Role of Divalent Substitution in Dielectric Behavior and Pressure Sensitivity of MgTi$_2$O$_5$

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Abstract

The synthesis of MgTi$_2$O$_5$ (MTO) is carried by using high temperature solid state reaction technique. Two more karrooites are also synthesized in identical manner by divalent substitution. They are Mg$_{0.9}$Ca$_{0.1}$Ti$_2$O$_5$ (MTC) and Mg$_{0.9}$Zn$_{0.1}$Ti$_2$O$_5$ (MTZ). The structural, electrical and dielectric parameters are measured as a function of temperature / frequency. The unit cell volume, particle size and dielectric constant (k') at 1 kHz (at room temperature) are maximum, whereas d. c. resistivity (at room temperature) and a. c. resistivity at 1 KHz (at room temperature) are minimum corresponding to MTC. Interestingly, the pressure coefficient of capacitance is observed to be maximum for MTC. The correlation between pressure sensitivity and the physical parameters is discussed and analyzed. On the basis of analysis, it is concluded that the divalent substitution of Mg by Ca enhances the pressure sensitivity owing to its ionic character and size.
Key words: MTO, MTC, MTZ, Dielectric, Thermal Hysteresis, Disorder

Introduction

MgTi2O5 occurs as a natural mineral it is added in microwave ceramics to improve permittivity, Q factor and thermal stability . Its addition improves both impact resistance and thermal strain and makes the ceramic highly compact, thus avoiding dielectric loss. Therefore, it becomes an important constituent also for refractory ceramics [1]. Also, MgTi2O5 is known to be pressure sensitive [2, 3].

A wide range of non-convergent cation order – disorder between two crystallographically distinct octahedral sites (M1 and M2) in MgTi$_2$O$_5$ is responsible for its high temperature stabilization [4]. The cation disorder can increase the compressibility of MgTi$_2$O$_5$ by as much as 6%, an order of magnitude greater than that predicted by bulk modulus volume systematic [3]. Therefore, the cation disorder in addition to composition and structure can also affect the elasticity of the crystalline phase . The influence of pressure on the interatomic angles has been observed to be small compared to the ineratomic distances, suggesting that the compression of the karrooite structure is controlled primarily by bond length shortening rather than bond angle bending. [2]. This suggests that in addition to structural and composition factors, cation order – disorder also plays an important role in determining the elastic properties of the crystalline phase.

CaO is used as reducing agent. It is an alloying agent in the production of Al- Mg alloys. It is used for hardening the material like making cement and mortar. It is also used as a semiconductor with a high dielectric constant. The ionic character of Ca-O bond is 0.77, which is higher than Mg-O (0.67). The ionic size of Ca^{2+} is also very much larger than Mg^{2+}.

ZnO is unique material that exhibits semi conducting and piezoelectric dual properties. It has higher excitation binding energy (60 meV) and is more resistant to radiation. Its polycrystalline form is used as piezoelectric transducers, varistors and transparent conducting film. Also ionic character of Zn-O bond is 0.55, which is smaller than Mg-O bond. The ionic size of Zn^{2+} is slightly larger but comparable with Mg^{2+}.

Therefore, it is thought interesting to modify the $MgTi_2O_5$ by 10% divalent substitution of Mg by Ca / Zn and investigate the influence of substitution on the pressure sensitivity as well as structural, electric and dielectric properties of $MgTi_2O_5$.

Experimental

All the samples have been synthesized by high temperature solid state technique. The samples in pellet form were sintered finally in air at 1200°C for 24 hours. A microprocessor based JEOL JDX – 8030 X – ray diffractometer was used to obtain the XRD data of the samples .. The FTIR spectra were taken to determine the vibrational frequencies of the dipoles at M1 and M2 sites. 'PERKIN – ELMER 683' spectrophotometer was used for this purpose. The dielectric parameters were determined in the temperature range 300 – 838 K at 1 kHz as well as at room temperature for frequency range from 10 kHz to 1000 kHz by using an impedance analyzer 'HP – 4192'. The d. c. resistivity at room temperature and a. c. resistivity at 1 kHz in the temperature range 300 – 838 K were also measured.

