Dielectric and Structural Analysis of Barium Titanate Nanoparticles Prepared by Nano Ball Milling Technique

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ABSTRACT

$BaTiO_3$ (BTO) is considered as a promising material because of its various electronic applications such as in multilayer ceramic capacitor, PTC–thermistors, piezoelectric transducers, sensors, dynamic RAM, MEMS, optical modulators and electromechanical devices (Ramakanth et al 2015, Tsivadze et al. 2016). The influence of nano ball milling frequency on the structural and dielectric properties of BTO samples prepared by solid-state reaction have been investigated. The BTO samples are prepared with different milling frequency ranging from 0 to 30 Hz. The samples are characterized by x-ray diffraction and dielectric measurement apparatus. XRD analysis shows that samples have pure tetragonal structure. Lattice parameters and grain size are calculated using data received from XRD analysis and it is observed that milling frequency has pronounced effect on crystallite size. Frequency dependent dielectric is determined for all samples. Increased dielectric constant at low frequencies is observed for all the samples.

1. INTRODUCTION

The ferroelectric materials with perovskite structure (ABO_3) have significant use in the fabrication of electromechanical devices. The outstanding electrical property is always required for practical applications. Among these ferroelectric materials, Barium Titanate ($BaTiO_3$) is a considerably attractive electroceramic material because of its ferroelectric properties with high dielectric constant. It is useful in applications such as thermistors, dynamic random access memory (DRAM), actuators, sensors and MLCC (Xu et al 2009, Nyutu et al. 2008, Ramoska et al. 2010, Fan et al. 2009, Wan et al. 2008). In addition, BTO is environmental friendly as compared to other ceramics like lead based materials due to its less toxic nature (Nath et al. 2010).

Dielectric properties depend on the particle size of the material. To improve particle size by growth conditions is open question among the researchers. Several research groups report that dielectric properties alter with the processing conditions (Kumar et al. 2016). There are many techniques such as sol-gel (Phule et al. 1988), hydrothermal (Kakihana et al. 1999), sol-precipitation (Salze et al. 1986) and organic

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polymeric (Kutty et al. 1984) for the production of nano-sized BTO powder. Among these techniques, ball milling based solid-state method is more beneficial for the fabrication of BTO because it is rapid, simple and cost effective method. The nanosized powder of material has been produced by a high-energy ball milling technique. In the ball milling, the grinding bowl, straddling on a turning support frame, also revolve about its axis. These two rotations form forces that are exerted on the milling balls and materials inside the bowl. These forces cause reduction of particle size and induce microstrains at the same time (Nath et al. 2010). In the present paper, the nano ball milling based solid-state process was used to produce BTO submicron sized powders by a new route which is much easier than other synthesis process. The influence of the milling condition and heating on the crystal structure and the dielectric properties of BTO powders were investigated, and the formation mechanism of the BTO powders would be discussed.

2. Experimental details

Barium titanate was prepared by solid state reaction. Mixture of BaO (99.99% pure) and TiO_2 (99.99%, Merck) was prepared at room temperature. The ratio between reactants was 1:1 relation by weight.

$$BaO + TiO_2 \rightarrow BaTiO_3$$

The mixture was ball milled [Fritsch, Germany] with five rotating balls at 900 rpm for two hours in a ceramic bowl. Then pellet was prepared using hydraulic press by applying pressure 27.58 MPa for 2 minutes. Area, thickness and diameter of pellet were 0.845 cm^2, 0.155 cm and 1.032 cm, respectively. Similarly more samples were prepared but with different milling rotations of 1200 rpm and 1800 rpm for two hours. The rotation speed, area and thickness of samples are listed in Table I. After this all samples were heated at 1200 ^oC in oxidizing environment for 12 hours. The crystal structure of prepared samples before and after heating was investigated by X-Ray Diffraction (Bruker D8). The Impedance analyzer (Wayne Kerr 6500 B) was used to determine the frequency dependent dielectric parameters.

