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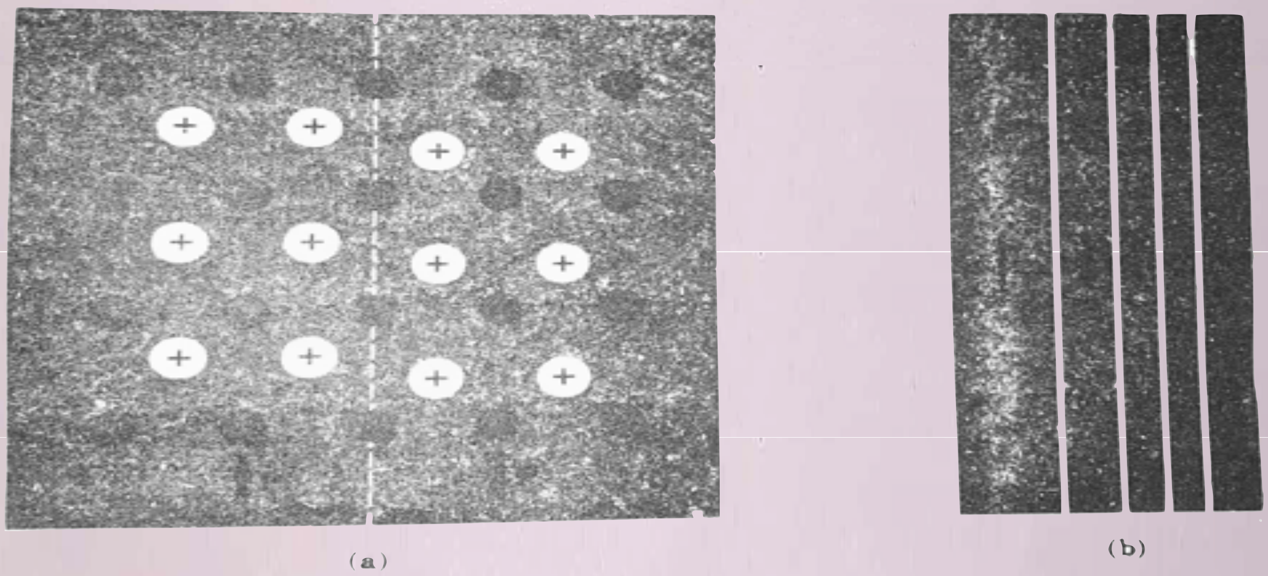
M.Sc (Physics) Semester IV

Topic: "Ferroelectrics"

Ferroelectric Domain

* defined as a small microscopic region in the material within which all the electric dipoles are oriented in the same direction due to a strong short-range interaction caused by internal electric fields.
* ferroelectric material consists of a large number of domains with each domain having a specific polarization direction
* domains are randomly oriented in the absence of an electric field
* when an external field is applied, the domains tend to get oriented in the direction of the applied field.
* the domains that are in the direction of external field grow in size at the expense of the other domains.

* as the external field is increased, more and more domains get oriented in the field direction.
* as a result, the material ideally consists of a single domain.
* the material in this state possesses maximum polarization
* the orientation of the domain is better facilitated if the material is maintained at a high temperature (close to T_c but less than T_c)



(a) Schematic drawing of atomic displacements on either side of a boundary between domains polarized in opposite directions in a ferroelectric crystal; (b) view of a domain structure, showing 180° boundaries between domains polarized in opposite directions.

