

## **SAMPLE PREPARATION AND DIELECTRIC SPECTRUM EQUIVALENT CIRCUITS MODELING FOR $\text{Bi}_2\text{Mn}_2\text{O}_7$**

Abdul Halim Shaari, Wan Mohd. Daud Wan Yusoff, Mansor Hashim,  
Zainal Abidin Talib, Lim Kean Pah, Tay Boon Ping

*Physics Department, Faculty Science, 43400 UPM Serdang,  
Selangor Darul Ehsan, Malaysia.*

### **ABSTRACT**

A  $\text{Bi}_2\text{Mn}_2\text{O}_7$  ceramic sample was prepared by solid state reaction method. Its dielectric property was then characterized by impedance analysis within frequencies range from  $10^2$  Hz to  $10^6$  Hz and temperatures range from room temperature to  $450^\circ\text{C}$ . All spectrums were then normalized into a single master curve. The dielectric response mechanism observed in the sample master curve spectrum were modeled by combinations of diffusive, quasi-dc, bound charge (dipole-like) elements with a non-dispersive capacitor. The experimental data are in close agreement with the value obtained from equivalent circuit.

### **INTRODUCTION**

Ferromagnetism and ferroelectricity are two ordering phenomena which are rather common among transition metal oxides. In contrast, magnetoelectric multiferroic, i.e. compounds which are simultaneously ferroelectric and ferromagnetic (or at least show some kind of magnetic ordering), are rather scarce [1]. They have recently attracted some attention [1-6], since one can envisage a whole recently of new applications by combining both phenomena. However, in almost all presently known multiferroic compounds, different ions are responsible for the ferroelectric and the magnetic ordering, respectively [7]. Therefore, there seems to be some empirical exclusion principle between both phenomena, but there exists no simple theoretical argument supporting this exclusion. Thus finding new multiferroics where the same ion is responsible for both phenomena would be stimulating. Exploring the fundamental physics behind the scarcity of multiferroics, it was suggested to look for compounds where a 3d-atom with a partially filled d-shell has an anisotropic coordination providing an asymmetric potential with double-well potential [1]. From the literature review, there is likely occurrence multiferroic magnetoelectric property in the simple perovskite  $\text{BiMnO}_3$  [8]. Base on this compound, we decide to prepare a new compound,  $\text{Bi}_2\text{Mn}_2\text{O}_7$  based on an idea that by the increment of the  $\text{Mn}^{3+}$  ion oxidation state in  $\text{BiMnO}_3$  from  $3+$  to  $4+$  may hold the key to improve the multiferroic magnetoelectric property of  $\text{BiMnO}_3$ . The investigation of  $\text{Bi}_2\text{Mn}_2\text{O}_7$  properties were first begins by studying its dielectric relaxation response.

In the dielectric studies, the dielectric master curve spectrum was fitted by using equivalent circuit modeling technique [9], with combination of Dissado-

Hill's quasi-dc model [10-13] and bound charges (or bound dipolar) model [12, 13] together a diffusion barrier and a non-dispersive capacitor element. In the model, the dielectric susceptibility can be expressed in the form of

$$\chi^*(\omega) = \chi(0)F(\omega/\omega_x) \quad (1)$$

where for the quasi-dc dispersion case ( $\omega_x = \omega_c$ ), asymptotic form of  $F(\omega/\omega_x)$  can be expressed in the fractional power law behavior as [10-13]

$$\chi^*(\omega) = \chi(0)(i\omega/\omega_c)^{-p} \quad \text{for } \omega \ll \omega_c \quad (2a)$$

and 
$$\chi^*(\omega) = \chi(0)(i\omega/\omega_c)^{n-1} \quad \text{for } \omega \gg \omega_c \quad (2b)$$

However, for the bound dipolar case ( $\omega_x = \omega_p$ ), asymptotic form of  $F(\omega/\omega_x)$  can be expressed in the fractional power law behavior as [12]

$$\chi^*(\omega) = \chi(0)(i\omega/\omega_p)^{n-1} \quad \text{for } \omega \gg \omega_p \quad (3a)$$

and 
$$\chi^*(\omega) = \chi(0) - \chi(0)(i\omega/\omega_p)^m \quad \text{for } \omega \ll \omega_p \quad (3b)$$

where  $\omega_c$  and  $\omega_p$  is the characteristic frequency and peak frequency respectively,  $\chi(0)$  is the susceptibility at very low frequency and  $n$  and  $p$  lie in the range from zero to unity. The diffusion barrier dielectric response has been expressed as

$$\chi^*(\omega) \propto \chi(\omega_d)(i\omega/\omega_d)^{-s} \quad s \cong 0.5 \quad (4)$$

which defines a diffusion susceptibility of magnitude  $\chi(\omega_d)$  at frequency  $\omega_d$ .

