C H A P T E R - III

: SOLID STATE BATTERY FORMATION :

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SOLID STATE BATTERY FORMATION

3.1   Introduction:

Ferroelectrics have been used for many years in devices requiring piezoelectricity, for example transducers. Also the uses of ferroelectric materials, in frequency controls, filters, miniature capacitors, thermal meters, modulating devices, frequency multipliers and dielectric amplifiers, and as switches and modulators for laser light. Nonlinear piezoelectric properties can be used in direct amplification of sound, and in computer circuits as matrix stores.

Solid state battery formation by ferroelectric materials, is another one of the interesting and promising applications. The report of solid state battery formation of KNo_3 was first given by Yoshihto Ishibashi, Michio Midorikwa and Yutaka Tauagi, Nagoya University, Chikusa Ku. Nagoya, (1969).

During the experimental study of Yukata Takagi and others, the effect of electric field on the ferroelectricity of KNo_3 crystals, it was found that the electromotive force (emt) of about 1 volt is observed between two electrodes sticked into the fused crystal after a d.c. electric field of about 1Kv/cm was once applied to the crystal at high temperature and then taken off. Platinum plates or stainless steel plates were used as electrodes. The magnitude of this

electromotive force, whose polarity is always the same as
that of the applied d.c. voltage, is temperature dependent.
It disappears at low temperatures, but recovers when the
samples are heated again. Drastic change in emf at about
$130^{\circ}C$ seems to correspond to the phase transition of KNo_3
crystals.

The emf decays with time, but decay constant is quite
long, while the time constant of a condeuser composed of KNo_3
and electrodes is estimated as less than 10^{-3} sec. Even after
the electrodes are short circuited the emf gradually recovers
almost the same value as expected without any short circuitry.
Usually at room temperature no large emf is observed. If we
put a drop of water on the sample, however, soon some emf
is seen to appear. From these facts, especially from a long
decay constant and recovery of emf after the short circuitry,
we can conclude that some chemical reaction is taking place
and a solid state battery is formed.

3.2   Experimental:

The experimental set-up is shown in the Fig.(3.1);
it consists of a globar furnace to heat the sample by keeping
it a so called crystal holder, the electronically regulated
power supply to provide d.c. electric fields digital milli-
voltmeter, temperature controller arrangement, and a
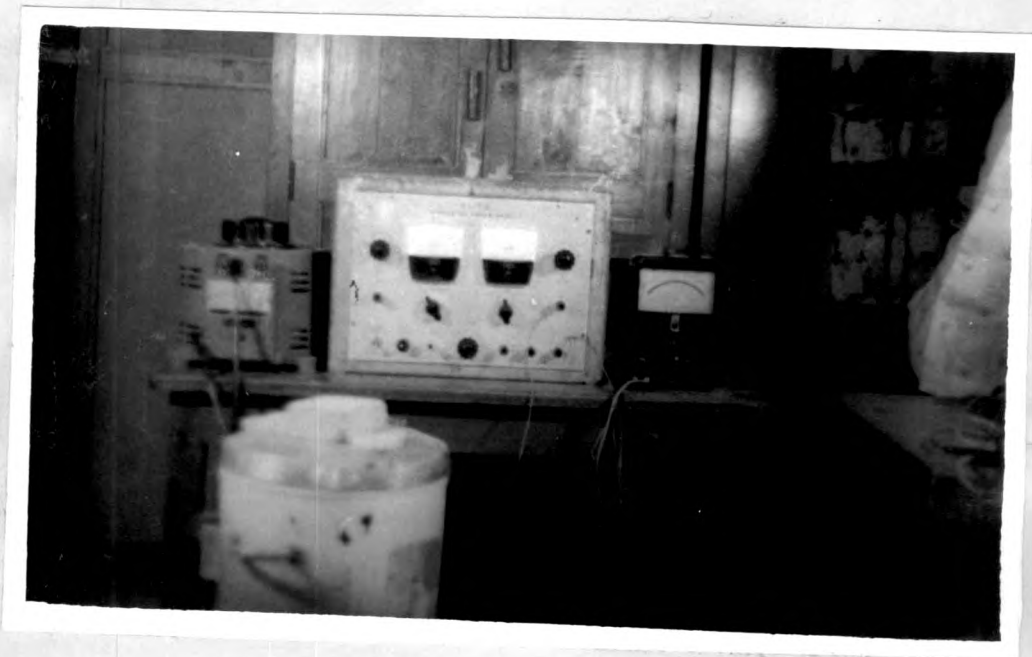millivoltmeter (d.c.) to measure the emf generated across

FIG. (3.1)

the sample. The dimensions of pellet (sample) were 0.12 cm.
steel electrodes are used. The sample is heated at high
temperature and then a d.c. electric field of 1 KV/cm was
applied. Immediately the emf generated was measured by a
millivotmeter.