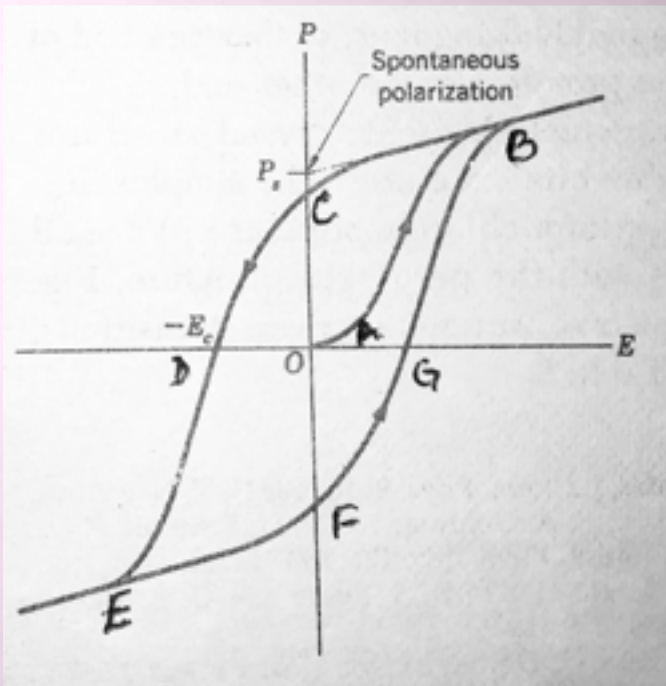
Ferroelectric Hysterisis

* A typical plot of polarization versus electric field for the ferroelectric state is closed loop, known as <u>hysterisis loop</u>

* when $E=0$, ferroelectric domains are randomly distributed so polarization is zero (Pt O)

* as E increases, domains get oriented in the direction of the field, polarization initially increases linearly

* as the field is further increased, more and more domains get oriented and curve becomes non-linear



Ferroelectric hyteresis loop

* when all the domains get oriented, the polarization attains the maximum value (Pt B), known as spontaneous or saturation polarization P_s
* At this point, the crystal has become a single domain.
* when E is reduced to zero, there remains finite polarization, called the remnant polarization P_R (OC)
* the polarization becomes zero at negative electric field i.e. $-E_c$, the coercive field.
* E is further increased in reverse direction beyond E_c, the domains get oriented in the direction of field, polarization attains maximum value in the reverse direction (pt E).
* if the field is again reduced back to zero, there will be remnant polarization $-P_R$ (pt F).
* If the field ~~the~~ is further increased from 0 to +ve value (direction), P_R disappears at field $+E_c$, further increase in the field will trace the path GB loop.
* the closed loop is called the <u>hysterisis curve</u>.

Applications of Ferroelectric materials

* several applications due to their special characteristics -

Property	Application
Large dielectric constt.	capacitor
Large piezoelectric coeff.	Sonar detectors, strain sensors, actuators
pyroelectricity	I.R. detectors, I.R. imaging
large non-linear polarizability	optical devices like optical memory, display, optical wave guide etc.
Bistable orientational state (ie. reversal of spontaneous polarization)	Binary memories, switching devices

Phase transition in Ferro-electric crystals

* phase transition in F.E. crystals/materials are divided in 2 classes

F.E. crystals

Order-disorder transistion	Displacive or Displacement transition
* transistion is associated with the individual ordering of ions	* transistion is associated with the displacement of a whole sublattice
* includes crystal with hydrogen bonds in which the motion of the proton is related to the F.E. properties	* includes ionic crystals structure closely related to the perovskite and ilmenite structure
* soft mode is only diffusive i.e. non-propogating	* soft mode can propogate in the crystal at the transition

Order-disorder transition

* there is really not a phonon at all, but only large amplitude hopping between the wells of the order-disorder system. Many ferroelectrics have soft modes that fall between two extremeties

eg. Potassium dihydrogen phosphate KH_2PO_4 ($T_C = 123\,K$)

Potassium dihydrogen arsenate KH_2AsO_4 ($T_C = 96\,K$)

Rubidium dihydrogen phosphate RbH_2PO_4

Displacive or Displacement transition

* Perovskite st - structure with a Chemical formula ABX_3

$AB \Rightarrow$ metals i.e. cation

$X \Rightarrow$ gas i.e. anion

$AB \Rightarrow$ two cations of different sizes and X is an anion that bonds to both

