CHAPTER 2

Background Science

2.1 Ferroelectricity

Ferroelectricity is the property of polar crystal of which the spontaneous polarization can be reversed by applying an electric field. Fig. 1 showed the classification for the 32 crystallographic point groups in relation to ferroelectric properties. Among the 32 classes of single crystal materials, 21 crystal classes are noncentrosymmetric and 20 of these give piezoelectric effects. The one exception is class 432 in the cubic system which cannot exhibit a piezoelectric effect. The subdivision of piezoelectric group consists of those 10 crystal classes which are spontaneously polarized in the absence of an external field ; such crystals are termed pyroelectric (changes to temperature alter the charge developed). If this pyroelectric crystal can reverse permanently polarization direction by applying a sufficiently intense external field, the crystal is said to be the ferroelectric effect.

Most ferroelectric materials have a domain structure which results from the transition from a non-polar to a polar phase accompanied by the appearance of spontaneous polarization in a ferroelectric body.

The presence of domains in a ferroelectric crystal is the reason for non-linear P-E hysteresis loops when an alternating field is applied and those loops are commonly accepted for ferroelectricity. A typical hysteresis curve for a ferroelectric crystal is given in fig.2. When a cyclical electric field is applied parallel to a crystallographic direction to a random domain state the domains in which polarization is close to the field direction grow in size by rearranging their structure (fig.2) , and total polarization of the crystal increases, curve OA. Maximum orientation of domains with the field occurs at point A and polarization is said to be saturated. Reducing the electric field to zero at point B , a number of domains retain their changed orientation so that the polarization does not return to zero, and so is called the remanent polarization , P_r. Increasing the field to the opposite direction will first reduce the polarization to zero at its E_c, the coercive field, and then saturates in the reverse direction at point C. Again, the process of reducing the field to zero traces a path to point D which is equal to $-P_r$. The hysteresis loop is completed by, once again, changing the field direction, increasing the polarization to saturation in the original direction and finally reducing it to zero at P_r.

A series typical P-E response of a ferroelectric can be observed as shown in fig. 3.

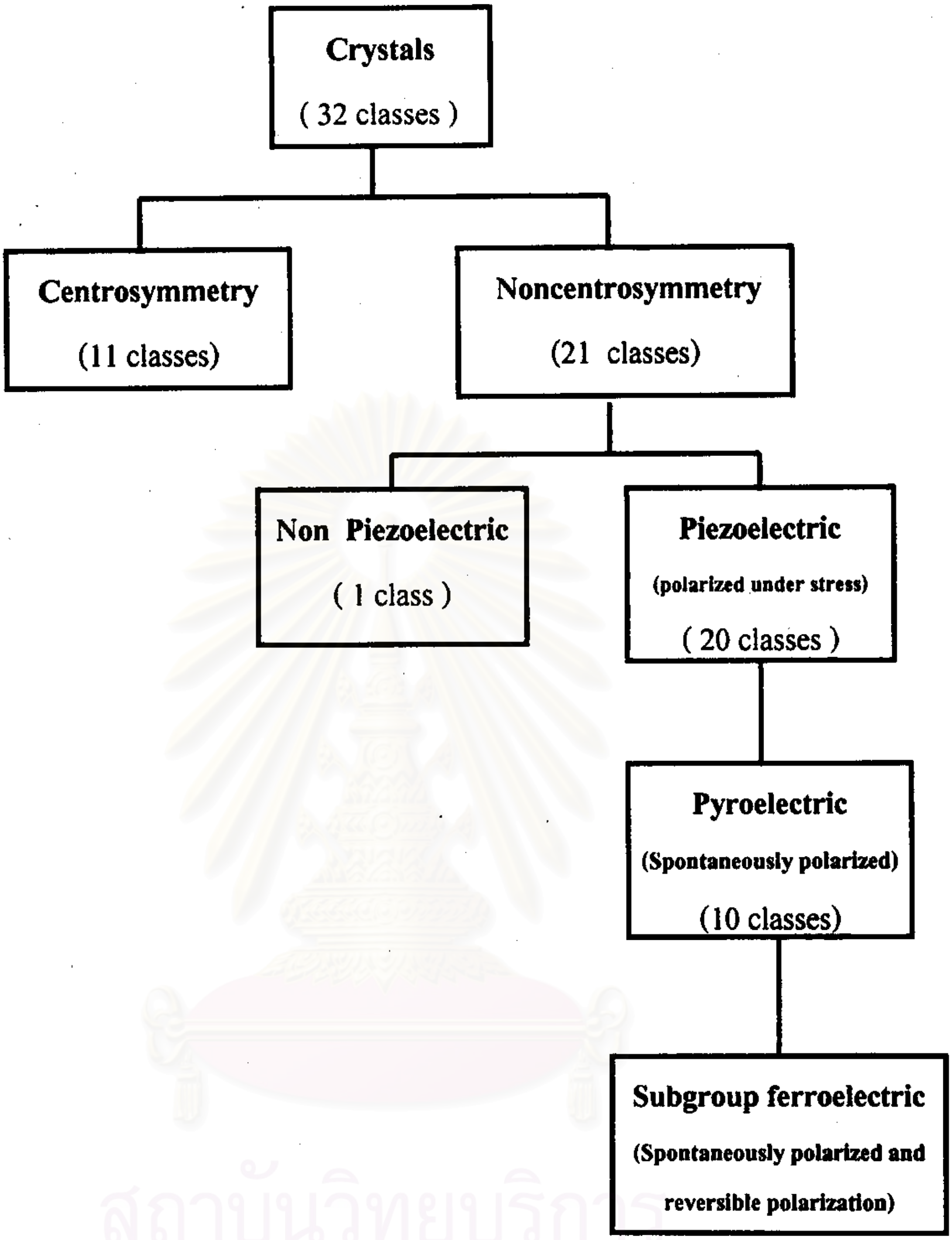

Fig. 1 A classification scheme of the 32 crystallographic point groups in relation to ferroelectric properties (4,5)