3.3   Solid State Battery Formation for (Pb, Sr) TiO$_3$:

A pellet of (Pb, Sr) TiO$_3$ was introduced in the
crystal holder, and heated to a high temperature. The d.c.
electric field was given by means of the regulated power supply.
The emf generated was measured by a milliroltmeter with the
change of temperature. As the temperature changes, the emf
also changes. The variation of emf with temperature for the
above solid solution is shown in the Fig.(3.2). The emf
decreases as the temperature decreases, it disappears at
low temperature, but recovers when the sample is heated.
Drastic change in emf at about 490°C seems to correspond to
the phase transition of (Pb, Sr) TiO$_3$ solid solution system.
Another fact also we can observe is that, the emf decays with
time, but decay constant is quite long and even when electrodes
are short circuited the emf gradually recovers almost the
same value as that expected without any short circuitry.

One of the plausible explainations of the mechanism
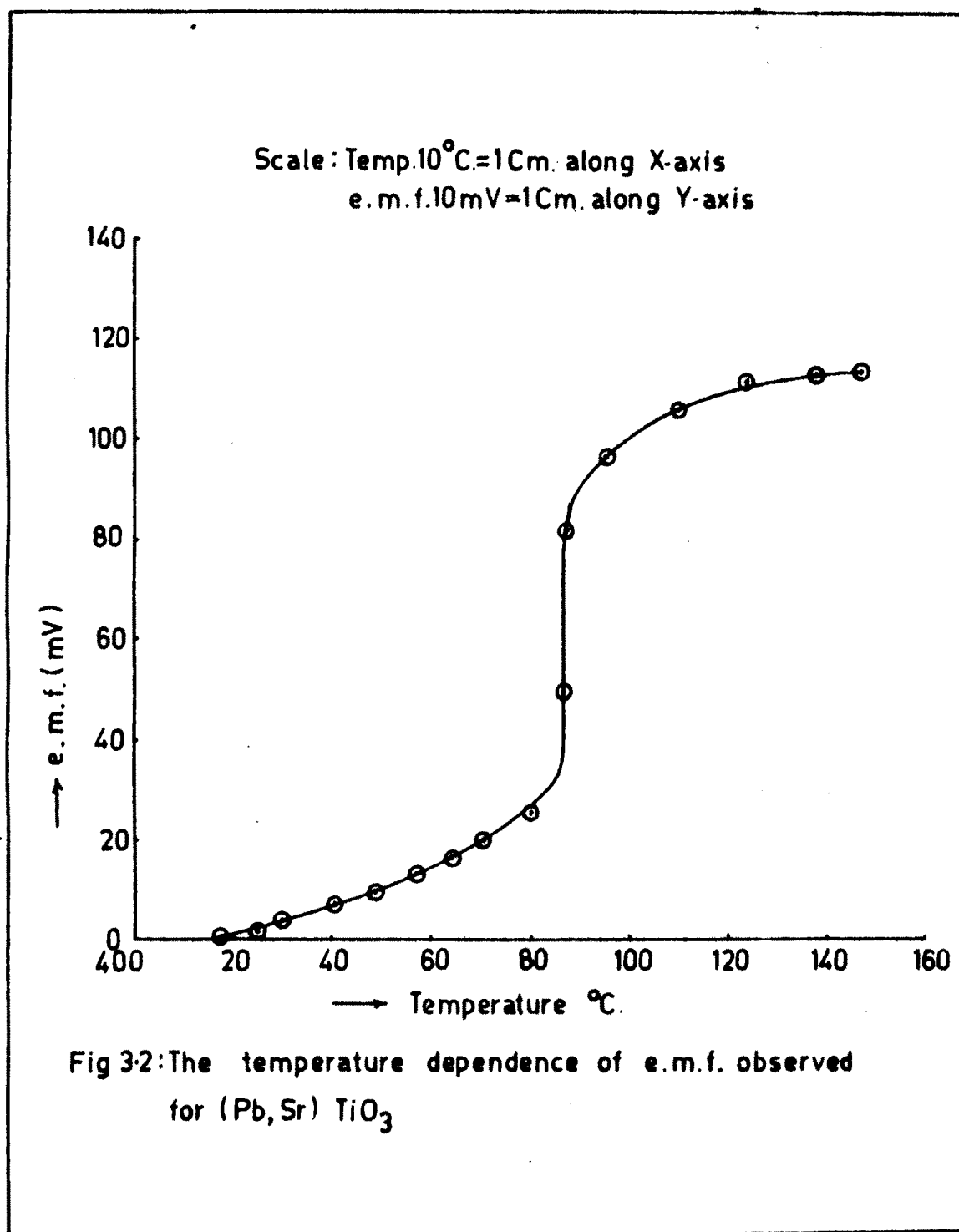can be given as follows.

