UNIVERSITI PUTRA MALAYSIA

DIELECTRIC AND MAGNETIC CHARACTERIZATION OF (La0.5-xPrxBa0.5)(Mn0.5Ti0.5)O3 PEROVSKITE AS A MULTIFERROIC MATERIAL SYNTHESIZED VIA SOLID STATE TECHNIQUE

NOR HAYATI BT. ALIAS
FS 2009 37
DIELECTRIC AND MAGNETIC CHARACTERIZATION OF 
(La_{0.5-x}Pr_xBa_{0.5})(Mn_{0.5}Ti_{0.5})O_3PEROVSKITE AS A MULTIFERROIC MATERIAL SYNTHESIZED VIA SOLID STATE TECHNIQUE

NOR HAYATI BT. ALIAS

MASTER OF SCIENCE
UNIVERSITI PUTRA MALAYSIA

2009
DIELECTRIC AND MAGNETIC CHARACTERIZATION OF 
(La_{0.5-x}Pr_xBa_{0.5})(Mn_{0.5}Ti_{0.5})O_3 PEROVSKITE AS A MULTIFERROIC 
MATERIAL SYNTHESIZED VIA SOLID STATE TECHNIQUE

NOR HAYATI BT. ALIAS

MASTER OF SCIENCE 
UNIVERSITI PUTRA MALAYSIA

2009
DIELECTRIC AND MAGNETIC CHARACTERIZATION OF (La_{0.5-x}Pr_xBa_{0.5})(Mn_{0.5}Ti_{0.5})O_3 PEROVSKITE AS A MULTIFERROIC MATERIAL SYNTHESIZED VIA SOLID STATE TECHNIQUE

By

NOR HAYATI BT. ALIAS

Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia, in Fulfilment of the Requirements for the Degree of Master of Science

October 2009
DEDICATION

To god, my children and Dear husband

For the remembrance of my beloved late mother and father,

Friends, Universiti Putra Malaysia and Agency Nuclear Malaysia
A new manganate perovskite \((\text{La}_{0.5-x}\text{Pr}_x\text{Ba}_{0.5})(\text{Mn}_{0.5}\text{Ti}_{0.5})\text{O}_3\) has been prepared by ceramic solid-state technique at sintering temperature 1300 °C for 24 hours. The \(x\) concentration of Praseodymium (Pr) in molar proportion in A site has been varied as \(x = 0, 0.01, 0.02, 0.03, 0.04, 0.05, 0.06, 0.07, 0.08, 0.09, 0.1, 0.2, 0.3\) and 0.4. The dielectric properties of the synthesized materials have been studied at frequency ranging from 5 Hz to 1 MHz from room temperature up to 200 °C. Furthermore, analyses have been carried out to determine the structural, magnetic and dielectric electrical properties of the synthesized material as a candidate of multiferroic material.

Pr (Praseodymium) addition would promote liquid phase sintering in the synthesized samples. This enhanced the agglomeration and porosity formation in the bulk volume. The defects and conducting liquid present would generate traps that
produce negative permittivity response at interfacial/space charge frequency region due to delay in transient current or situation in which inertial conducting current of the trap presents, exceeding the charging-discharging current component. The XRD (X-Ray Diffractometry) results indicate all samples possess a single phase monoclinic structure with space group P112. Multiferroic magnetodielectric coupling in material with ferromagnetic and high dielectric constant ($>30$) is able to achieve in sample with $x$ molar concentration $= 0.07$ at room temperature. The dielectric value obtained is 176 with loss tan $\delta$ value 0.62. SEM/EDX analysis of the sample shows fine grain microstructure and high manganese (Mn) content ($>0.6$ wt %) which favours the double exchange mechanism.

Comparing to unsubstituted Pr sample, $x=0$; sample with $x$ molar concentration 0.2 and 0.4 shows enhanced dielectric values with additional loss. The ranged of dielectric value obtained for unsubstituted sample $x=0$ is 3117 to 12396 while for $x=0.2$ and $x=0.4$ the value range obtained is 1611 to 16316 and 967 to 13185 respectively. The increment is associated with both polarization and conduction mechanism process. Where, the dielectric constant and loss is contribution from the effect of space charge polarization and/or ion conducting motion. Respectively, generally higher values of dielectric constant is obtained in unsubstituted sample $x = 0$ and high $x$ substituted concentration 0.1, 0.2, 0.3 and 0.4 as a results of dual relaxational polarization mechanisms existed in the frequency ranged studied. Dc conduction is found to be dominated the sample at high temperature regime and for low substituted sample with $x$ molar concentration 0.01, 0.02, 0.03, 0.04, 0.05, 0.06, 0.07, 0.08 and 0.09. This is to suggest of enhanced mobility of localized charge carriers in liquid phase region. Whereas in sample Pr(X)0.07, dominated dc
conduction effect is due to fast ion hopping conduction in its fine grain microstructure with high Mn content.
Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan Ijazah Master Sains

