

Magnetic, Electrical Properties and Spin-Glass Effect of Substitution of Ca for Pr in $\text{Ca}_{2-x}\text{Pr}_x\text{MnO}_4$ Compounds

M.T. Tlili^{*a}, M. Bejar^a, E. Dhahri^a, M.A. Valente^b, L.C. Costa^b and E.K. Hlil^c

^aLaboratoire de Physique Appliquée, Faculté des Sciences de Sfax, B.P. 802, Sfax 3018, Tunisie

^bI3N and Physics Department, University of Aveiro, 3810-193 Aveiro, Portugal

^cLaboratoire de Cristallographie CNRS, Institut de Néel, Département MCMF BP.166,38042 Grenoble, France

Abstract: $\text{Ca}_{2-x}\text{Pr}_x\text{MnO}_4$ ($x = 0.000$ to 0.200) manganites were synthesized by a sol-gel method and then characterized by X-ray diffraction (XRD) at room temperature. Rietveld refinement technique shows that all samples can be indexed in orthorhombic system except for Ca_2MnO_4 ($x = 0.000$) which can be indexed in the tetragonal system. Magnetic and electrical measurements show that magnetization and resistivity have a large dependence of the fractional composition x and temperature. The applied magnetic field has also a large influence on magnetization level. Spin-glass behavior was detected at low temperature for the samples with $x \geq 0.175$. For all x -values, all compounds exhibit semiconductor behavior and the ferromagnetic (FM) transition temperature T_C (Curie temperature) is around 105 K , whatever the applied field.

Keywords: Manganites, perovskite, ferromagnetic, spin-glass.

1. INTRODUCTION

Besides the perovskite family, the Ruddlesden–Popper manganites, which consist of a regular intergrowth of single rock-salt with multiple perovskite layers, were studied most extensively. The crystal chemistry of these oxides shown in numerous studies, are complex and subject to controversy [1-14]. The $\text{Ca}_{2-x}\text{Ln}_x\text{MnO}_4$ compounds (Ln = Pr, Sm, Gd, Ho) are good examples of Ruddlesden–Popper manganites. These compounds display diverse magnetic and electronic phases such as antiferromagnetic (AFM)-insulating, ferromagnetic (FM)-conductor, paramagnetic (PM)-insulating [15], spin-glass [16-26] and charge-ordering [27]. On the other hand, these Ruddlesden–Popper manganites display interesting magnetic properties, depending on the materials-doping, multiple phase transitions, saturation and no-saturation magnetization. The Ln-doped manganites of Ca_2MnO_4 compound induces a mixed valence state ($\text{Mn}^{3+}/\text{Mn}^{4+}$) and enhances magnetic behavior transition; which can be explained by the double exchange interaction between Mn^{3+} and Mn^{4+} ions [28]. It has been shown that $\text{Ca}_{2-x}\text{Ln}_x\text{MnO}_4$ (Ln = Pr, Sm, Gd, Ho) compounds, which despite their pure bidimensional character, submit a spin-glass transition at low temperatures. For the praseodymium phases $\text{Ca}_{2-x}\text{Pr}_x\text{MnO}_4$, all compounds exhibit semiconductor behavior. In this paper, we report the effect of Pr doping on the magnetic and electrical properties of $\text{Ca}_{2-x}\text{Pr}_x\text{MnO}_4$ compounds. A detailed experimental study of the dependence of magnetization and resistivity with temperature and composition x is reported.

2. EXPERIMENTAL SECTION

$\text{Ca}_{2-x}\text{Pr}_x\text{MnO}_4$ compounds ($x = 0.000$ to 0.200) were synthesized by a sol-gel method. The reaction starts from a

stoichiometric mixture of high purity materials: $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (98%), MnO_6 (99%) and Pr_6O_{11} (99.9%). The samples were subjected to five cycles of sintering for 48 h at 500°C , 900°C , 1000°C , 1100°C , 1200°C and a last cycle at 900°C for two weeks. Before every cycle, the samples were grinded and pressed with less than 2 tons, into a disc shape of 8 mm diameter. Samples were characterized at room temperature by a Siemens D5000 X-ray powder diffractometer (XRD) with a graphite monochromatized $\text{CuK}\alpha$ radiation ($\lambda = 1.54056\text{ \AA}$) and $10^\circ \leq 2\theta \leq 100^\circ$ with a step size of 0.02° and a counting time of 18 s per step. The magnetization measurements were performed using a Foner magnetometer equipped with a super-conducting coil in different magnetic field. The DC electrical resistivity was measured with Keithley electrometer equipment, model 617, as a function of the temperature (80-400 K).

