

## Crystalline Phase, Surface Morphology and Electrical Properties of Monovalent Doped $\text{Pr}_{0.75}\text{Na}_{0.25}\text{Mn}_{1-y}\text{Co}_y\text{O}_3$ Ceramics

Nurhabibah Nabilah AB MANNAN<sup>1,a\*</sup>, Suhadir SHAMSUDDIN<sup>1,b</sup>,

Mohamad Zaky NOH<sup>1,c</sup> and Zakiah MOHAMED<sup>2,d</sup>

<sup>1</sup>Materials Physics Laboratory, Faculty of Science, Technology and Human Development, Universiti Tun Hussein Onn Malaysia, 86400 Parit Raja, Batu Pahat, Johor, Malaysia.

<sup>2</sup>Faculty of Applied Sciences, Universiti Teknologi MARA, 40450 Shah Alam, Selangor, Malaysia.

<sup>a</sup>habibah.nabilah@gmail.com, <sup>b</sup>suhadir@uthm.edu.my, <sup>c</sup>zaky@uthm.edu.my,

<sup>d</sup>zakiah626@salam.uitm.edu.my

**ABSTRACT.** This paper reports effects of cobalt (Co) doped at Mn-site of  $\text{Pr}_{0.75}\text{Na}_{0.25}\text{Mn}_{1-y}\text{Co}_y\text{O}_3$  ( $y = 0, 0.02$  and  $0.05$ ) on structure and electrical properties along with the surface morphology. All the samples were synthesized using standard solid state reaction method. Powder X-ray diffraction measurement shows that all samples were crystallized in an orthorhombic structure with  $Pnma$  space group. The unit cell volume was decreased suggestively due to the different ionic radius between Mn and Co as Co increases. Resistivity measurement shows that the  $y = 0$  sample exhibits an insulating behavior down to lower temperature and interestingly the metal-insulator (MI) transition was found at 108 K and 84 K for  $y = 0.02$  and  $y = 0.05$  respectively. The shifting of the MI transition to lower temperature indicates a weakening of the double-exchange mechanism. On the other hand, scanning electron microscope (SEM) measurement showed that a different surface morphology was observed for all samples. A different pattern of grain boundaries was observed with increasing of Co content. Grains connection of  $y = 0$  samples was observed slightly denser compare to the  $y = 0.02$  and  $0.05$  samples in conjunction with increasing of the value of porosity. This can be suggested due to the successful of doping of Co ions in the compound.

**Keywords:** X-ray diffraction, Scanning electron microscope, Double-exchange mechanism;

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### 1. INTRODUCTION

Mixed valence perovskite manganites with general formula  $\text{RE}_{1-x}\text{A}_x\text{MnO}_3$  (where RE= Pr, Nd, La; and A= Ca, Sr, Ba) received noticeable attention due to varieties of physical and chemical properties as well as potential applications in technology such as magnetic sensor, magnetic recording, etc [1-3]. The Pr-based manganites have been studied widely as they exhibit charge ordering (CO) which can be destabilized or destruct in order to tune the physical properties [4] and  $\text{Pr}_{0.75}\text{Na}_{0.25}\text{MnO}_3$  has caught attention as this compound is CO insulator at relatively high temperature,  $T_{CO} \sim 220$  K compared to antiferromagnetic interaction with Neel temperature,  $T_N \sim 180$  K [5,6].

The doping at Mn-site with other transitional metal ions whether magnetic or non-magnetic ions could be a very effective ways to alter the properties and charge ordering of the manganites due to the changes of  $\text{Mn}^{3+}/\text{Mn}^{4+}$  ratio [7]. Generally, the Curie temperature ( $T_c$ ) as well as metal-insulator transition temperature ( $T_{MI}$ ) will decrease dramatically when other elements are substituted at Mn site due to the destroyed double-

exchange ferromagnetism [8]. For instance, the CO of  $\text{Nd}_{0.75}\text{Na}_{0.25}\text{Mn}_{1-x}\text{Cr}_x\text{O}_3$  [9] is said to be decreased as the concentration of  $\text{Cr}^{3+}$  increased. The metal-insulator (MI) transition of the samples appeared at ( $x = 0.04$ ) and disappeared with further Cr doping. Besides, the electrical study of  $\text{La}_{0.8}\text{Ca}_{0.2}\text{Mn}_{1-x}\text{Cr}_x\text{O}_3$  shows the  $T_{MI}$  shifts towards lower temperature as the Cr content increased probably due to the weakening of double exchange (DE) mechanism by reducing the ratio of  $\text{Mn}^{3+}/\text{Mn}^{4+}$  [10]. However, the behavior of CO affected by the elemental substitution at Mn-site of mixed valence perovskite manganites is still not clearly understood.

