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Pr_{0.7}Ca_{0.3}Mn_{0.8}Cr_{0.2}O₃ as a promising candidate for sensor and thermistor applications: investigation of TCR, SF, β , and α parameters

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Motivated by potential sensor and thermistor applications, a detailed study of the electrical behavior of Pr_{0.7}Ca_{0.3}Mn_{0.8}Cr_{0.2}O₃ (PCMCO) ceramic was carried out. Additionally, to gain deeper insight into the charge transport mechanisms in the studied material, different theoretical conduction models were employed. Indeed, DC-conductance measurements confirm the semiconducting behavior over the investigated temperature range. According to Holstein's theory, the charge transport mechanism in Pr_{0.7}Ca_{0.3}Mn_{0.8}Cr_{0.2}O₃ at elevated temperatures is primarily controlled by non-adiabatic small polaron hopping (NSPH). At low temperatures, the variable range hopping (VRH) mechanism becomes dominant. Furthermore, the temperature coefficient of resistance (TCR) was evaluated to characterize the material's thermo-resistive behavior, highlighting its potential for application in technological devices. It was found that the studied material exhibits a high TCR, reaching $-20.72\% \text{ K}^{-1}$ at 100 K, indicating its promise for use in sensor devices. By determining key thermistor parameters such as the stability factor (SF), sensitivity parameter (β), and sensitivity factor (α), Pr_{0.7}Ca_{0.3}Mn_{0.8}Cr_{0.2}O₃ is considered a promising candidate for thermistor applications. The frequency-dependent conductance spectrum, observed between 80 K and 280 K, is well described by Jonscher's power law, revealing both hopping and tunneling transport processes.

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1. Introduction

Manganite systems with the general formula AMnO₃, particularly those doped with rare-earth elements have attracted extensive scientific interest due to their distinctive structural, electrical and magnetic properties.^{1–9} These properties render them promising candidates for various technological applications. Notably, owing to their favorable mixed ionic–electronic conductivity and high thermal stability, manganites have demonstrated significant potential for solid oxide fuel cells (SOFCs).^{10,11} These materials are also used in spintronic devices and magnetic sensors due to their pronounced magnetoresistive behavior and transport anisotropy arising from lattice distortions.^{11–15} Furthermore, manganites are deemed suitable for use in photovoltaic devices as well as optoelectronic applications, as reported in previous studies^{16,17} and in our prior work.⁴ Therefore, several research teams have extensively investigated the physical properties of these systems. Among the extensively studied manganite systems, praseodymium-based manganites have attracted significant attention due to their diverse physical properties. The

properties of these materials are strongly influenced by the complex interplay between their spin, charge orbital and magnetic degrees of freedom.^{9,18,19} Accordingly, the improvement of their physical properties is principally controlled by the modification of several factors such as the nature of the dopant element, its concentration, and appropriate substitution at the A site, the Mn site, or simultaneously at both the A and Mn sites.^{8,20–25} In recent years, several studies have extensively explored the effects of doping at the Mn site in manganite materials.^{2,4,7,8,26–29} Such an approach offers an effective strategy of tuning their structural, electrical, and magnetic properties by directly altering the Mn³⁺/Mn⁴⁺ ratio. Additionally, it influences the double-exchange (DE) interactions and the dynamics of polarons.² Furthermore, Mn-site substitution can induce significant changes in the relative cooling power (RCP) and the magnetoresistance response; therefore, modification of the transport properties of these materials.^{28,30–33} In this regard, substituting Mn with other transition metals possessing different electronic configurations results in significant changes to the electronic structures of both Mn and the substituting elements. As a result, the type of dopant element and the microstructure play a major role in governing the conduction mechanisms, the dynamics of the charge carriers, and thermally activated transport phenomena. It equally influences the

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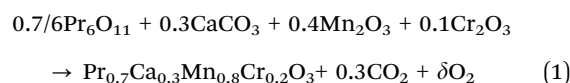


colossal magnetoresistance, which in turn modifies the overall physical properties of manganite systems.¹ Among the various dopant elements at the Mn site, doping by chromium (Cr³⁺) ions is one of the most intensively studied substitutions by many research groups.^{31,32,34–36} Its electronic configuration is similar to that of the Mn³⁺ ion; however, it is devoid of an itinerant (e_g) electron.³⁷ As a result, Jahn–Teller distortions are effectively suppressed, leading to significant alterations in the Mn–O–Mn super-exchange channels.³⁷ In ref. 2, the authors reported that the introduction of Cr element at the Mn site might disturb long-range double-exchange conduction. Accordingly, it strengthens electron–phonon coupling and favors the formation of small polarons. According to the reported results in ref. 38, chromium ion act as effective dopants for inducing a metal–insulator transition in charge-ordering (CO) manganite compounds, leading to an enhancement of the colossal magnetoresistance effect. It is worth noting that the level of Cr substitution plays a crucial role in determining the transport properties of Pr–Ca manganites. While low Cr concentrations generally induce moderate perturbations in the Mn³⁺/Mn⁴⁺ network, higher substitution levels can lead to significant modifications of the electronic structure and charge transport mechanisms. In particular, a Cr content as high as 20% is expected to strongly disrupt the double-exchange interaction and enhance carrier localization effects. This can result in a qualitative transition from partially delocalized transport to a regime dominated by hopping conduction processes. In this context, the composition Pr_{0.7}Ca_{0.3}Mn_{0.8}Cr_{0.2}O₃ offers an interesting platform to explore the interplay between strong localization, hopping dynamics, and thermo-resistive performance. However, despite its potential, such a high Cr substitution level has not been sufficiently investigated in terms of its combined impact on electrical transport and thermistor-related properties, which motivates the present study. To understand the dynamics of charge carriers within several oxides, numerous theoretical approaches have been developed to explain the electrical transport properties of manganites in both DC and AC regimes.^{39–46} In the DC regime, the small polaron hopping (SPH), and the variable range hopping (VRH) models are principally used to explain the origin of the semiconducting behavior observed in various classes of oxides. At elevated temperatures, the adiabatic and the non-adiabatic models developed within Holstein's theory have been extensively used to analyze the electrical behavior of a wide range of materials.⁴⁷ Nevertheless, in the AC regime, the high-frequency conductance spectra typically exhibit a power-law behavior. Accordingly, the transport properties in this region arise from the combined contributions of both hopping and tunneling conduction mechanisms.^{44–46,48} Tang *et al.*⁴⁹ and Pi *et al.*⁵⁰ have found that, in perovskite systems, the solubility of certain dopants is limited to $x = 0.2$. Thus, a large Cr content was deliberately chosen to enhance the electrical properties of Pr_{0.7}Ca_{0.3}MnO₃ manganite while remaining within the permissible concentration limit in perovskite systems. This enhancement with higher Cr amount is particularly relevant for the negative temperature coefficient (NTC) behavior and the temperature coefficient of resistance (TCR) in praseodymium-based