'A' atoms are larger than the 'B' atoms

* Ileminite st. - structure with a Chemical formula ABX_3

$AB \Rightarrow$ two cation of almost same size

eg.. $BaTiO_3$ ($T_c = 393\,K$), $PbTiO_3$ ($T_c = 763\,K$)

In $BaTiO_3$, ionic displacement is relative position of titanium ion with oxygen ion

Structural Phase transition -

* Occurs when a material changes its crystallographic structure
* transformation from one crystal to other if temperature, pressure, chemical composition, magnetic or electric field is varied.
* stable structure 'A' at absolute zero generally has the lowest accessible internal energy of all the possible structures
* structure 'A' can be varied if P or T is varied
  eg. Hydrogen and Xenon become metallic under extreme pressure
* consider another structure 'B' has softer or lower frequency phonon spectrum than 'A'
* As T is raised, the phonons in 'B' become highly excited than phonons in 'A'

* highly excited means higher thermal average occupancies and entropy increases with occupancy
* therefore entropy of B > entropy of A as the temperature is increased.
* phase transition require a change in entropy of the system
* the stable structure at a temp T is determined by the minimum of the free energy $F = U - TS$
* at transition temperature T_c, the free energy of the two phases will be equal
* thus the transformation of st. A to st. B may take place at critical or transition temperature such that $F_A(T_c) = F_B(T_c)$
* Some structural phase transitions have only small effects on the macroscopic physical properties of the material whereas some may have considerable effects on the macroscopic physical prop.
* Ferroelectric transitions are a subgroup of structural phase transition,

* eg in $BaTiO_3$, at T_c, F.E. state from tetragonal phase changes into paraelectric cubic phase

* Ferroelectrics are important due to unusually temperature dependent values of dielectric constant, the piezoelectric effect, the pyroelectric effect.

* eg in $PbTiO_3$, when $T > T_c$ ⇒ cubic structure
  when $T < T_c$ ⇒ tetragonal structure

Soft mode

* Soft mode concept was proposed to describe the mechanism of the ferroelectric structural phase transitions.
* the soft mode concept is that on cooling a material from a temperature above T_c, a normal mode of vibration of the crystal decreases to a zero frequency when the crystal becomes unstable and distorts
* based on the assumption that the crystal gets unstable against a particular normal vibration of lattice.
* the optical phonons associated with the distorted lattice is referred to as soft phonons.
* in high temperature phase, there exists a certain unstable phonon known as soft mode phonons whose frequency goes down as temperature approaches to the T_c (the phonon softens)
* at T_c, correspondent vibration (or atomic position) become frozen and produce a structure of another symmetry with a definite dipole moment.

* From LST relation; $\omega_T^2 / \omega_L^2 = \epsilon_\infty / \epsilon_0$
* the static dielectric constant increases when the transverse optical phonon frequency ω_T decreases.
* when ω_T has a low value, ϵ_0 has a high value 100 to 10k
* when $\omega_T = 0$, the crystal is unstable and distorts to a new structure because there is no effective restoring force
* soft mode is defined as an oscillatory mode that has a frequency near zero.

Antiferroelectricity -

* property of a material and can appear or disappear depending on temp, pressure, external electric field etc.
* the induced phase transition in antiferroelectrics has a double hysteresis loop.
* thus an antiferroelectric crystal is defined as a crystal whose structure can be considered as being composed of two sublattices polarized spontaneously in antiparallel direction.
* antiferroelectric state may be changed into F.E. state under the influence of strong external field or upon cooling to a very low temperature.
* eg $PbZrO_3 - PbTiO_3$ system show transistions between para, ferro and antiferroelectric state.

Numericals for practice

1. Determine the percentage of ionic polarization in a NaCl crystal which has the optical index of refraction and static dielectric constant as 1.5 and 5.6 respectively.

2. If the molecular dipoles in a 10^{-3} m radius water drops are pointed in the same direction, calculate the polarization. Dipole moment of the water molecule is 6×10^{-30} C-m.