Recently, a mixed valence perovskite manganites has become the focus of investigation as the system was reported to exhibit a variety of magnetic and electrical transport properties [11,12]. For instance, N. Dhahri et al. [13] reported decreasing  $T_{MI}$  varied from 360 K to 210 K as the Co concentration increased in  $\text{La}_{0.67}\text{Pb}_{0.33}\text{MnO}_3$  most probably due to the enhancement of superexchange and weakening of DE mechanism as Co replaces Mn site. Similar observations also have been reported in  $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$  where the  $T_c$  decreased gradually with increasing Co content due to the reduction of ferromagnetic (FM) interaction thus enhanced the antiferromagnetic interactions between Co and Mn ions [14]. By considering the literatures mentioned above, we expect the Co doping in the compound  $\text{Pr}_{0.75}\text{Na}_{0.25}\text{MnO}_3$  may influence the physical properties of the materials. However to the best of our knowledge, such study on the  $\text{Pr}_{0.75}\text{Na}_{0.25}\text{MnO}_3$  has not been reported. Thus, the doping effect of Co at Mn-site on the  $\text{Pr}_{0.75}\text{Na}_{0.25}\text{Mn}_{1-y}\text{Co}_y\text{O}_3$  would be particular interest as it is expected to induce the MI transition as well as suppress the CO state. In addition, the monovalent doped manganites is believed having advantage of creation or the required concentration in  $\text{Mn}^{3+}/\text{Mn}^{4+}$  ions with relatively small doping concentration. In this paper, the crystal structure, morphology and electrical transport properties of monovalent doped materials, PNMCoO are reported. In addition, values of density and porosity are also presented and discussed.

## 2. MATERIALS AND METHODS

The manganite samples of  $\text{Pr}_{0.75}\text{Na}_{0.25}\text{Mn}_{1-y}\text{Co}_y\text{O}_3$  ( $y = 0, 0.02, \text{ and } 0.05$ ) were synthesized using standard solid state reaction method. A stoichiometric amounts of high purity ( $\geq 99.99\%$ )  $\text{Pr}_2\text{O}_3$ ,  $\text{Na}_2\text{O}_3$ ,  $\text{MnO}_2$  and  $\text{Co}_2\text{O}_3$  were ground in agate mortar with pestle and calcined in air at 1000 °C by using Protherm furnace Model PLF130/15 for 24 hours with heating rate of 15 °C/min and slowly cooled to room temperature at rate of 1 °C/min followed by several intermediate grindings process. The obtained powder were compacted into pellets with 13 mm diameter and thickness around 3 mm under 5 tons and then sintered at 1200 °C for 24 hours. X-ray diffraction (XRD) was performed using Bruker D8 Advance Diffractometer system. The radiation employed was Cu-K $\alpha$  ( $\lambda = 0.15406$  nm) which were operated at 40 KV and 40 mA. The sample was scanned continuously in the range of  $20^\circ \leq 2\theta \leq 80^\circ$  with a scanning rate of 2 °/min. The XRD patterns was then analyzed by using X'Pert HighScore software to confirm the crystalline phase of the samples. Electrical resistivity measurement were carried out using the DC electrical resistivity measurement along with four-point probe technique. The measurement was performed in the temperature range of 20 - 300 K using a four point probe technique in a Janis model CCS 350T cryostat. The morphology of the synthesis samples were determined by using Phenom ProX, scanning electron microscopy (SEM) with 5kx magnification. Bulk density of the samples were determined by employing the Archimedes principle using acetone as the liquid buoyant. The percentage of porosity was calculated by using this relation.

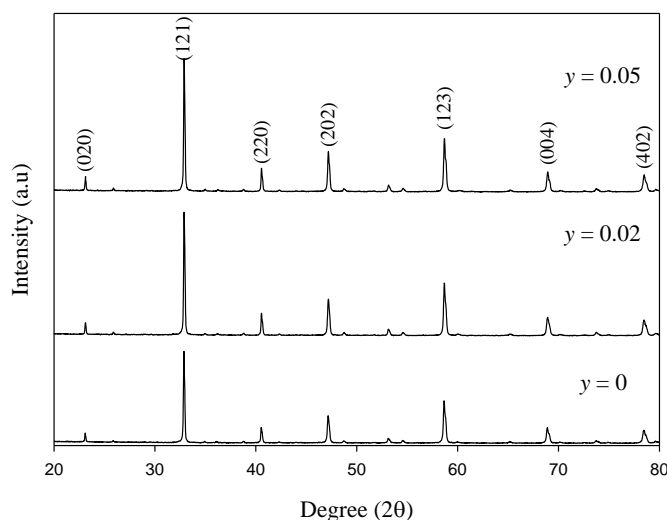
$$\text{Porosity}\% = \left( \frac{\rho_{\text{theoretical}} - \rho_{\text{bulk}}}{\rho_{\text{theoretical}}} \right) \times 100\% \quad (1)$$

Where  $\rho_{\text{theoretical}}$  and  $\rho_{\text{bulk}}$  are the theoretical and bulk density respectively.

