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Enhancement of Double-Exchange Mechanism in Charge-Ordered $Pr_{0.75}Na_{0.25}MnO_3$ Ceramics by Cr Doped at Mn-Site

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ABSTRACT. Charge ordered $Pr_{0.75}Na_{0.25}Mn_{1-x}Cr_xO_3$ (x = 0 - 0.04) ceramics has been investigated to study the effect of Cr doping on structure and electrical transport properties as well as surface morphology which synthesized using the solid-state reaction method. X-ray diffraction (XRD) analysis revealed the crystalline phase of all samples consists of essentially single phase and crystallized in an orthorhombic structure. The Cr doping were influence the lattice parameters and the unit cell volume suggestively due to the different of ionic radius between Mn^{3+} ions and Cr^{3+} ions. DC electrical resistance measurement showed that, the x = 0 sample exhibited an insulating behaviour down to the lower temperature. Interestingly, the metal-insulator (MI) transition temperature for x = 0.02 and x = 0.04 samples were found to be around T_{MI}~120 K and T_{MI}~122 K respectively indicating the enhancement of double-exchange (DE) mechanism as a result of weakening the Jahn-Teller (JT) effect which caused the charge ordered (CO) state to be weakened. scanning electron microscope (SEM) images of $Pr_{0.75}Na_{0.25}Mn_{1-x}Cr_xO_3$ compound showed the morphology of the samples were quite uniform suggestively due to the good crystalline nature.

Keywords: *Double-exchange mechanism, Charge ordering, Electrical properties;*

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1. INTRODUCTION

Rare-earth manganites with perovskite structure of the general composition of type $Re_{1-x}A_xMnO_3$ where Re is a trivalent rare-earth ion such as La, Nd, Dy, Pr and A is a divalent alkaline-earth such as Ca, Sr or Ba has been received remarkable attention due to their unique physical properties as well as potential applications [1-6]. In addition, studies on these rare-earth manganites have revealed that colossal magnetoresistance (CMR) effect which is commonly attributed to the double-exchange (DE) mechanism is also suggested to be related to the Jahn-Teller (JT) effect and charge ordering (CO) [7]. Interestingly, the $Pr_{0.75}Na_{0.25}MnO_3$ has attracted interest due to the existence of CO transition at a higher temperature compared to anti-ferromagnetic (AFM) ordering (T_{CO}~260 K, T_N~160 K) [8,9].

Many reports showed that substitution directly at Mn-sites with a certain amount of transition metal element have influenced the physical properties of the material as well as charge-ordered (CO) state [7-11]. For instance, previous study on $Pr_{0.75}Na_{0.25}Mn_{1-x}Fe_xO_3$ [7] have shown the resistivity decreases with Fe content up to $x \leq 0.05$, and then increases subsequently with further Fe doping indicating a suppression of double exchange (DE) mechanism. Meanwhile, for $Pr_{0.8}Na_{0.2}Mn_{1-x}Co_xO_3$ [10], the composition of x = 0.04

showed metal-insulator (MI) transition connected with a ferromagnetic (FM) arrangement [10]. However, very few studies on effect of magnetic ion-doped at Mn-site are available in the literatures.

The Cr^{3+} ion was suggested to be very effective element to suppress CO as well as induced the phase transition. In addition, Cr doping on the half-doped manganite also reveals a lot of anomalous electrical transport properties [11]. For example, in $Nd_{0.75}Na_{0.25}Mn_{1-x}Cr_xO_3$ manganite, the electrical resistivity measurement for $x = 0$ sample showed a signal at 170 K indicates the signal on development of CO state. A MI transition at temperature 75 K was reported by $x = 0.03$ sample and increasing of Cr doped up to $x \geq 0.05$ was caused the MI transition to be disappeared suggestively due to reduction of DE mechanism [11]. Meanwhile, increasing of Cr doped up to $x = 0.07$ for $La_{0.8}Ca_{0.2}Mn_{1-x}Cr_xO_3$ compound caused a MI transition to shifted to lower temperature [12]. Thus, considering the entire study above, Cr doped at the Mn-site in $Pr_{0.75}Na_{0.25}Mn_{1-x}Cr_xO_3$ is expected to induce a MI transition as well as weakened the CO state as a result of weakening of the JT effect. However, to the best of our knowledge, such study on the $Pr_{0.75}Na_{0.25}Mn_{1-x}Cr_xO_3$ compound has not been previously reported.