Table 1: Summary of the samples obtained in this study

Sample ID	**Rotation speed (rpm)**	**Area (cm^2)**	**Thickness (cm)**
A	0	0.845	0.155
B	900	0.836	0.199
C	1200	0831	0.148
D	1800	0.832	0.185

3. Results and discussion

The XRD patterns of samples A-D before heating are shown in Fig. 1. It is found that number of peaks were same in all samples (A-D) with different intensity. The high intensity peaks were observed at around 2θ = 24.1° and 25.35°. The diffracted peak at 24.1° can be attributed to the orthorhombic structure of barium carbonate as confirmed by JCPDS card (pdf 41-0373). The characteristic peak at 2θ = 25.35° originated by anatase phase of titanium oxide having tetragonal structure as approved by card (pdf 89-4921). The weak peaks correspond to barium carbonate and titanium oxide. Fig. 2 illustrates the XRD measurements of samples A-D after heating at 1200 ^{o}C. It was observed that diffraction angles changed by heating. The diffraction peaks at 2θ = 22°, 32°, 39°, 45°, 46°, 50°, 66°, 70° and 75° can be indexed to the (001), (110), (111), (002), (200), (102), (112), (220), (212) and (310) planes of tetragonal structure of $BaTiO_3$ with the help of JCPDS card number 05-0626. Additionally, characteristic diffraction peaks of $BaTiO_3$ are consistent in all cases, which indicate that the crystal phase structure of $BaTiO_3$ was not changed with milling frequency. The highest peak (110) of tetragonal structure of $BaTiO_3$ diffracted at 32^{o}. Hsing et al. (1996) reported that splitting of peak (002) diffracted at angle 45^{o}-46^{o} indicated the tetragonal phase of BTO. In our samples, this splitting was also observed. The lattice parameters were found by using equation.

$$\frac{1}{d^2} = \frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2}$$

where, all constants comprise the usual meanings. The calculated lattice parameters were 3.94 and 4.03 **Å**. XRD findings are consistent with already available literature (Sandeep et al. 2016, Mahmood et al. 2011). The crystallite size and dislocation