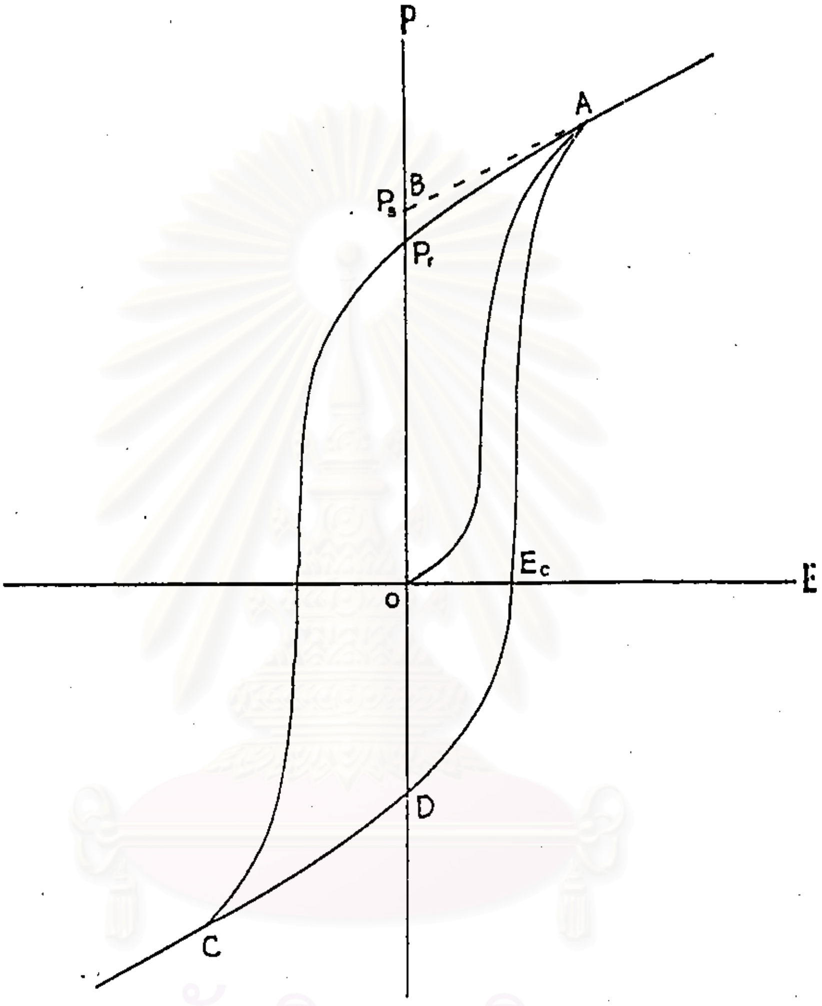

Fig. 2 Hysteresis loop behavior for typical ferroelectric ceramic showing important properties. P_r, remanent polarization; P_s spontaneous polarization; E_c coercive field.

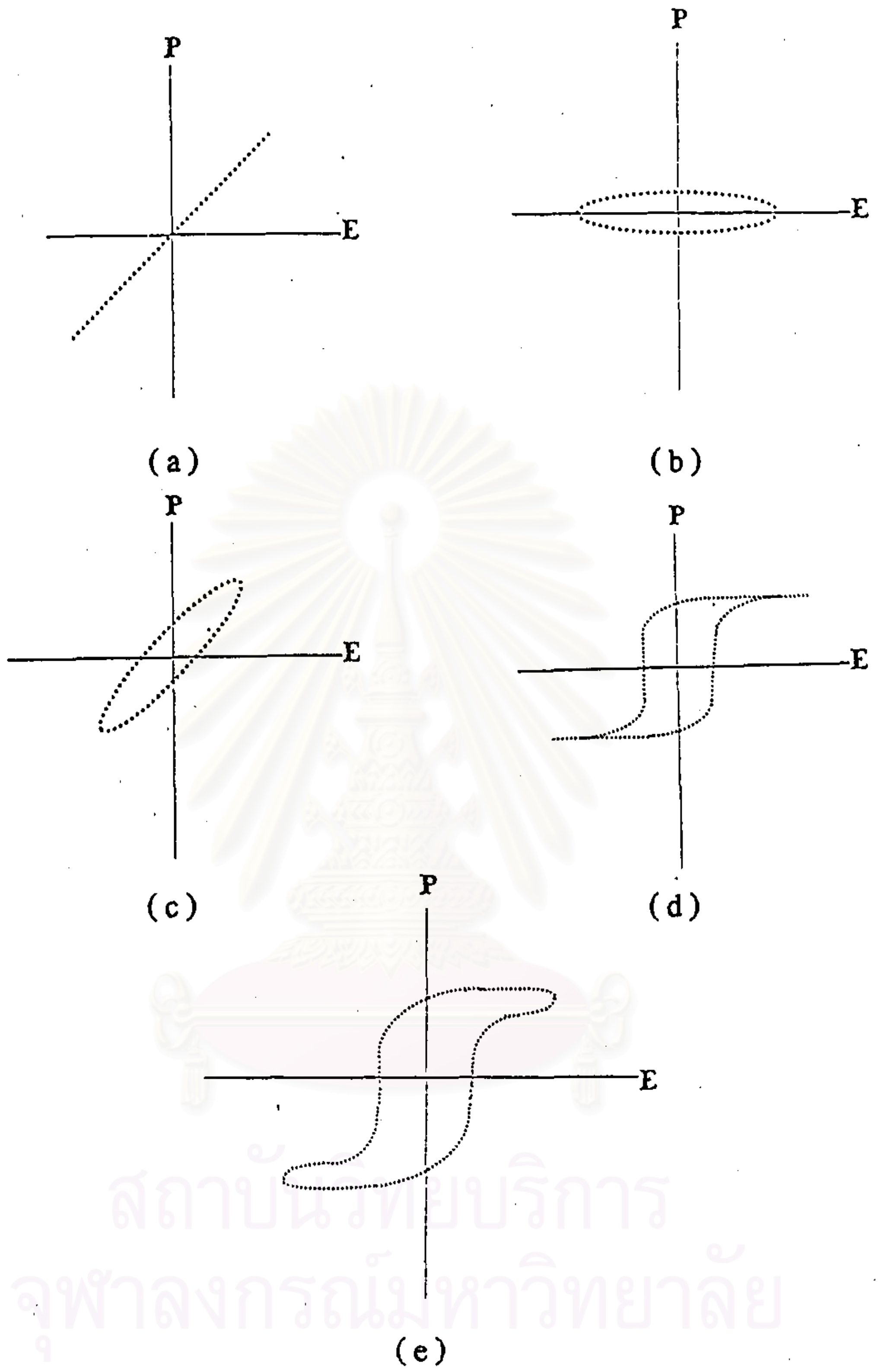

Fig. 3 A series of P-E response of a ferroelectric showing : (a) linear dielectric; (b) linear resistor; (c) lossy capacitor ; (d) nonlinear ferroelectric and (e) increasing the electric field extends the P-E hysteresis loop, ultimately to breakdown.

