UNIVERSITI TEKNOLOGI MARA

EFFECT OF Fe AND Cr SUBSTITUTION AT Mn-SITE ON STRUCTURE, MAGNETIC, MAGNETOTESISTANCE BEHAVIOUR AND DIELECTRIC PROPERTIES IN Pr-BASED MANGANITES

SITI SUMAIYAH BINTI SHEIKH ABDUL AZIZ

PhD

July 2024

ABSTRACT

The substitution of Fe or Cr at the Mn site was suggested to directly impact the interaction between Mn ions in manganites and have different effects on the compound properties which required detailed investigations. Thus, Pr_{0.75}Na_{0.05}K_{0.20}Mn_{1-x}Fe_xO₃ and $Pr_{0.75}Na_{0.05}K_{0.20}Mn_{1-x}Cr_xO_3$ (x =0.00-0.05) manganites were prepared using solid-state synthesis to elucidate their structural, magnetic, electrical, and dielectric properties as well as magnetoresistance (MR) effect. For Pr_{0.75}Na_{0.05}K_{0.20}Mn_{1-x}Fe_xO₃ series, all samples (x = 0-0.05) exhibited ferromagnetic (FM)-paramagnetic (PM) transition behaviour and a decrease of Curie temperature (T_C). The reduction in T_C indicates the weakening of the FM interaction involving Mn³⁺ and Mn⁴⁺ ions as Fe³⁺ replaces Mn³⁺ site. The observed large increased in resistivity with Fe substitution with the decreased in the metal-insulator transition temperature (T_{MI}) from 122 K (x = 0) to 80 K (x = 0.02). Under a 0.8 T applied field, all samples showed a decrease in resistivity between 30 K - 300 K, indicating the presence of MR effects. The intrinsic MR effect increase from 22% (x = 0.0) to 40% (x = 0.02) near T_{MI} indicates Fe³⁺ substitution enhanced intrinsic MR effect, which may be related to the reduction of spin disordering. The extrinsic MR effect increased to 42% (x = 0.04), due to enhancement of the spin polarised tunnelling process. While for Pr_{0.75}Na_{0.05}K_{0.20}Mn_{1-x}Cr_xO₃ series, Cr³⁺ substitution increased the unit cell volume and distorted the MnO $_6$ octahedra. The T_C value slightly decreased from 140.7 K (x = 0.00) to 139.3 K (x = 0.02) and increased with higher concentration of Cr^{3+} to 143.4 K (x = 0.05). The observed large increased in resistivity with Cr^{3+} substitution and the decrease in T_{MI} from 122 K (x = 0) to 90 K (x = 0.05) samples. The observed absence of GP in all Fe and Cr-substituted samples, on the other hand, may be related to variations in magnetic interaction in the studied compounds. The dielectric constant, dielectric loss, and tangent loss all drop with frequency, owing to the dominant contributions of Maxwell-Wagner interfacial polarisation and grain boundary resistance. The observed change in the metal-insulator transition temperature and resistivity due to Fe and Cr substitution, implies a potential approach for precisely enhancing the electrical characteristics of these materials, which is essential in spintronic applications. Thus, Fe and Cr substitutions at Mn-sites Pr_{0.75}Na_{0.05}K_{0.20}MnO₃ play an important role in structure, magnetic, electrical, magnetoresistance behaviour and dielectric properties but not in GP.

ACKNOWLEDGEMENT

Assalamualaikum w.b.t.

This thesis summarises my research work as a PhD student in the Superconductor Lab at Universiti Teknologi MARA (UiTM) Shah Alam between October 2021 and October 2023. Alhamdulillah, praise be to Allah, the Almighty of God. My heartfelt thankfulness to Allah S.W.T for his blessing in allowing and providing me with the opportunity to successfully complete my PhD studies.

First and foremost, I would like to express my deepest gratitude to my supervisor, Dr. Norazila Ibrahim, for the opportunity to pursue my PhD in the field of manganites materials. With her priceless guidance, and knowledge, and for consistently providing excellent feedback, constantly reviewing my progress, and guiding me through my PhD studies. Special thanks to my co-supervisors, Dr. Zakiah Mohamed, and Dr. Rozilah Rajmi, for their contributions and advice on my research.