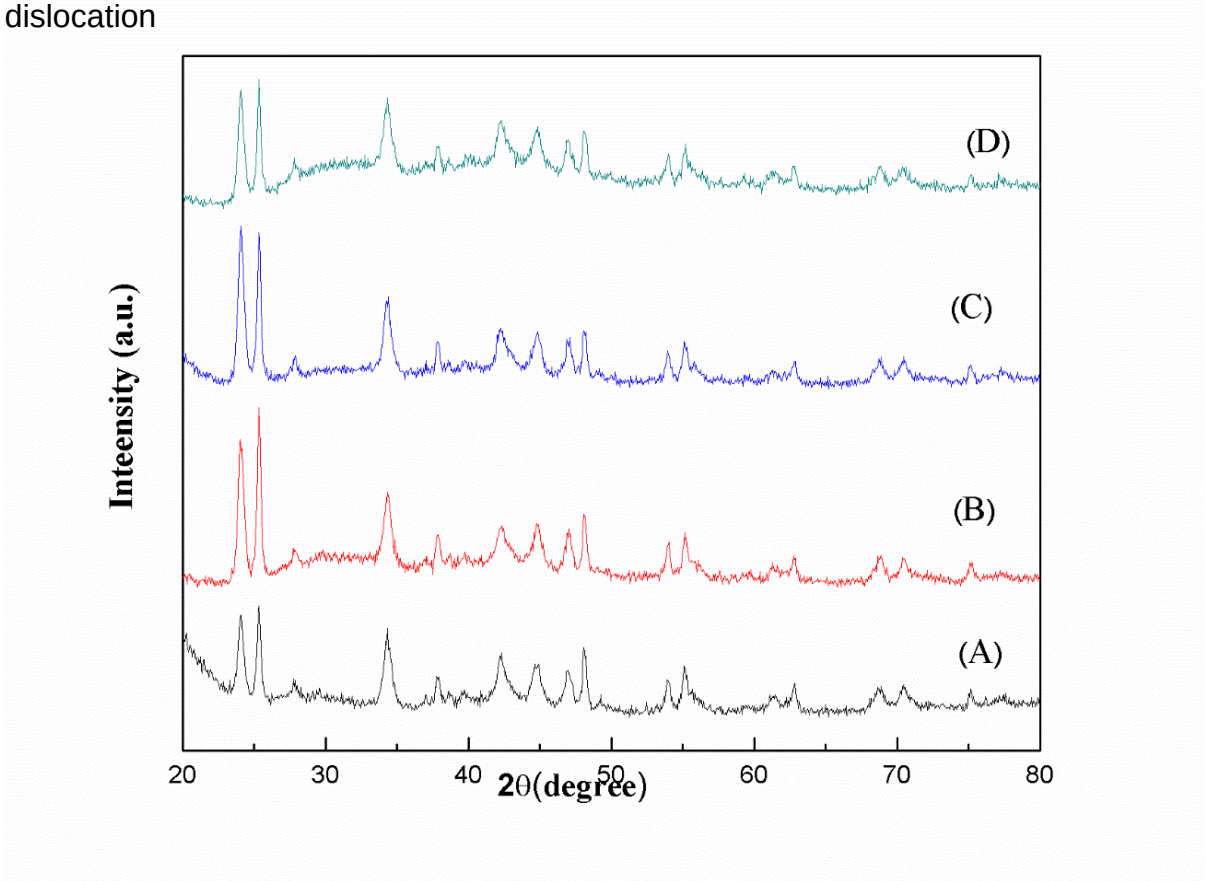

Fig. 1 X-ray diffraction pattern of samples A-D before heating.

density of highest peak (110) as a function of milling frequency is plotted in Fig. 3. Initially the crystallite size increases with milling frequency but it decreases with further increase of milling frequency. The reduction in crystallite size is due to the induction of strain that produces high dislocation density as shown in Fig. 3.