2.2 Structure and properties of lead titanate ($PbTiO_3$)

2.2.1 Unmodified lead titanate ($PbTiO_3$)

Lead Titanate ($PbTiO_3$) has a perovskite-type ferroelectric (ABO_3) structure below the Curie Temperature (T_c) at 490°C. Above T_c its structure can be viewed as a similar cubic $BaTiO_3$ as shown in fig. 4(5). This unit cell is composed of Pb^{2+} ions (A-site) on the corners, oxygen (O) anion on each face center ,and Ti^{4+} ions (B-site) at the center of the unit cell in an octahedral intersitce surrounded by six co-ordinating oxygen anions.

At room temperature, $PbTiO_3$ has a tetragonal structure with lattice parameters of a = 3.894 A° , c = 4.140 A° , and the tetragonal distortion c/a ratio is equal to 1.063 (6) which is much greater than that of $BaTiO_3$ (c/a = 1.01) (7,8). As $PbTiO_3$ is heated through T_c ~ 490 °C, it transforms to a cubic structure with the Ti^{4+} ion being distorted from its position to the center of TiO_6 octahedral as shown in fig. 5(7).

In addition, the other transitions have been reported at around -100°C by X-ray diffraction method (9) and -150°C by dielectric measurement (10). These results were confirmed by Ikegami et al.(11), and Tanaka et al. (12). When Remeika and Glass (13) studied dielectric and piezoelectric properties of lead titanate ($PbTiO_3$), the phase transitions at -100°C and -150°C were not identified. A similar result was reported by Glazer and Mabud (14). The main reason of the different results was due to the quality of single crystal. It is difficult to prepare pure single domain crystals used for X-ray study (15-16). Y. Uesa et al (17) succeeded to grow dendritic crystals with good quality by Fesenko's method (18) and measured these crystals by using X-ray diffractometer. Their lattice constants a and c or lattice volume begin to decrease at -90°C (T_1) as shown in fig 6. At this temperature, $PbTiO_3$ structure transformed from tetragonal to orthorhombic.

$PbTiO_3$ is the stable compound in the PbO - TiO_2 system as shown in fig 7 (7). In this phase diagram, the system contains two eutectics and $PbTiO_3$ melts incongruently at 1285°C. A pyrochlore structure of $PbTiO_3$ has been reported in forms of $PbTi_3O_7$ (19) and $Pb_2Ti_2O_6$ (20).

The various flux systems such as $PbO\text{-}B_2O_3$ (21), KF (22) and $KF\text{-}KBF_4\text{-}PbF_4$ (23) have been used to prepare most single crystals of $PbTiO_3$. However, the fabrication of high quality single crystals of $PbTiO_3$ with sufficient size (up to 1 cm) and no defects is difficult to prepare. A number of $PbTiO_3$ single crystals have been investigated.

Single crystal measurements (24) have shown the dielectric constant to obey the Curie-Weiss law above the Curie point with a peak dielectric constant value closed to 10,000 at 495°C. The measurement of spontaneous polarization of 75 $\mu C/cm^2$ (25) has been decreased to 57±3 $\mu C/cm^2$ (26) as a result of the different quality of single crystal used in these two experiments.

Hydrostatic pressure can change the lattice constants of $PbTiO_3$ (27), c decreasing and a increasing with increasing pressure. The Curie point was estimated to be lowered by 1.8×10^{-2} °C/atm.

Crack-free polycrystalline ceramics of pure $PbTiO_3$ are difficult to prepare highly dense due to the large anisotropy in lattice constant (c/a = 1.063). This leads to a large strain resulting from during cooling through the Curie point at 490°C. Therefore cracks occur during sintering and poling. Some additives were selected to improve the micro- and macro cracks-free upon sintering and subsequent cooling through the Curie point. These additives may act to reduce the tetragonal distortion of the $PbTiO_3$ unit-cell, the spontaneous strain and/or inhibit grain growth. The additives substituting for Pb^{2+} at A- site are isovalent type additives such as Ca^{2+}, Sr^{2+}, Ba^{2+} and Cd^{2+} and donor type additives, e.g. Bi^{3+}, La^{3+} and Sm^{3+}. The additives substituting for Ti^{4+} at B-site are isovalent type additives such as Nb^{5+} or Ta^{5+} and acceptor type additives, e.g. Sc^{3+}, Mn^{3+} and Fe^{3+}. The use of additives with $PbTiO_3$ results in the changes of structure and properties. These may be used to tailor properties of modified $PbTiO_3$ for specific application.

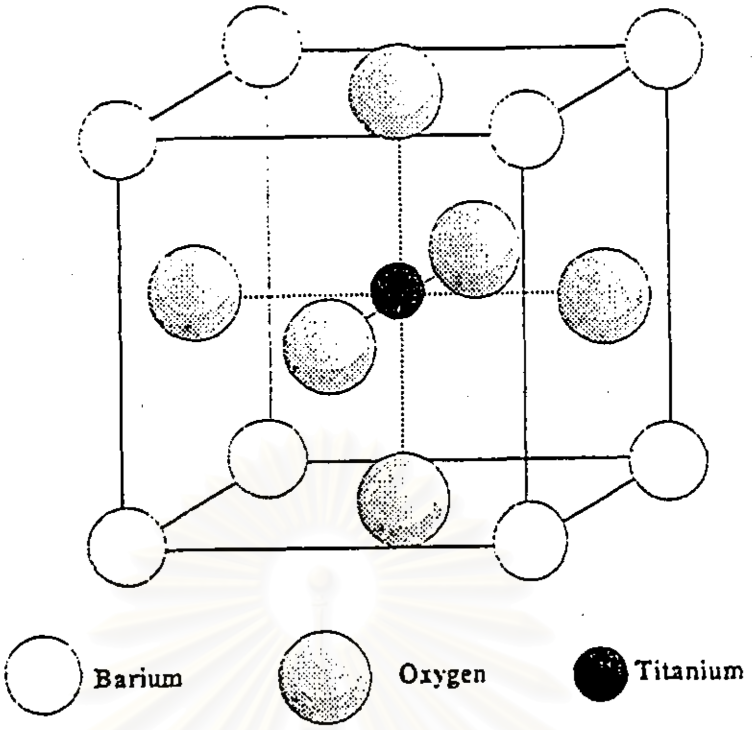

Fig. 4 The perovskite structure of $BaTiO_3$ (after Moulson and Herbert(5))