PENCIRIAN DIELEKTRIK DAN MAGNET (La_{0.5-x}Pr_xBa_{0.5})(Mn_{0.5}Ti_{0.5})O_3 PEROVSKITE SEBAGAI BAHAN MULTIFEROIC MELALUI TEKNIK KEADAAN PEPEJAL

Oleh

NOR HAYATI BT. ALIAS

Oktober 2009

Pengerusi: Abdul Halim Shaari, PhD.

Fakulti: Sains

Satu bahan baru seramik perovskite dari kumpulan manganit (La_{0.5-x}Pr_xBa_{0.5})(Mn_{0.5}Ti_{0.5})O_3 telah disediakan melalui teknik tindak balas keadaan pepejal pada suhu pensinteran 1300 °C selama 24 jam. Kepekatan x molar Praseodymium (Pr) pada kedudukan A pada perovskite telah ditetapkan sebagai x = 0, 0.01, 0.02, 0.03, 0.04, 0.05, 0.06, 007, 0.08, 0.09, 0.1, 0.2, 0.3 and 0.4. Kajian dielektrik telah dikendalikan pada julat frekuensi 5 Hz sehingga 1 MHz dalam keadaan suhu bilik sehingga suhu mencapai 200° C. Analisa juga dilakukan untuk mengkaji sifat struktur, magnet dan dielektrik bahan yang telah disintesis serta melihat kesan pengkupelan multiferoik pada bahan yang dikaji.

Telah didapati bahawa kesan penggantian Pr (Praseodymium) ke atas bahan telah meningkatkan kesan pembentukan fasa solidus ceair pada mikrostruktur bahan.
Kesan agglomerasi dan pembentukan liang pada bahan juga adalah agak ketara. Ini memberi kesan kecacatan dalam bahan. Kecacatan serta kandungan fasa solidus cecair dalam mikrostruktur bahan telah mewujudkan kawasan negatif permiittiviti spektra pada julat frekuensi interfasial. Ini adalah mungkin disebabkan oleh kesan kelambatan pada pergerakan arus peralihan elektrik atau disebabkan oleh kesan penghasilan arus inertia daripada perangkap kecacatan yang lebih besar. Analisis XRD (X-Ray Difraktometri) telah menunjukkan bahan yang disintesis mempunyai fasa tunggal hablur monoklinik P112. Adalah didapati juga bahawa kesan pengkupelan sifat dielektrik dan magnet berjaya diperolehi pada x dengan kepekatan molar 0.07. Sifatnya adalah feromagnetik dengan nilai pemalar dielektrik bahan 176 dan tan δ 0.76 pada suhu bilik. Bahan ini juga didapati mempunyai mikrostruktur dengan saiz butiran yang kecil serta kandungan Mangan (Mn) yang agak tinggi (> 0.6 bt %) lantas menambahkan kesan mekanisma pertukaran ganda dua (DE) pada bahan.

Jika dibandingkan dengan bahan tanpa penggantian Pr iaitu x=0; sampel x=0.2 dan x=0.4 menunjukkan peningkatan nilai pemalar dielektrik juga nilai tan δ nya. Julat nilai dielektrik yang diperoleh untuk sampel x=0 adalah 3117 to 12396. Sementara julat nilai yang diperoleh dari sampel dengan x molar kepekatan x=0.2 dan x=0.4 ialah 1611 - 16316 dan 967 - 13185. Keadaan ini adalah disebabkan oleh kedua-dua jenis mekanisma yang hadir pada bahan iaitu kesan relaksasi polarisasi serta kekonduksian. Dimana nilai pemalar dielektrik dan tan δ yang diperolehi adalah gabungan daripada kesan polarisasi interfasial dan/atau konduksi pergerakan ion. Nilai pemalar dielektrik dengan x molar = 0, 0.1, 0.2, 0.3 dan 0.4 juga didapati lebih tinggi berbanding sampel x molar rendah. Ini disebabkan oleh wujudnya kesan dwi-
relaksasi polarisasi bahan pada campuran kepekatan tersebut. Bahan x molar rendah
x = 0.01, 0.02, 0.03, 0.04, 0.05, 0.06, 0.07, 0.08 dan 0.09 menunjukkan kesan
kekonduksian dc yang ketara terutamanya pada suhu tinggi. Ini mungkin disebabkan
oleh kesan peningkatan cas yang bergerak pada kawasan solidus ceair bahan.
Bagaimanapun kesan kekonduksian dc pada sampel Pr(X)0.07 ialah disebabkan oleh
penambahan kelincahan pelompatan kekonduksian ion bebas bagi mikrostrukturnya
yang bersaiz butiran lebih kecil dengan kandungan Mn yang lebih tinggi.
ACKNOWLEDGEMENTS

