A Transition From Relaxor To Normal Ferroelectric: An Overview

Band S. A.

Yeshwantrao Chavan College of Engineering, Wanadongari Nagpur, 4441110, (M.S.)

Takarkhede M .V.

J D College of Engineering ,Near Asaram Bapu Ashram,Kalmeshwar road,Nagpur-441501(M.S.)

Abstract

Relaxors like PMN and PMN based materials proved to be promising candidate for multilayer capacitors (MLCs) and electrostriction actuators , pyroelectric bolometers, piezoelectric sensors replacing normal ferroelectrics such as $BaTiO_3$ and PZT. The compositional heterogeneity resulting from scale of ordering at the B-site influences relaxor to normal ferroelectric behavior .The genesis and growth of PMR resulted in ferroelectric transition. The distribution of curie points in PMR leads to DPT behavior. The dielectric relaxation is attributed to the relaxation of domain walls. Strong charge effects developed as a result of 1:1 ordering at the B-site limits the ordering of domains hence the size growth. The difference between NFE and RFE along with mechanism influencing the transition from RFE to NFE have been discussed.

[Key words: Relaxor ferroelectrics (RFE), normal ferroelectrics (NFE), Polar micro-regions (PMR), diffuse phase transition (DPT)]

Introduction

The Spontaneous polarization 'Ps' ,its reversibility and anomaly in physical properties and change in crystal structure at transition temperature(T_c) are the most fundamental properties of ferroelectric materials. They exhibit high relative permittivity (ε_r) which is non-linear and exhibit hysteresis. Domains get disrupted by thermal agitation above Tc .When interactions between atoms is large spontaneous polarization is produced. At T_C spontaneous polarization (Ps) sets in. It is the temperature dependant part of polarization called orientation polarization, its switching from one orientation state to other with electric field causes anomalies in physical properties around the transition temperature. The change in crystal phase with temperature transforms ferroelectric materials into non-ferroelectric state. In general ferroelectric materials are polar materials in their ferroelectric state.

Ferroelectrics can be divided into two groups normal and relaxors. Complex lead perovskites discovered by Smolenskii etal 1958 , encompasses largest family of relaxors Some prominent relaxors are PMN , PZN ,PSN ,PST and normal ferroelectrics are $BaTiO_3$,PZT , PT , $KNbO_3$,Lead Germanate ,TGS , KH_2PO_4 ,$LiNbO_3$ .Some important differences between NFE and RFE are given below .

❖ NFE shows 1st or 2nd order transition at curie point i.e. at T_c undergoing structural transition changing ferroelectric phase completely into paraelectric phase above T_c.

On the other hand RFE shows broad phase transition which is diffused (gradual decrease of Ps with rising temperature) at T_c .Both ferroelectric and paraelectric phase coexist above T_c up to certain temperature range, No clear evidence of structure transition is observed (Fig 1.1)
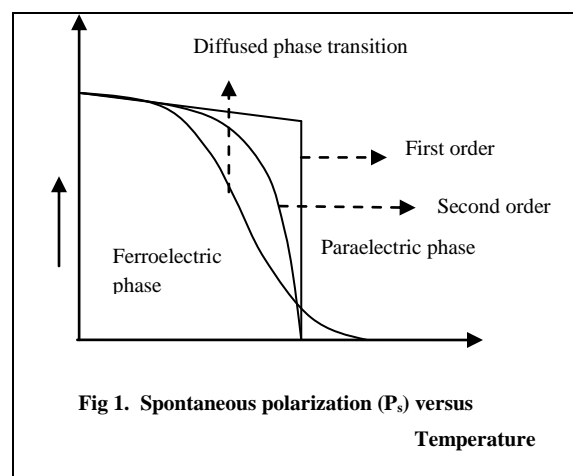

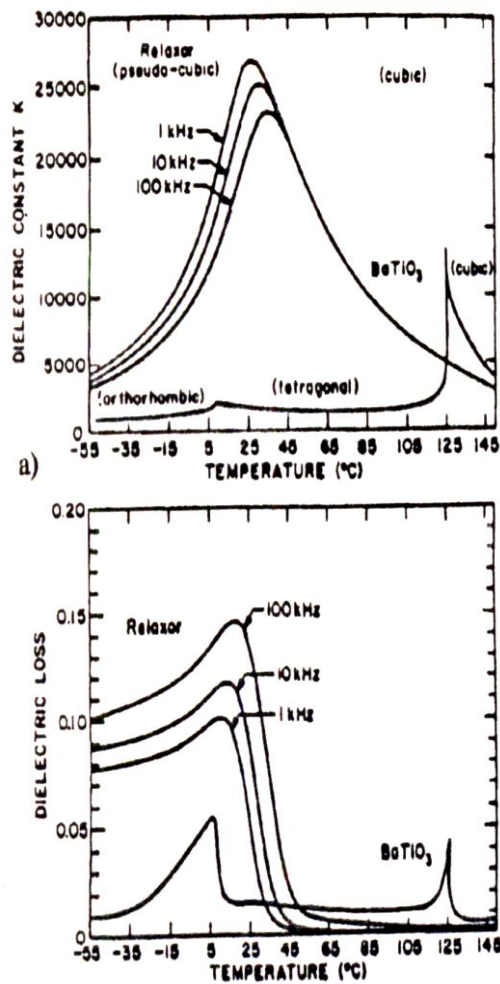**Fig 1. Spontaneous polarization (P_s) versus Temperature**