3. RESULTS AND DISCUSSIONS

a) Structural Properties

In order to make sure that all the samples are single phase and all chemical elements (Ca, Pr, Mn, and O) are present in $\text{Ca}_{2-x}\text{Pr}_x\text{MnO}_4$ compounds, XRD and EDAX analysis have been realized. Using Fullprof program, the diffraction peaks corresponding to $x = 0.000$ can be indexed in the tetragonal system with $I41/acd$ space group. The substitution of Ca with Pr generates spectral modifications (Fig. 1) and the diffraction peaks can be indexed in the orthorhombic system with $Aba2$ space group. Fig. (2) shows an example of EDAX spectrum analyzed at room temperature of the $\text{Ca}_{1.9}\text{Pr}_{0.1}\text{MnO}_4$ compound ($x = 0.100$). This analysis reveals that, for all the compositions, all elements (Ca, Pr, Mn and O) remain present in the course of the sintering.

b) Magnetic Properties

Using constant applied magnetic field of 0.045 T , the temperature (T) dependence of the magnetization (M), for

*Address correspondence to this author at the Laboratoire de Physique Appliquée, Faculté des Sciences de Sfax, B.P. 802, Sfax 3018, Tunisie ; E-mail: medtahir59@yahoo.fr

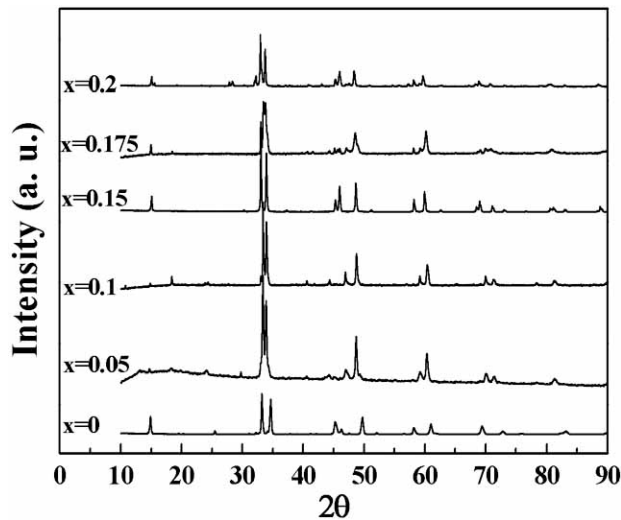


Fig. (1). X-ray diffraction patterns at room temperature of $Ca_{2-x}Pr_xMnO_4$ compounds ($x = 0.0$ to 0.2).

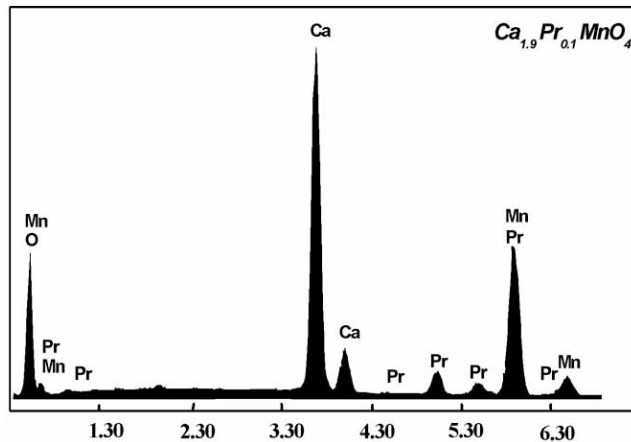


Fig. (2). Example of EDAX analysis spectral at room temperature of $Ca_{1.9}Pr_{0.1}MnO_4$ sample ($x = 0.100$).