Result and Discussion

Structural properties

The XRD data of all the samples confirmed the single phase Orthorhombic structure of karrooite. It is interesting to note that the unit cell volume of MTZ is the least (Table 1), which indicates an efficient packing of the octahedras whereas it is the largest for MTC. The Debye particle size is the largest for MTC perhaps due to strain free growth of lattice which is indicated by smaller inhomogeneity (5) .. The divalent substitution promotes the grain size as shown by SEM photographs [Fig. 1 (a), (b) and (c)]. The density and grain size are found to be the largest in MTZ (Table 2) because Zn promotes densification [6] and grain growth.

Table 1 Comparison of Lattice parameters modified karrooites.

Sample	a (°A)	b (°A)	c (°A)	Volume
MTO	9.7160	9.9652	3.7365	361.78
MTC	9.7190	9.9852	3.7394	362.89
MTZ	9.6636	9.9872	3.7192	358.95

Table 2 : Comparison of density, pore fraction, particle size, grain size & inhomogeneity of modified karrooites.

Sample	Density (XRD) (g/c.c.)	Density (Pract) (g/c.c.)	Pore Fraction	Particle size °A	Grain size (μm)	Inhomo-geneity
MTO	3.6720	3.489	0.050	670.86	1.837	-0.0039
MTC	3.6896	2.902	0.213	1122.5	2.490	-0.0019
MTZ	3.7770	3.444	0.088	613.09	3.382	-0.0021

Degree of disorder (x)

The karrooite exhibits different cation distribution in the M1 and M2 sites depending on the heat treatment. The cation distribution is well described by the degree of disorder [7, 8]. It is now established that the degree of disorder (x) depends on lattice parameters [9]. An empirical model based on the knowledge of lattice parameters has also been proposed [1]. However, knowing the sensitivity of lattice parameters to many factors such as grain size of basic ingredients, impurities, heat treatment etc., we proposed a new model to determine the degree of disorder (x), which depends mainly on the relative values, or ratios of lattice parameters.

$$x = 586.241\left[\frac{c}{b}\right] - 188.154\left[\frac{c}{a}\right] - 150.822\left[\frac{a}{b}\right]$$

This equation is very well calibrated with Brown – Navrotsky's data [9]. Taking the clue from the linear relationships between the degree of disorder and average bond lengths L_1 and L_2 of M1 and M2 sites respectively, we have determined ratios of bond lengths L_1/L_2 using Brown – Navrotsky's data [28] to eliminate the effects of other parameters on L_1 and L_2. The plot between the degree of disorder and the ratio L_1/L_2, which is perfectly linear (Fig. 2). Similarly, relation between degree of disorder (x) and ratio q_1/q_2 of charges (based on ionic character and valency) on M1 and M2 sites respectively is plotted, which is also perfectly linear (see Fig. 3).
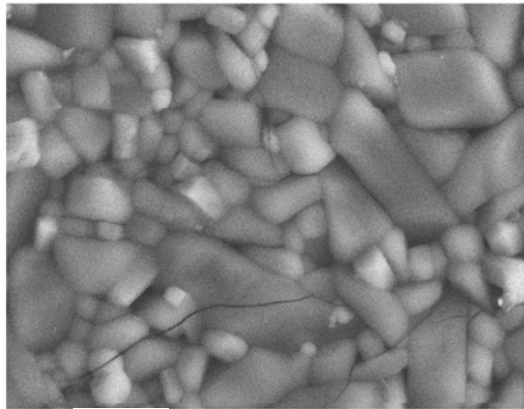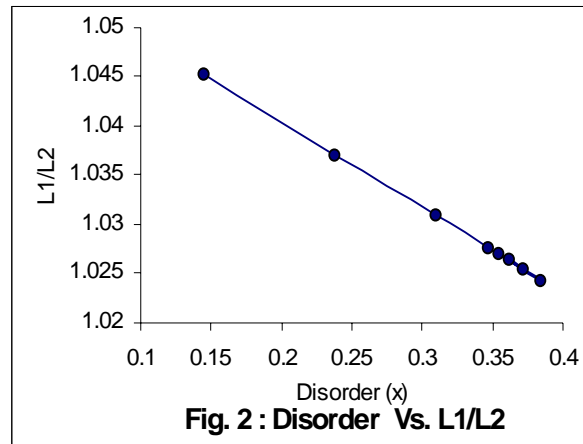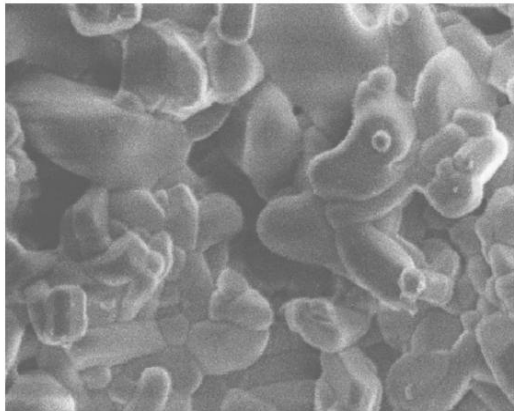
Fig. 1 (a) : SEM of MTO

