Phase transition in Pb[(Mg\(_{3/4}\)Cu\(_{1/4}\))\(_{1/3}\)Nb\(_{2/3}\)]O\(_3\) ceramic

Amit Kumar\(^a\), K Prasad\(^a\), S N Choudhary\(^a\) & T P Sinha\(^b\)

\(^a\)Materials Research Laboratory, University Department of Physics, T. M. Bhagalpur University, Bhagalpur 812 007, India

\(^b\)Department of Physics, Bose Institute, 93/1 A.P.C. Road, Kolkata 700 009, India

Received 22 March 2004; accepted 10 October 2005

Single phase perovskite-type cubic ceramics of Pb[(Mg\(_{3/4}\)Cu\(_{1/4}\))\(_{1/3}\)Nb\(_{2/3}\)]O\(_3\) (PMCN) were synthesized by high temperature double step solid state reaction technique. Dielectric studies show relaxor behaviour with diffuse phase transition. The phase transition (\(T_m\)) occurs at \(-22^\circ\text{C}\) at 10 kHz. The frequency dependence of \(T_m\) has been modeled using Vogel-Fulcher relation. The dielectric relaxation in PMCN is found analogous to the magnetic relaxation in spin-glass system. The relaxor behaviour in PMCN has also been examined through admittance spectroscopy.

IPC Code: C04B33/00, G01N33/38

In recent years, there has been a growing interest in Pb-based relaxor ferroelectrics having perovskite type A(B′B′′)O\(_3\) structure. Among these, lead magnesium niobate, Pb(Mg\(_{1/3}\)Nb\(_{2/3}\))O\(_3\) (abbreviated as PMN) is one of the most interesting and extensively studied system, which has already shown its potential in various electronic devices such as in multilayer capacitors (MLCs), actuators, electrostrictive devices, and as a suitable alternative for the SiO\(_2\) layer in MOSFET\(^{1-3}\). Since the discovery of PMN, numerous pure and modified PMN and its isomorphous compounds, e.g., Pb(Zn\(_{1/3}\)Nb\(_{2/3}\))O\(_3\), Pb(Ni\(_{1/3}\)Nb\(_{2/3}\))O\(_3\), Pb(Fe\(_{1/2}\)Nb\(_{1/2}\))O\(_3\), Pb(I\(_{1/2}\)Nb\(_{1/2}\))O\(_3\), Pb(Mg\(_{1/4}\)Cd\(_{1/4}\) Nb\(_{1/2}\))O\(_3\), Pb(Fe\(_{1/2}\)Nb\(_{1/2}\))O\(_3\) + PbTiO\(_3\), (Pb,Ba) [(Zn\(_{1/3}\)Nb\(_{2/3}\))-(Mg\(_{1/3}\)Nb\(_{2/3}\))Ti]O\(_3\), Pb(Mg\(_{1/3}\)Nb\(_{2/3}\))O\(_3\) + PbTiO\(_3\) + BaTiO\(_3\), Pb(Zn\(_{1/3}\)Nb\(_{2/3}\))O\(_3\) + PbTiO\(_3\) + BaTiO\(_3\), and Pb(Mg\(_{1/3}\)Nb\(_{2/3}\))O\(_3\) + PbTiO\(_3\) + Ba(Zn\(_{1/3}\)Nb\(_{2/3}\))O\(_3\) have already been investigated\(^4-14\). Some of these are found to be technologically important. Promising electrical properties of these materials have given a tremendous boost to carry out the fundamental and applied research on relaxor ferroelectrics. Further PMN exhibits high dielectric constant with diffuse phase transition (DPT) characterized by frequency dependent dielectric maximum (\(\varepsilon_m\)). In spite of the intensive investigations, the mechanism responsible for freezing process in PMN is yet to be understood. It is believed that PMN is analogous to the spin-glass system with existence of thermally activated polarization fluctuations above \(T_f\) (static freezing temperature). Based on this analogy one can consider the relaxor ferroelectric to behave as a polar-glassy system which can be modeled through Vogel-Fulcher law\(^{15}\). Also, PMN undergoes a transition in the vicinity of \(T_f = 220 \text{ K}\) into a non-ergodic state\(^{15}\) which is similar to the dipolar glass state\(^{16}\). Further, it has been concluded that the assemblage of the relaxor elements with broad distribution of relaxation times give rise to the glassy behaviour of the relaxor ferroelectrics\(^{16-18}\). As PMN is having a highly tolerant ABO\(_3\)-structure, it provides enough scope for modification either at A or B-sites. It has also been observed that the electrical properties and ferro-paraelectric phase transition temperature of PMN can be controlled effectively by proper doping at B-site.