By the application of d.c. electric field some part of ($PbTiO_3$ and $SrTiO_3$) may have decomposed into ($Pb + Sr$) and TiO_2 and O_2 ions. The TiO_2 and O_2 get out positive terminal as gas and ($Pb + Sr$) stay near negative terminal electrode. Therefore we obtain the battery of

Steel, ($Pb + Sr$)/ TiO_2, O_2 , steel.

By putting the drop of water the emf is generated. This fact may be explained as, ($Pb + Sr$) which exists near the negative terminal reacts with water, and ($Pb + Sr$) $(OH)_2$ and H_2 are formed. Thus we have H_2 gas at negative terminal and O_2 gas at positive terminal. This pair can also produce some emf.
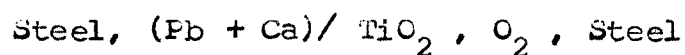
3.4   Solid State Battery Formation for (Pb,Ca) TiO_3:

The sample was replaced by the solid solution system (Pb,Ca) TiO_3 and heated in a furnace to a high temperature. The d.c. electric field was given by means of the regulated power supply. The emf generated by (Pb,Ca) TiO_3 solid solution was measured by a millivoltmeter. The variation of emf with temperature is shown graphically by the Fig. (3.3). The emf decreases with temperature, it disappears at low temperature, but recovers when the sample is heated again. Drastic change in emf at about $490^{\circ}C$ seems to correspond to the phase transition of (Pb,Ca) TiO_3 solid solution system. Here again we can observe that, emf decays with time but decay constant

Scale : Temp.10°C.=1Cm. along X-axis
e.m.f.10mV=1Cm. along Y-axis

Fig 3·2 : The temperature dependence of e.m.f. observed
for (Pb,Sr) TiO_3

is quite long. Even when electrodes are short circuited
the emf gradually recovers almost the same value as that
expected without any short circuitry.