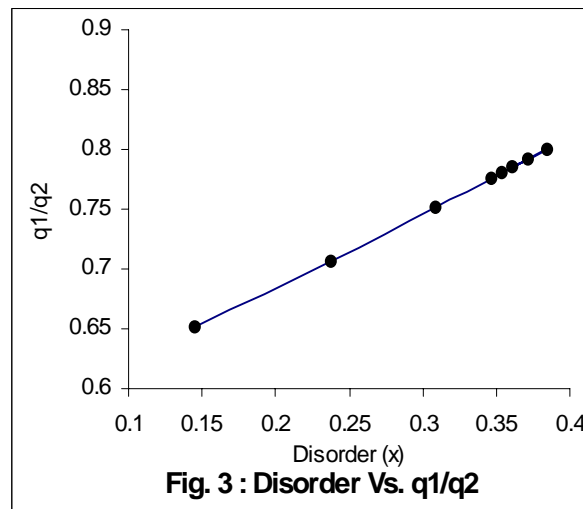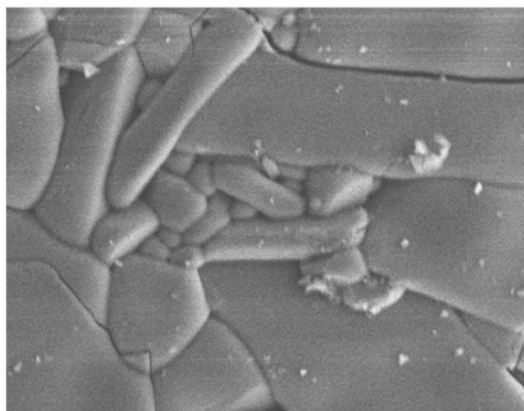
Fig. 2 : Disorder Vs. L1/L2