manganites. In contrast to our previous studies on Cr-doped Pr–Ca manganites, which mainly focused on fundamental transport behavior, the present work aims to establish a direct link between charge transport mechanisms and thermistor functionality. Particular attention is devoted to the composition Pr_{0.7}Ca_{0.3}Mn_{0.8}Cr_{0.2}O₃, for which a comprehensive investigation of both DC and AC electrical properties is performed in conjunction with a detailed evaluation of key thermistor parameters, including the temperature coefficient of resistance (TCR), sensitivity parameter (β), sensitivity factor (α), and stability factor (SF). Notably, the material exhibits an enhanced TCR in the low-temperature regime, highlighting its potential for sensitive thermal detection. By correlating the dominant conduction mechanisms namely, non-adiabatic small polaron hopping at high temperatures and variable range hopping at low temperatures with device-relevant performance metrics, this study provides a more application-oriented perspective that goes beyond conventional transport analysis.

2. Experimental details

Manganite-based oxide systems can generally be prepared using a variety of preparation techniques, each providing specific advantages depending on the desired material properties. In the present investigation, the solid-state reaction method was employed to synthesize the Pr_{0.7}Ca_{0.3}Mn_{0.8}Cr_{0.2}O₃ compound due to its simplicity and suitability for large-scale production. Additionally, high-purity precursors Pr₆O₁₁, CaCO₃, Cr₂O₃, and Mn₂O₃ were used to prepare the studied manganite, mixed in the desired stoichiometric ratios according to the following chemical reaction:



The resulting powders are subsequently pressed into pellets. They are then sintered sequentially at 800, 1000, 1100, and 1300 °C for 24 h per cycle.³⁰ Intermediate regrinding and re-pelletizing are performed to ensure privileged crystallization.³⁰ The obtained compound is finally cooled from the high sintering temperature to room temperature following the cooling inertia of the furnace (~8 h). For structural characterization, the crystal structure for Pr_{0.7}Ca_{0.3}Mn_{0.8}Cr_{0.2}O₃ sample was performed at room temperature by X-ray powder diffraction (XRD) with Cu K α radiation. As reported in ref. 30, this manganite forms a single phase without detectable impurities, crystallizing an orthorhombic structure with the Pnma space group. For the electrical characterization, all the achieved electrical measurements are affected using impedance spectroscopy technique over a wide frequency range [40–4 × 10⁶ Hz]. A thin layer of silver is deposited on the two opposite faces of the pellet form a plate capacitor configuration, allowing for electrical measurements. After that, the investigated Pr_{0.7}Ca_{0.3}Mn_{0.8}Cr_{0.2}O₃ is installed in Janis VPF-800 cryostat to control the temperature between 80 K and 300 K. Under vacuum and in



darkness, measurements are taken using an Agilent 4294 analyzer with a 20 mV excitation signal.

3. Results and discussion

3.1 DC-conductance analysis

The temperature dependence of the DC electrical conductance (G_{dc}) of $\text{Pr}_{0.7}\text{Ca}_{0.3}\text{Mn}_{0.8}\text{Cr}_{0.2}\text{O}_3$ manganite is shown in Fig. 1(a). Over the investigated temperature region (from $T = 80$ K to $T = 300$ K), G_{dc} is found to increase monotonically with increasing temperature indicating the semiconducting behavior of the studied system. According to the results reported in ref. 17, such experimental observation can be associated with the localization of charge carriers, which arises from the enhancement of electron–phonon interaction coupled with lattice distortions. Additionally, in $\text{Pr}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ manganite structure, the electrical transport properties are principally controlled by the double-exchange (DE) mechanism between Mn^{3+} cations and Mn^{4+} cations *via* oxygen anions.⁵¹ This process facilitates the movement of electrons from one site to another. In our system, substituting chromium at the Mn site disturbs the Mn conduction pathways. This effect suppresses the DE interaction leading to a reduction in charge carrier mobility as commonly reported for Cr-substituted manganites.⁵² As a result, an enhancement in carrier localization, accompanied by thermally activated transport, results in an increase in G_{dc} with temperature. On the other hand, the electrical transport properties of the manganite are strongly influenced by the microstructure of the material. It has been reported that the introduction of Cr at the Mn site primarily affects the grain boundaries, which play an important role in controlling the movement of the charge carriers.² These grain boundaries, which are more resistive than the grain interiors, act as barriers that hinder the movement of charge carriers, thereby enhancing their localization. To overcome these barriers, the charge carriers need sufficient thermal energy. Therefore, the electrical conductance of $\text{Pr}_{0.7}\text{Ca}_{0.3}\text{Mn}_{0.8}\text{Cr}_{0.2}\text{O}_3$ increases with increasing temperature, which is a characteristic feature of semiconducting behavior. In the DC conductance regime, the observed semiconducting behavior is principally related to the contribution of different conduction processes. The small polaron hopping (SPH) and the variable range hopping (VRH) models are the two mechanisms that can be used to describe the transport properties of $\text{Pr}_{0.7}\text{Ca}_{0.3}\text{Mn}_{0.8}\text{Cr}_{0.2}\text{O}_3$ system. At high temperatures and beyond half of the Debye temperature ($\theta_D/2$), the electrical conductance evolution is related to the thermal activation of the SPH mechanism. Therefore, the electrical conduction in this process occurs between nearest-neighbor sites. Additionally, the temperature at which the high-temperature linear region begins to deviate from linear behavior is commonly associated with $\theta_D/2$, where θ_D denotes as the Debye temperature.⁵³ In the literature,^{54–56} the SPH mechanism is explained in terms of the adiabatic SPH (ASPH) and the non-adiabatic SPH (NSPH) models. The latter is mainly introduced to justify the transport properties at elevated temperatures. According to these models,