$Ca_{2-x}Pr_xMnO_4$ compounds ($x = 0.000$ to 0.200) is visualized in Fig. (3). From $x = 0.000$ to 0.150 , the magnetization level increases and reaches the maximum at $x = 0.150$ and then exhibit an abrupt decrease for $x = 0.175$ and 0.200 . On the other hand, all the samples present a magnetic transition from a paramagnetic to a ferromagnetic state, by decreasing the temperature. This transition occurs at the Curie temperature (T_C) determined from the peak of $(-dM/dT)$ vs T curves (Fig. 4). For all the x -values, T_C is around 105 K and independent of the applied field (Fig. 5). For $x < 0.150$, the PM-FM transitions is induced by the partial substitution of the Ca^{2+} sites by a trivalent alkaline earth ion Pr^{3+} in $Ca_{2-x}^{2+}Pr_x^{3+}Mn_{1-x}^{4+}O_4^{2-}$ compounds. This magnetic behavior can be explained by the increase of the Mn^{3+}/Mn^{4+} ratio. So that, the rise of x -value means a partial substitution of the tetravalent ions Mn^{4+} by the trivalent ions Mn^{3+} . The mixed valence state induces a double exchange (DE) interaction between Mn^{3+} and Mn^{4+} ions [16], which increases until $x = 0.150$ (Figs. 3, 6). Fig. (6) shows the magnetic results of Pr-doping. For all the temperatures less than 110 K, the

magnetization reaches the maximum around $x = 0.15$. For $x > 0.150$, the superexchange (SE) interactions become dominant and increase with x increasing. As a further consequence, the magnetization undergoes an abrupt decreasing. The PM-FM phase transition is relatively sharp for $x = 0.100$ to 0.150 . However, in compounds with $x > 0.150$, the magnetic behavior is different. A second phase transition appears below Curie temperature and becomes clearly visible by increasing Pr-doping level. $-dM/dT$ vs T curves (Fig. 4) show two peaks for higher values of x ($x > 0.150$). The first one, at $T = T_C$, is attributed to PM-FM phase transition. The second one, detected at T_{sg} (spin-glass temperature) around 90 K, can be attributed to the competition between the ferromagnetic (FM) and the antiferromagnetic (AFM) interaction, leading to the appearance of an antiferromagnetic spin-glass state [29, 30]. This state becomes dominating for $x = 0.175$ and $x = 0.200$, which explains the decrease of the magnetization.

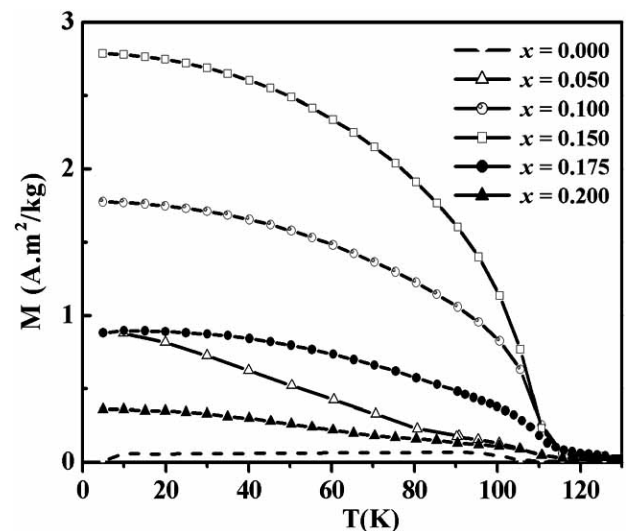


Fig. (3). Magnetization vs temperature for $Ca_{2-x}Pr_xMnO_4$ compounds ($x = 0.000$ to 0.200), at an applied magnetic field of 0.045 T.

c) Electrical Properties

From resistivity curves $\rho(T)$ (Fig. 7), we can conclude that all samples present a semiconductor behaviour at high temperatures ($T > 100$ K). On the other hand, at fixed temperatures (Fig. 8), each $\rho(x)$ curve goes over a minimum at $x = x_{min}$ depending on the temperature. At low temperatures ($T < 155$ K), the minimum of the resistivity (ρ_{min}) corresponds to $x_{min} = 0.15$. This result is in good agreement with that found for the magnetic study, which reveals that the maximum of the magnetization corresponds to $x = 0.15$. When the temperature increases, x_{min} shifts towards higher x -values. From Fig. (7), it can clearly be seen that $x_{min} = 0.175$ for the temperature range 155 - 210 K, and $x_{min} = 0.2$ for higher temperatures ($T > 210$ K). For $x < x_{min}$, the decrease of the resistivity with x increasing (Fig. 8) can be explained by the increase of the transfer of electron between neighbouring Mn^{3+} and Mn^{4+} ions through the path $Mn-O-Mn$ indicating an amplification of the double-exchange (DE)