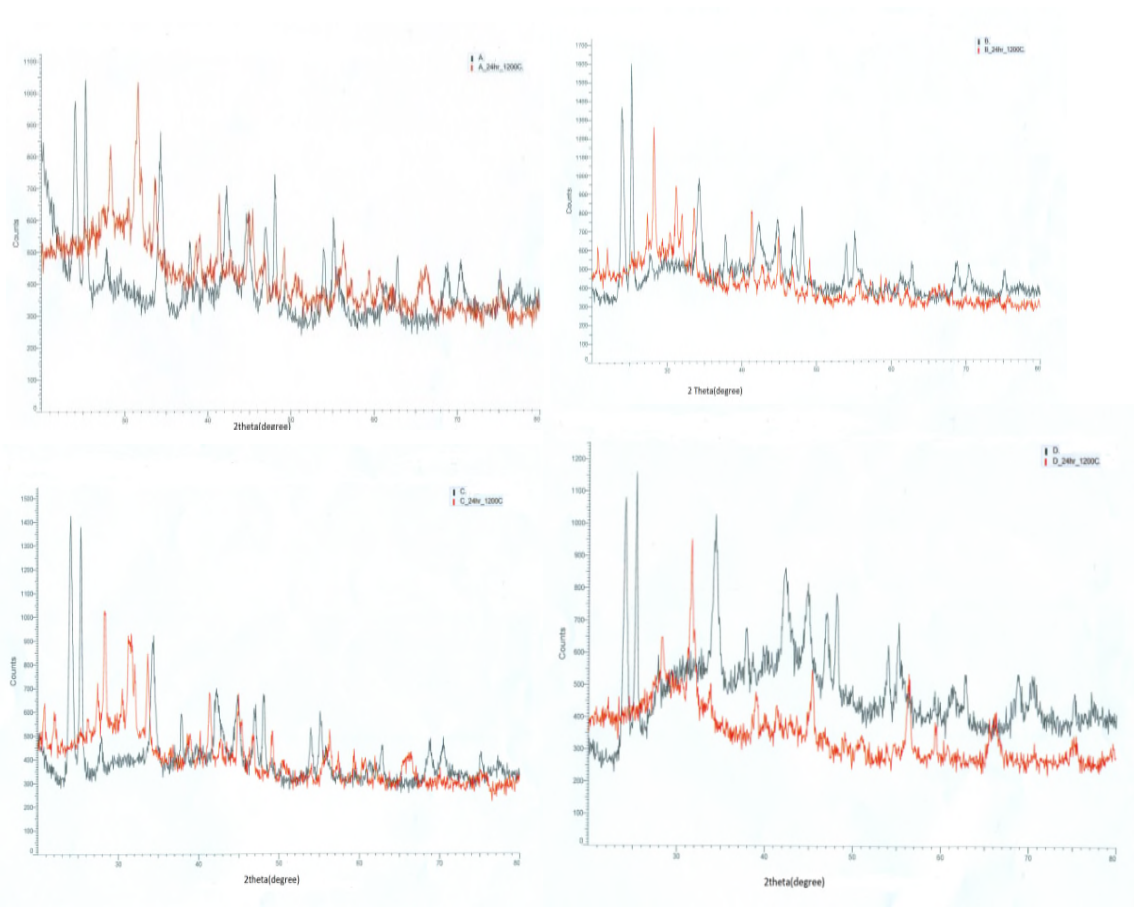

Fig. 2 X-ray diffraction pattern of samples A-D after heating

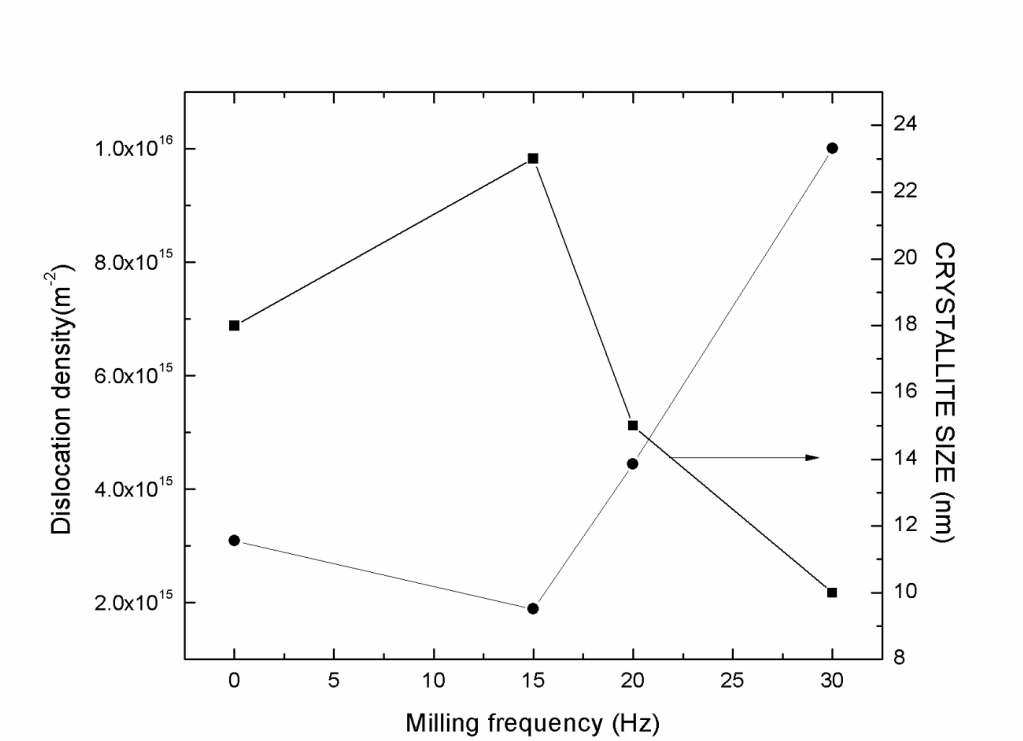

Fig. 3 A plot of crystallite size and dislocation density of highest peak of BTO as function of milling frequency.

Fig. 4 shows the dielectric constant of samples A-D before heating as a function of frequency. All the prepared samples show high values of dielectric constant (ε_r) at lower frequency which is usual behavior of ferroelectric material. The high value of dielectric constant is due to polarization. The space charge/interface (grain-boundaries), dipolar, atomic and electronic are four types of polarizations. The dipolar and interfacial polarizations play dominant role at low frequencies (Cole et al. 1941, Anderson 1964). The decrease in dielectric constant is due to filtration of different polarization mechanisms such as ionic, electronic and orientation polarizability (and finally disappearance) at high frequencies. There is also release of space charge polarization that is responsible for decrease in dielectric constant value (Smith and Wijn 1965). However, dielectric constant becomes constant at high frequency because electric dipoles are unable to follow such alternating applied electric field due to inertia, which indicates the phenomenon of dielectric dispersion that can be explained on the basis of change in space charge polarization.