Fig. 1 (b) : SEM of MTC
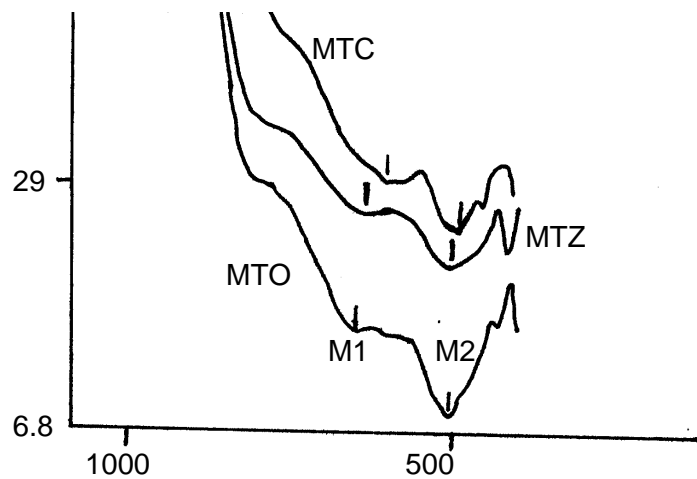

Fig. 3 : Disorder Vs. q1/q2

Fig. 1 (c) : of MTZ

Fig. 4 : IR specta of Modified karrooites

Using this equation and graphs, we have determined the degree of disorder (x) and cation distribution of our samples, which is shown in Table 3. It is observed that the divalent substitution of Ca / Zn decreases the degree of disorder. The negative degree of disorder corresponding to MTZ may be due to the size of Zn, which is slightly larger than Mg, which results in larger value of L_1/L_2 than the L_1/L_2 corresponding to zero disorder. The perfect order in MTZ (Table 3, column 3) derived from the above technique implies small unit cell volume, which matched with reported data [10].

Table 3 Degree of disorder (x), cation distribution, L_1/L_2 and q_1/q_2 corresponding to modified karrooites.

Sample	x	Cation distribution	L_1/L_2	q_1/q_2
MTO	0.405	$[Mg_{0.595}Ti_{0.405}]_{M1}[Mg_{0.405}Ti_{1.595}]_{M2}$	1.0226	0.8135
MTC	0.350	$[Mg_{0.615}Ca_{0.035}Ti_{0.35}]_{M1}[Mg_{0.285}Ca_{0.065}Ti_{1.65}]_{M2}$	1.0275	0.7788
MTZ	-0.036	$[Mg_{0.1}Zn_{0.1}]_{M1}[Ti_2]_{M2}$	1.0591	0.5576

IR Spectra

The IR spectra of all samples are reproduced in Fig. 4 and the IR frequencies of FTIR absorption bands are given in Table 4. The bands at around 630 cm^{-1} and 500 cm^{-1} are assigned to octahedral stretching modes corresponding to the M1 and M2 sites respectively, whereas band at around 425 cm^{-1} is assigned to octahedral bending mode [11, 12, 13]. It is observed that the separation in bands ($v_1 - v_2$) decreases by the divalent substitution which is attributed to greater content of Ti on M2 site. This gives stronger coupling between M1 and M2 sites. The separation is the least in MTC, which may be due to greater ionic character of Ca – O bond and occupancy of Ca on both the M1 and M2 sites.

Table 4 : IR band frequencies of modified karrooites.

Sample	v_1 cm^{-1}	v_2 cm^{-1}	v_3 cm^{-1}	$v_1 - v_2$
MTO	648.03	505.30	425.99	142.73
MTC	604.00	500.00	456.00	104.00
MTZ	629.93	507.90	416.30	122.03

Electrical properties

The plot of Log ρ_{ac} (at 1 kHz) versus 1/T is reproduced in Fig. 5. It is observed that above 460 K there are two activation energies for each sample, which are reported in Table 6. The activation energy (E_a) above 630 K is attributed to the commencement of the change in cation distribution whereas in lower temperature range (460 – 630 K), it is due to instrinsic conduction. The PTCR characteristic is observed below 450 K, which is attributed to recombination and impurity (disorder) scattering of M1 and M2 sites. It is prominent in MTC as can be seen from the PTCR coefficient of resistivity (Table 5, last column).