Next, I want to express profound appreciation to my parents, En. Sheikh Abdul Aziz and , as well as the rest of my family, for their unwavering faith, love, and encouragement throughout my studies. I am eternally grateful to my husband, En. Muhammad Shahrul Azren, and my children (Azim, Azmya, Azhfar) for their sacrifice, patience, and love during my studies. This journey would not have been possible without their permission, blessing and prayers.

I'm thankful to my lab mates, especially Nur Amirah Zahrin and Nor Asmira Amaran, who always took the time to help me with lab things and were always available for discussions about anything I was unsure about, as well as Liyana, Athirah, Atiqah, Farhana, Naim, and Afiq, who were wonderful people both in and out of the lab, and to my friends, who were always there for me when I needed them.

Finally, I am grateful to the Ministry of Higher Education (MOHE) for financial support through Skim Latihan Akademi Bumiputera (SLAB), as well as the management of the Faculty of Applied Sciences (FSG) and UiTM for providing a good environment and facilities for me to complete my studies. Alhamdulilah.

Thank you.

TABLE OF CONTENTS

			Page				
CONFIRMATION BY PANEL OF EXAMINERS			ii				
AUTHOR'S DECLARATION			iii				
ABSTRACT			iv				
ACKNOWLEDGEMENT TABLE OF CONTENTS LIST OF TABLES			v vi x				
				LIST OF FIGURES			xiv
				LIST OF SYMBOLS			xxiii
LIST OF ABBREVIATIONS			xxvi				
CHA	APTER	1 INTRODUCTION	28				
1.1	Resea	arch Background	28				
1.2	Proble	Problem Statement					
1.3	Resea	Research Objectives					
1.4	Scope and Limitation of study		34				
1.5	Significance of Study		34				
CHA	APTER 2	2 LITERATURE REVIEW	36				
2.1	Introd	luction	36				
2.2	Physical Properties of Perovskite Manganites		36				
	2.2.1	Crystal Structure of manganites	37				
	2.2.2	Electrical Properties	38				
	2.2.3	Electrical Properties in Pr _{0.75} Na _{0.25-x} K _x MnO ₃	48				
	2.2.4	Magnetic Properties in Manganites	49				
	2.2.5	Magnetic Properties in Pr _{0.75} Na _{0.25-x} K _x MnO ₃	53				
	2.2.6	Magnetoresistance (MR) Effect in Manganites	54				

CHAPTER 1

INTRODUCTION

1.1 Research Background

Manganite materials have recently emerged as one of the most intriguing research topics due to their physical properties and colossal magnetoresistance (CMR) [1]–[3]. Furthermore, manganite have unique properties which can be considered for a new class of electronic devices based on the MR effect [4] which predicted an increase in wide applications area such in consumer, automotive, medical, industrial, and other applications [5]. With the rapid development of electronic devices towards integration and miniaturisation, the feature sizes of microelectronic devices based on rare-earthdoped perovskite manganite are now down-scaled to nanoscale dimensions [6]. Based on the need and demand from society for effective technologies and communication, more research should be focused on next generation nanoelectronics devices [7]. A wide range of study has been conducted, focusing on various methods and chemicals [8] for improving the magnetic, electrical, and dielectric properties of these compounds, which may be potential candidates for industrial applications such as spintronic-based devices [1], [2], [9], magnetic sensors [1], non-volatile memory elements [9], and supercapacitor electrodes [8]. Furthermore, manganite exhibit tuneable electrical and magnetic properties that are switchable in an external applied field, implying a wide range of applications. In addition to the stated above properties, some manganite have high dielectric permittivity values, which improve their multiferroic properties and industrial applications due to spontaneous polarisation [10]. Belmabrouk et al. reported that the substitution of Mn by a transition metal such as Aluminium (Al) caused structural disorder, which was responsible for high dielectric properties of material, making the study sample a potential candidate for a wide range of applications such as microelectronic devices, energy industry applications, multilayer ceramic capacitors, and high density energy storage [8].