I would like to thank you to my supervisor Professor Dr. Addul Halim bin Shaari for accepting me as his master student. Your scientific insight has helped me in understanding my research. It is a pleasure for me to embark in a scientific journey in discovering and understanding of a new advanced material.

I would like also to express my gratitude to both of my co-supervisors Assoc. Prof. Dr. Wan Mohamad Daud bin Wan Yusoff and Dr Che Seman bin Mahmood for their support during the period of research study.

Thank you also to my friends Zalita, Walter, Mazni, Ina, Nini, Emma and Josephine for their encouragement and help.

The most appreciation goes to my beloved children Nurul Ain Najiha, Muhammad Zahiruddin and my Dear husband Mohd Khalid Matori for their support and prayer.

Finally, my foremost gratitude is for Agency Nuclear Malaysia for the scholarship study in Universiti Putra Malaysia.
I certify that a Thesis Examination Committee has met on 19 October 2009 to conduct the final examination of Nor Hayati binti Alias on her thesis entitled “Dielectric and Magnetic Characterization of \((La_{0.5-x}Pr_xBa_{0.5})(Mn_{0.5}Ti_{0.5})O_3\) Perovskite as a Multiferroic Material via Solid State Technique” in accordance with the Universities and University Colleges Act 1971 and the Constitution of the Universiti Putra Malaysia [P.U.(A) 106] 15 March 1998. The Committee recommends that the student be awarded the Master of Science.

Members of the Examination Committee are as follows:
This thesis was submitted to the Senate of Universiti Putra Malaysia and has been accepted as fulfillment of the requirement of the degree of Master of Science. The members of the Supervisory Committee were as follows:

**Abdul Halim Shaari, PhD**  
Professor  
Faculty of Science  
Universiti Putra Malaysia  
(Chairman)

**Wan Mohamad Daud Wan Yusoff**  
Associate Professor  
Faculty of Science  
Universiti Putra Malaysia  
(Member)

**Che Seman Mahmood**  
Dr  
Industrial Technology Group  
Malaysian Technology Group  
(Member)

---

**HASANAH MOHD GHAZALI, PhD**  
Professor and Dean  
School of Graduate Studies  
Universiti Putra Malaysia

Date: 14 January 2010
DECLARATION

I hereby declare that the thesis is based on my original work except for quotations and citations which have been duly acknowledged. I also declare that it has not been previously or concurrently submitted for any other degree at UPM or other institutions.