## EXPERIMENTAL DETAILS

In this study, a  $\text{Bi}_2\text{Mn}_2\text{O}_7$  sample was prepared by conventional solid state reaction method with high purity raw materials  $\text{Bi}_2\text{O}_3$  (99.975%) and  $\text{MnO}_2$  (99.9+%). Because  $\text{Bi}_2\text{Mn}_2\text{O}_7$  is a new compound, which does not have any literature review; therefore at the beginning of sample preparation, the Thermogravimetry analysis (TGA) was done upon the pre-sintering mixture for the sintering temperature confirmation. It is followed by XRD for samples sintered at various temperatures until a stable XRD pattern has been found. The pellet type sample was then prepared by sintering at 780°C for 5 hours in open air condition. Sample's dielectric property was then measured by using HP 4192A impedance analyzer within frequencies range from  $10^2$  Hz to  $10^6$  Hz at room temperature, 50°C, 100°C, 150°C, 200°C, 250°C, 300°C, 400°C and 450°C.

## RESULTS AND DISCUSSION

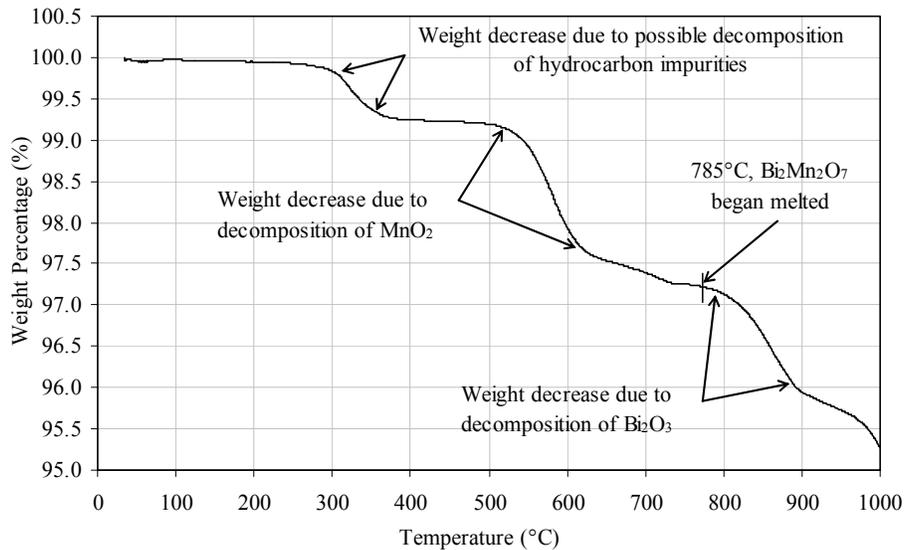


Figure 1: TGA result of pre-sinter Bi<sub>2</sub>Mn<sub>2</sub>O<sub>7</sub> mixture

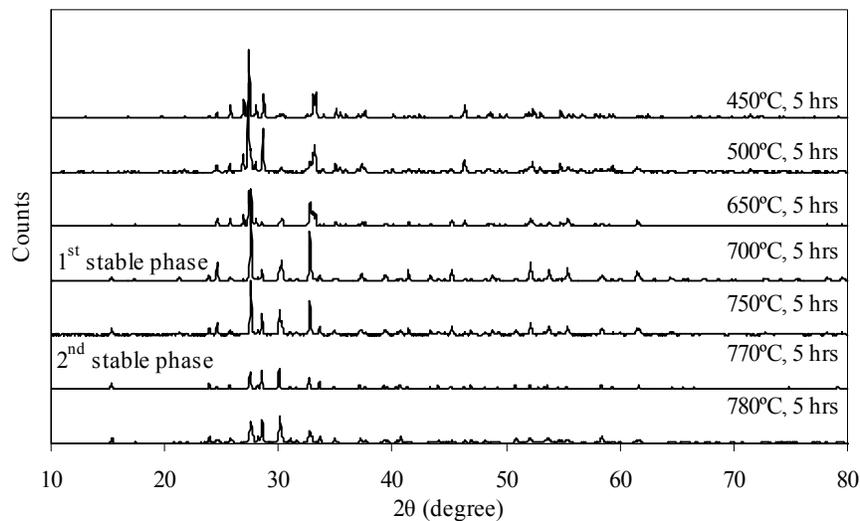


Figure 2: XRD pattern of Bi<sub>2</sub>Mn<sub>2</sub>O<sub>7</sub> sintered at varies temperatures