The octahedras corresponding to larger cation Ca^{2+} are more distorted as well as the IR band frequency (ν_3) corresponding to MTC is maximum. These factors increase the probability of electron-hole recombination, which results in greater PTCR. The band gap is maximum in MTO may be due to large degree of disorder (x). The larger band in MTO may be due to large degree of disorder (x). The band gap appears to increase with the degree of disorder. The least activation energy corresponding to MTC in intrinsic conduction region is responsible for low d.c. resistivity (ρ_{dc}) as well as a.c. resistivity (ρ_{ac}) at 1 kHz at room temperature.
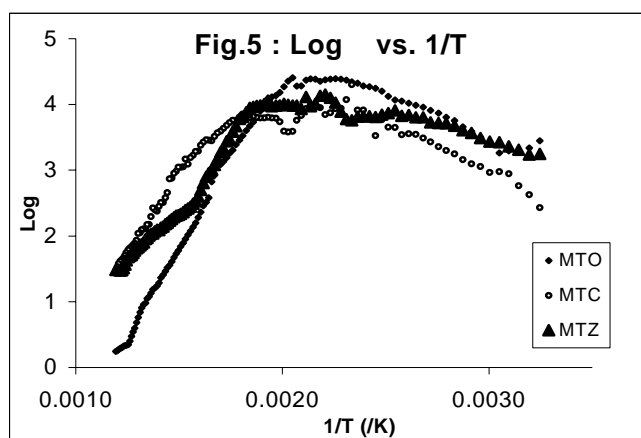

Fig.5 : Log   vs. 1/T

Table 5: Electrical parameters of modified karrooites.

Sample	E_a (eV)		Band Gap E_g (eV)	ρ_{dc} (kΩ.m) at room temp.	ρ_{ac} (kΩ.m) at room temp. & at 1 kHz	PTCR Coefficient $= \dfrac{d\rho}{\rho.dT}$ … (K^{-1})
	Intrinsic conduction region	Change in cation distribution				
MTO	0.730	1.071	2.142	4280	2958	0.0536
MTC	0.150	0.963	1.926	2692	209.6	0.2760
MTZ	0.456	0.550	1.100	3956	836.0	0.0334

Dielectric properties

The dielectric constant (k') is measured as a function of temperature for all samples and reproduced in Fig 6 (a), (b) and (c). It is observed that the dielectric constant remain almost constant in MTO and MTZ from room temperature up to certain temperature called transition temperature (T_t) and then suddenly starts rising rapidly. This rise is attributed to change in cation distribution. However, in MTC, there is significant decrease in dielectric constant with temperature near room temperature.