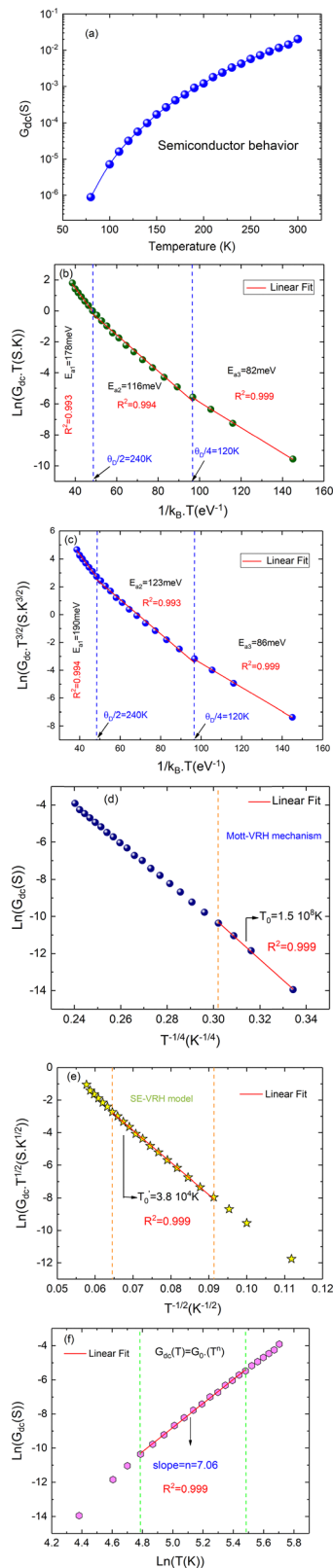


Fig. 1 (a)–(f) Temperature dependence of the DC-conductance (G_{dc}) for $\text{Pr}_{0.7}\text{Ca}_{0.3}\text{Mn}_{0.8}\text{Cr}_{0.2}\text{O}_3$ compound. (a). Evolution of $\ln(G_{dc} \cdot T)$ (b) and $\ln(G_{dc} \cdot T^{3/2})$ (c) against $1/k_B T$. Variation of $\ln(G_{dc})$ versus $T^{-1/4}$ (d). Variation of $\ln(G_{dc} \cdot T^{1/2})$ against $T^{-1/2}$ (e). Variation of $\ln(G_{dc})$ as a function of $\ln(T)$ (f).



the temperature dependence of the dc-conductance is given by eqn (2) and (3), respectively, for ASPH and NSPH processes as follows:⁴⁷

$$G_{\text{dc}} \cdot T = A \exp\left(\frac{-E_a}{k_B T}\right) \quad (2)$$

$$G_{\text{dc}} \cdot T^{3/2} = A \exp\left(\frac{-E_a}{k_B T}\right) \quad (3)$$

where E_a is the activation energy, required for the displacement of charge carriers between two states. It can be expressed according to the following relation:⁵⁷

$$E_a = E_H + E_D/2 \quad \text{for } T > \theta_D/2 \quad (4)$$

$$E_a = E_D \quad \text{for } T < \theta_D/4 \quad (5)$$

E_H , and E_D represent respectively the polaron hopping and disorder energy. The appearance of disorder energy arises from the local arrangement of the ions variation.^{39,40,42,43} For ASPH and NSPH models, the variation of $\ln(G_{\text{dc}} \cdot T)$ and $\ln(G_{\text{dc}} \cdot T^{3/2})$ as a function of the inverse temperature for $\text{Pr}_{0.7}\text{Ca}_{0.3}\text{Mn}_{0.8}\text{Cr}_{0.2}\text{O}_3$ compound are shown in Fig. 1(b) and (c). At high temperatures and for $T > \theta_D/2$, each conductance curve exhibits a linear behavior, that confirms the thermally activation of the adiabatic SPH (ASPH) or the non-adiabatic SPH (NSPH) mechanisms. For the investigated $\text{Pr}_{0.7}\text{Ca}_{0.3}\text{Mn}_{0.8}\text{Cr}_{0.2}\text{O}_3$, the deduced Debye temperature is $\theta_D = 480$ K. Based on the Holstein's theory,^{54,55} the dominant mechanism of the SPH process can be defined by comparing the ratio between both polaron bandwidth J as well as the critical polaron energy bandwidth Φ . If $\frac{J}{\Phi} > 1$, the transport properties of the investigated material at high temperatures are dominated by the ASPH model.

Conversely, for the NSPH model, $\frac{J}{\Phi} < 1$. In this case, the parameters J and Φ are deduced using the following expressions:^{54,55}

$$J = 0.67h\vartheta_{\text{ph}}\left(\frac{T}{\theta_D}\right)^{1/4} \quad (6)$$

$$\Phi = \left(\frac{2k_B T E_a}{\pi}\right)^{1/4} \left(\frac{h\vartheta_{\text{ph}}}{\pi}\right)^{1/2} \quad (7)$$

The parameters h and k_B correspond respectively to the Planck and Boltzmann constants ($h = 4.14375 \times 10^{-15}$ eV s and $k_B = 8.617333 \times 10^{-5}$ eV K⁻¹). ϑ_{ph} is the optical phonon frequency as evaluated from the expression:⁵⁸ $h\vartheta_{\text{ph}} = k_B\theta_D$. From the linear fits of the ASPH and NSPH models, the extracted electrical parameters values are summarized in Table 1. It is found that

Table 1 The deduced parameters from the adiabatic and the non-adiabatic models for $\text{Pr}_{0.7}\text{Ca}_{0.3}\text{Mn}_{0.8}\text{Cr}_{0.2}\text{O}_3$

	E_{a1} (eV)	E_H (eV)	E_D (eV)	θ_D (K)	ϑ_{ph} (Hz)	$\frac{J}{\Phi}$	γ_p
ASPH	0.178	0.137	0.082	480	0.99×10^{13}	0.92	6.67
NSPH	0.190	0.147	0.086	480	0.99×10^{13}	0.90	7.16

the calculated values of $\frac{J}{\Phi}$ are 0.92 and 0.90 for the ASPH and NSPH models, respectively. In this case, the calculated $\frac{J}{\Phi}$ ratio is less than 1 after the application of both models, indicating that the NSPH is the most adequate model for describing the observed high-temperature behavior of $\text{Pr}_{0.7}\text{Ca}_{0.3}\text{Mn}_{0.8}\text{Cr}_{0.2}\text{O}_3$. Accordingly, the temperature dependence of dc-conductance obeys the eqn (3). To get insight into the type of electron-phonon interaction, it is useful to calculate the value of the coupling polaron (γ_p) using the formula:⁵⁹ $\gamma_p = \frac{2E_H}{h\vartheta_{\text{ph}}}$. Based on