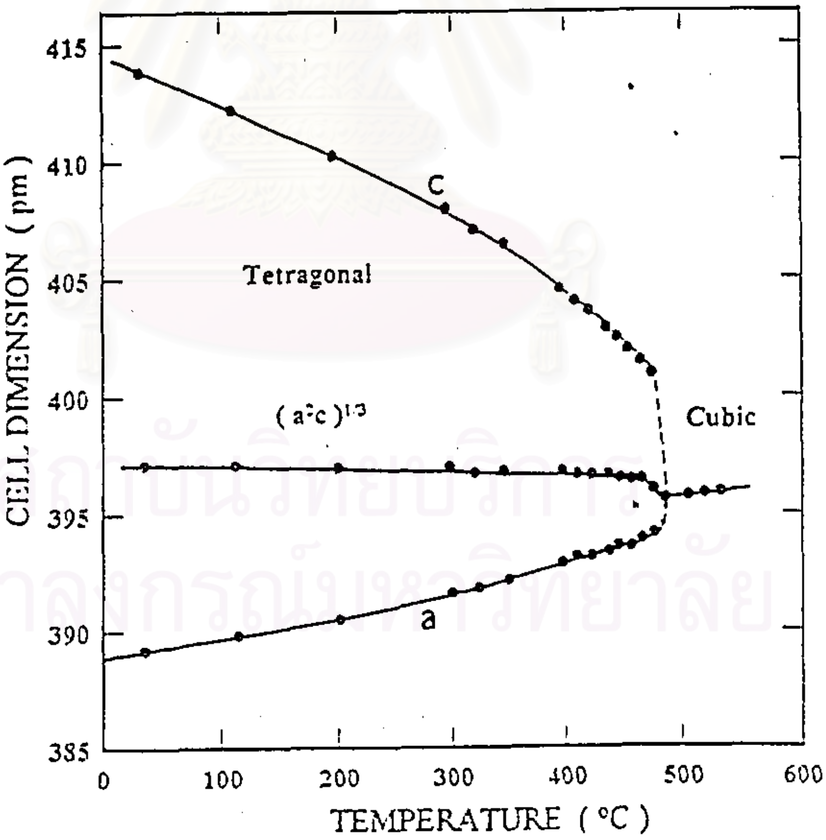

Fig. 5 Change in lattice constants of $PbTiO_3$ versus temperature (after Jaffe et al.(7))

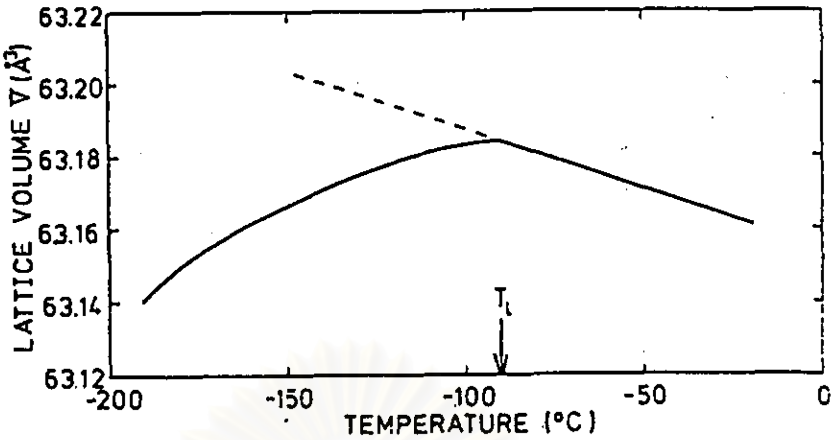

Fig. 6 Temperature dependence of the lattice volume of $PbTiO_3$ (after Y. Uesu et al. (17))

