

# Influence of polarization and iron content on the transport properties of praseodymium–barium manganite



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## ABSTRACT

Polarization and iron effects on the electrical properties of  $\text{Pr}_{0.67}\text{Ba}_{0.33}\text{Mn}_{1-x}\text{Fe}_x\text{O}_3$  have been studied using impedance measurements. When iron is introduced, the insulator–metal transition (MI), observed in free compound, disappears and destroying such transition needs an iron concentration less than 5%. We also found that electrical conductance decreases when increasing Fe content. Such results are attributed to the decrease of  $\text{Mn}^{3+}/\text{Mn}^{4+}$  ratio. Also, they are ascribed to the high probability of encountering  $\text{Fe}^{3+}-\text{O}-\text{Fe}^{3+}$  and  $\text{Mn}^{3+}-\text{O}-\text{Fe}^{3+}$  interactions, which greatly weakens the influence of  $\text{Mn}^{3+}-\text{O}-\text{Mn}^{4+}$  interactions. The AC conductivity studies indicate that different types of hopping are involved. The contribution of hopping mechanism is confirmed by the temperature dependence of the frequency exponent 's'. Conductivity analysis shows that small polaron hopping (SPH) and variable range hopping (VRH) models are present in the conduction process. For small iron concentrations ( $x < 0.1$ ), we found that activation energy ( $E_a$ ) does not change significantly. Such result is in good agreement with the literature. But, for high iron concentrations ( $x > 0.1$ ), we found that  $E_a$  depend strongly in Fe content. We also found in this work that DC-bias does not affect the conduction process but proves its thermal activation. The variation of the conductance with polarization is a proof of an electro-resistance effect.

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## 1. Introduction

Manganese perovskite materials attract a great deal of interest because they have potential applications [1–3]. They can be used in magnetic recording, sensing, refrigeration [4,5] and as cathodes in solid oxide fuel cells (SOFC) [6]. Manganites are known to exhibit interesting electronic properties which are explained by many mechanisms [7–10]. During the last few years, the manganites of the type  $\text{Ln}_{1-x}\text{A}_x\text{MnO}_3$ , where Ln is a trivalent element (Pr, La, Nd, ...) and A is a divalent one (Ba, Ca, Sr, ...) are widely studied [11,12]. The magnetic and transport properties of these compounds depend on several factors such as the ratio of the divalent ion, the ionic radii of the metal ion, the elaboration method of the samples, etc. In a similar way, the substitution of Mn by Fe can produce important modifications in the magnetic and transport properties of these materials [13]. Different substitutions in these systems lead to different transport properties. The replacement of the trivalent element by a divalent or a monovalent one produces an inhomogeneous distribution of  $\text{Mn}^{3+}$  and  $\text{Mn}^{4+}$  ions to

maintain charge neutrality and subsequently, this modifies both of the magnetic and transport properties. Such modifications can be understood on the basis of the interactions between the spin of  $\text{Mn}^{3+}$  and  $\text{Mn}^{4+}$  ions. In doped manganites, many efforts are devoted to highlight the central role of the  $\text{Mn}^{4+}-\text{O}-\text{Mn}^{3+}$  interactions. In the last few years, various researches [14–16] have suggested that doping at Mn-site influences the polaronic transport. The effect of substituting Mn by Sn, Fe, Cr and Ti is well studied by our group [17–22]. Also, the effects of introducing Ag in manganite-system on electric and dielectric properties are recently studied [23–26]. Different conduction mechanisms appear when changing the dopant element, its concentration and the substitution sites. The most observed mechanisms are hopping and percolation ones. Recently, we have investigated the iron effects in the electrical properties of  $\text{LaBaMnO}_3$  system [22]. On one hand, we found that electrical properties are strongly dependent on the iron content. On the other hand, the composition  $x=0.1$  represents the limit value of Fe concentration which destroys the metallic–insulator transition. Few works and less discussions have been done on the electrical properties of  $\text{PrBaMnO}_3$  [27] and Fe doped  $\text{PrBaMnO}_3$  [28,29]. In this work, we introduced iron in  $\text{Pr}_{0.67}\text{Ba}_{0.33}\text{MnO}_3$  and we study its effect on the electrical properties of this compound. Also, polarization effects are investigated.