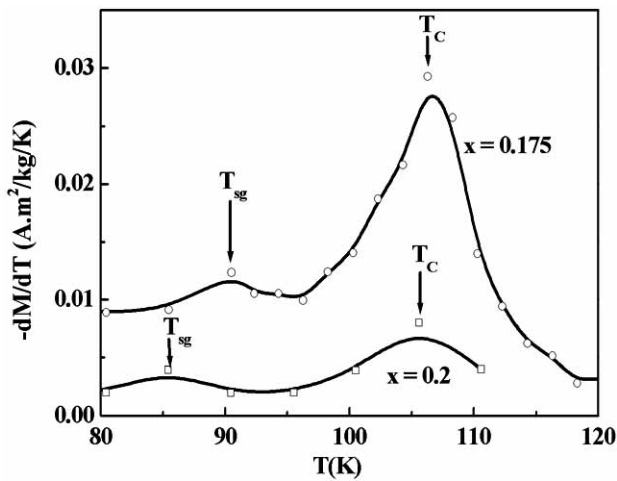
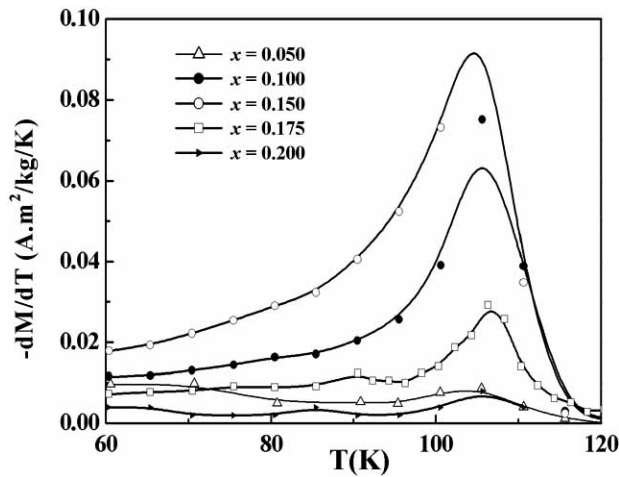


Fig. (4). Variation of $(-dM/dT)$ as function of temperature T for $Ca_{2-x}Pr_xMnO_4$ compounds ($x = 0.000, 0.100, 0.150, 0.175, 0.200$), at an applied magnetic field of $0.045 T$.

mechanism. When x exceeds x_{min} ($x > x_{min}$), the local antiferromagnetic interactions, induced by the higher praseodymium concentration, become important and compete with the long-range ferromagnetism from the double exchange interactions between the Mn ions. So that, the increase of the Pr-doping level enhances the localization of the conduction electrons, which explains the increase of resistivity. The increase in x_{min} and the decrease of the resistivity level with the temperature increasing, as it shown in isothermal curves (Fig. 8), can be attributed to the increase of the vibration frequency which dominates the conductivity phenomenon at high temperatures.

4. CONCLUSIONS

$Ca_{2-x}Pr_xMnO_4$ compounds ($x = 0.000$ to 0.200) were synthesized by a sol-gel method. X-ray diffraction peaks can be indexed in the tetragonal system for $I41/acd$ space group for $x = 0.000$ and in the orthorhombic system for $Aba2$ space group, after doping with the praseodymium. The Curie temperature, T_C , is found to be around $105 K$ for all samples. At low temperatures, the minimum of the resistivity corresponds to $x_{min} = 0.15$, which is in good agreement with