Figure 1 shows that there are three thermal stable weight ratio states which exist in the TGA result of pre-sinter Bi<sub>2</sub>Mn<sub>2</sub>O<sub>7</sub> mixture, due to the decomposition of hydrocarbon impurity, MnO<sub>2</sub> and molten of Bi<sub>2</sub>O<sub>3</sub> at ~300°C, ~535°C and ~817°C respectively. Few pre-suitable sintering temperatures were defined according to these thermal stable states temperatures. Figure 2 shows the XRD patterns of samples sintered at these temperatures. Two stable XRD structural phases were observed at 700°C and 770°C. Moreover, the sample melted at 785°C. Finally, the

optimum sintering temperature was taken as 780°C.

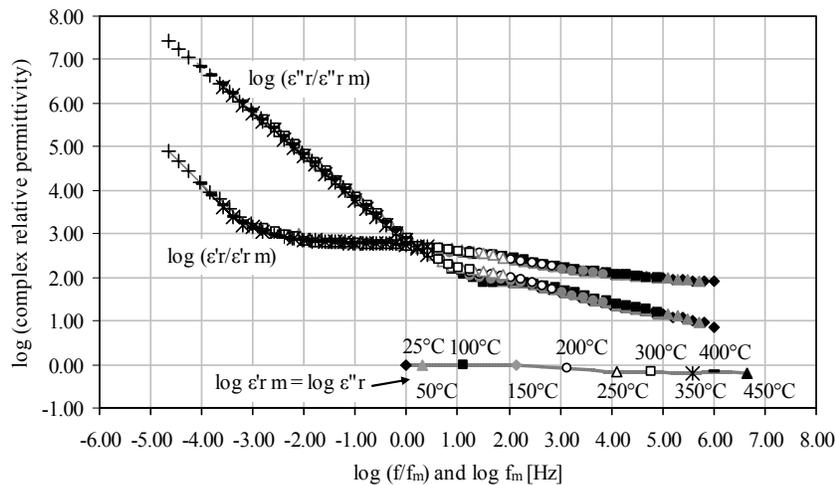


Figure 3: Dielectric spectrum master curve of  $\text{Bi}_2\text{Mn}_2\text{O}_7$  sintered at 780°C for 5 hrs

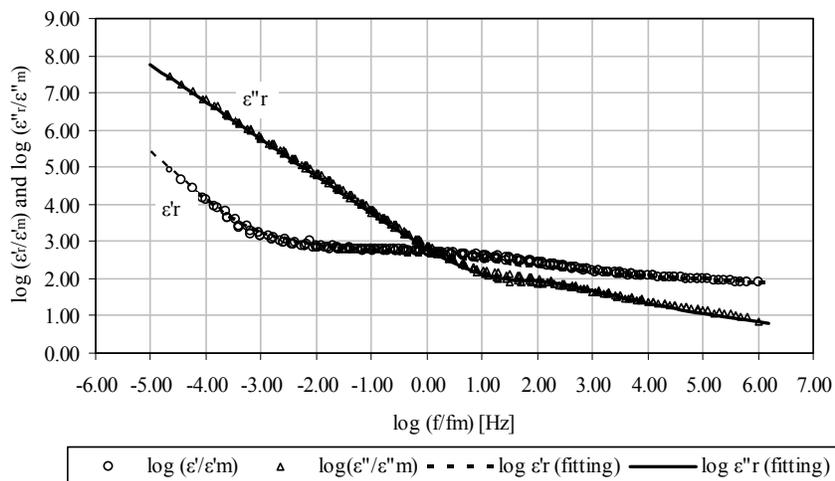


Figure 4: Graph fitted by using the equivalent circuits modeling for  $\text{Bi}_2\text{Mn}_2\text{O}_7$  sintered at 780°C for 5 hours

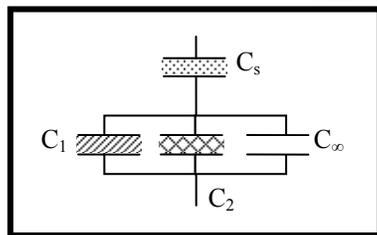


Figure 5: Schematic of circuit used in equivalent circuit modeling analysis in Figure 4, where the  $C_1$  represents bound-charge relaxation,  $C_2$  represents quasi-dc dispersion,  $C_s$  represents the diffusion mechanism and  $C_\infty$  is non-dispersive infinite frequency capacitor.

