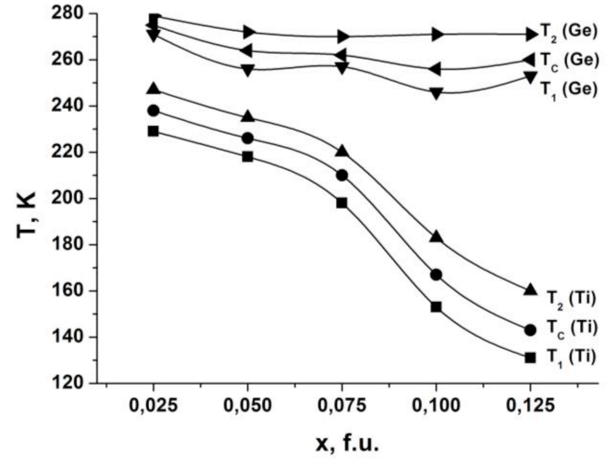

Fig. 1. Dependencies of “ferromagnetic-paramagnetic” transition temperatures for initial (sintered) Ge- and Ti-substituted manganites with c=0.19 (T_1, T_2 – temperatures at beginning and at termination of transition)

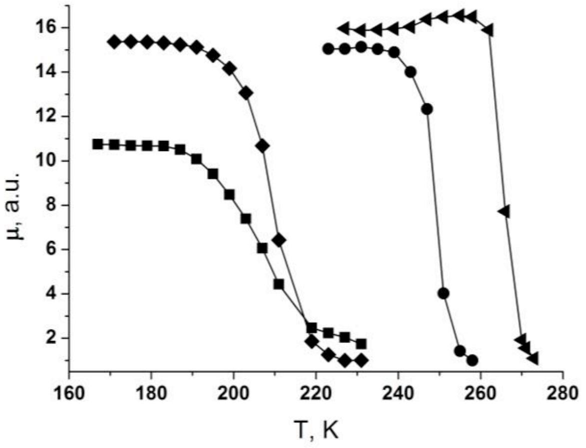

Fig. 2. Temperature dependencies of magnetic permeability for initial samples of manganites with x=0.075:
■- Me=Ti, c=0.17; ◆- Me=Ti, c=0.19;
●- Me=Ge, c=0.17; ◀- Me=Ge, c=0.19

rises with Ti content increasing, in spite of the lowering of T_c and σ at 80 K. This fact can be ascribed to more pronounced formation of clusters and magnetic inhomogeneities with higher magnetization and higher transition temperature [15] in Ti- than in Ge-substituted manganites. Temperature interval of transition in Ti-contained compositions is overextended over analogous compositions with Ge (Figures 1, 2).

Ge-substituted manganites with c=0.19 at all x, and with c=0.15, 0.17 at x≤0.075 in initial state revealed metallic type of temperature dependence of resistivity in appropriate low temperature regions. After annealing the resistivity rose sharply, the “metal-semiconductor” transition temperature decreased, and the metal-similar region of the sample with c=0.15, x=0.075 vanished (Figure3).

On the contrary, Ti-substituted manganites with all “c” at x≥0.075 had semiconducting type of conductivity, and metallic behaviour was observed in sintered samples with c=0.19 only at x≤0.05 (Figure 4).

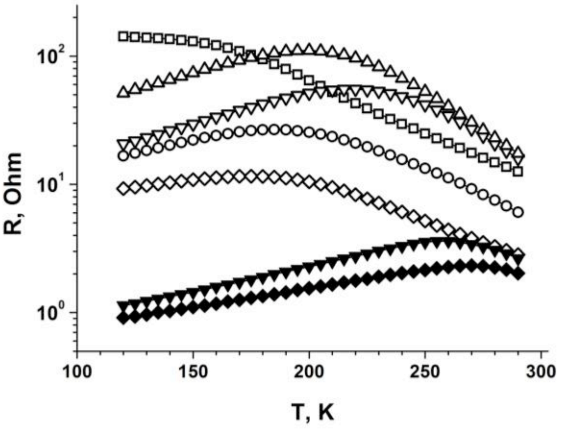

Fig. 3. Temperature dependencies of resistivity for Ge-substituted manganites: ◆- c=0.19, x=0.050, initial sample; ◇- c=0.19, x=0.050, annealed; ▼- c=0.19, x=0.100, initial; ▽- c=0.19, x=0.100, annealed; ○- c=0.17, x=0.075, annealed; △- c=0.19, x=0.125, annealed; □- c=0.15, x=0.075, annealed

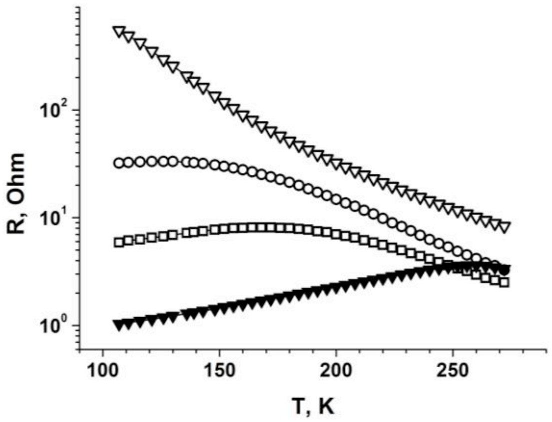

Fig. 4. Temperature dependencies of resistivity for initial samples of manganites with c=0.19:
▼- Me=Ge, x=0.100; ▽- Me=Ti, x=0.100;
□- Me=Ti, x=0.025; ○- Me=Ti, x=0.050

4 Conclusion

From the data obtained it might be inferred that substituting Ge^{4+} and Ti^{4+} ions shift phase boundary “rhombohedral-orthorhombic structure” to lower value of c, moreover, the effect of Ge is most significant.

Sintered manganites (before vacuum annealing) have an excess of oxygen content over stoichiometric one, that promotes the existence of rhombohedral and metallic phases. There is a correlation between the shift of boundary “rhombohedral-orthorhombic structure” and the change of tolerance factor depending on the type and concentration of substituting ion.

Simultaneously, concentration transition “semiconductor-metal” displaces in the region of higher “c”.

Ge-substituted manganites have essentially higher values of magnetization and Curie temperature, which decreases more slowly upon substitution, than analogous compositions with Ti. The "ferromagnetic-paramagnetic" transition temperature interval is more broad in Ti-contained manganites, that can be associated with the distinction in formation of magnetic clusters and inhomogeneities.

Metal-similar state of manganites is more stable to substitution of Ge for Mn than of Ti.

The dilution of octahedral sublattice of Mn^{3+} ions by Ge^{4+}, Ti^{4+}, and cation vacancies has significant effect on double-exchange interaction, magnetic ordering and transport properties, inducing semiconducting behaviour of manganites.

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