NOR HAYATI BT. ALIAS

Date: 4 December 2009
TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Chapter</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>TABLE OF CONTENTS</td>
<td></td>
</tr>
<tr>
<td></td>
<td>DEDICATION</td>
<td>II</td>
</tr>
<tr>
<td></td>
<td>ABSTRACT</td>
<td>III</td>
</tr>
<tr>
<td></td>
<td>ABSTRAK</td>
<td>VI</td>
</tr>
<tr>
<td></td>
<td>ACKNOWLEDGEMENTS</td>
<td>IX</td>
</tr>
<tr>
<td></td>
<td>APPROVAL</td>
<td>X</td>
</tr>
<tr>
<td></td>
<td>DECLARATION</td>
<td>XII</td>
</tr>
<tr>
<td></td>
<td>LIST OF TABLES</td>
<td>XV</td>
</tr>
<tr>
<td></td>
<td>LIST OF FIGURES</td>
<td>XVI</td>
</tr>
<tr>
<td></td>
<td>LIST OF ABBREVIATIONS AND KEY WORD</td>
<td>XXV</td>
</tr>
<tr>
<td></td>
<td>CHAPTER</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>INTRODUCTION</td>
<td>1</td>
</tr>
<tr>
<td>1.1</td>
<td>Multiferroic Material and its Relevance</td>
<td>1</td>
</tr>
<tr>
<td>1.2</td>
<td>Manganite Perovskite</td>
<td>5</td>
</tr>
<tr>
<td>1.3</td>
<td>Research Objective</td>
<td>6</td>
</tr>
<tr>
<td>2</td>
<td>LITERATURE REVIEW</td>
<td>8</td>
</tr>
<tr>
<td>2.1</td>
<td>Introduction</td>
<td>8</td>
</tr>
<tr>
<td>2.2</td>
<td>Previous Study</td>
<td>8</td>
</tr>
<tr>
<td>3</td>
<td>THEORY</td>
<td>16</td>
</tr>
<tr>
<td>3.1</td>
<td>Classification of Materials</td>
<td>16</td>
</tr>
<tr>
<td>3.2</td>
<td>Importance of Dielectric Study in Material</td>
<td>16</td>
</tr>
<tr>
<td>3.3</td>
<td>Complex Impedance Spectroscopy</td>
<td>17</td>
</tr>
<tr>
<td>3.4</td>
<td>Polarization Mechanism</td>
<td>18</td>
</tr>
<tr>
<td>3.5</td>
<td>Dielectric Theory</td>
<td>22</td>
</tr>
<tr>
<td>3.6</td>
<td>Analysis of Ac Electrical Data and Dielectric Relaxational Model</td>
<td>27</td>
</tr>
<tr>
<td>3.6.1</td>
<td>Susceptibility Function in Various Model Response</td>
<td>30</td>
</tr>
<tr>
<td>3.6.2</td>
<td>Impedance (Z*) Complex Plot Analysis (Z'/Z'')</td>
<td>33</td>
</tr>
<tr>
<td></td>
<td>3.6.3 Grain Structure and Boundary</td>
<td>34</td>
</tr>
<tr>
<td>4</td>
<td>METHODOLOGY</td>
<td>36</td>
</tr>
<tr>
<td>4.1</td>
<td>Introduction</td>
<td>36</td>
</tr>
<tr>
<td>4.2</td>
<td>Sample Preparation</td>
<td>36</td>
</tr>
<tr>
<td>4.3</td>
<td>Dielectric Measurement</td>
<td>40</td>
</tr>
<tr>
<td>4.4</td>
<td>SEM (Scanning Electron Microscopy)/EDAX (Energy Dispersive X-Ray Analysis)</td>
<td>41</td>
</tr>
<tr>
<td>4.5</td>
<td>XRD (X-Ray Diffraction) Study</td>
<td>42</td>
</tr>
<tr>
<td>4.6</td>
<td>VSM (Vibrating Sample Magnetometer)</td>
<td>43</td>
</tr>
<tr>
<td>4.7</td>
<td>TGA/DTA (Thermogravimetry and Differential Analysis)</td>
<td>43</td>
</tr>
</tbody>
</table>
4.8 FTIR (Fourier Transform Infrared) Spectrometer Analysis
4.9 Dilatometer Study

5 RESULTS AND DISCUSSION
5.1 SEM Micrograph Analysis
5.1.1 High Percentage Substitution of Pr(X) Variant Samples
5.1.2 Low Percentage Substitution of Pr(X) Variant Samples
5.2 EDAX Analysis
5.3 Density Analysis
5.4 Thermal Expansion Coefficient Analysis
5.5 TGA/DTA Analysis
5.6 XRD Analysis
5.7 Electrical Properties
5.7.1 Dielectric Relaxational Studies
5.7.2 Proposed Dielectric Relaxational Model
5.7.3 Dielectric Constant (\(\varepsilon\)) and Dielectric Loss (\(\tan\delta\)) Studies
5.7.4 Impedance Characteristic
5.7.5 Electrical Ac Conductivity Analysis
5.7.6 Conductivity Model Fitting
5.8 FTIR (Fourier Transform Infrared) Spectrometer Analysis
5.9 Magnetization Curve Analysis