the found results in Table 1, and for the NSPH process γ_p is equal to 7.16. As reported by Millis⁶⁰ a powerful electron-phonon interaction takes place when $\gamma_p > 4$, whereas a weak electron-phonon interaction dominates when $\gamma_p < 4$. As a result, the coupling polaron γ_p plays a crucial role in determining the main properties of the material. Consequently, the γ_p value is an effective parameter for characterizing the electron-phonon interaction. In our investigation, the obtained value of γ_p clearly satisfies this condition ($\gamma_p = 7.16 > 4$). Such result confirms the appearance of strong electron-phonon interaction in $\text{Pr}_{0.7}\text{Ca}_{0.3}\text{Mn}_{0.8}\text{Cr}_{0.2}\text{O}_3$. The same behavior is recently observed in other manganite systems like $\text{La}_{0.8}\text{Ca}_{0.2}\text{Mn}_{0.5}\text{Ni}_{0.5}\text{O}_3$ oxide.⁶¹ To affirm again this strong interaction in the studied compound, we can evaluate the value of $\frac{m_p}{m^*}$ according to the formula:⁵⁸

$$\frac{m_p}{m^*} = \left(\frac{h^2}{m^* 8\pi^2 J R^2}\right) \exp(\gamma_p) = \exp(\gamma_p) \quad (8)$$

where m_p , and m^* are respectively the polaron mass and the rigid lattice effective mass. It is found that the $\frac{m_p}{m^*}$ value from the NSPH approach is $\frac{m_p}{m^*} = 1286$. Such a large value further indicates the strong electron-phonon interaction.

Fig. 1(d) shows the variation of $\ln(G_{\text{dc}})$ versus $T^{-1/4}$. Below $\theta_D/4$, the observed linearity of the plotted curve indicates that the charge transport in the studied compound is governed by the Mott-VRH mechanism. Hence, the temperature dependence of G_{dc} is expressed by the following equation:^{62,63}

$$G_{\text{dc}}(T) = G_0 \exp\left(\frac{-T_0}{T}\right)^{1/4} \quad (9)$$

G_0 is the pre-exponential factor. T_0 is a characteristic temperature, which was used to determine the density of states value ($N(E_F)$) at the Fermi level. Such a parameter was obtained using the relation cited below:

$$N(E_F) = \frac{16\alpha^3}{k_B T_0} \quad (10)$$

Here α represents the inverse localization length (*i.e.*, the spatial extent of the localized wave function). From the linear fit of Fig. 1(d), the experimental value of T_0 was deduced and found to be 1.5×10^8 K. This value is in good agreement with predictions of Mott's assumption,^{39,40,42,43} which mentioned a characteristic T_0 in the order of 10^8 K. Based on the expression



(10), the value of $N(E_F)$ was calculated, $N(E_F) = 1.23 \times 10^{24} \text{ eV}^{-1} \text{ cm}^{-3}$ for $\alpha^{-1} = 10 \text{ \AA}$.⁶⁴ At temperatures surpassing $\theta_D/4$, the increase in temperature leads to an improvement in the density of mobile charge carriers, inducing a strong electron-lattice coupling.^{39,40,42,43} Therefore, the contribution of the Mott-variable range hopping mechanism to the transport phenomenon becomes less significant. A high concentration of electrons gives rise to enhance interaction between the charge carriers mobile.³⁹ Such behavior can be associated with the effect of the temperature rise on the dynamics of electrons.

Fig. 1(e) presents the variation of $\ln(G_{dc} \cdot T^{1/2})$ as a function of $T^{-1/2}$. In the intermediate temperature interval, the linear slope indicates that the electrical conduction of $\text{Pr}_{0.7}\text{Ca}_{0.3}\text{Mn}_{0.8}\text{Cr}_{0.2}\text{O}_3$ can be described by the Shklovskii-Efros variable range hopping (SE-VRH) mechanism. In this regime, Coulomb interactions between charge carriers play a major role. So, the temperature dependence of G_{dc} can be explained using SE-VRH model:^{65,66}

$$G_{dc} \cdot T = A \exp\left(\frac{-T'_0}{T}\right)^{1/2} \quad (11)$$

A is a pre-exponential factor, whereas the SE-VRH characteristic temperature T'_0 is estimated as $3.8 \times 10^4 \text{ K}$. Furthermore, within the same temperature range, the charge transport can be analyzed using the Shimakawa method.^{40,67} According to this approach, the electrical conductance can be explained by tunneling mechanisms. For $\theta_D/4 \leq T \leq \theta_D/2$, the variation of G_{dc} versus temperature can be investigated using the relation: $G_{dc}(T) = G_0 \cdot (T)^n$ (Fig. 1(f)). The deduced value of the exponent parameter is $n = 7.06$. This suggests that multi-phonon-assisted tunneling processes predominantly govern the conductance.

3.2 Negative temperature coefficient characteristic

A negative temperature coefficient (NTC) thermistor, also known as a negative thermal resistor, is a semiconductor device in which the electrical resistance decreases with increasing temperature. This behavior originates from the effect of temperature on the mobility of the charge carriers. Fig. 2(a) shows the variation of $\ln(R)$ as a function $1/k_B T$ of the $\text{Pr}_{0.7}\text{Ca}_{0.3}\text{Mn}_{0.8}\text{Cr}_{0.2}\text{O}_3$ oxide. Over the explored temperature region, a linear variation is observed. This behavior is characteristic of materials presenting a pronounced negative temperature coefficient (NTC), in which the electrical resistance decreases with increasing temperature. This indicates the semiconductor nature of the prepared compound. Accordingly, the temperature dependence of the electrical resistance is described by ref. 68 and 69:

$$R = R_0 \exp\left(\frac{E_a}{k_B T}\right) \quad (12)$$

R_0 is the resistance at infinite temperature. From the linear Fit of Fig. 2(a), the value of the thermistor constant β is deduced through the relation:^{70,71} $\beta = E_a/k_B$, giving a value of $\beta = 1496 \text{ K}$. Comparing with other systems displaying a thermistor constant (β) varying from 654.68 to 8417.895,^{72,73} our elaborated system is a suitable candidate for thermistor applications. In addition, to explore the stability performance of $\text{Pr}_{0.7}\text{Ca}_{0.3}\text{Mn}_{0.8}\text{Cr}_{0.2}\text{O}_3$