In this paper, the structural and dielectric properties of Cu-modified PMN ceramic having chemical formula Pb[(Mg\(_{3/4}\)Cu\(_{1/4}\))\(_{1/3}\)Nb\(_{2/3}\)]O\(_3\) (abbreviated PMCN) have been reported. The results have been modeled through Vogel-Fulcher relation to understand the phase transition mechanism in the present system. Further the relaxor behaviour in PMCN has been probed through admittance spectroscopy.

**Experimental Procedure**

The polycrystalline samples of PMCN were prepared by the columbite precursor method using high-purity AR/GR grade (99.5%+ pure) chemicals (PbO, MgO, CuO and Nb\(_2\)O\(_5\)) in the desired stoichiometry. In the first step, mixture of MgO, CuO

*For correspondence (E-mail: k_prasad65@yahoo.co.in)*
and Nb2O5 were thoroughly mixed and ground in an agate-mortar for about 3 h in dry medium. The powder was then calcined in an alumina crucible at 1000°C for 8 h in the air atmosphere to obtain the pyrochlore Mg3/4Cu1/4Nb2O6. The thermochemical reaction taking place at this stage can be described as follows:

\[
\frac{3}{4} \text{MgO} + \frac{1}{4} \text{CuO} + \text{Nb}_2\text{O}_5 \rightarrow \text{Mg}_{3/4}\text{Cu}_{1/4}\text{Nb}_2\text{O}_6.
\]

Again, this precursor in powder form was mixed with PbO and the process of mixing was carried for another 3 h in a methanol medium. The fine powder thus obtained was calcined at 900°C in an alumina crucible in a closed medium for 6 h. The thermochemical reaction taking place is:

\[
PbO + \frac{1}{3} \text{Mg}_{3/4}\text{Cu}_{1/4}\text{Nb}_2\text{O}_6 \rightarrow \text{Pb}[(\text{Mg}_{3/4}\text{Cu}_{1/4})_{1/3}\text{Nb}_{2/3}]\text{O}_3.
\]

To compensate the lead loss and suppress the pyrochlore formation in the final compound excess of 0.5 wt% of PbO and 0.3 wt% of MgO were added to the initial composition. Finally, the powder of PMCN was used to make cylindrical pellets of diameter 9-10 mm and thickness 1-2 mm under an isostatic pressure of 4×10⁷ Nm⁻². Polyvinyl alcohol (PVA) was used as a binder to reduce the brittleness of the pellets. The binder was burnt off during the sintering process. The pellets were then sintered in an alumina crucible at 1200°C for 4 h in lead environment to minimize the lead loss. The formation and quality of the compound were checked by an X-ray diffraction (XRD) technique using Philips PW1710 diffractometer, Holland with CuKα-radiation (λ = 1.5418 Å) in a wide range of Bragg’s angles (20° ≤ 2θ ≤ 80°). To study the dielectric properties, both flat surfaces of the pellets were electroded with fine silver paste and were kept at 200°C for 1 h prior to conducting the experiment. Impedance (Z), admittance (Y), phase angle (θ), dielectric constant (ε) and loss tangent (tanδ) of the sample were measured as a function of frequency (0.1 kHz-1 MHz) and temperature (-30°C -150°C) using a computer controlled LCR-meter (3532-50 HIOKI, Japan).