6 SUMMARY, CONCLUSION AND RECOMMENDATION FOR FUTURE RESEARCH

REFERENCES
APPENDICES
BIODATA OF STUDENT
## LIST OF TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Pr(X) concentration sample labeling.</td>
<td>37</td>
</tr>
<tr>
<td>2</td>
<td>Relaxation and conduction activation energy for grain-boundary and bulk of Pr(X) samples compositions.</td>
<td>146</td>
</tr>
<tr>
<td>3</td>
<td>Conductivity parameters obtained at 50°C for Pr(X) composition variants.</td>
<td>159</td>
</tr>
<tr>
<td>4</td>
<td>Dc Conductivity (Ea $\sigma_{dc}$) and Ac Conductivity (Ea $\sigma_{ac}$) Activation Energy Obtained from Arrhenius Plot</td>
<td>165</td>
</tr>
</tbody>
</table>
### LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Common structure in perovskite $\text{ABO}_3$.</td>
<td>3</td>
</tr>
<tr>
<td>2</td>
<td>Ideal perovskite structure.</td>
<td>4</td>
</tr>
<tr>
<td>3</td>
<td>The resultant dielectric spectrum.</td>
<td>19</td>
</tr>
<tr>
<td>4</td>
<td>Frequency dependence of polarization mechanism.</td>
<td>19</td>
</tr>
<tr>
<td>5</td>
<td>Different polarization mechanism.</td>
<td>21</td>
</tr>
<tr>
<td>6</td>
<td>Dielectric capacitors (a) in vacuum and (b) with dielectric material between plate, (c) represents a charge distribution built in dielectric material.</td>
<td>22</td>
</tr>
<tr>
<td>7</td>
<td>Phase diagrams for (a) perfect capacitor (b) real capacitor.</td>
<td>22</td>
</tr>
<tr>
<td>8</td>
<td>Dielectric dispersion (a) and absorption (b) in ideal debye dielectric relaxational spectra.</td>
<td>29</td>
</tr>
<tr>
<td>9</td>
<td>Complex impedance plot of ($Z''$ vs $Z'$) for parallel RC circuit.</td>
<td>33</td>
</tr>
<tr>
<td>10</td>
<td>Schematic representation of grains separated by discontinuous grain boundary phase.</td>
<td>34</td>
</tr>
<tr>
<td>11</td>
<td>Flow chart of sample preparation.</td>
<td>38</td>
</tr>
<tr>
<td>12</td>
<td>Pre-sintering heating-cooling cycle profile.</td>
<td>39</td>
</tr>
<tr>
<td>13</td>
<td>Sintering heating-cooling cycle profile.</td>
<td>39</td>
</tr>
<tr>
<td>14</td>
<td>SEM micrographs of substituted concentration of samples (a) $\text{Pr}(X)0$; (b) $\text{Pr}(X)0.1$; (c) $\text{Pr}(X)0.2$; (d) $\text{Pr}(X)0.3$; and (e) $\text{Pr}(X)0.4$.</td>
<td>45</td>
</tr>
<tr>
<td>15</td>
<td>SEM micrographs of substituted Pr samples (a) $\text{Pr}(X)0$; (b) $\text{Pr}(X)0.1$; (c) $\text{Pr}(X)0.2$; (d) $\text{Pr}(X)0.3$ and (e) $\text{Pr}(X)0.4$ after further polishing.</td>
<td>47</td>
</tr>
<tr>
<td>16</td>
<td>SEM micrographs of low substituted Pr samples (a) $\text{Pr}(X)0.01$; (b) $\text{Pr}(X)0.02$; (c) $\text{Pr}(X)0.03$; (d) $\text{Pr}(X)0.04$; (e) $\text{Pr}(X)0.05$; (f) $\text{Pr}(X)0.06$; (g) $\text{Pr}(X)0.07$; (h) $\text{Pr}(X)0.08$ and (i) $\text{Pr}(X)0.09$.</td>
<td>48</td>
</tr>
<tr>
<td>17</td>
<td>Elemental concentration of (a) La, Pr, Ba in active A site and (b) Mn, Ti in active B site by EDAX analysis.</td>
<td>50</td>
</tr>
</tbody>
</table>
18 Density profile plot of synthesized sample.

19 Thermal expansion plot of synthesized samples.

20 TG/DTG curves of sample (a) Pr(X)0; (b) Pr(X)0.1; (c) Pr(X)0.2; (d) Pr(X)0.3 and (e) Pr(X)0.4.

21 TG/DTG curves of sample (a) Pr(X)0.01; (b) Pr(X)0.02; (c) Pr(X)0.03; (d) Pr(X)0.04; (e) Pr(X)0.05; (f) Pr(X)0.06; (g) Pr(X)0.07; (h) Pr(X)0.08 and (i) Pr(X)0.09.

22 Percentage weight loss of Pr(X) variant concentration.

23 XRD diffractogram profile of Pr(X) substituted samples variant.

24 d spacing data of Pr(X) substituted variant concentration.