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The complex impedance spectroscopy is used to study the electrical properties of samples with different Fe concentrations. This technique provides a simple method to determine the contribution of different mechanisms to the total conductivity of materials and allows studying the polarization effects.

## 2. Experimental details

Perovskite manganese oxides with nominal composition  $\text{Pr}_{0.67}\text{Ba}_{0.33}\text{Mn}_{1-x}\text{Fe}_x\text{O}_3$  (PBMO-Fe) ( $0 \leq x \leq 0.2$ ) are prepared by standard solid state reaction using stoichiometric amounts of precursors,  $\text{Pr}_6\text{O}_{11}$ ,  $\text{BaCO}_3$ ,  $\text{Mn}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$ , with a purity better than 99.9%. The powder is fired at 700 °C for 24 h. Then, we performed several cycles of grinding, pelletizing and heating for 24 h at 1100 °C and then 1200 °C to obtain a well crystallized phase. The powders are pelleted at a pressure of 105 N cm<sup>-2</sup>. The samples are finally annealed at 1453 K for 24 h in air. In previous works [28,29], powder X-ray diffraction and powder neutron diffraction are used to investigate the structure and the morphology of the compound. They have shown that the structural parameters and the grain sizes are not affected by Fe doping.

Pellets with a diameter of 10 mm and a height around 1 mm are used for electrical measurement. An indium ball of a diameter of one millimeter is cut in two pieces. The cut faces are directly deposited on one side of the pellet separated by a distance of 5 mm. Then, the pellet is heated to 170 °C to obtain ohmic contact. The other side is bounded to the cold finger of liquid nitrogen cooled cryostat to vary the sample temperature between 77 and 320 K. The two indium pads are connected to the electrodes of an Agilent 4294 A impedance analyzer to measure the sample conductance. Samples is modeled by a parallel circuit and excited by an alternating signal of an amplitude of 50 mV.

## 3. Result and discussion

### 3.1. DC conductivity analysis

The temperature dependence of dc-conductance  $G_{DC}$  of PBMO-Fe is shown in Fig. 1a. The material exhibits a semiconductor behavior throughout the whole temperature range. The metal-insulator (MI) transition is not observed for all iron concentrations. So, introducing iron in PBMO system suppresses the MI transition observed in free compound [28]. This effect of iron was observed in the  $\text{La}_{0.67}\text{Ba}_{0.33}\text{MnO}_3$  compound [22]. In the temperature range (80–320 K), we observe that DC conductance decreases with increasing Fe content. The decrease of  $G_{DC}$  is due to the replacement of  $\text{Mn}^{3+}$  ion by  $\text{Fe}^{3+}$  one. The eg band of manganese is responsible for the hop of the electron from  $\text{Mn}^{3+}$  to  $\text{Mn}^{4+}$  via oxygen. So the replacement of  $\text{Mn}^{3+}$  by  $\text{Fe}^{3+}$ , which has a completely filled eg band, causes the blocking of the electron hopping between  $\text{Mn}^{3+}$  and  $\text{Fe}^{3+}$  [30,31].

The electron executing hop from one site of  $\text{Mn}^{3+}$  will find  $\text{Fe}^{3+}$ , i.e.  $\text{Mn}^{3+}\text{-O-Fe}^{3+}$  network, around itself. The  $\text{Fe}^{3+}$  could hinder the  $\text{Mn}^{3+}\text{-O-Mn}^{4+}$  networks, which are responsible for carrier hopping, and reduces the available sites for hopping [32]. The decrease in  $G_{DC}$  with Fe doping in our system with nominal stoichiometry was early explained by considering the electronic band structure of the material [22]. It is found that doping with Fe causes depletion in the number of hopping electrons and hence weakens the  $\text{Mn}^{3+}\text{-O-Mn}^{4+}$  interaction, which suppresses metallicity and leads to a compound with a semiconductor behavior. In the literature, Jonker [33] studied the conductivity in the  $\text{LaBaMnFeO}_3$  systems. Such study shows that the  $\text{Fe}^{3+}$ ,  $\text{Mn}^{3+}$  and  $\text{Mn}^{4+}$  ions are present when iron content does not exceed  $x=0.85$ .