Fig. 6 (a) : K' vs. T

Fig. 6(b) : K' vs. T

Fig. 6 (c) : K' vs. T

Fig. 7(a) : K' vs. Log F

Fig. 7 (b) : K'' vs. Log F
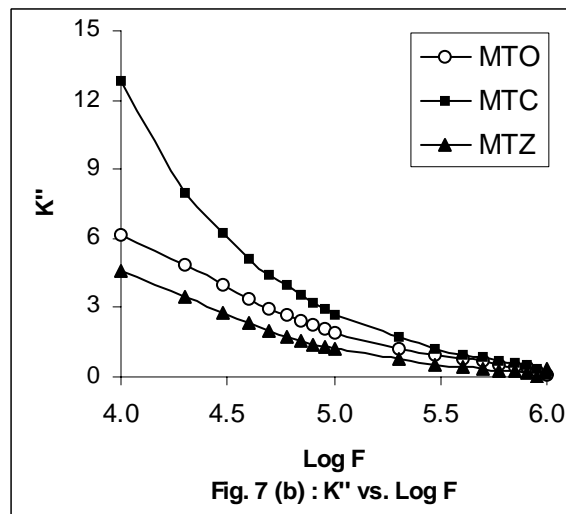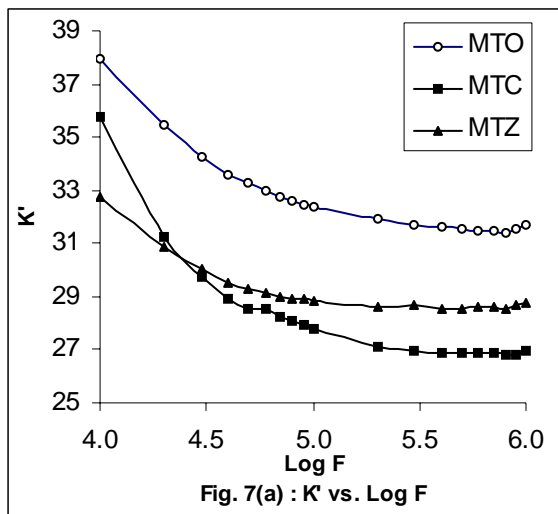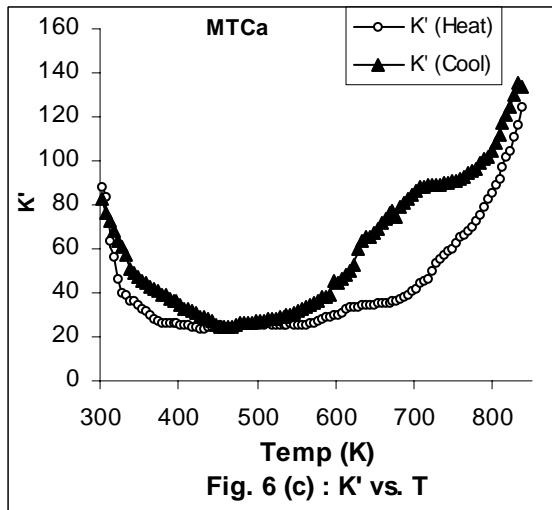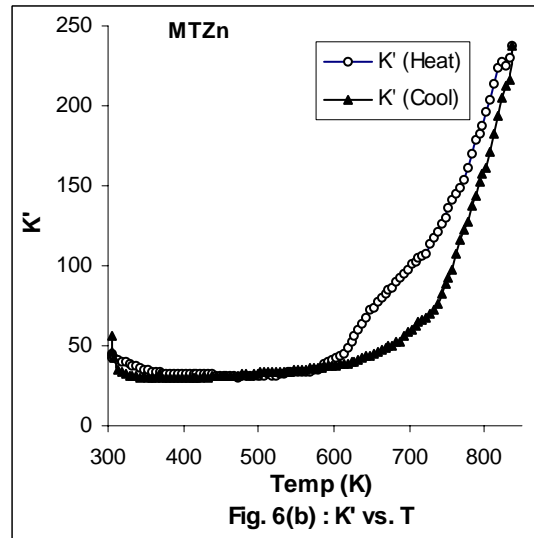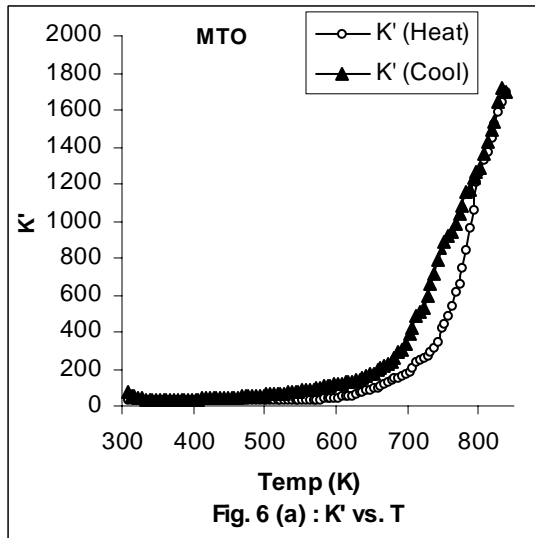
The rate of rise in dielectric constant is characterized by temperature coefficient of dielectric constant (K_T'). The K_T' and T_t are found to be largest in MTO and decrease by the divalent substitution (see Table 6) but increase with increase in degree of disorder. The strong coupling between M1 and M2 octahedra may oppose the change in cation distribution, which results in low K_T' in MTC and MTZ. It is interesting to note that heating and cooling cycles [Figures 6 (a), (b) and (c)] form a distinct loop, which shows the energy dissipation and area of the loop also increases with degree of disorder. It is, therefore, concluded that the interfacial polarization is maximum in MTC and the dielectric loop and its characteristics are correlated with the order – disorder (i.e. cation distribution) transition.