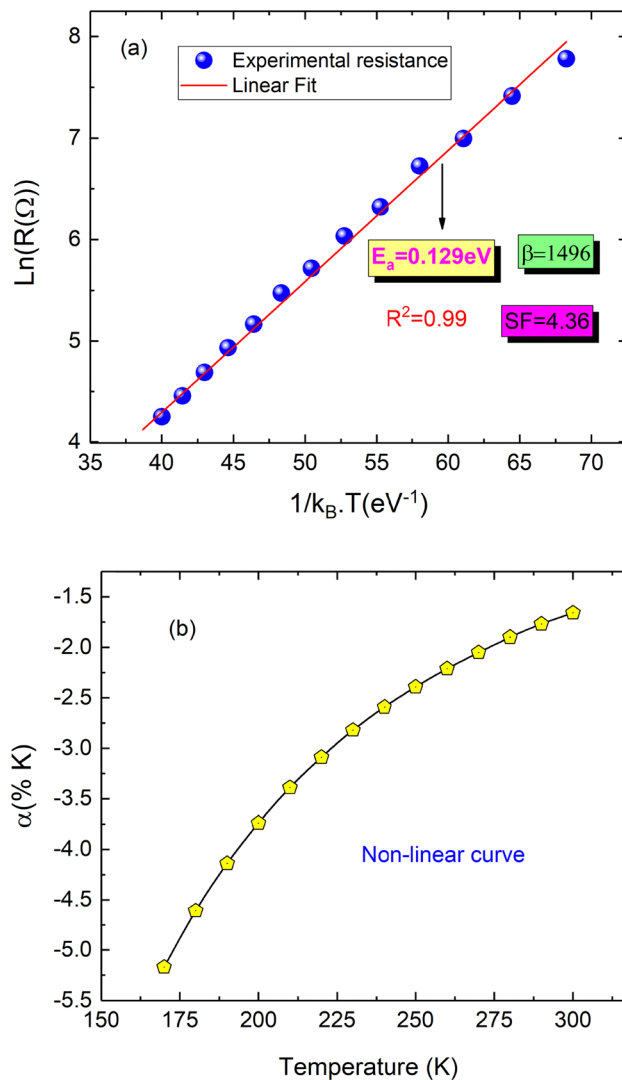


Fig. 2 (a) Evolution of $\ln(R)$ against $1/k_B T$ and the deduced electrical parameters for $\text{Pr}_{0.7}\text{Ca}_{0.3}\text{Mn}_{0.8}\text{Cr}_{0.2}\text{O}_3$. Temperature dependence of the sensitivity parameter (α) (b).

manganite, the stability factor (SF) value was calculated according to the following relation:^{73,74}

$$\text{SF} = \log\left(\frac{R_{\max}}{R_{\min}}\right) \quad (13)$$

For the investigated $\text{Pr}_{0.7}\text{Ca}_{0.3}\text{Mn}_{0.8}\text{Cr}_{0.2}\text{O}_3$, SF is found to be 4.36. Such a significant value indicates a strong temperature dependence of the electrical resistance response, implying that this compound is a promising candidate for sensor applications.^{75,76} Generally, using the factor β , the temperature coefficient or sensitivity parameter (α) can be determined using the following expression:⁷⁷

$$\alpha(T) = -\frac{\beta}{T^2} \times 100 \quad (14)$$

Fig. 2(b) displays the temperature dependence of α for the studied system. The obtained experimental results reveal that α increases in a nonlinear manner, which is a typical behavior



observed in NTC thermistor materials. This nonlinearity is frequently associated with the fast thermal response of sensing materials.⁷⁷ In comparison with previously reported results in the literature,⁷⁵ the present sample can be considered suitable for thermistor applications. The obtained α value is consistent with those reported by Priyambada Mallick *et al.*, who noted that thermistors exhibiting satisfactory performance generally possess a sensitivity parameter α within the range of -1% to -9% .⁷⁵ In the present work, the α values are found to vary between -1% and -4% , demonstrating a good agreement with the desired range. According to previous studies, the variation in the temperature coefficient is mainly attributed to the presence of extrinsic charge carriers in the grain regions, which significantly affect the electrical transport properties.⁷³

3.3 The temperature coefficient of resistance

To describe the sensitivity of a compound's electrical resistance to temperature variations, the temperature coefficient of resistance (TCR) is an important parameter. In semiconducting and NTC thermistor materials, the TCR commonly displays negative values, indicating a decrease in the resistance values with increasing temperature.^{78–80} Consequently, the TCR analysis is crucial for estimating the potential of materials for temperature-sensing and thermistor applications. The temperature coefficient of resistance (TCR) values are evaluated according to the following expression:^{4,78–80}

$$\text{TCR} = \frac{1}{R} \left(\frac{dR}{dT} \right) \times 100\% \quad (15)$$

The temperature coefficient of resistance (TCR %) *versus* temperature for $\text{Pr}_{0.7}\text{Ca}_{0.3}\text{Mn}_{0.8}\text{Cr}_{0.2}\text{O}_3$ is depicted in Fig. 3. It is evident that the compound exhibits a remarkably high TCR, reaching $-20.72 \pm 0.5\% \text{ K}^{-1}$ at $T = 100 \text{ K}$, with an activation energy $E_a = 0.129 \pm 0.003 \text{ eV}$, and a sensitivity parameter $\beta = 1496 \pm 35 \text{ K}$. These values indicate a pronounced carrier

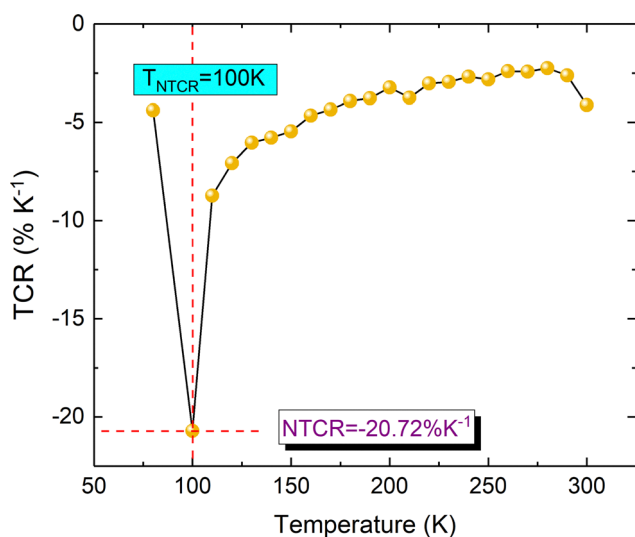


Fig. 3 Variation of the temperature coefficient of resistance (TCR) against temperature $\text{Pr}_{0.7}\text{Ca}_{0.3}\text{Mn}_{0.8}\text{Cr}_{0.2}\text{O}_3$ compound.