## 3. RESULTS AND DISCUSSION

The powder XRD patterns for all the  $\text{Pr}_{0.75}\text{Na}_{0.25}\text{Mn}_{1-y}\text{Co}_y\text{O}_3$  ( $0 \leq y \leq 0.05$ ) samples are shown in Fig. 1. XRD analysis revealed all samples consist of essentially single phase and crystallized in orthorhombic structure

with *Pnma* space group reliable with the structure reported from the previous study [15]. Table 1 shows the values of MI transition temperature ( $T_{MI}$ ), lattice parameters, calculated unit cell volume ( $V$ ), density ( $D$ ) and porosity of each samples. It can be seen that, the values of  $V$  was observed to be decreased as the concentration of Co increased, which points to the possibility that Co ions with smaller ionic radius (0.61 Å) substitutes Mn ions with larger ionic radius in the lattice structure. Successful of substitution for  $Mn^{3+}$  has also been previously reported [16]. Apart from that, the decrease in values of  $D$  with Co content shows a good agreement with the calculated unit cell volume indicating that  $Co^{3+}$  which has smaller ionic radius compared to  $Mn^{3+}$  is successfully doped in the system which is in line with the previous study [17].



**Fig. 1** XRD patterns for  $Pr_{0.75}Na_{0.25}Mn_{1-y}Co_yO_3$  ( $0 \leq y \leq 0.05$ )

**Table 1** M-I transition temperature ( $T_{MI}$ ), Lattice parameters, unit cell volume, density and percentage of porosity of  $Pr_{0.75}Na_{0.25}Mn_{1-y}Co_yO_3$  ( $0 \leq y \leq 0.05$ )

| Sample     | $T_{MI}$<br>(K) | Lattice parameter |                 |                 | $V$<br>(Å) <sup>3</sup><br>±0.1 | $D$<br>(g/cm <sup>3</sup> )<br>±0.01 | Percentage<br>of porosity<br>(%)<br>±0.01 |
|------------|-----------------|-------------------|-----------------|-----------------|---------------------------------|--------------------------------------|---|
|            |                 | a (Å)<br>±0.001   | b (Å)<br>±0.002 | c (Å)<br>±0.001 |                                 |                                      |   |
| $y = 0$    | -               | 5.446             | 7.696           | 5.445           | 228.2                           | 6.13                                 | 1.75                                      |
| $y = 0.02$ | 108             | 5.444             | 7.690           | 5.443           | 227.9                           | 5.87                                 | 5.90                                      |
| $y = 0.05$ | 84              | 5.443             | 7.680           | 5.444           | 227.6                           | 5.68                                 | 8.96                                      |

The effect of Co-doped on temperature dependence of electrical resistivity for all samples are shown in Fig. 2. It was found that, the  $y = 0$  sample showed an insulating behaviour as there are no MI transition observed in the temperature range of 80 K - 300 K. Interestingly the  $y = 0.02$  and  $y = 0.05$  samples showed distinct a metal-insulator transition at 108 K and 84 K respectively suggestively due to the DE mechanism. Meanwhile, the shifting of the MI transition to lower temperature as Co increased could be suggested due to replacements of Co ions at Mn site which leads to the depletion of the Mn ion ratio and the decreasing of resistivity can be connected to the hopping process. Thus, the DE is weakened and caused to the destruction of long range ferromagnetic order [12,19,20].

The effect of Co-doped on the surface morphology of the  $y = 0-0.05$  fractured samples are shown as in Fig. 3. Different surface morphology characterized by a change in grain boundary and the grain size as well as apparent porosity was observed for all samples. The  $y = 0$  sample showed a uniform grain compared to the  $y = 0.02$  sample. This can be said the uniformity and disorder of the grain size of the samples change according to the concentration of the Co doped most probably due to the difference of ionic radii between  $\text{Co}^{3+}$  and  $\text{Mn}^{3+}$  in line with the previous study [20].