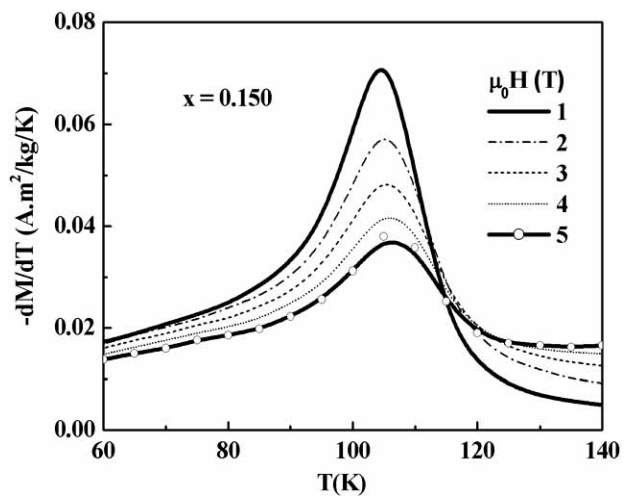
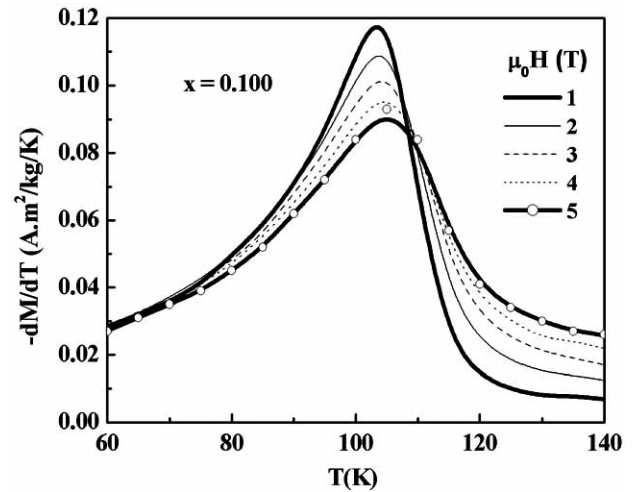


Fig. (5). Variation of $(-dM/dT)$ as function of temperature T for $Ca_{2-x}Pr_xMnO_4$ compounds ($x = 0.100$ and $x = 0.150$), at different applied magnetic fields $\mu_0 H$.

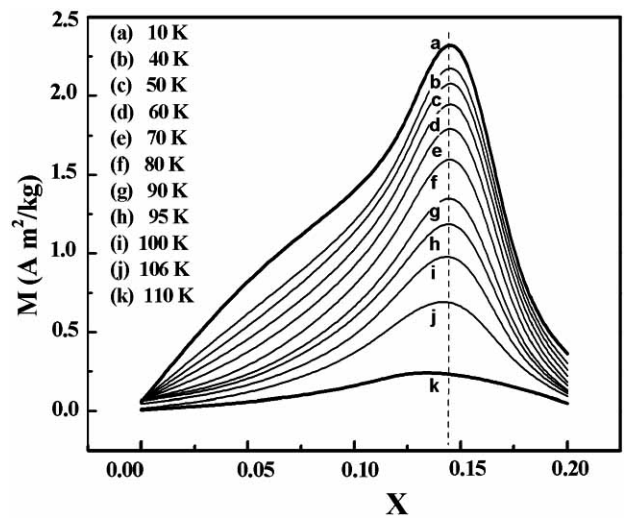


Fig. (6). Magnetization vs x for $Ca_{2-x}Pr_xMnO_4$ compounds at low applied magnetic field ($0.045 T$), at different temperatures.

that found for the magnetic study. For a temperatures range 155-210 K, and for temperatures higher than 210 K, $x_{min} = 0.175$ and 0.2, respectively. For low x -values ($x < x_{min}$), the increase of magnetization and the decrease of resistivity, can be explained by the importance of the double-exchange mechanism. For $x > x_{min}$, the antiferromagnetic interactions, become dominate and prevent the transfer of electrons between Mn^{3+} and Mn^{4+} ions, which reverses the variation senses of the magnetization and the resistivity.

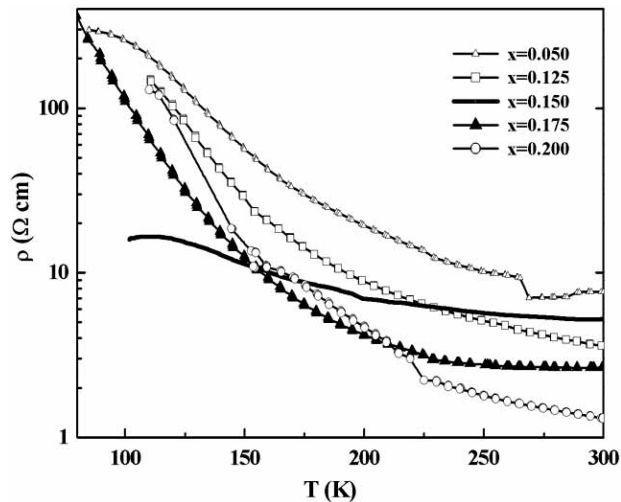


Fig. (7). Resistivity vs temperature without applied magnetic field for $Ca_{2-x}Pr_xMnO_4$ compounds ($x = 0.050$ to 0.200).