**Results and Discussion**

A standard computer program ‘PowdMult’¹⁹ was used for the X-ray diffraction profile (Fig. 1) fitting. A least squares regression fit of the diffraction data yielded the cubic structure having the lattice parameter, \(a = 4.047 \pm 7\) Å with an estimated error of ±10⁻³ Å. The criterion adopted for evaluating the rightness, reliability of the indexing and the structure of PMCN was the sum of differences in observed and calculated \(d\)-values \(\{\text{Σ}(d_{\text{obs}} - d_{\text{cal}})\}\) found to be minimum. The observed and calculated \(d\)-values of PMCN have been compared in Table 1.

Fig. 2 shows the variation of dielectric constant (ε) and tangent loss (tanδ) as a function of frequency at room temperature (30°C). It is observed that both ε and tanδ decrease with the increase in frequency, which is normal trend of a ferroelectric material. The higher value of ε at low frequencies may be due to the presence of all types (electronic, atomic, dipolar and interfacial) of polarization. At low frequencies dipoles are able to follow the field (thereby high ε) and as the frequency increases dipoles begin to lag behind and no longer follow the field at the higher frequencies and hence ε decreases.

<table>
<thead>
<tr>
<th>h k l</th>
<th>(d_{\text{obs}})</th>
<th>(d_{\text{cal}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 0 0</td>
<td>4.0493</td>
<td>4.0477</td>
</tr>
<tr>
<td>1 1 0</td>
<td>2.8622</td>
<td>2.8622</td>
</tr>
<tr>
<td>1 1 1</td>
<td>2.3355</td>
<td>2.3370</td>
</tr>
<tr>
<td>2 0 0</td>
<td>2.0230</td>
<td>2.0239</td>
</tr>
<tr>
<td>2 1 0</td>
<td>1.8106</td>
<td>1.8102</td>
</tr>
<tr>
<td>2 1 1</td>
<td>1.6529</td>
<td>1.6525</td>
</tr>
<tr>
<td>2 2 0</td>
<td>1.4308</td>
<td>1.4311</td>
</tr>
<tr>
<td>3 1 0</td>
<td>1.2802</td>
<td>1.2800</td>
</tr>
<tr>
<td>3 1 1</td>
<td>1.2210</td>
<td>1.2204</td>
</tr>
</tbody>
</table>

**Table 1—Comparison of observed and calculated \(d\)-value of \(\text{Pb}[(\text{Mg}_{3/4}\text{Cu}_{1/4})_{1/3}\text{Nb}_{2/3}]\text{O}_3\) at room temperature**

![Fig. 1—XRD pattern of \(\text{Pb}[(\text{Mg}_{3/4}\text{Cu}_{1/4})_{1/3}\text{Nb}_{2/3}]\text{O}_3\) at room temperature.](image-url)
Fig. 3 shows the temperature dependence of dielectric constant of PMCN at different frequencies. The plots show a broad maximum (diffuse phase transition, DPT) in the region of 15-20°C and strong frequency dispersion, which indicates the relaxor behaviour of PMCN. It has been observed that the temperature at which the relative permittivity was maximum (i.e. phase transition temperature, $T_m$) shifted to higher temperature (from -22°C at 10 kHz to -9°C at 1 MHz) (inset Fig. 5) and $\varepsilon_m$ decreases (inset Fig. 3) with the increase in frequency. It can be seen from the inset Fig. 3 that dielectric constant is very high at 10 kHz and decreases sharply with the increase in frequency. In case of polycrystalline ceramics, this is commonly observed if the grains are semiconducting and the grain boundaries are insulating. The semiconductive grains in PMCN ceramics is believed to be due to the loss of oxygen during firing at higher temperatures in accordance with the reaction $O_2 ⇄ \frac{1}{2}O_2 \uparrow + V^{**}_o + 2e^-$ where all the species are written in accordance with Kröger Vink notation of defects. These defects affect impedance and capacitance in the formation of barrier layers at the grain-grain boundary interface. During cooling after sintering, the reverse reaction occurs. But due to insufficient time available during cooling, the re-oxidation takes place and is restricted to grain boundaries only. This results in difference between resistance of grain boundary and grain, giving rise to barrier. The build-up of charges at grain-grain boundary interface causes large polarization results in large dielectric constant at lower frequencies.