In this paper, we report the effect of Cr doping on structure and electrical transport properties as well as surface morphology of charge ordered $Pr_{0.75}Na_{0.25}Mn_{1-x}Cr_xO_3$ ceramics. Cr doping has been chosen in this work due to the special nature where Cr^{3+} ion which is iso-electronic in configuration with Mn^{4+} ion. In addition, result of density and porosity are also presented and discussed.

2. MATERIALS AND METHODS

The $Pr_{0.75}Na_{0.25}Mn_{1-x}Cr_xO_3$ magnetic ceramics samples were synthesized using the solid state reaction method. A stoichiometric amount of Pr_2O_3, Na_2CO_3, MnO_2, and Cr_2O_3 powders with high purity (≥99.99%) were carefully mixed and ground in an agate mortar with pestle for approximately 2 hours to ensure a homogenous mixture and fine powder was obtained. The mixture powder were then calcined in air at 1000 °C for 24 hours at the rate of 15 °C/min on heating in a Protherm Furnace Model PLF130/15 with several intermediate grinding followed by cooling at rate of 1 °C/min. The powder were then reground again for another a few hours and pressed into pellets in a 13 mm diameter and 2-3 mm thickness using Specac Dice Mole under a load of 6-7 tones using hydraulic pressure equipment. The pellets were then sintered at 1200 °C for 24 hours in air at the rate of 15 °C/min and slow cooled at room temperature at rate of 1 °C/min.

All the synthesized samples were ground again into fine powder and then characterized by X-ray diffraction (XRD) using Bruker D8 Advance model with a CuK_α (1.544 Å) radiation at room temperature. The samples were scanned continuously in the range of $20° \leq 2\theta \leq 80°$ with scanning rate 2°/min. The result from XRD was analysed using X'Pert HighScore programme to confirm the crystalline phase of material. Resistivity of the samples was measured using the standard four probe method. The current leads and voltage leads were attached to the sample (typically, ~10 mm long , ~3 mm wide and ~1 mm thick) with silver paste and this characterization was performed in a Janis Cryostat Model CCS-350ST under zero magnetic fields. Microstructural characterization of the pellets sample was done using scanning electron microscope (SEM) by Hitachi SU1310 operating at 5 KV. Bulk density of the samples was determined by employing the Archimedes principle using acetone as the liquid buoyant.

3. RESULTS AND DISCUSSION

Fig. 1 shows the powder XRD patterns for all the $Pr_{0.75}Na_{0.25}Mn_{1-x}Cr_xO_3$ ($x = 0$-0.04) samples. XRD analysis revealed all the samples are essentially single phased and the peaks can be indexed to an orthorhombic structure with space group *Pnma* with no detectable impurity peaks and it is in line with the structure reported from the previous study [13,14]. Table 1 shows values of MI transition temperature (T_{MI}), lattice parameters, calculated unit cell volume (V), density (D) and porosity for all samples. It is interesting to seen that the lattice parameters as well as calculated unit cell volume, V decrease continuously with Cr content. In addition, the lack of existence of secondary phase from the XRD diffractogram and the decreasing of the V of the samples with Cr content indicate some form of substitution involving of Cr^{3+} ion taking place in the crystal

lattice which can be suggested to be due to the Cr^{3+} ions has a smaller ionic radius (0.615 Å) continuously replaces the Mn^{3+} ion with higher ionic radius (0.645 Å) [15,16]. A similar suggestion was also proposed for $Nd_{0.5}Ca_{0.5}Mn_{1-x}Cr_xO_3$ [15]. Apart from that, the substitution of Cr^{3+} was also suggested to induce the lattice distortion and rearrangement of atom as a results of smaller cation in the B-site of the ABO_3 perovskite structure is responsible for the reduction in unit cell volume [17-19].