25 Lattice parameter obtained from XRD profile (a) lattice a, (b) lattice b and (c) lattice c.

26 $\varepsilon', \varepsilon''$ vs frequency plot at room temperature for sample (a) Pr(X)0; (b) Pr(X)0.1; (c) Pr(X)0.2; (d) Pr(X)0.3 and (e) Pr(X)0.4 at 25 °C.

27 $\varepsilon', \varepsilon''$ vs frequency plot for sample (a) Pr(X)0; (b) Pr(X)0.1; (c) Pr(X)0.2; (d) Pr(X)0.3 and (e) Pr(X)0.4 at 50 °C.

28 $\varepsilon', \varepsilon''$ vs frequency plot for sample (a) Pr(X)0; (b) Pr(X)0.1; (c) Pr(X)0.2; (d) Pr(X)0.3 and (e) Pr(X)0.4 at 75 °C.

29 $\varepsilon', \varepsilon''$ vs frequency plot for sample (a) Pr(X)0; (b) Pr(X)0.1; (c) Pr(X)0.2; (d) Pr(X)0.3 and (e) Pr(X)0.4 at 100 °C.

30 $\varepsilon', \varepsilon''$ vs frequency plot for sample (a) Pr(X)0; (b) Pr(X)0.1; (c) Pr(X)0.2; (d) Pr(X)0.3 and (e) Pr(X)0.4 at 125 °C.

31 $\varepsilon', \varepsilon''$ vs frequency plot for sample (a) Pr(X)0; (b) Pr(X)0.1; (c) Pr(X)0.2; (d) Pr(X)0.3 and (e) Pr(X)0.4 at 150 °C.

32 $\varepsilon', \varepsilon''$ vs frequency plot for sample (a) Pr(X)0; (b) Pr(X)0.1; (c) Pr(X)0.2; (d) Pr(X)0.3 and (e) Pr(X)0.4 at 175 °C.
$\varepsilon', \varepsilon''$ vs frequency plot for sample (a) Pr(X)0; (b) Pr(X)0.1; (c) Pr(X)0.2; (d) Pr(X)0.3 and (e) Pr(X)0.4 at 200 °C.

$\varepsilon', \varepsilon''$ vs frequency plot for sample (a) Pr(X)0.01; (b) Pr(X)0.02; (c) Pr(X)0.03; (d) Pr(X)0.04; (e) Pr(X)0.05; (f) Pr(X)0.06; (g) Pr(X)0.07; (h) Pr(X)0.08 and (i) Pr(X)0.09 at 25 °C.

$\varepsilon', \varepsilon''$ vs frequency plot for sample (a) Pr(X)0.01; (b) Pr(X)0.02; (c) Pr(X)0.03; (d) Pr(X)0.04; (e) Pr(X)0.05; (f) Pr(X)0.06; (g) Pr(X)0.07; (h) Pr(X)0.08 and (i) Pr(X)0.09 at 50 °C.

$\varepsilon', \varepsilon''$ vs frequency plot for sample (a) Pr(X)0.01; (b) Pr(X)0.02; (c) Pr(X)0.03; (d) Pr(X)0.04; (e) Pr(X)0.05; (f) Pr(X)0.06; (g) Pr(X)0.07; (h) Pr(X)0.08 and (i) Pr(X)0.09 at 75 °C.

$\varepsilon', \varepsilon''$ vs frequency plot for sample (a) Pr(X)0.01; (b) Pr(X)0.02; (c) Pr(X)0.03; (d) Pr(X)0.04; (e) Pr(X)0.05; (f) Pr(X)0.06; (g) Pr(X)0.07; (h) Pr(X)0.08 and (i) Pr(X)0.09 at 100 °C.

$\varepsilon', \varepsilon''$ vs frequency plot for sample (a) Pr(X)0.01; (b) Pr(X)0.02; (c) Pr(X)0.03; (d) Pr(X)0.04; (e) Pr(X)0.05; (f) Pr(X)0.06; (g) Pr(X)0.07; (h) Pr(X)0.08 and (i) Pr(X)0.09 at 125 °C.

$\varepsilon', \varepsilon''$ vs frequency plot for sample (a) Pr(X)0.01; (b) Pr(X)0.02; (c) Pr(X)0.03; (d) Pr(X)0.04; (e) Pr(X)0.05; (f) Pr(X)0.06; (g) Pr(X)0.07; (h) Pr(X)0.08 and (i) Pr(X)0.09 at 150 °C.