Fig .2. ε_r Vs T and tanδ Vs T for Relaxor ferroelectrics

(PMN-PT) and normal ferroelectrics (Ba TiO₃)

❖ RFE exhibit strong frequency dependence in curie range 100Hz to 1MHz in ε_r and tanδ. However NFE exhibit weak frequency dependence in curie range. At high temperature ε_r'' is almost zero .Upon cooling a sudden increase of ε_r'' implies appearance of a domain state whose relaxation frequency drops in the low frequency range ε_r'' peaks at a temperature T_{max} then it decreases continuously, shrout etal 1990.

❖ NFE obey Curie Weiss above T_c ie ε_r = C/T-T_o where T_o= T_c for continuous transition (2nd order) and few degrees less than T_c for discontinuous transition. (Ist order). On the other hand RFE obey quadratic law $1/\varepsilon r$ = $1/\varepsilon_{rmax}$ +(T-Tc)^2/2$\varepsilon_{rmax}\delta^2$ where δ =diffuseness coefficient, a measure of diffuseness of transition

❖ NFE shows strong optical anisotropy with light whereas RFE shows weak optical anisotropy.
❖ NFE shows strong remnant polarization on the other hand RFE shows weak remnant polarization.
❖ Line splitting is observed owing to spontaneous deformation from paraelectric to ferroelectric phase   in NFE .Whereas no x-ray line splitting giving a pseudo cubic structure is observed in case of RFE.

Discussion

The dielectric response of relaxor are generally explained in terms of separate polar micro-regions called PMR , originated due to composition fluctuations which possess spontaneous polarization vector Ps . The dielectric response is viewed as result of reorientation of local polarization vector Ps under applied electric field. The PMR size varies from 2-10 nm. The phase transition in the polar state occurs in separate regions of crystal independent of one another with local transition temperature depending upon the composition of the individual regions. In these relaxor materials randomly oriented polar micro-regions exists or appear at temperature far above T_c say Td where Td >> T_{max}(100-200°C above T_{max} .) It should be noted that polar clusters are randomly formed. Hence it is easier to form clusters of small size .The Polar Regions are considered as the nuclei of ferroelectric phase in paraelectric matrix and cannot be   smaller than critical size. Since in ferroelectric transition Tc is strongly dependent on composition, the PMR possess different T_c s. This model involving distribution of sizes and a temperature dependent size gives the best qualitative fit to the relaxor behavior, Smolenskii etal, 1961, Smolenskii 1970, Bokov etal 1961 .

The dielectric response was interpreted as the switching of local spontaneous polarization between states with different orientation of vector Ps.   At a given temperature T, only regions of which the local T_c is close to T contribute to the macroscopic (bulk) dielectric response since activation energy required to switch polarization in the region increases drastically with temperature below Tc . Size of nano-domains begins to increase strongly upon cooling through T_{max} giving rise to a peak of εr which does not result from a true phase transition ie structure change.   Some researchers argued random electric field originated from charged compositional fluctuations limits the size of the domains which accounts for the diffuse character of the transition. Small variation in cluster size can

induce a dielectric dispersion covering several decades Westphal etal 1992.

Random etal 1990 suggested polar clusters or domains dispersed in paraelectric matrix resembles in many aspects as that of super magnetic clusters in spin glasses Randall etal1980 ,. Setter etal 1980 and Cross etal 1987, suggested non-interacting polar clusters (with local spontaneous polarization) which are super paraelectric with polarization vector thermally fluctuating between equivalent potential well .Ferro-electricity is a cooperative phenomenon , an energy involved with every polar regions must scale with volume .The size of polar clusters determine size (value) of activation energy between degenerate dipolar states .Then for sufficient thermal energy a flipping of orientation from one state to other can occur and that for regions with a size of 10nm ,the potential barrier required to reorient the local polarization vector would be comparable to thermal energy of the crystal. The local polarization fluctuates under thermal agitation. According to this model, all the polar regions contribute to the orientation polarization and on cooling the temperature and frequency dependence of ε_r is observed due to the slowing down of fluctuation of local polarization vectors. It refers to thermal agitation of the orientation of spontaneous dielectric polarization in polar clusters. The flipping frequency 'υ' is expressed as υ = υ_D exp –E_a / k_B T where $\upsilon_D = 10^{12}$ to 10^{13} Hz