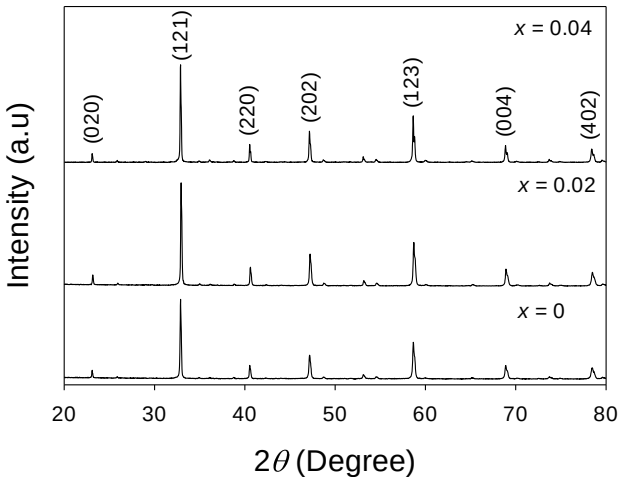

Fig. 1 X-ray powder diffraction (XRD) pattern of $Pr_{0.75}Na_{0.25}Mn_{1-x}Cr_xO_3$ ($0 \le x \le 0.04$) samples

Fig. 2 shows the temperature dependence of the electrical resistivity for x = 0-0.04 samples. The x = 0 sample showed an insulating behavior in the temperature range of 80 K-300 K. Interestingly, a MI transition was observed at around T_{MI}~120 K and T_{MI}~122 K for the x = 0.02 and x = 0.04 samples respectively. The shifting of the MI transition to higher temperatures can be suggested to be due to the enhancement of double-exchange (DE) mechanism (Cr^{3+}-O-Mn^{3+}) as a result of weakening the Jahn-Teller (JT) effect indicating the CO state to be weakened. In fact, it is in line with a previous report [15]. The DE mechanism between Mn^{3+} ion and Cr^{3+} ion has been suggested to be possible occurs in this study due to the Cr^{3+} ion may have a similar role with Mn^{4+} where the Cr^{3+} ($t^3_{2g}e^0_g$) ion have same electronic configuration with Mn^{4+} ($t^3_{2g}e^0_g$) ion [15,20]. Apart from that, the increasing of Cr content also influenced the intensity of the resistivity where this can be suggested to be due to the increase of carrier concentration as result of enhancement of the DE mechanism [15].

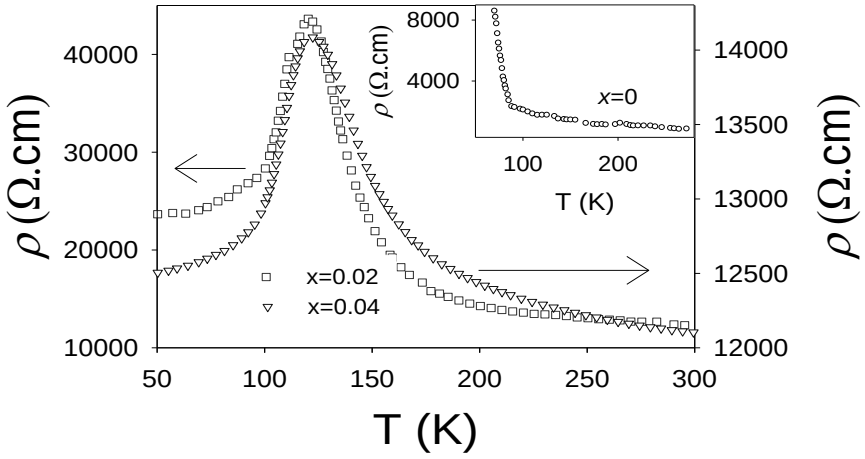

Fig. 2 Temperature dependence of the electrical resistivity of $Pr_{0.75}Na_{0.25}Mn_{1-x}Cr_xO_3$ ($0 \le x \le 0.04$)