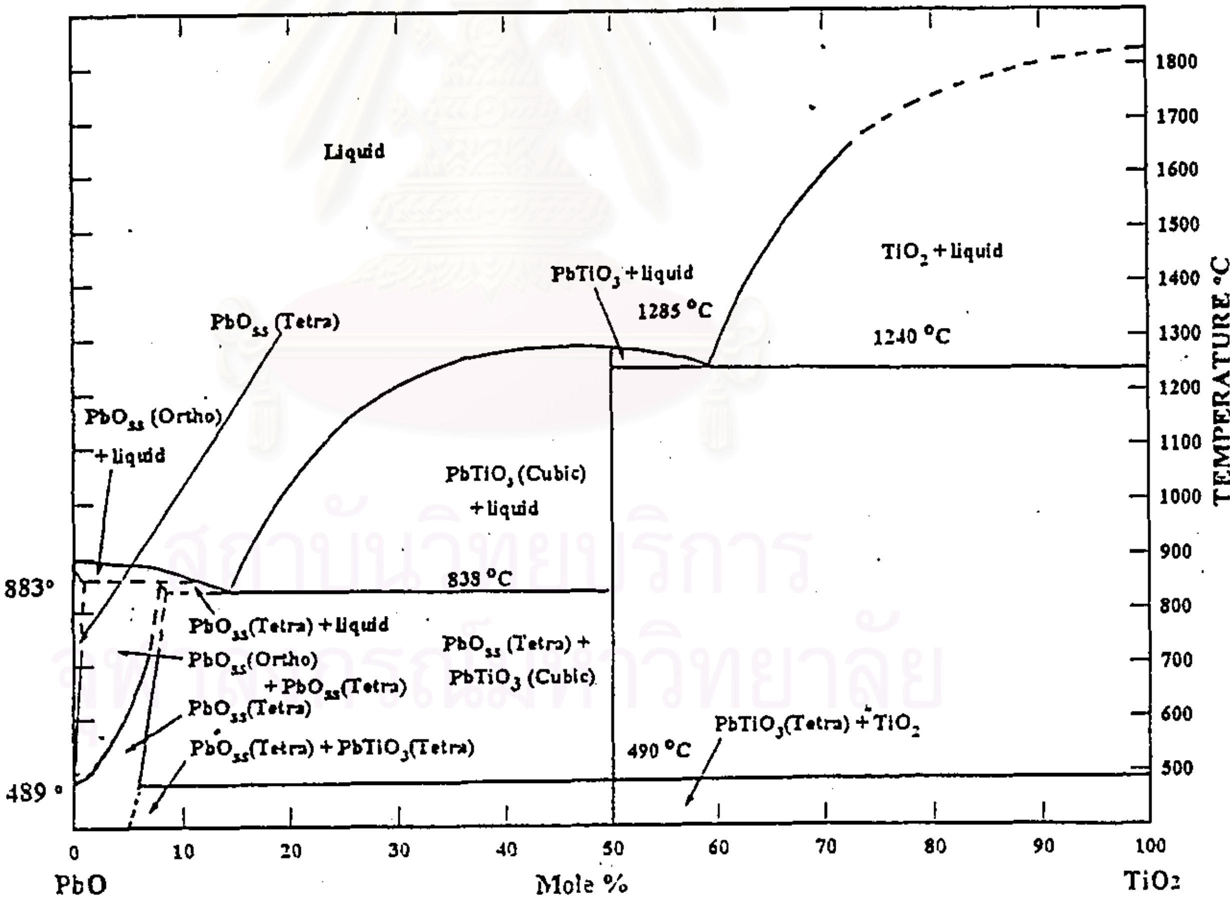

Fig. 7 PbO-TiO_2 phase diagram (after Jaffe et al. (7))

2.2.2 Ca^{2+}- Modified lead titanate

A large number of additives have been investigated to improve the sinterability of lead titanate ceramics. It has been shown that highly dense materials having superior dielectric and piezoelectric properties can be produced by doping lead titanate with a variety of alkaline-earth and rare-earth oxides.

Ca^{2+} is an isovalent substitutent for A site ions. Substituting Ca^{2+} for Pb^{2+} site have been reported in study of the (Ba,Ca,Pb)TiO_3 system. The phase relation of the $PbTiO_3$- $CaTiO_3$ system exhibited that increasing Ca^{2+} concentration resulted to decrease in the tetragonality of the $PbTiO_3$ unit cell(31-35) as shown in fig.9. At room temperature crystal structure of composition from 0 to 40% $CaTiO_3$ was reported to be tetragonal type. Above this amount it was presented as cubic type structure (31,32). Another study showed that the $PbTiO_3$-$CaTiO_3$ system (33,48) presented a tetragonal phase as compositions containing $PbTiO_3$ from 100 to ~50 mole%; a cubic paraelectric phase for composition between 50 and ~ 27 mole%$PbTiO_3$; mixed two phases of paraelectric cubic and antiferroelectric orthorhombic of ~27 to 23%$PbTiO_3$ compositions. The remaining compositions up to without $PbTiO_3$ (100 mole%$CaTiO_3$) exhibited only the orthorhombic phase. These resulting phase regions agreed with other report of the similar system(36).

Crystal structure of ordered $(Pb_{1-x}Ca_x)TiO_3$ ceramics ,with x ranging from 0.3125 to 0.5165, was investigated by transmission electron microscopy(37). The structure was determined to be tetragonal belonging to point group *4mm*. Pb and Ca ions were in an ordered face center arrangement of the A-sites.

G.King et al.(37) found that the strain-induced ferroelectric domain structure in tetragonal $Pb_{1-x}Ca_xTiO_3$ disappeared when $x \geq 0.39$, because the c/a ratio approached unity with increasing x and the grains presented random domains.

The hysteresis loops of $(Pb,Ca)TiO_3$ bulk ceramics were studied by Sawaguchi et al.(34). They found that at room temperature the hysteresis loop of the compositions between 0 and 0.30 mole of $Ca^{2+}$was very narrow. The hysteresis loop of 0.50 mole of Ca^{2+} content was also reported and its Curie point was at ~80°C . Nevertheless, the results in fig. 8 showed that $Pb_{0.5}Ca_{0.5}TiO_3$ should be paraelectric at room temperature. However the values of spontaneous polarization, coercive field and dielectric constant were not reported(34). After few year, they found the aging on double hysteresis loops of $Pb_{0.5}Ca_{0.5}TiO_3$ (38). The dielectric constant versus temperature curve of the aged specimen shows two maxima, compared to one peak observed in the non-aged specimen as shown in fig. 10. There are many reasons to explain the aging effect. Mason(39) proposed that the cause of aging was a reduction of the effective polarization caused by a very slow motion of the domain walls in the ceramics. McQuarrie and Buessem (40) suggested that an increase in the depth of domain-wall potential wells by a diffusion process of a mechanical creep was the cause of aging. Sawaguchi(38) et al.'s studies suggest that aging is the result of a separation of the original single phase into two or more phases.

A number of the $Pb_{1-x}Ca_xTiO_3$ thin films have been investigated. G.Tewee et al.(41) prepared $Pb_{1-x}Ca_xTiO_3$ thin films by sol-gel method on platinized Si substrates. They found the remanent polarization values were 3-7 $\mu C/cm^2$ and reached a maximum at $x = 0.3$. The relatively small values of polarization and dielectric constant may be caused by the small grain size. In 1997, S.Chewasatn et al.(42) synthesized $Pb_{1-x}Ca_xTiO_3$ thin films by dial based sol-gel route. The average values of remanent polarization and coercive field decreased with increasing Ca^{2+} contents from ~11 μC/cm^2 and ~ 125 kV/cm. for $x = 0.10$, to ~ 8 μC/cm^2 and 80 kV/cm for $x = 0.30$.

Studies of dielectric properties as a function of temperature for $Pb_{1-x}Ca_xTiO_3$ showed that an increasing Ca^{2+} concentration resulted the broad transition region and lowered the Curie point (40,42). The maximum dielectric constant of $x = 0.2$ was 9030 at 334°C, and $x = 0.3$ was 7995 at 254°C. A transition of $Pb_{0.6}Ca_{0.4}TiO_3$ transferred from paraelectric to a ferroelectric state at 14°C and changed to paraelectric at –50°C for the compositions of x is > 0.6.

Other researchers have been attempted to modify $PbTiO_3$ ceramics by using another complex systems. Y. Yamashita et al(43) investigated the complex system of $(Pb,Me)(Co_{0.5}W_{0.5})TiO_3$ (Me = Ca, Sr or Ba) ; A-sites substitution; containing small amounts of MnO and NiO. These materials showed high apparent density, small dielectric constant and facility in poling procedure. The $(Pb,Ca)(Co_{0.5}W_{0.5})TiO_3$ ceramic was excellent characteristics for ultrasonic transducers for nondestructive testing of metals. A.Ahmad et al.(44) studied the composition of $Pb_{0.725}Ca_{0.275}(Mn_{0.015}Fe_{0.01}Me_{0.02}Ti_{0.955})O_3$(Me = V, Ta, Nb) that was B-site substitution. All of three additives can improve sintering to high density (>97%). Both Ta and Nb-doped materials showed attractive dielectric, piezoelectric and pyroelectric properties, which offered a great potential for device applications. Doped with vanadium, these materials were relatively more conductive and more lost and hence could not be poled at fields > 35 kV/cm.