localization, characteristic of small polaron hopping conduction. Relative to other reported manganites in the literature (see Table 2), the present compound shows a significantly enhanced TCR. For instance for $\text{Sm}_{0.45}\text{Pr}_{0.1}\text{Sr}_{0.45}\text{MnO}_3$ ($\text{TCR} = -7\% \text{ K}^{-1}$),⁸¹ $\text{La}_{0.7}(\text{Sr}_{5/6}\text{Na}_{1/6})_{0.3}\text{Mn}_{0.7}\text{Ti}_{0.3}\text{O}_3$ ($\text{TCR} = -13.36\% \text{ K}^{-1}$),⁸² $\text{La}_{0.14}\text{Nd}_{0.35}\text{Sr}_{0.3}\text{MnO}_3$ ($\text{TCR} = 2.7\% \text{ K}^{-1}$),⁸³ and $\text{La}_{0.7}\text{K}_{0.25}\text{Sr}_{0.05}\text{MnO}_3$ ($\text{TCR} = 11.9\% \text{ K}^{-1}$),⁸⁴ $\text{Pr}_{0.8}\text{K}_{0.1}\text{Na}_{0.1}\text{MnO}_3$ ($\text{TCR} = -3.79\% \text{ K}^{-1}$),⁸⁵ $\text{Pr}_{0.8}\text{K}_{0.15}\text{Na}_{0.05}\text{MnO}_3$ ($\text{TCR} = -4.037\% \text{ K}^{-1}$),⁸⁵ and $\text{Pr}_{0.7}\text{Ca}_{0.3}\text{Mn}_{0.85}\text{Cr}_{0.15}\text{O}_3$ ($\sim 18\% \text{ K}^{-1}$).⁵ Alongside the previously mentioned oxides, varieties of additional oxide systems exhibiting different crystal structures and transport behaviors have been examined for use in thermistor applications.^{86–89} $\text{Ba}_3\text{Bi}_2\text{Fe}_2\text{O}_9$ ($\beta \approx 1683 \text{ K}$)⁸⁶ and KBiFeMnO_5 ($\beta \approx 4634 \text{ K}$)⁸⁹ are representative examples of defect perovskites and complex oxides that demonstrate comparatively high thermistor constants. Nevertheless, in spite of these elevated β values, their temperature coefficients are either moderate or not expressly indicated, thereby hindering their effectiveness for high-sensitivity temperature sensing applications. The detailed comparison in Table 2, which includes the synthesis method, peak TCR temperature, activation energy (E_a), and sensitivity parameter (β), demonstrates that the present sample achieves an optimal combination of high TCR and moderate activation energy. This combination enables a rapid response and dependable performance across the operating temperature range, highlighting the material's suitability for low-temperature sensing. Compared with the TCR values reported for the above-mentioned oxides, the $\text{Pr}_{0.7}\text{Ca}_{0.3}\text{Mn}_{0.8}\text{Cr}_{0.2}\text{O}_3$ sample demonstrates significant potential for applications in low-temperature sensors, such as detectors.

3.4 AC-conductance study

3.4.1 Effect of the frequency variation on the electrical behavior. The temperature dependence of the electrical conductance for $\text{Pr}_{0.7}\text{Ca}_{0.3}\text{Mn}_{0.8}\text{Cr}_{0.2}\text{O}_3$ at different frequencies is shown in Fig. 4(a). For all the chosen frequency values, it is clearly observed that the conductance values increase with increasing temperature. Such behavior confirms the semiconductor character of the investigated compound. This behavior arises from the existence of cation–anion–cation interactions within the entire temperature domain examined. As a function of increasing temperature, each conductance curve can be split into two distinct domains. Below $T_d = 170 \text{ K}$, a noticeable impact on the frequency increase on the electrical conductance is observed at very low temperatures. Indeed, the conductance response is found to increase proportionally with frequency. In such temperature regions, the transport properties of $\text{Pr}_{0.7}\text{Ca}_{0.3}\text{Mn}_{0.8}\text{Cr}_{0.2}\text{O}_3$ are dominated by the Mott-VRH conduction process. Therefore, increasing the frequency has a negligible influence on the cationic disorder of the mentioned system. For $T > T_d = 170 \text{ K}$, the electrical conductance is solely controlled by temperature variation. In fact, the rise in frequency does not influence its behavior or order.

Fig. 4(b) presents the variation of $\ln(G_{ac} \cdot T)$ *versus* $1/k_B T$. This kind of representation allows us to deduce the activation energy (E_a) value in different temperature intervals and at multiple



Table 2 Comparison of thermistor parameters of the studied material with comparable oxide-based thermistors from literature

Materials	Synthesis method	TCR (% K ⁻¹)	Peak TCR temperature (K)	E _a (eV)	β (K)	Ref.
Pr _{0.7} Ca _{0.3} Mn _{0.8} Cr _{0.2} O ₃	Solid-state reaction	-20.72	100	0.129	1496	This work
Sm _{0.45} Pr _{0.1} Sr _{0.45} MnO ₃	Solid-state reaction	-7	160	0.168	—	81
La _{0.7} (Sr _{5/6} Na _{1/6}) _{0.3} Mn _{0.7} Ti _{0.3} O ₃	Solid-state reaction	-13.36	115	0.196	—	82
La _{0.14} Nd _{0.35} Sr _{0.3} MnO ₃	Solid-state reaction	2.7	289	—	—	83
La _{0.7} K _{0.25} Sr _{0.05} MnO ₃	Sol-gel spin-coating technique	11.9	291.2	—	—	84
Pr _{0.8} K _{0.1} Na _{0.1} MnO ₃	Sol-gel method	-3.79	200	—	—	85
Pr _{0.8} K _{0.15} Na _{0.05} MnO ₃	Sol-gel method	-4.037	180	—	—	85
Pr _{0.7} Ca _{0.3} Mn _{0.85} Cr _{0.15} O ₃	Solid-state reaction	18	90	0.115	1350	5
Ba ₃ Bi ₂ Fe ₂ O ₉	Solid-state sintering technique	—	—	—	≈ 1683	86
KBiFeMnO ₅	Solid-state sintering technique	—	—	≈ 0.399	≈ 4634	89