Table 6 : Dielectric parameters of modified karrooites.

Sample	T_t (K)	K_T' (K^{-1})	Loop area
MTO	713	0.0412	37964
MTC	688	0.0199	8723
MTZ	600	0.0190	6112

Relaxation spectra

The presence of space charge in the family of pseudobrookite prompted us to study their relaxation spectra. The relaxation spectra of these samples at room temperature are investigated between the range 10 kHz and 1000 kHz. For each sample the dielectric constant (k') and dielectric loss (k'') fall with increase in frequency as shown in Fig. 7 (a) and (b) respectively. In divalent substitution, space charge contribution is the least in MTZ but maximum in MTC. This may be due to large grain size or greater ionic character Ca – O than Zn – O, which may release more space charge. The dielectric loss is observed to be most in MTC, which may be attributed to space charge polarization.

Pressure sensing property

It is observed that the capacitance of each sample is sensitive to pressure and increases linearly with pressure as shown in Fig. 8. The pressure sensitivity is measured in terms of pressure coefficient of capacitance (C_p') at 1 kHz and at room temperature. It is maximum in MTC (Table 7). Bond lengths are more sensitive to pressure than bond angles in karrooite [11]. The large ionic size and ionic character of Ca may be responsible for increasing pressure sensitivity.

Table 7 Pressure sensing parameter of karrooites

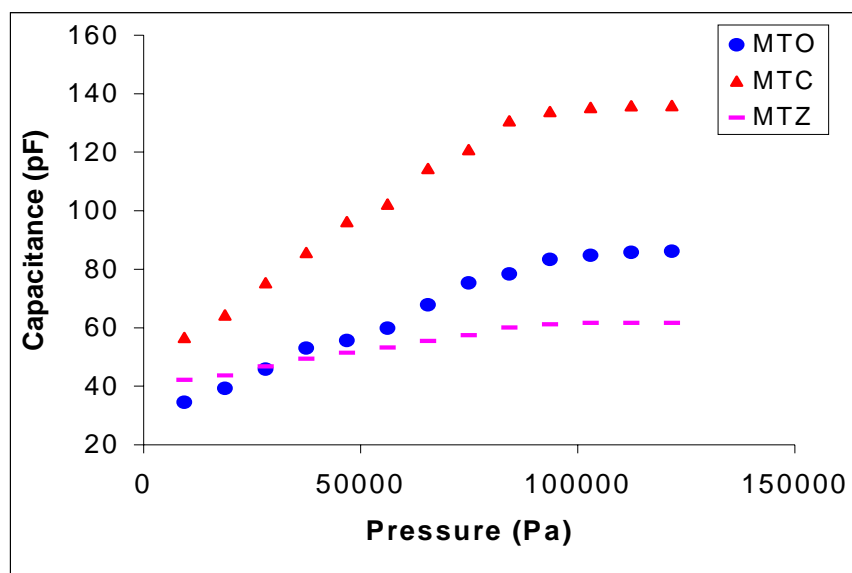| Sample	$C_P' = \dfrac{\partial C}{C.\partial P}$ … (Pa^{-1})
MTO	1.6827×10^{-5}
MTC	1.8020×10^{-5}
MTZ	0.4996×10^{-5}

Figure 8 : Capacitance versus pressure

Conclusion

The Zn / Ca substitution increases grain size and dielectric constant at 1 kHz and at room temperature whereas reduces degree of disorder, resistivity, band gap and energy dissipation. The dielectric and most of the electrical properties have changed with the degree of disorder / change in cation distribution. The pressure sensitivity towards the capacitance is increased by substitution of Ca, which may be attributed to large unit cell volume, particle size and large ionic character and size of Ca^{2+}.

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