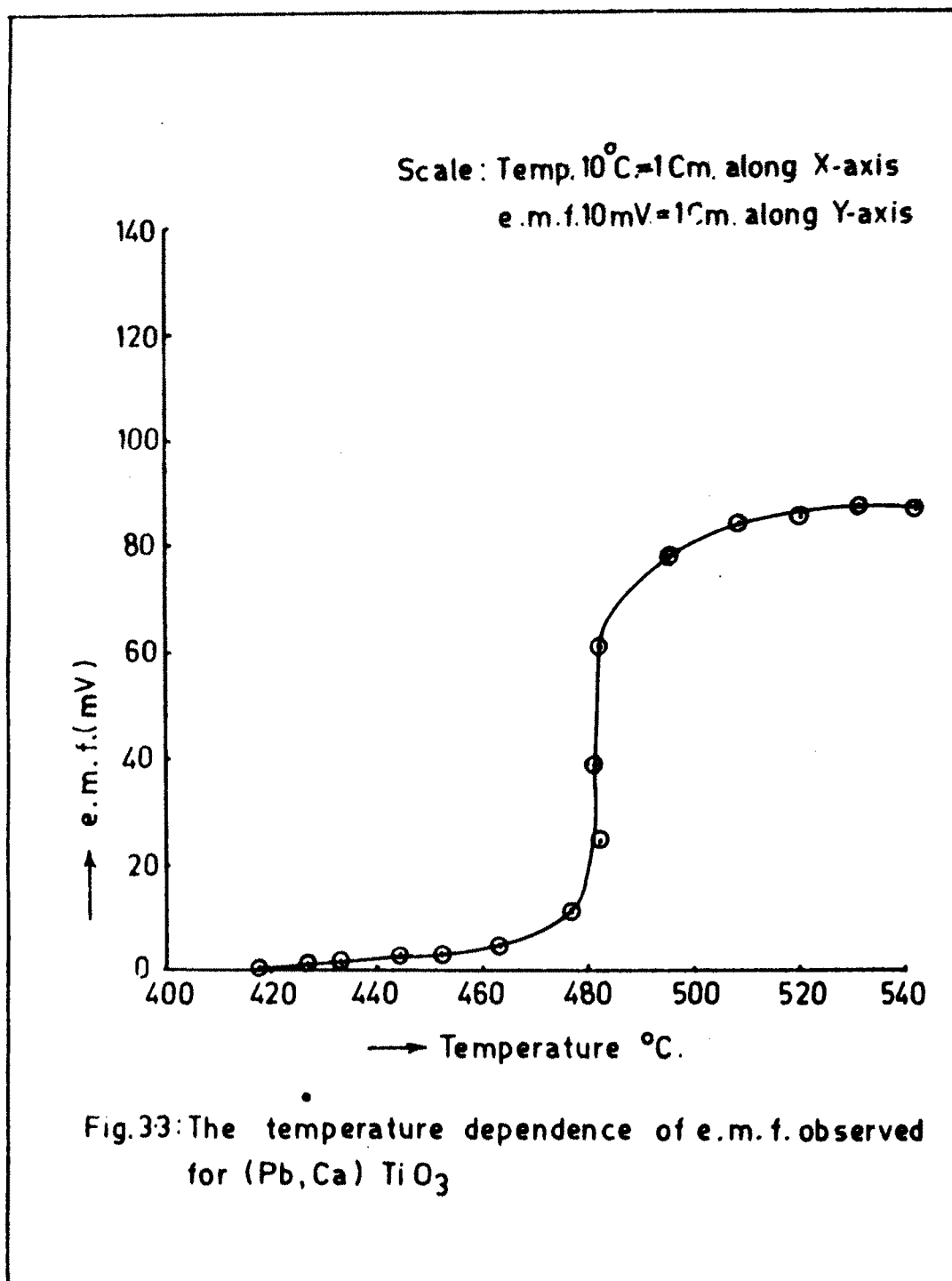The plausible explaination of the mechanism may be
given as follows:

By the application of d.c. electric field some part
of ($PbTiO_3$ and $CaTiO_3$) may have decomposed into (Pb + Ca)
and TiO_2 and O_2 ions. The TiO_2 and O_2 get out of positive
terminal as gas and (Pb + Ca) stay near negative terminal.
Therefore, we obtain the battery of

Steel, (Pb + Ca)/ TiO_2 , O_2 , Steel

By the drop of water on the sample the emf is generated.
This fact can be explained as, (Pb + Ca) which exists near the
negative terminal reacts with water and (Pb + Ca) $(OH)_2$ i.e.
lead and calcium hydroxide and H_2 are formed. This we have
H_2 gas at negative terminal and O_2 gas at positive terminal
electrode. This pair can also produce some emf.

3.5   Results and Discussion:

By applying d.c. electric field the emf generated tells
that solid state battery is formed for both of the solid
solutions (Pb,Sr) TiO_3 and (Pb,Ca) TiO_3 . The drastic change
in emf seems to correspond to the phase transition at $487^{O}C$
for (Pb,Sr) solid solution and at $483^{O}C$ for (Pb,Ca) solid
solution which is shown respectively from the Fig.(3.2) and
Fig.(3.3). Emf. decays with time but decay constant is

Fig. 3·3: The temperature dependence of e.m.f. observed for (Pb, Ca) Ti O₃

quite long. The emf gradually recovers almost the same value even when electrodes are short circuited, as that expected without any short circuitry.

Since solid state battery is formed for both of the solid solutions $(Pb,Sr)TiO_3$ and $(Pb,Ca)TiO_3$ by the application of a d.c. electric field, it will be quite difficult, sometimes even impossible, to study d c electric field effects on ferroelectricity of these solid solutions such as the shift of ferroelectric phase transition temperature and as the change of dielectric constant due to d.c. electric field.

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