Table 1 MI transition temperature (T_{MI}), lattice parameters, unit cell volume (V), density (D) and porosity of $Pr_{0.75}Na_{0.25}Mn_{1-x}Cr_xO_3$ ($0 \leq x \leq 0.04$)

Sample	T_{MI} (K) (± 0.1)	Lattice parameter (±0.001)			V (Å)^3 (±0.1)	D (g/cm^3) (±0.01)	Porosity (%) (±0.1)
		a (Å)	b (Å)	c (Å)			
x = 0.0	-	5.446	7.696	5.445	228.2	5.71	11.0
x = 0.02	120.0	5.448	7.669	5.443	227.4	5.68	13.0
x = 0.04	122.0	5.449	7.659	5.444	227.2	5.51	14.0

On the other hand, the effect of Cr-doped on the surface morphology of the x = 0-0.04 samples are shown as in Fig. 3. The microstructure of the samples were discussed based on the images obtained from SEM. It can be seen that, all samples showed nearly spherical shape and the morphology of the samples were quite uniform suggestively due to the good crystalline nature of these sample [19]. Meanwhile, the values of porosity was observed to be increase with the increase of Cr doping in conjunction with the values of calculated unit cell for the samples which can be suggested to be due to difference of ionic radius between Cr^{3+} ions and Mn^{3+} ions.

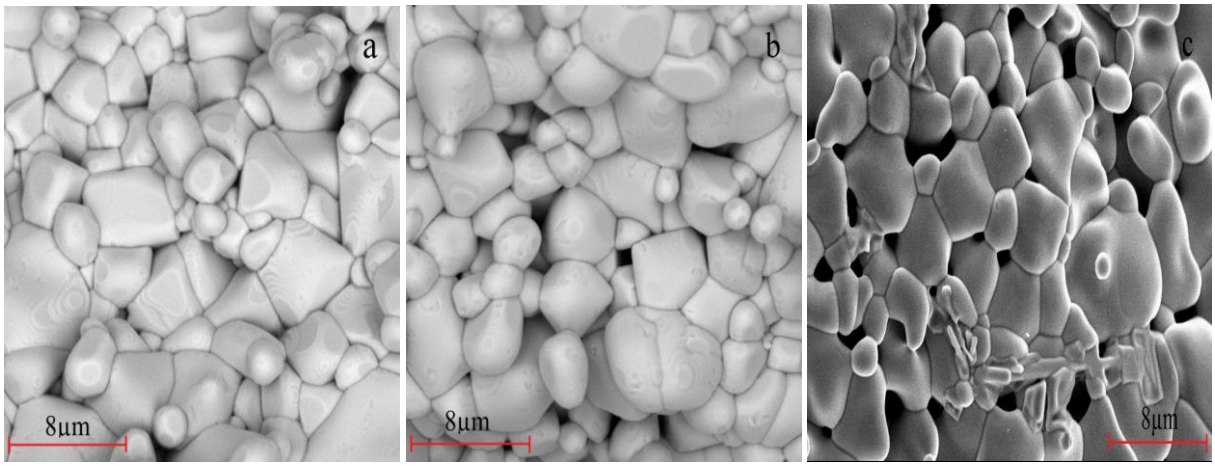

Fig. 3 SEM images for $Pr_{0.75}Na_{0.25}Mn_{1-x}Cr_xO_3$ samples (a) x = 0.0, (b) x = 0.02 and (c) x = 0.04

4. SUMMARY

In conclusion, the influence of Cr doped in $Pr_{0.75}Na_{0.25}Mn_{1-x}Cr_xO_3$ ($0 \leq x \leq 0.04$) magnetic ceramics has been studied. It was found that, the calculated unit cell volume, V decrease continuously with Cr content suggestively due to the Cr^{3+} ion has a smaller ionic radius compare to Mn^{3+} ion. Increasing of Cr doped induced a MI transition for x = 0.02 (T_{MI}~120 K) and x = 0.04 (T_{MI}~122 K) samples suggested to be due to the enhancement of double exchange (DE) mechanism as a result of a weakening of the JT effect. Apart from that, increasing of Cr content also caused a different surface morphology for the all samples indicating the Cr doped play an important role on influencing the properties of materials.

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