Figure 3 shows the a normalized dielectric spectrum master curve for  $\text{Bi}_2\text{Mn}_2\text{O}_7$  sintered at 780°C for 5 hours over the temperature range from 25°C to 450°C by using the locus point translation technique [14-16]. The normalized

master curve had extended the effective frequency range from 4 decades to 11 decades, thereby increasing the confidence in the consistency of the results [15]. The pre-normalized spectrums shape is relatively invariant with frequency; this means that the local structure of the material does not change appreciably in the temperature range as mentioned above [15]. This also implies that the nature of the sample dielectric process remains invariant and only the rate process changes in thermally activated manner [16].

The master curve was then fitted by equivalent circuit modeling technique (Figure 4) in order to understand the nature process of sample's dielectric response. It was found that the process is dominated by series combination of quasi-dc dispersion and a diffusion mechanism (Figure 5). The characterization detail of the responses used in the equivalent circuit modeling is shown in Table 1.

Table 1: Characterization of responses shown in Figure 4 and 5 for the sample

Process	Type	Parameters
C <sub>1</sub>	Bound charge	$\chi_0 = 1.00 \cdot 10^{-09}$ F/m; m = 1.0000; n = 0.5000; $\omega_p = 6.28 \cdot 10^{+02}$ Hz
C <sub>2</sub>	Quasi-DC	$\chi_0 = 2.00 \cdot 10^{-09}$ F/m; p = 0.9995; n = 0.8100; $\omega_c = 1.58 \cdot 10^{+01}$ Hz
C <sub>s</sub>	Diffusion	$\chi_0 = 7.08 \cdot 10^{-04}$ F/m; p = 0.5000
C <sub>∞</sub>	Non-dispersive	$\epsilon_\infty = 5.62 \cdot 10^{-10}$ F/m

## CONCLUSION

From the TGA and XRD results, a Bi<sub>2</sub>Mn<sub>2</sub>O<sub>7</sub> sample was chosen to be sintered at 780°C for 5 hours. The compound's formula is based on primary stoichiometry formula in the sample preparation which does not reflect the real elemental composition of the sample. The well normalized dielectric spectrums implied that the local structure of the sample does not change appreciably in temperature 25°C – 450°C. The well fitted normalized master curve to the circuit model implied that the sample dielectric relaxation is dominated by a series combination of quasi-dc dispersion and diffusive mechanism.

## ACKNOWLEDGEMENT

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## REFERENCES

- [1]. N.A. Hill (2000); *J. Phys. Chem. B* **104**, 6694
- [2]. Alessio Filippetti and N.A. Hill (2001); *J. Magn. Magn. Mater.* **236**,176
- [3]. N.A. Hill and Alessio Filippetti (2002); *J. Magn. Magn. Mater.* **242-245**, 976
- [4]. T. Atou, H. Chiba, K. Ohoyama, Y. Yamaguchi and Y. Syono (1999); *J. Solid State Chem.* **145**, 639
- [5]. C.W. Nam, L. Liu, N. Cai, J. Zhai, Y.H. Lin, L. J. Dong, C. X. Xiong (2002); *Appl. Phys. Lett.* **81**, 3831
- [6]. L. Fuentes, M. García, J. Matutes-Aquino and D. Ríos-Jara (2003); *J. Alloys and Compounds* **xxx**, xxxx
- [7]. V. Bohnar, P. Lunkenheimer, A. Loidl, E.E. Kaul and C. Geibel (2002); *Solid State Comm.* **122**, 595
- [8]. A. Moreira dos Santos, S. Parashar, A.R. Raju, Y.S. Zhao, A.K. Cheetham, C.N.R. Rao, (2002); *Solid State Comm.* **122**, 49
- [9]. M.F. Kabir, W. M. Daud, K. Khalid and H.A.A. Sidek (2000); *Wood and Fiber Science* **32(4)**, 450
- [10]. L. A. Dissado and R. M. Hill (1984); *J. Chem. Soc., Faraday Trans. 2* **80**, 291
- [11]. T. Ramdeen, L. A. Dissado, R. M. Hill (1984); *J. Chem. Soc., Faraday Trans. 1* **80**, 325
- [12]. R. M. Hill and Colin Pickup (1985); *J. Mater. Sci.* **20**, 4431
- [13]. L. A. Dissado, R. C. Rowe, A. Haidar, and R. M. Hill (1987); *J. Colloid Interface Sci.* **117(2)**, 310
- [14]. A. K. Jonscher (1983); *Dielectric Relaxation in Solids*; Chelsea Dielectrics Press Ltd, London; Chap3, pp. 101-110
- [15]. A. K. Jonscher (1983); *Thin Solid Films* **100**, 329
- [16]. A. K. Jonscher (1996); *Universal Relaxation Law*; Chelsea Dielectric Press Ltd, London; Chap 10, pp. 299 – 300