$\varepsilon', \varepsilon''$ vs frequency plot for sample (a) Pr(X)0.01; (b) Pr(X)0.02; (c) Pr(X)0.03; (d) Pr(X)0.04; (e) Pr(X)0.05; (f) Pr(X)0.06; (g) Pr(X)0.07; (h) Pr(X)0.08 and (i) Pr(X)0.09 at 175 °C.

(a-b) Suggested Circuit Model Fitting for (a) Dual Relaxation and (b) Single Relaxation Mechanism.

Fitting of $\varepsilon', \varepsilon''$ vs Frequency plot for sample Pr(X)0 at
25 °C.

44 Fitting of $\varepsilon^\prime$, $\varepsilon^\prime\prime$ vs Frequency Plot for Sample Pr(X)0.1 at 25 °C.

45 Fitting of $\varepsilon^\prime$, $\varepsilon^\prime\prime$ vs Frequency Plot for Sample Pr(X)0.1 at 100 °C.

46 Fitting of $\varepsilon^\prime$, $\varepsilon^\prime\prime$ vs Frequency Plot for Sample Pr(X)0.2 at 25 °C.

47 Fitting of $\varepsilon^\prime$, $\varepsilon^\prime\prime$ vs Frequency Plot for sample Pr(X)0.3 at 50 °C.

48 Fitting of $\varepsilon^\prime$, $\varepsilon^\prime\prime$ vs Frequency Plot for Sample Pr(X)=0.4 at 25 °C.

49 Fitting of $\varepsilon^\prime$, $\varepsilon^\prime\prime$ vs Frequency Plot for Sample Pr(X)=0.01 at 25 °C.

50 Fitting of $\varepsilon^\prime$, $\varepsilon^\prime\prime$ vs Frequency Plot for Sample Pr(X)=0.08 at 25 °C.

51 Dielectric Constant and Loss (Tan $\delta$) Values at Temperature 25 °C to 200 °C for (a) Pr(X)0 and High Substituted Samples (b) Pr(X)0.1; (c) Pr(X)0.2; (d) Pr(X)0.3 and (e) Pr(X)0.4 at 1 MHz.

52 Dielectric Constant and Loss (Tan $\delta$) Values at Temperature 25 °C to 200 °C for Low Substituted Samples (a) Pr(X) 0.01; (b) Pr(X)0.02; (c) Pr(X)0.03; (d) Pr(X)0.04; (e) Pr(X)0.05; (f) Pr(X)0.06; (g) Pr(X)0.07; (h) Pr(X)0.08 and (i) Pr(X) 0.09 at 1 MHz.

53 Equivalent circuit for impedance fitting.

54 $Z'$/$Z''$ plot of sample Pr(X)0 at 25 °C.

55 $Z'$/$Z''$ plot of sample Pr(X)0 at 50 °C.

56 $Z'$/$Z''$ plot of sample Pr(X)0 at 75 °C.

57 $Z'$/$Z''$ plot of sample Pr(X)0 at 100 °C.

58 $Z'$/$Z''$ plot of sample Pr(X)0 at 125 °C.
Z'/Z'' plot of sample Pr(X)0 at 150 °C.

Z'/Z'' plot of sample Pr(X)0 at 175 °C.

Z'/Z'' plot of sample Pr(X)0 at 200 °C.

Variation of resistance, capacitance and relaxation time of grain boundary (gb) and bulk (b) with temperature for Pr (X)0.

ln ω Arrhenius plot of (a) grain boundary and (b) bulk for sample Pr(X)0.

ln σ Arrhenius plot of (a) grain boundary and (b) bulk for sample Pr (X)0.

Z'/Z'' plot of sample Pr(X)0.1 at 100 °C.

Z'/Z'' plot of sample Pr(X)0.1 at 125 °C.

Z'/Z'' plot of sample Pr(X)0.1 at 150 °C.

Z'/Z'' plot of sample Pr(X)0.1 at 175 °C.

Z'/Z'' plot of sample Pr(X)0.1 at 200 °C.

Variation of resistance, capacitance and relaxation time of grain boundary (gb) and bulk (b) with temperature for Pr (X)0.1.

ln ω Arrhenius plot of (a) grain boundary and (b) bulk for sample Pr(X) 0.1.

ln σ Arrhenius plot of (a) grain boundary and (b) bulk for sample Pr(X) 0.1.

Z'/Z'' plot of sample Pr(X)0.2 at 25 °C.

Z'/Z'' plot of sample Pr(X)0.2 at 50 °C.