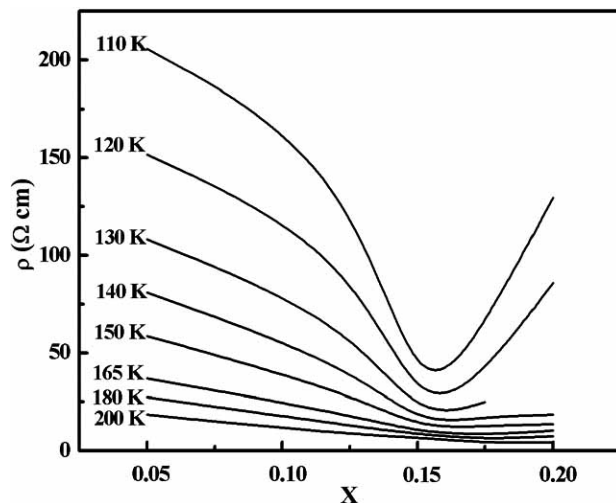


Fig. (8). Resistivity vs x for $Ca_{2-x}Pr_xMnO_4$ compounds at different temperatures without applied magnetic field.

REFERENCES

- [1] Han DK, Kim SH, Hong KP, *et al.* Crystal structure and magnetism of layered $Ln_2Ca_2MnNiO_8$ ($Ln = Pr, Nd, Sm, \text{ and } Gd$) compounds. *J Solid State Chem* 2004; 177: 1078-86.
- [2] Daoudi A, Le Flem G. J Sur une série de solutions solides de formule $Ca_{2-x}Ln_xMnO_4$ ($Ln = Pr, Nd, Sm, Eu, Gd$). *J Solid State Chem* 1972; 5: 57-61.
- [3] Chaumont C, Daoudi A, Le Flem G, Hagenmuller P. Préparation, propriétés cristallographiques, magnétiques et électriques de la solution solide $Ca_{2-x}Y_xMnO_4$. *J Solid State Chem* 1975; 14: 335-41.
- [4] Kamegashira N, Shimono A, Xu HW, Satoh H, Hayashi K, Kikuchi T. Phase transition of the $Ca_{1.5}Nd_{0.5}MnO_4$ phase. *Mater Chem Phys* 1990; 26: 483-92.
- [5] Bednorz JG, Müller KA. Possible high T_c superconductivity in the Ba-La-Cu-O system. *Z Phys* 1986; B 64: 189-93.
- [6] Chi EO, Kim WS, Hong CS, Hur NH, Choi YN. Metal-insulator transition induced by short range magnetic ordering in monolayered manganite. *Bull Korean Chem Soc* 2003; 24: 573.
- [7] Bao W, Chen CH, Carter SA, Cheong SW. Electronic phase separation and charge ordering in $(Sr,La)_2MnO_4$: Indication of triplet bipolarons. *Solid State Commun* 1996; 98:55-9.
- [8] Sternlieb BJ, Hill JP, Wildgruber UC, *et al.* Charge and magnetic order in $La_{0.5}Sr_{1.5}MnO_4$. *Phys Rev Lett* 1996; 76: 2169.
- [9] Hong CS, Kim WS, Chi EO, Hur NH, Choi TN. Role of rare earth ion in spin-glass behaviour in $R_{0.7}Sr_{1.3}MnO_4$. *Chem Mater* 2002; 14: 1832.
- [10] Choy JH, Kwon SJ, Park GS. High- T_c Superconductors in the Two-Dimensional Limit: $[(Py-C_nH_{2n+1})_2HgI_4]-Bi_2Sr_2Ca_{m-1}Cu_mO_y$ ($m = 1$ and 2). *Science* 1998; 280: 1589-92.
- [11] Wheatly JM, Hsu TC, Anderson PW. Interlayer effects in high- T_c superconductors. *Nature* 1988; 333: 121.
- [12] Harshman DR, Mills AP. Concerning the nature of high- T_c superconductivity: survey of experimental properties and implications for interlayer coupling. *Phys Rev* 1992; B45: 10684.
- [13] Varela M, Arias D, Sefrioui Z, *et al.* Direct correlation between T_c and CuO_2 bilayer spacing in $YBa_2Cu_3O_{7-x}$. *Phys Rev* 2002; B 66: 134517.
- [14] Michel CR, Amigo R, Casan-Pastor N. dramatic change in magnetic properties of manganates $Ca_{2-x}Ln_xMnO_4$ by low temperature electrochemical oxidation in fused. Nitrates *Chem Mater* 1999; 11: 195-7.
- [15] Maignan A, Martin C, Van Tendeloo G, Hervieu M, Raveau B. Ferromagnetism and magnetoresistance in monolayered manganites $Ca_{2-x}Ln_xMnO_4$. *J Mater Chem* 1998; 8: 2411-6.