The DPT can conveniently be described by modified Curie-Weiss law:

$$\frac{1}{\varepsilon} - \frac{1}{\varepsilon_m} = \left( T - T_m \right)^\gamma / C'$$

where $C' = 2\varepsilon_m^{\delta / \gamma}$ is modified Curie-Weiss constant, $\delta$ is diffusivity parameter and $\gamma$ is the critical exponent can vary from 1, for normal ferroelectrics to 1-2 for relaxor ferroelectrics. Eq. (1) can be solved graphically using a log-log plot as shown in Fig. 4. The slope of the curve represents the value of the critical exponent while the intercept gives the diffuseness parameter according to the following equation:

$$\delta = \left( \frac{2\varepsilon_m \text{intercept}}{1/\varepsilon_m} \right)^{1/\gamma}$$

The linear regression analysis given the value of $\gamma = 1.44$, $\delta = 111.52$ and $C' = 19.614 \times 10^5$ °C at 10 kHz which clearly indicates the DPT. It has been observed...
that the diffuse phase transition and relaxor behaviour in Pb(B\textsuperscript{I}/\textsubscript{3}B\textsuperscript{II}/\textsubscript{3})O\textsubscript{3}-type compounds have been considered generally due to the B-site compositional fluctuation (B\textsuperscript{I}/B\textsuperscript{II} ratio) caused by the formation of the 1:1 non-stoichiometric short-range ordered microdomains\textsuperscript{1,2,3,4}. In fact, in Pb(B\textsuperscript{I}/\textsubscript{3}B\textsuperscript{II}/\textsubscript{3})O\textsubscript{3} the bonding preference for 1:1 local ordering is incompatible with the global 1:2 stoichiometry, leading to a frustrated state with only incomplete and short-range order\textsuperscript{24}. Therefore, the diffuse phase transition and relaxor behaviour in Pb[(Mg\textsubscript{3/4}Cu\textsubscript{1/4})\textsubscript{1/3}Nb\textsubscript{2/3}]O\textsubscript{3} ceramic may be due to the compositional fluctuation at the B-site which can be estimated by the ratio of Mg/Nb and/or Cu/Nb.

Recent studies\textsuperscript{8,16,25,26} showed that, like in spin and structural glass, the frequency dependence of T\textsubscript{m} obeys the empirical Vogel-Fulcher law\textsuperscript{27,28}:

\[
f = f_0 \exp\left[-\frac{E_a}{k_B(T_m - T_f)}\right]
\]

where \(f\) is the operating frequency, \(f_0\) is the pre-exponential factor (Debye frequency), \(E_a\) is the activation energy and \(k_B\) is Boltzmann constant. Fig. 5 shows the variation of (ln\(f_0\) - ln\(f\))^\textsuperscript{-1} with temperature \(T_m\) where the solid circles represent the experimental data. Excellent fitting of Vogel-Fulcher relation with experimental data, suggests that the above mechanism can be employed to explain relaxor behaviour in PMCN ceramics. The value of the phenomenological parameters \(E_a, f_0\) and \(T_f\) using linear least-squares fit to Eq. (3) were respectively found to 0.029133 eV, 5.722x10\textsuperscript{9} Hz and -47.7263ºC, which are consistent with the earlier report on a similar system\textsuperscript{15,16,26}. The value of \(f_0\) corresponding to the optical frequency range of the lattice vibrations.