Other research groups have modified $(Pb,Ca)TiO_3$ ceramics by using MnO additives(45-46) leading to increase electrical resistivity varying from 1×10^9 to 4×10^{11} (Ωcm.) (47) and inhibit grain growth. Nevertheless, more than 1.0 mole% of

MnO decreased electrical resistivity and increased average grain size. It can believe that smaller grain boundary area induced by large grain size may be decrease resistivity of this specimen. H. Iwasaki et al (46) studied MnO doping in a range of 0-4 mole% in $(Pb_{0.75}Ca_{0.25})(Mg_{1/3}Nb_{2/3})_{0.0625}Ti_{0.9375})O_3$ ceramics could increase grain size linearly from 1.5 μm to 8 μm but the Curie temperature decreased from 270°C to 240°C, respectively.

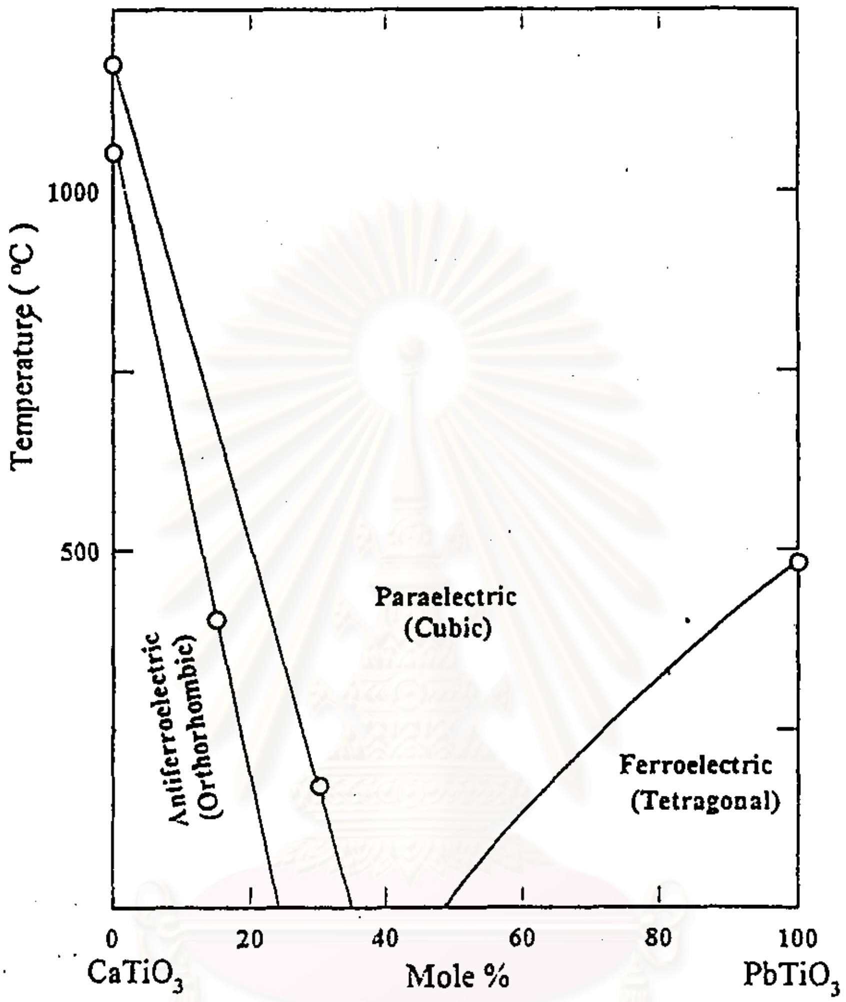

Fig. 8 Phase diagram of the $PbTiO_3$ – $CaTiO_3$ solid solution

(after Ikeda (48))

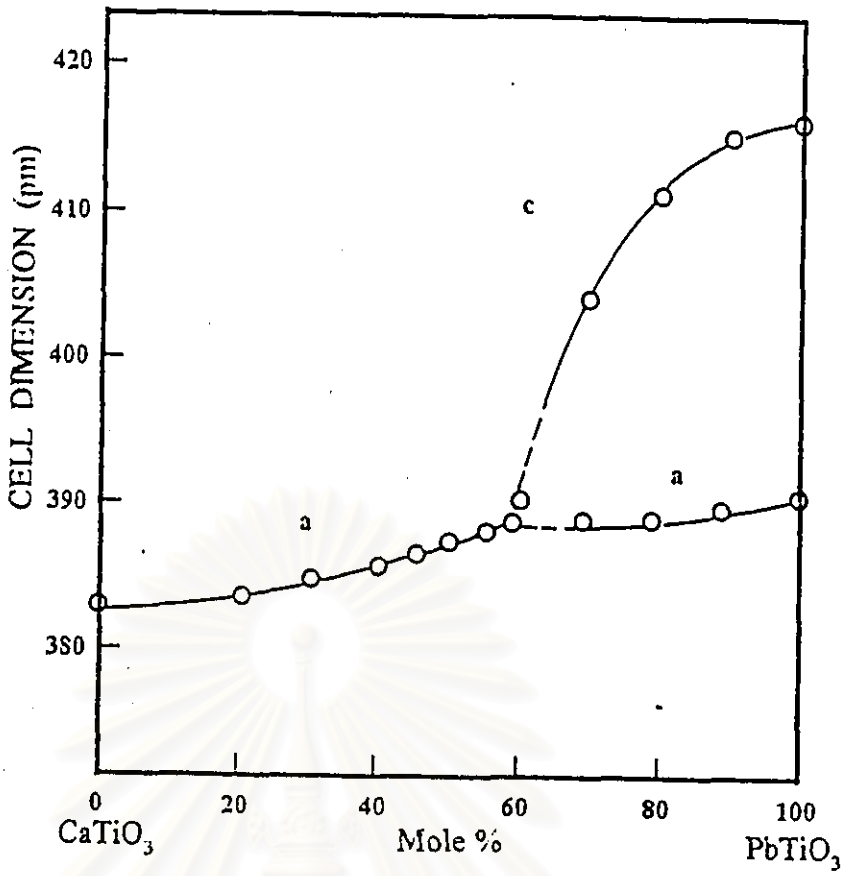

Fig. 9 Lattice spacing of $PbTiO_3$-$CaTiO_3$ system at room temperature (after Sawaguchi et al. (34))