frequencies. It also highlights the effect of frequency on E_a . Thus, the activation energy value for each selected frequency was determined from the observed slopes. At low frequencies, the calculated activation energy is found to be $E_a = 170$ meV, which is very close to the value obtained from the DC-conductance analysis ($E_a = 178$ meV) within the same temperature range (Fig. 1(b)). This close indicates a strong correlation between AC and DC conductance, suggesting that they originate from the same mechanism. Fig. 4(c) displays the frequency dependence of the disorder E_D and hopping E_H energies. From the variation of E_D , it is observed that the increase in frequency leads to decreased E_D values, which is in agreement with Miller-Abrahams theory:^{47,90}

$$E_D = \frac{0.3e^2}{\epsilon_s \times R_{\text{hop}}} \quad (16)$$

The factors e and ϵ_s present respectively the electronic charge and the static dielectric constant. The variation in the disorder energy with frequency may be associated with a modification in the average distance between the hop centers (R_{hop}). However, an increase in the hopping energy (E_H) with rising frequency is observed. Following the theories of Mott *et al.*,^{39,40,42,43} E_H can be determined using the following equation:

$$E_H = \frac{E_p}{2} = \frac{e^2}{4\epsilon_p} \left(\frac{1}{R_{\text{pol}}} - \frac{1}{R_{\text{hop}}} \right) \quad (17)$$

R_{pol} is the radius of polaron and ϵ_p is the effective dielectric constant.

3.4.2 Conductance spectrum analysis. To elucidate the charge transport mechanism and explain the origin of the electrical conduction in the AC region, the investigation of the electrical conductance as a function of frequency is an effective approach. Such measurements provide valuable insight into the models governing transport properties. For manganite materials, it has been widely reported that the conductance spectra in the dispersive zone generally follow Jonscher's or double Jonscher power laws. Within this framework, the dominant conduction mechanisms associated with charge carrier displacement between sites can be identified through the analysis of the frequency exponent s . In the present section, the frequency dependence of the ac-conductance (G_{ac}) for the investigated Pr_{0.7}Ca_{0.3}Mn_{0.8}Cr_{0.2}O₃ is shown in Fig. 5(a). As a function of the frequency rise, each conductance curve is characterized by the presence of two distinct regions. At low

frequencies, the ac-conductance remains almost constant, indicating that the transport process is not influenced by frequency variation. Hence, the conductance spectrum shows a DC plateau, which arises from long-range charge transport.^{8,91,92} This behavior is generally associated to the thermally activated nature of the small polaron hopping. At high frequencies, and in the temperature range [80–280 K], each conductance spectrum exhibits a single dispersive region. In this region, G_{ac} depends strongly on frequency and increases as the frequency rises. Thus, the Jonscher power law (JPL) is valid for explaining the electrical response of the system, expressed as:^{57,93}

$$G_{\text{ac}} = G_{\text{dc}} + A\omega^s \quad (18)$$

The parameter s is the frequency exponent, which varies with temperature. It expresses the coupling between the charge carriers and the lattice. For recent oxide and brownmillerite-based materials, authors have reported similar conductivity spectra, suitable for thermistor and electronic applications.^{94–96} For example, in their study of the defect brownmillerite LiBiFeMnO₅, Panda *et al.*⁹⁴ reported conductivity spectra characterized by a low-frequency plateau, ascribed to long-range charge transport, accompanied by a dispersive high-frequency region associated with thermally activated hopping among localized states. A JPL-type response was also observed over a wide temperature range in complex molybdate materials such as Sr–Bi–Mo–O ceramics,⁹⁶ where the dispersive range was attributed to short-range hopping of charge carriers across grain boundaries and defect sites. These results suggest that the JPL is an effective approach for describing the AC conductivity of different material classes, such as manganites. Beyond $T = 280$ K, a decrease in the conductance is observed. Although this behavior may appear metallic-like behavior, however, in polaronic manganites, it should be interpreted with precaution. In fact, the reduction in the electrical conductance with increasing temperature can be related to strengthened carrier scattering. This behavior occurs due to strong electron-phonon interactions, which reduce carrier mobility. As the temperature increases, the scattering mechanism becomes more pronounced. This leads to a hindrance of charge transport and therefore to the observed decrease in the conductance. In this temperature range, the transport mechanism wanders a crossover from a thermally activated regime, commonly described by small polaron hopping,^{39,40} toward a regime of delocalized carriers with significant scattering, as widely reported in manganite systems.^{4,6}



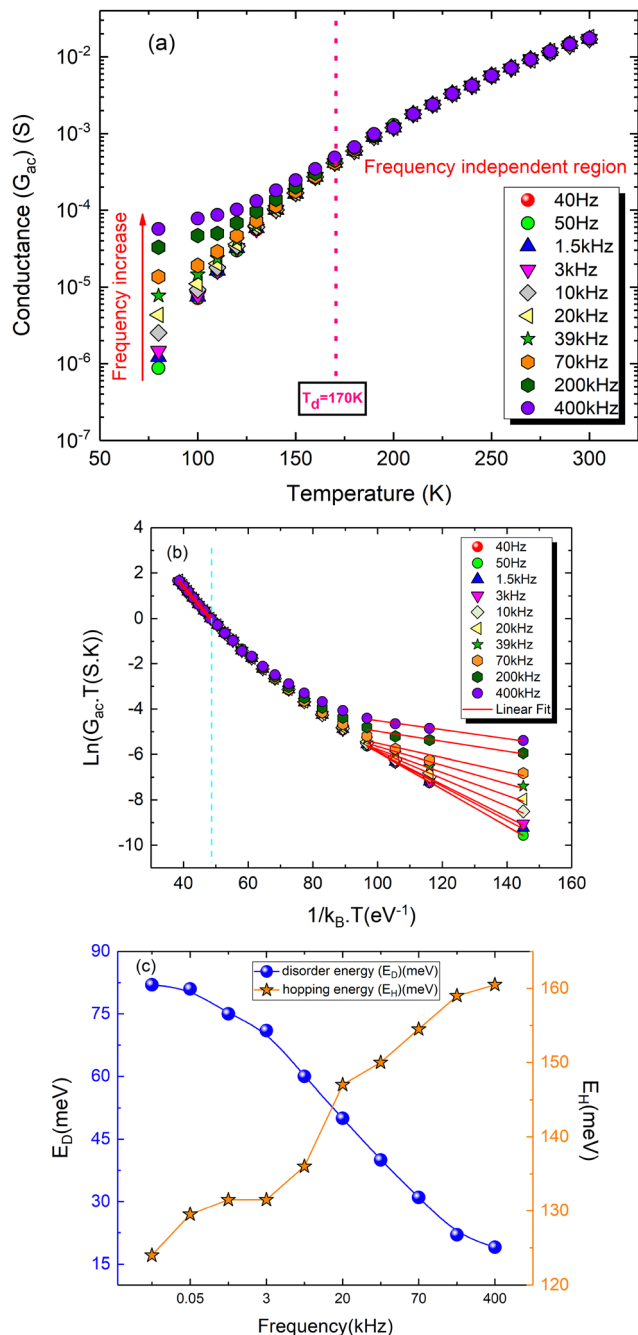


Fig. 4 (a) Temperature dependence of G_{ac} at selected frequencies for $\text{Pr}_{0.7}\text{Ca}_{0.3}\text{Mn}_{0.8}\text{Cr}_{0.2}\text{O}_3$. Plot of $\ln(G_{ac} \cdot T)$ against $1/k_B T$ (b). Frequency dependence of the disorder E_D and hopping E_H energies (c).