The high value of dielectric constant at lower frequency region is attributed to Maxwell Wagner interfacial type of polarization (Van Uitert 1956, Abdeen 1999) that explains the involvement of inhomogeneous double layers of dielectric structure which support the Koop's phenomenological theory that corresponds to resistors and capacitors (Pandit et al. 2005, Zaki 2005). As inhomogeneous dielectric structure contains two layers, the first layer consists of grains that are conducting. These grains

are detached by grain boundaries which have low conductivity. The role of grain boundaries having low conductivity dominates at low frequencies that increase the dielectric constant. In the same manner, low dielectric constant at high frequencies is observed due to effective role of grains. In the beginning, there was rise in dielectric constant with milling frequency. It is suggested that thickness of the insulating grain boundaries reduced with milling that caused an enhancement of grain size. Consequently, high dielectric constant is produced because of large polarization by an improvement of displacement of electrons. The dielectric constant values decreased with further increase in milling frequencies. It may be possible that milling at high frequencies induces defects in material that produces inhomogeneous strain in the lattice. The grain sizes reduced due to this strain.

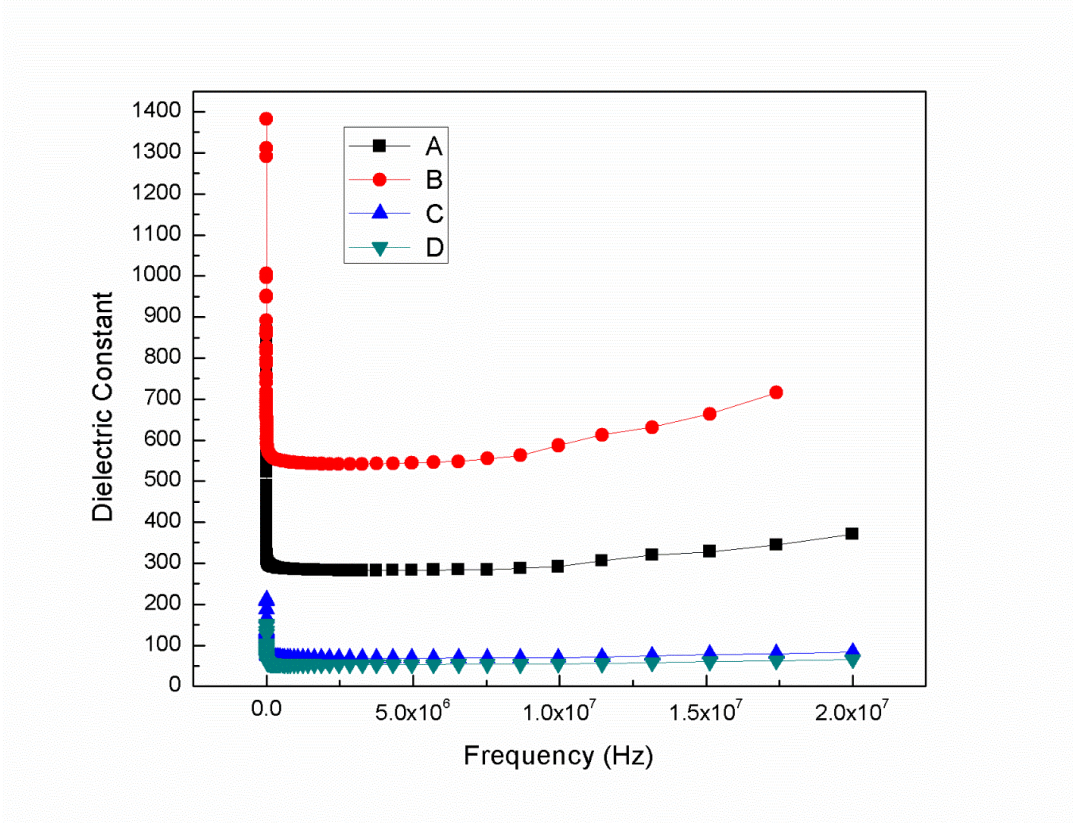

Fig. 4 Dielectric constant of samples A-D before heating.

4. Conclusions

Barium titanate has been successfully prepared by frequency dependent nano-milling based solid-state method through a new easy, simple and flexible route that exhibits excellent structure properties. XRD measurements confirmed the tetragonal structure of BTO. The lattice parameters, crystallite size and dislocation density were found. A relation was establish between crystallite size and milling frequencies. Therefore, it is reasonable to consider the potential applications of barium titanate for fabrication of electronic devices.

REFERENCES

Nyutu, E.K., Chen, C.H., Dutta, P.K. and Suib, S.L. (2008), "Effect of microwave frequency on hydrothermal synthesis of nanocrystalline tetragonal barium titanate" *J. Phys. Chem. C.,* Vol. **112**, 9659-9667.