- [16] Sdiri N, Bejar M, Dhahri E. The effect of the B-site size on the structural, magnetic and electrical properties of $La_{0.7}Ca_{0.3}MnO_{3-\delta}$ compounds. *J Magn Magn Mater* 2007; 311: 512-6.
- [17] Sternlieb BJ, Hill JP, Wildgruber UC, *et al.* Charge and magnetic order in $La_{0.5}Sr_{1.5}MnO_4$. *Phys Rev Lett* 1996; 76: 2169-72.
- [18] Du J, Zheng Q, Li YB, *et al.* Large magnetocaloric effect and enhanced magnetic refrigeration in ternary Gd-based bulk metallic glasses. *J Appl Phys* 2008; 103: 023918.
- [19] Binder K, Young AP. Spin glasses: experimental facts, theoretical concepts, and open questions. *Rev Mod Phys* 1986; 58: 801-976.
- [20] Chudnovsky EM, Saslow WM, Serota RA. Ordering in ferromagnets with random anisotropy. *Phys Rev* 1986; B33: 251-61.
- [21] Billoni OV, Cannas SA, Tamarit FA. Spin-glass behaviour in the random-anisotropy heisenberg model. *Phys Rev* 2005; B72: 104407.
- [22] Chen JH, Lubensky TC. Mean field and ϵ -expansion study of spin glasses. *Phys Rev* 1977; B16: 2106-14.
- [23] Luo Q, Zhao DQ, Pan MX, Wang WH. Multiwavelength Raman spectroscopy of diamond nanowires present in n -type ultrananocrystalline films. *Appl Phys Lett* 2007; 90: 211903.
- [24] Luo Q, Zhao DQ, Pan MX, Wang WH. Critical and slow dynamics in a bulk metallic glass exhibiting strong random magnetic anisotropy. *Appl Phys Lett* 2008; 92: 011923.
- [25] Moritomo Y, Tomioka Y, Asamitsu A, Tokura Y. Magnetic and electronic properties in hole-doped manganese oxides with layered structures: $La_{1-x}Sr_{1+x}MnO_4$. *Phys Rev* 1995; B51: 3297-300.
- [26] Moritomo Y, Asamitsu A, Kuwahara H, Tokura Y. Giant magnetoresistance in layered structure of manganese oxides. *Nature* 1996; 340: 141.
- [27] Autret C, Retoux R, Hervieu M, Raveau B. Charge ordering in a 2D manganite, $Pr_{0.25}Ca_{1.75}MnO_4$. *Chem Mater* 2001; 13: 4745-52.

- [28] Zener C. Interaction between the *d*-shells in the transition metals. II. ferromagnetic compounds of manganese with perovskite structure. *Phys Rev* 1951; 82 (3): 403-5.
- [29] Sudyoadsuk T, Suryanarayanan R, Winotai P, Wenger LE. Suppression of charge-ordering and appearance of magnetoresistance in a spin-cluster glass manganite $\text{La}_{0.3}\text{Ca}_{0.7}\text{Mn}_{0.8}\text{Cr}_{0.2}\text{O}_3$. *J Magn Magn Mat* 2004; 278: 96-106.
- [30] El-Hagary M, Shoker YA, Mohamed S, Moustafa AM. Structural and magnetic properties of polycrystalline $\text{La}_{0.77}\text{Sr}_{0.23}\text{Mn}_{1-x}\text{Cu}_x\text{O}_3$ manganites. *J Alloys Comp* 2009; 468: 47-53.

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