The super-paraelectric model accounts for many of the relaxor features including broad dielectric dispersion .According to Viehland etal 1990 , ferroelectric relaxors are envisaged as that of spin glasses with freezing temperature obeying Vogel Fulcher relationship and explain the dielectric dispersion in relaxors. They have emphasized the influence of the cluster dispersion on the width of the relaxation time spectrum. They showed that spherical clusters of diameter 4-5 nm have fluctuation frequencies of approximately 10^7 to 10^8 respectively .The relaxation time increases sharply with the size. RFE has thermally activated polarization fluctuations above a static freezing temperature 'T_f' . Based on these considerations the Vogel fulcher relationship was introduced to characterize the relation between w and Tm of RFE as

f = f_o exp [-Ea/(T_{max}-T_f)],where f_o= Debye frequency = 10^{12} and E_a = activation energy , Tm= curie temp independent of w , T_f = freeing temp few degrees below T_{max}

The dielectric constant peaks at a temperature for which the size of the polar clusters becomes so large that they begin to fail to follow the applied field .It

appears therefore natural that Tmax increases with frequency.

In order to explain unique frequency dependence of the relaxor dielectric response, Thomos 1990, Rolov 1965 presented a theoretical network of PMN in terms of contribution made by individual NbO_6 and MgO_6 octahedra considered as polar units . With this theory although important trends in relaxor frequency behavior have been correctly predicted but this theory could not account for the absence of dielectric dispersion for $T > T_{max}$ region .

In relaxors as the equivalent site are occupied by different cations , PMN ceramics involves the coexistence of some micro-domains containing as many Mg as Nb ions and micro-domains richer in niobium in order to restore the global stoichiometry. This leads to more heterogeneous distribution of cations on the B –site of the pervoskite .The 1: 1 ordering being electrically unbalanced, strong charge effects are induced in the material which dominates the kinetics of the ordering process and inhibit the development of the long range order. Large size differences between cations and anions favors the ordering of 1:1 type as lattice strain is less than 1:2 disordering. The electrostatic energy or random electric field however will increase an ordering because of charge imbalance between ordered and disordered region which accounts for the DPT behavior. The observed nanometer scale ordering in these systems represent a balance between electric and elastic strain consideration.

In Pb B_x B'_x O_3 where x = ½ materials stoichiometric order reduces chemical inhomogeneity therefore favors more normal dielectric behavior. In Pb B_x B'_{2x} O_3 where x = 1/3 materials stoichiometric order promotes space charge fluctuations and the corresponding dielectric data shows an enhancement of the relaxor characteristics. Charge fluctuations with Mg and Nb ions order at alternate B lattice sites arrest ordering process as the lattice is no longer able to compensate for such charges with existing lattice defects. **Thus the scale of B-site ordering limits the growth of PMR and leads to relaxor behavior.**

Chen etal 1989 discovered that La doping in PMN decreases charge effects and increases size of micro-domains .Na doping increases charge effects and decreases size of macro-domains.. **It is observed that charge fluctuations which occur in relaxor materials affect the ordering and dielectric behavior**. It has been also observed the size of ordered domains is reduced with increasing PT addition in PMN. PT addition dilutes the forces responsible for the ordering process and result in less diffused transition, Band

etal 1997, Hilton 1990.In certain composition as PMN-PT and PZN-PT there is a weakening of super lattice as the PT content increases. Eventually there is a point where super lattice cannot be detectable .This happens near MPB composition PMT-PT(0.65-0.35) and PZN-PT near (0.9-0.1)and correspondingly NFE behavior is observed .

Conclusion

It is a well understood fact that DPT in PMN is due to microscopic variation in Stoichiometry which results in micro volumes with conventional ferroelectric behavior but with variety of curie temperature scaled with volume of PMR . Relaxation is attributed to time dependant ferroelectric switching .It is the scale of B-site order occupying equivalent positions by different cations leads to compositional heterogeneity , develops charge effect which limits the size of domains and influences RFE -NFE- behavior.
La doping in PMN decreases charge effects and increases size of micro-domains leading toward more relaxor behavior .Na doping increases charge effects and decreases size of macro-domains and leading towards normal behavior. It is observed that charge fluctuations which occur in relaxor materials affect the ordering and dielectric behavior. Either complete disorder or full range order appears to give rise to normal ferroelectric behavior .It is limited nano scale ordering which appears to favor the development of small scale polar regions and RFE behavior .

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