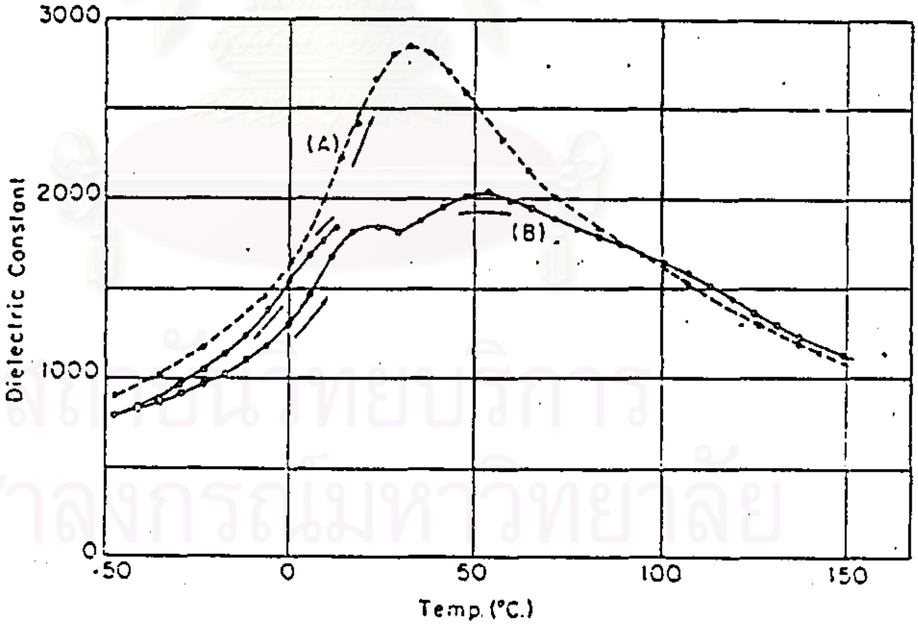

Fig.10 Dielectric constant as a function of temperature for $Pb_{0.5}Ca_{0.5}TiO_3$. (A) Specimen measured immediately after cooling and, (B) measured after aging at room temperature for 7 days. (after Sawaguchi et al. (38))

2.2.3 La^{3+}Modified lead titanate

Lanthanum (La^{3+}) is a donor type additive of which various studies showed improvement of sinterability and electrical properties of $PbTiO_3$ ceramics.

Reports of $Pb_{1-3/2x}La_xTiO_3$ ceramic prepared by conventional technique (48,51) displayed a decreasing of tetragonality (c/a ratio) with increasing La^{3+} contents. The XRD result of c/a ratio of calcined powder was higher than that of sintered powder. This may be due to the formation of a homogeneous solid solution during sintering (51). The average grain size increased from 0.5 to 3 μm with increasing La^{3+}content(48). Dielectric measurements of similar composition showed the Curie point decreasing from about 320°C for 10%La^{3+} to 150°C for 20% La^{3+} at a frequency of 1 kHz and their dielectric values at room temperature were between 300 and 800(50). T. Yamamoto et al.'s report (49) for 15%La^{3+} resulted in the Curie temperature of 245°C and its dielectric value was about 9700. The highest value of dielectric constant (~1200) could be obtained at 28 mole% of La^{3+} on PLT films (50).

Polarization measurements of PLT showed a maximum value of $P_r = 11$ $\mu C/cm^2$ and E_c 3.9 kV/cm for 10%mole of La^{3+}. When La^{3+} concentration was higher than 10 mole% the remanent polarization (P_r) and coercive field (E_c) decreased (49). In contrast, the result of P.L.Tan's studies(51) showed that $E_c \sim 0.5$ kV/mm and $P_r \sim 12$ $\mu C/cm^2$ could be obtained from 20% La-PT. When 2.5 mole% of La_2O_3 and 1.0 mole% of MnO were added into $PbTiO_3$ ceramics(51), the remanent polarization values were about 2 and 3.5 $\mu C/cm^2$ at 100°C and 200°C, respectively. While its Curie point was about 470°C. These features gave advantageous electromechanical device applications at high frequency.

In recent reports, thin films ($PbTiO_3$, PLT, PLZT) have been fabricated (52-53) to give highly c-axis oriented film leading to production of pyroelectric currents on the films even without a poling treatment. The figure of merit for voltage responsivity R_v ,(F_v) of highly c- axis orientated $PbTiO_3$ thin films was 2.3 times as large as that of $PbTiO_3$ ceramics (54). A $Pb_{1-x}La_xTi_{1-x/4}O_3$ composition could be prepared to obtain the highly c-axis oriented PLT thin films and its dielectric and pyroelectric measurement showed higher values than those of the $PbTiO_3$ thin film(54). R. Takayama et al. (55) found that $Pb_{0.9}La_{0.1}Ti_{0.975}O_3$ (PL10T) thin films with x = 0.1 were the most suitable materials for use in the infrared sensors. Because both F_v and F_m (figure of merit for specific detectivity D*) of the PL10T thin films were three times as large as those of $PbTiO_3$ ceramics.

2.3 Fabrication of $(Pb_{1-x}Ca_x)TiO_3$ and $(Pb_{1-x}La_x)Ti_{1-x/4}O_3$ ceramics

During the sixty's, some researchers tried to get the $PbTiO_3$ dense ceramics with the use of additives and succeeded to prepare more highly dense $PbTiO_3$ ceramics. Eventhough modified-$PbTiO_3$ ceramics presented lower crystal anisotropy than pure $PbTiO_3$, they have reached a high interest as piezoelectric ceramics.

The conventional powder processing technique was used to prepared modified-$PbTiO_3$ ceramics such as Ca^{2+} and La^{3+} modified $PbTiO_3$ ceramics. Pure grades or reagent grades of mixed oxides; PbO, TiO_2, $CaCO_3$ or La_2O_3 were weighed in a stoichiometric ratio and mixed by ball milling in a polyethylene container (47). The milled powder was calcined at 850-900 °C for 2-5 hours in air for $Pb_{1-x}\,Ca_xTiO_3$ powder (32,33,36,47) and 800-900 °C for 2-5 hours in air for $Pb_{1-x}\,La_xTi_{1-x/4}O_3$ powder(48-49,55) respectively. The calcined powder was ground thoroughly and pressed into disks and then sintered at 1100-1300°C for 2-5 hours (35,54-55) in a covered alumina crucible that was loosely packed with powder of the same composition to minimize the loss of lead, because of volatilization. It was found that the density was up to 93% of theoretical density(36). The best dispersing of particles is generally obtained by milling in a liquid medium, such as water or alcohol. For the electronic application use of in processing, water may reduce the electrical properties.