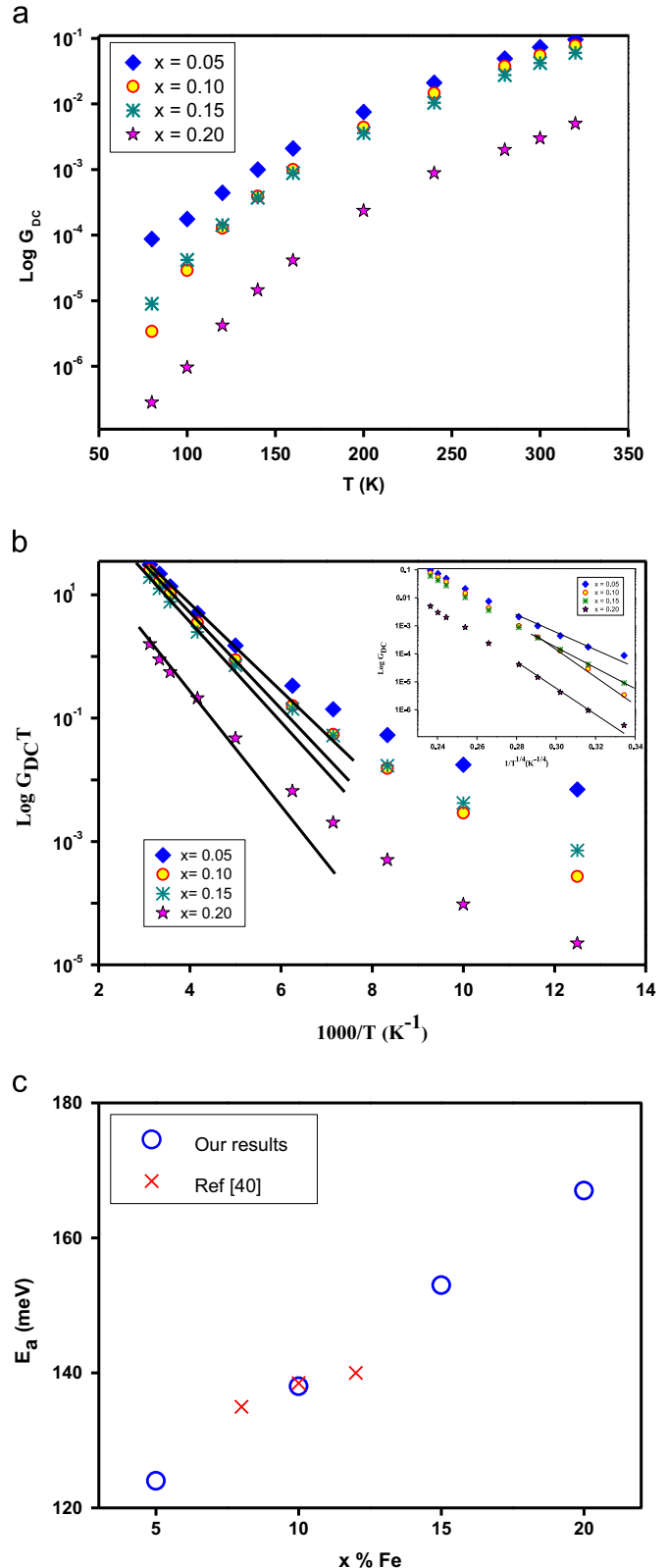


Fig. 1. (a) Temperature dependence of the conductance  $G_{DC}$  of  $\text{Pr}_{0.67}\text{Ba}_{0.33}\text{Mn}_{1-x}\text{Fe}_x\text{O}_3 \equiv \text{PBMO-Fe}$ . (b)  $\text{Log}(G_{DC}T)$  vs  $(1000/T)$ . The inset is  $\text{log}(G_{DC})$  vs  $(T^{-1/4})$ . (c) Variation of activation energy as a function of Fe concentration ( $V_p=0$  V).

For  $x > 0.85$ ,  $\text{Fe}^{3+}$ ,  $\text{Fe}^{4+}$  and  $\text{Mn}^{4+}$  are present. Also, the investigation of physical properties of  $\text{LaCaMnFeO}_3$  by Banks and Tshima [34] shows that hopping mechanism can occur

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