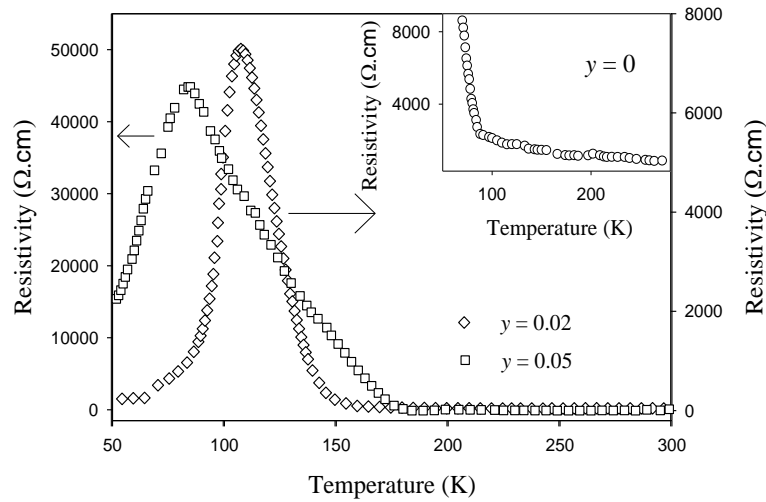


Fig. 2 Temperature dependence of electrical resistivity of  $\text{Pr}_{0.75}\text{Na}_{0.25}\text{Mn}_{1-y}\text{Co}_y\text{O}_3$  ( $0 \leq y \leq 0.05$ )

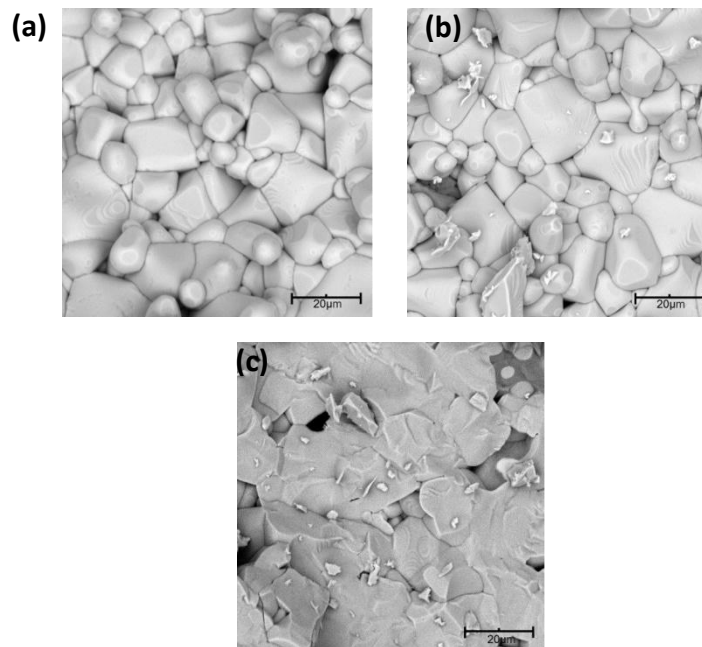


Fig. 3 SEM images with 10kx magnification for  $\text{Pr}_{0.75}\text{Na}_{0.25}\text{Mn}_{1-y}\text{Co}_y\text{O}_3$  samples (a)  $y = 0$ , (b)  $y = 0.02$  and (c)  $y = 0$

However for  $y = 0.05$ , the observation of grain boundaries was not clearly seen. Apart from that, the calculated porosity as shown in Table 1 was increased from 1.75% to 8.96% with increasing of Co content in line the apparent porosity as observed in SEM morphology indicated a successful doped of Co in the Mn-site in the compound.

#### 4. SUMMARY

In conclusion, crystalline phase, electrical properties and surface morphology of the monovalent doped of  $\text{Pr}_{0.75}\text{Na}_{0.25}\text{Mn}_{1-y}\text{Co}_y\text{O}_3$  ( $y = 0, 0.02$  and  $0.05$ ) samples have been investigated. Powder X-ray diffraction measurement show that all the synthesized samples were crystallized in the orthorhombic structure with *Pnma* space group. Analysis of lattice parameters and unit cell volume from the XRD results showed these values were decreased in conjunction with the value of calculated sample of bulk density suggestively due to smaller ionic radii of  $\text{Co}^{3+}$ . Increasing of Co content from  $y = 0.02$  to  $y = 0.05$  caused a MI transition to shifted to lower temperature which can be suggested due to the weakening of DE mechanism. On the other hand, investigation on the surface morphology of  $\text{Pr}_{0.75}\text{Na}_{0.25}\text{Mn}_{1-y}\text{Co}_y\text{O}_3$  samples showed an improvement of grain boundaries with increasing Co content accompanying with the increasing values of calculated porosity.

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