Ramakanth, S., Hamad, S., Rao, S.V. and Raju, K.C.J (2015), "Magnetic and nonlinear optical properties of $BaTiO_3$ nanoparticles" *AIP Adv*., **5**, 057139.

Tsivadze, A.Y., Ionova, G.V., Mikhalko, V.K., Ionova, I.S. and Gerasimova, G.A. (2016), "Ferroelectric $BaTiO_3$ nanoparticles: Electron structure and properties" *Nanoscal. Nanostruct. Mater. Coat*., **52,** 61-65.

Xu, J.B., Zhai, J.W. and Yao, X. (2009), "Structure and dielectric nonlinear characteristics of $BaTiO_3$ thin films prepared by low temperature process" *J. Alloys Compd*., **467,** 567-571.

Ramoska, T., Banys, J., Sobiestianskas, R., Bobic, M.V.J and Stojanovic B. (2010), *Processing and Application of Ceramics,* Vol. **4[3],** 193-198.

Fan, H and Liu, L. (2009), "Optimizating design of the microstructure of sol-gel derived $BaTiO_3$ ceramics by artificial neural networks", *J. Electroceram*., **22**, 291-296.

Wan, F., Han, J.G. and Zhu, Z.Y. (2008), "Dielectric response in ferroelectric $BaTiO_3$", *Phys. Lett. A*., Vol. 372, 2137-2140.

Nath, A.K. and Jiten, C. (2010), "Influence of ball milling parameters on the particle size of barium titanate nanocrystalline powders", *Physica B.* **405**, 430–434.

Kumar, S., and Ahlawat, N. (2016), "Microwaves sintering time optimization to boost structural and electrical properties in $BaTiO_3$ ceramics", *J. Integ. Sci. Technol.*, **4(1)**, 10-16.

Phule, P.P. and Risbud, S.H. (1988) ″Sol-gel synthesis of barium titanate using barium acetate and titanium (IV) isoprop oxide", *Adv. Ceram. Mater*., **3**, 183-185.

Kakihana, M., Arima, M., Nakamura, Y., Yashima, M. and Yoshimura, M. (1999), ″Characterization of precursors used in the pichini-type polymerizable complex processing of barium titanate", *Chem. Mater*., **11**, 438-450.

Salze, H., Odier, P and Cales, B. (1986), ″Elaboration of fine micro powders from organometallic polymeric precursors", *J. Non-Cryst. Solids*, **82**, 314-320.

Kutty, T.R.N. and Balachandran, R. (1984), ″Direct precipitation of lead zirconate titanate by the hydrothermal method" *Mater. Res. Bull*. **19**, 1479-1488.

Hsing, H. and Yen, F.S. (1996), "Effect of crystallite size on the ferroelectric domains growth of ultrafine $BaTiO_3$ powders", *J. Amer. Ceram. Soc*., **79**, 1053-1060.

Mahmood, N.B. and Al-Shakarchi, E.K. (2011), "Three techniques used to produce $BaTiO_3$ fine powder", *J. Mod. Phys*. **2**, 1420-1428.

Cole, K.S. and Cole R.H. (1941), "Dispersion and absorption in dielectrics - Alternating Current Characteristics", *J. Chem. Phys*., **9**, 341- 352.

Anderson, J.C. (1964), "*Dielectrics*", Spottiswoode, Ballantyne & Co Ltd., London and Colchester.

Smith, J. and Wijn, H.P.J. (1965), "*Ferrites*", Philips Technical Library, Eindhoven, The Netherlands.

Van Uitert, L.G. (1956), “Dielectric properties of and conductivity in ferrites”, *Proc. IRE*. **44**, 1294-1303.

Abdeen, A.M. (1999), “Dielectric behaviour in Ni–Zn ferrites”, *J. Magn. Magn. Mater.* **192**, 121-129.

Pandit, A.A., Shitre, A.R., Shengule, D.R. and Jadhav, K.M. (2005), “Magnetic and dielectric properties of $Mg_{1+x}Mn_x Fe_{2-2x}O_4$ ferrite system”, *J. Mater. Sci*., **40**, 423–428.

Zaki, H.M. (2005), “AC conductivity and frequency dependence of the dielectric properties for copper doped magnetite”, *Physica - B*, **363**, 232–244.