The dielectric relaxation in relaxor ferroelectrics is believed to be similar as spin glass system\textsuperscript{16-18}. The glassy relaxation characterizes a broad and equal probability distribution of relaxation times\textsuperscript{17,18}. For linear relaxation processes of the type modelled by the series RC-branch, the principle of superposition allows the complex admittance to be described as:

\[
Y^* = \int_0^\infty \frac{y^*(\tau,T)d\tau}{\pi}\]

where \(y^* = i\omega C_0 \varepsilon_0 / (1 + i\omega \tau)\) is equivalent admittance of a series RC element, which represents the nature of Debye relaxation, the relaxation time \(\tau = RC\) and \(g(\tau,T)\) represents the distribution of relaxation times. The distribution should normalize \(\int_0^\infty g(\tau,T)d\tau = 1\). The real and imaginary part of admittance can be written as\textsuperscript{18}:

\[
Y' = \frac{\pi}{2}\omega C_0 \varepsilon_0 \exp\left[(T - T_f)/U\right]
\]

and \(Y'' = \frac{\pi}{2}Y'\ln[A(T)/Y']\)

where \(A(T) = (\pi/2)\omega_0 C_0 \varepsilon_0 [(T - T_f)/U]\)

\(=(\pi/2)\omega_0 \varepsilon_0 C \left[1/ \ln(\omega_0/\omega)\right]\).

If the leakage current is also considered then a constant term \(G_o\) is to be added in Eq. (6). Therefore,

\[
Y'' = \frac{\pi}{2}Y'\ln[A(T)/Y'] + G_o
\]

It is known that Eq. (4) expresses the superposition of admittance of RC series elements with continuous...
distribution of relaxation times and each RC series element is representative of a polar cluster. These polar clusters with different size are corresponding to the series RC elements with different $R_iC_i$ values. The broad distribution of sizes of polar clusters gives rise to the broad distribution of relaxation times because of relaxation time $\tau_i (=R_iC_i)$ is proportional to the size of polar cluster. All these series elements are in parallel and the assemblage of all these polar clusters makes the relaxor ferroelectrics to follow the glassy relaxation behaviour\superscript{18}. Therefore, a relaxor ferroelectric system could be considered as the sum of responses of relaxators in widely distributed spectrum of their relaxation times. Fig. 6 shows the experimental point along with simulated results between 100 Hz-3 MHz frequency using Eq. (8) at 303 K. It can be seen that Eq. (8) fits well with the experimental results of glassy behaviour in the investigated frequency range. Hence, based on the above results, the dielectric relaxation in PMCN may be considered analogous to magnetic relaxation in a spin-glass system with polarization fluctuations above $T_f$.

Conclusions

Single-phase perovskite-type cubic PMCN ceramic prepared by Coulombite precursor method showed relaxor behaviour with diffuse phase transition. The diffuse phase transition in PMCN may be due to the B-site compositional fluctuation caused by the formation of the 1:1 short-range ordered microdomains. Modelling of dielectric relaxation using Vogel-Fulcher relationship shows strong evidence for a static freezing temperature of thermally activated polarization fluctuations in PMCN. Therefore, the dielectric relaxation in PMCN may be considered analogous to magnetic relaxation in spin-glass system with polarization fluctuations above a static freezing temperature.

Acknowledgement

This work has been supported by the Department of Science & Technology, New Delhi (Ref. No.: SP/S2/M-15/97). One of us (KP) wishes to thank Dr. A. A. Bokov, Simon Fraser University, British Columbia, Canada, for useful discussion.

References

19. PowdMult - An interactive powder diffraction data interpretation and indexing programme, Ver. 2.1, E. Wu, School of Physical Science, S.A. 5042, Australia.
27. Vogel H, Z Phys, 22 (1921) 645.