Such transition is also supported by the change in the temperature dependence of conductance, such as variation in the slope, which indicates a shift from localized to partially delocalized charge transport. Based on the above results, the ac-conductance is well fitted by the Drude model:⁹⁷

$$G_{ac} = \frac{G_{dc}}{1 + \omega^2 \tau_s^2} \quad (19)$$

The parameter τ_s is the time between two consecutive collisions.

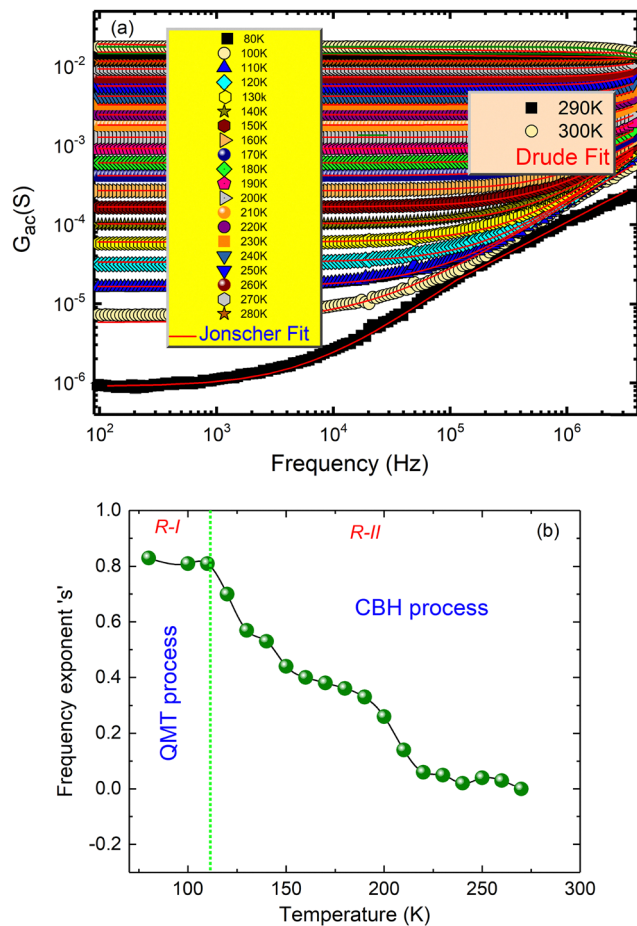


Fig. 5 (a) Frequency dependence of AC-conductance (G_{ac}) for $\text{Pr}_{0.7}\text{Ca}_{0.3}\text{Mn}_{0.8}\text{Cr}_{0.2}\text{O}_3$. Temperature dependence of the frequency exponent 's' (b).

In accordance with the Drude model, the metallic-like behavior observed in $\text{Pr}_{0.7}\text{Ca}_{0.3}\text{Mn}_{0.8}\text{Cr}_{0.2}\text{O}_3$ manganite, at elevated frequencies can be associated with the polaronic charge carriers. This behavior is further influenced by the double-exchange mechanism, which promotes the creation of effectively free hopping electrons. Such a process improves free electron collisions and strengthens the direct interaction between the Mn cations. To clarify the origin of the conductance increase in the dispersive zone and to identify the dominant AC conduction processes, the temperature dependence of the frequency exponent 's' is shown in Fig. 5(b). According to the found results in ref. 6, 8 and 61, it is identified that the transport properties can be dominated by the contribution of both tunneling and hopping conduction models. As shown in Fig. 5(b), that the obtained values of 's' are less than the unity indicating that the charge carriers transport occurs through translation motion accompanied by sudden hopping. In the investigated temperature region, it is clearly observed that the conductance increase in the dispersive range is mainly due to the contribution of two dissimilar conduction mechanisms. In the first region (R-I), corresponding to the temperature range $T = 80$ – 110 K, the frequency exponent 's' appears temperature independent. It



achieved a value of $s = 0.81$. This is in good agreement with the quantum–mechanical tunneling process (QMT). As reported in ref. 27, 47 and 61 that the temperature independent of the tunneling distance and the constancy of the frequency exponent 's' with temperature may be the responsible for the occurrence of the QMT model. In the second region (R-II), defined over the temperature range $T = 110$ – 280 K, the parameter 's' is found to increase with decreasing temperature, reaching a value of 0.8 at $T = 110$ K. In such case, we can assume that the correlated barrier hopping (CBH) model can be considered as the appropriate model for describing the charge transport properties of the investigated system within this temperature region. The same evolution has also been reported in Co-PCMO manganites.⁸

4. Conclusion

A comprehensive investigation of the transport properties of $\text{Pr}_{0.7}\text{Ca}_{0.3}\text{Mn}_{0.8}\text{Cr}_{0.2}\text{O}_3$ has been carried out to evaluate its potential in thermistor and sensor applications. The obtained results demonstrate that $\text{Pr}_{0.7}\text{Ca}_{0.3}\text{Mn}_{0.8}\text{Cr}_{0.2}\text{O}_3$ exhibits not only well-defined semiconducting transport governed by non-adiabatic small polaron hopping and variable range hopping mechanisms, but also promising thermistor characteristics. The relatively high TCR value obtained at low temperature, together with favorable sensitivity (β , α) and stability (SF) parameters, underscores the potential of this compound for thermal sensing applications. The observed dispersive conductance range arises from the combined contribution of both hopping and tunneling processes, including QMT, and the CBH models. Importantly, the present study goes beyond conventional transport modeling by establishing a clear correlation between the underlying conduction processes and the resulting functional performance. This approach provides new insight into the design and optimization of manganite-based materials for thermistor devices, thereby offering a benefit compared to previous investigations on similar systems.

Conflicts of interest

The authors declare no conflicts of interest.

Data availability

All the data that support this research are included within the article.

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