Z'/Z'' plot of sample Pr(X)0.2 at 75 °C.

Z'/Z'' plot of sample Pr(X)0.2 at 100 °C.

Z'/Z'' plot of sample Pr(X)0.2 at 125 °C.

Z'/Z'' plot of sample Pr(X)0.2 at 150 °C.

Z'/Z'' plot of sample Pr(X)0.2 at 175 °C.
80 $Z'/Z''$ plot of sample Pr(X)0.2 at 200 °C.

81(a-c) Variation of resistance, capacitance and relaxation time of grain boundary (gb) and bulk (b) with temperature for Pr(X)0.2.

82 In $\omega$ Arrhenius plot of (a) grain boundary and (b) bulk for sample Pr(X)0.2.

83 In $\sigma$ Arrhenius plot of (a) grain boundary and (b) bulk for sample Pr(X)0.2.

84 $Z'/Z''$ plot of sample Pr(X)0.3 at 50 °C.

85 $Z'/Z''$ plot of sample Pr(X)0.3 at 75 °C.

86 $Z'/Z''$ plot of sample Pr(X)0.3 at 100 °C.

87 $Z'/Z''$ plot of sample Pr(X)0.3 at 125 °C.

88 $Z'/Z''$ plot of sample Pr(X)0.3 at 150 °C.

89 $Z'/Z''$ plot of sample Pr(X)0.3 at 175 °C.

90 $Z'/Z''$ plot of sample Pr(X)0.3 at 200 °C.

91(a-c) Variation of resistance, capacitance and relaxation time of grain boundary (gb) and bulk (b) with temperature for Pr(X)0.3.

92 In $\omega$ Arrhenius plot of (a) grain boundary and (b) bulk for sample Pr(X) 0.3.

93 In $\sigma$ Arrhenius plot of (a) grain boundary and (b) bulk for sample Pr(X)0.3.

94 $Z'/Z''$ plot of sample Pr(X)0.4 at 25 °C.

95 $Z'/Z''$ plot of sample Pr(X)0.4 at 50 °C.

96 $Z'/Z''$ plot of sample Pr(X)0.4 at 75 °C.

97 $Z'/Z''$ plot of sample Pr(X)0.4 at 100 °C.

98 $Z'/Z''$ plot of sample Pr(X)0.4 at 125 °C.

99 $Z'/Z''$ plot of sample Pr(X)0.4 at 150 °C.

100 $Z'/Z''$ plot of sample Pr(X)0.4 at 175 °C.
101 Z'/Z'' plot of sample Pr(X)0.4 at 200 °C.

102(a-c) Variation of resistance, capacitance and relaxation time of grain boundary (gb) and bulk (b) with temperature for Pr (X)0.4.

103 In ωp Arrhenius plot of (a) grain boundary and (b) bulk for sample Pr(X)0.4.

104 In σ Arrhenius plot of (a) grain boundary and (b) bulk for sample Pr(X)0.4.

105 Z'/Z'' plot of sample Pr(X)0.01 at 25 °C.

106 Z'/Z'' plot of sample Pr(X)0.01 at 50 °C.

107 Z'/Z'' plot of sample Pr(X)0.01 at 75 °C.

108 Z'/Z'' plot of sample Pr(X)0.01 at 100 °C.

109 Z'/Z'' plot of sample Pr(X)0.01 at 125 °C.

110 Z'/Z'' plot of sample Pr(X)0.01 at 150 °C.

111(a-c) Variation of resistance, capacitance and relaxation time of bulk (b) with temperature for Pr(X)0.01.

112 In ωp Arrhenius plot of bulk for sample Pr(X)0.01.

113 In σ Arrhenius plot of bulk for sample Pr(X)0.01.

114 Z'/Z'' plot of sample Pr(X)0.08 at 25 °C.

115 Z'/Z'' plot of sample Pr(X)0.08 at 50 °C.

116 Z'/Z'' plot of sample Pr(X)0.08 at 75 °C.

117 Z'/Z'' plot of sample Pr(X)0.08 at 100 °C.

118 Z'/Z'' plot of sample Pr(X)0.08 at 125 °C.

119 Z'/Z'' plot of sample Pr(X)0.08 at 150 °C.

120(a-c) Variation of resistance, capacitance and relaxation time of bulk (b) with temperature for Pr(X)0.08.

121 In ωp Arrhenius plot of bulk for sample Pr(X)0.08.

122 In σ Arrhenius plot of bulk for sample Pr(X)0.08.