Other researchers have been studying the preparation of $PbTiO_3$ and modified-$PbTiO_3$ thin films by sol gel process(41,42) , rf magnetron sputtering (56) and laser ablation(57) or composite materials based on $PbTiO_3$. In these way, highly oriented lead titanate films give important piezo and pyroelectric response without poling(58). On the other hand, interesting piezoelectric composites have also been prepared using a polymer matrix and $PbTiO_3$ ceramics. Ferroelectric glass ceramics based on lead titanate may be suitable for some applications like sensors and filters.

Three different routes; a sol gel process, a coprecipitation route and conventional attrition milling method were investigated to synthesis the precursor powder by A. Ahmad et al.(44). All of precursor powders calcined in air at 750°C for 2 hours, pressed into disks forms at 25,000 psi and sintered at 1050°C for 3 hours indicated that a sol gel processing provided the most reactive precursor powders. A single phase was obtained at 750°C. Both coprecipitated and attrition milled powders exhibited trace amounts of unreacted materials. However, all three powders showed a single phase composition after sintering. As compared to the dielectric, piezoelectric and pyroelectric properties of these materials the material prepared from attrition milling exhibited the most favorable piezoelectric properties; while a sol gel processed material showed the highest pyroelectric coefficient.

2.4 Applications of $PbTiO_3$ based material

Lead titanate ($PbTiO_3$) based materials have been extensively studied for application to pyroelectric infrared sensor, medical diagnostic, ultrasonic transducers for nondestructive material, SAW devices and memory devices because of their excellent pyroelectric, piezoelectric and dielectric properties (32,59,60) as shown in table 1. Bulk ceramics are also used but their dimensions restrict their utilization to low frequencies.

In recent year, a pyroelectric sensor, which functions as a non-contact temperature sensor for microcomputer devices, has become the source of great interest lately because it can be used at room temperature. Table 2 shows properties of various materials for pyroelectric sensors(61).

In general, the following conditions must be satisfied in order to use a pyroelectric material as a sensor :

1. When the material absorbs thermal energy, the change in the temperature of the material must be large.
2. The pyroelectric coefficient must be large.

The pyroelectric coefficient is described as following equation (5)

$$D = \varepsilon_o E + P_{total} \qquad (1)$$

$$= \varepsilon_o E + (P_s + P_{induced}) \qquad (2)$$

where D is total dielectric displacement , E is an electric field and ε_o is the permittivity of free space (8.85×10^{-12} Fm^{-1})

If the dielectric is 'linear', so that polarization is proportional to the electric field within the material, which is commonly the case,

$$P_{induced} = \chi_e \varepsilon_o E \qquad (3)$$

Where χ_e is the electric susceptibility.

If follows from (1) and (3) that

$$D = \varepsilon_o E + (P_s + \chi_e \varepsilon_o E)$$

$$= (1+\chi_e)\varepsilon_o E + P_s \qquad (4)$$

The permittivity ε of dielectric is defined by

$$\varepsilon = (1+\chi_e)\varepsilon_o \qquad (5)$$

which, from equations (3) and (5), is

$$D = \varepsilon E + P_s \qquad (6)$$

Therefore

$$\partial D/\partial T = \partial P_s / \partial T + E(\partial \varepsilon/\partial T) \qquad (7)$$

(assuming constant E), and

$$p_g = p + E(\partial \varepsilon/\partial T) \qquad (8)$$

where $p = \partial Ps / \partial T$ is the true pyroelectric coefficient

$p_g = \partial D/\partial T$ is sometimes referred to as a generalized pyroelectric coefficient.

Since a temperature change, ΔT, produces a change in the polarization vector, the pyroelectric coefficient has three components defined by

$$\Delta P_i = p_i \Delta T \quad , \quad i = 1, 2, 3 \qquad (9)$$

3. The capacitance of the material must be small.

The satisfy condition for pyroelectric sensor should have :

- Small the heat capacity of the material, determined by the volume specific heat C
- Small dielectric constant
- Large "figure of merit for voltage responsivity (F_v) = $\lambda/\varepsilon_r C$ "

The performance factors for the pyroelectric sensor are the high voltage responsivity R_v, low the noise voltage ,V_N and large the detectivity D* value.

Recently a number of reviews on progress in thin film processing have shown that the pyroelectric properties of $PbTiO_3$ based materials including Ca^{2+} and La^{3+} modified $PbTiO_3$ can be candidates for use as infrared device applications, as shown in table 3.

Table 1 Types of application exploiting properties of $PbTiO_3$ based material

Property	Capability Utilized
Piezoelectric	– Ultrasonic transducers for nondestructive material – Surface acoustic wave (SAW) devices – Microactuator
Pyroelectric	– Infrared detectors / sensors – Temperature sensors – Thermal imaging cameras
Ferroelectric	Ferroelectric random access memories (FRAMS)

Table 2 Characteristics of pyroelectric materials $^{(61)}$

Material	Pyroelectric coefficient λ (C/cm^2.K)	Dielectric constant ε_r	Curie Temperature Tc ($^\circ$C)	Figure of Merit $\lambda/\varepsilon C$ (C.cm/J)
TGS	4.0×10^{-8}	35	49	4.6×10^{-10}
$LiTaO_3$	2.3	54	618	1.3
$LiNbO_3$	0.4	30	1200	0.46
$PbTiO_3$	6.0	200	470	0.94
SBN	6.5	380	115	0.8
PVF_2	0.24	11	120	0.9

Table 3 Summary of pyroelectirc properties of $PbTiO_3$ based materials and some selected materials

Material	λ (C/cm^2.K)	ε_r	Tan δ	Ref.
PVDF polymer	27	12	0.015	62
$LiTaO_3$ crystal	230	47	0.005	62
Ca modified $PbTiO_3$ ceramics	490	210	0.014	63
La modified $PbTiO_3$ ceramics	650	110	0.004	64
$PbTiO_3$ ceramics	750-960	80-120	0.018-0.03	64