BAÜ FBE Dergisi
Cilt:12, Sayı:1, 75-90
Temmuz 2010

Organic pyroelectric materials for device applications

R. ÇAPAN[*]
Balikesir University, Science& Literature Faculty, Physics Department,
10145 Balikesir TURKEY

Abstract

The wide range of applications of thermal imaging devices existing in military, industrial and space fields attract researchers to study pyroelectric materials which exhibit a temperature-dependent spontaneous polarisation. A brief review of pyroelectricity, pyroelectric materials and some commercial applications of these materials we will be given in this paper.

Keywords: *Pyroelectric effect, pyroelectric materials, applications of pyroelectricity*

Özet

Termal görüntüleme cihazlarının, askeri, endüstri ve uzay araştırmaları gibi geniş uygulama alanlarından dolayı, sıcaklığa bağlı polarize olan pyroelektrik maddeleri üzerindeki çalışmalar, araştırmacıların ilgisini çekmektedir. Bu maklede, pyroelektrik olayın, pyroelektrik maddelerin ve bu maddelere ait bazı uygulamaların genel bir değerlendirilmesi verilecektir.

Anahtar Kelimeler: *Pyroelektrik olay, pyroelektrik maddeleri, pyroelektriğin uygulamaları*

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[*] Rifat ÇAPAN, rcapan@balikesir.edu.tr, Tel: (266) 612 10 00.

1. Introduction

The origin of the pyroelectric effect goes back as far as the Ancient Greek period and was discovered by a Greek philosopher Theophrastus around 300 B.C. Further details about the history of pyroelectricity can be found in Lang's book [1]. In 1707, Johann Georg Schmidt wrote a book called "Curiöse Speculationes bey Schaflosen Nächten (Curious speculations during sleepless nights) about tourmaline behaviour and at the beginning of the eighteen century, pyroelectricity, as exhibited by tourmaline, was re-introduced into Europe. The electrical properties of tourmaline were described by Franz Aepinus in 1756. He noted that tourmaline always has positive electricity and negative electricity at the same time and the charges result not from a surface effect but from changes in the internal structure [2]. During the nineteenth century, the amount of research on pyroelectricity increased and became more quantitative. In 1824 the word "pyroelectricity" was used the first time by David Brewster in his paper entitled, "Observations on the Pyro-Electricity of Minerals" [3]. Jean-Mothee Gaugain [2] made the first precise measurement of pyroelectric charge in the middle of nineteenth century and established the three following laws for a pyroelectric material:

1- The total charge developed, ΔQ, by a crystal depends upon the total change of temperature, ΔT, and not upon the rate of change of temperature.

2- Within the same temperature limits, the charge developed by the effect of heating or cooling are of equal magnitude but the signs of the charge are reversed.

3- The quantity of charge developed is proportional to the cross-sectional area and independent of the length of the crystal.
These can be summarised by,

$$\Delta Q = \Gamma A \Delta T \tag{1}$$

where ρ_S is the surface charge density, Γ is the pyroelectric coefficient and A is the electrode area. These three laws comprise the basis of the present thermodynamic interpretation of the pyroelectric effect. Pyroelectricity became more interesting at the beginning of the twentieth century and most research involved the study of ferroelectricity and the detection and measurement of electromagnetic radiation fluxes and temperature changes using pyroelectric materials. The number of publications has dramatically increased in this area since the discovery of the ferroelectric effect [4] and the first use of a pyroelectric infrared detector was published by Yeou Ta in 1938 [5]. The technological applications of pyroelectricity in thermal infrared (IR) detectors using pyroelectric single crystals, ceramics and polymers have been employed for a range of modern technologies since the1960s [6-7]. Later on pyroelectric materials have been applied to security systems (intruder and fire alarms), vidicon cameras, geology and biology [7-8]. In pyroelectric material research, thin film deposition methods such as Langmuir-Blodget (LB), Sol-Gel and Spin Coating, and others have been extensively involved to prepare pyroelectric devices using inorganic and organic materials since the beginning of 1980s. The number of research studies in this area since then has dramatically increased up until today. We will give a brief theory of pyroelectricity and review pyroelectric materials and some of their applications.

2. Pyroelectric properties

If a pyroelectric material fabricated as a metal-insulator-metal (MIM) device are short-circuited, the polarization of the sample attracts charges onto the electrodes and the changes of the polarization of the sample can be described by:

$$P = \frac{Q}{A} \qquad (2)$$

where A is the overlap electrode area and Q is the charge.

The pyroelectric coefficient at the constant stress (σ) is only depend on the temperature change pyroelectric effect and is given by:

$$\Gamma = \left(\frac{\delta P}{\delta T}\right) \qquad (3)$$

$$\Gamma = \frac{1}{A}\left(\frac{\delta Q}{\delta T}\right) - \frac{Q}{A^2}\left(\frac{\delta A}{\delta T}\right) \qquad (4)$$

It is difficult to make any change in the electrode area; therefore the second term goes to the zero. The macroscopic pyroelectric coefficient can be defined using only first term of the equation. It can be noted that all measurements are taken under short-circuit conditions, Q can be treated as a function of temperature and strain (ε) and it can be written by:

$$dQ = \left(\frac{\delta Q}{\delta T}\right)_{\varepsilon} dT + \sum_{i=1}^{3}\left(\frac{\delta Q}{\delta \varepsilon_i}\right)_{T,\varepsilon} d\varepsilon_i \qquad (5)$$

where ε implies the total strain matrix. Thus:

$$\frac{1}{A}\left(\frac{\delta Q}{\delta T}\right)_{\sigma} = \frac{1}{A}\left(\frac{\delta Q}{\delta T}\right)_{\varepsilon} + \frac{1}{A}\left(\frac{\delta Q}{\delta \varepsilon_i}\right)_{T}\left(\frac{\delta \varepsilon_i}{\delta T}\right)_{\sigma} \qquad (6)$$

The primary pyroelectric effect can be defined by:

$$\Gamma_P^m = \frac{1}{A}\left(\frac{\delta Q}{\delta T}\right)_{\sigma} \qquad (7)$$

A piezoelectric stress coefficient is given by:

$$e_{3i}^{m}=\frac{1}{A}\left(\frac{\delta Q}{\delta\varepsilon_i}\right)_T \qquad (8)$$

The thermal expansion coefficient is given by:

$$\alpha_i=\left(\frac{\delta\,\varepsilon_i}{\delta T}\right)_\sigma \qquad (9)$$

Now the total macroscopic pyroelectricity can be defined by:

$$\Gamma^{m}=\Gamma_{P}^{m}+e_{3i}^{m}\,\alpha_i \qquad (10)$$

The total macroscopic pyroelectric effect of a material may be created from sum of primary and secondary pyroelectric effects. The total macroscopic pyroelectric effect can be defined as:

$$\Gamma_{Total}=\Gamma_{\mathrm{Pr}\,imary}+\Gamma_{Secondary} \qquad (11)$$

where $\Gamma_{primary}$ is the primary pyroelectric effect and $\Gamma_{Secondary}$ is the secondary pyroelectric effect. It is well known that the primary pyroelectric effect is a temperature-dependent spontaneous polarisation. The secondary pyroelectric effect arises from any mechanical stress, which is the result of thermal expansion.

2.1. Pyroelectric effect

A pyroelectric material exhibits a spontaneous electric polarisation, the magnitude of which is temperature-dependent. The pyroelectric effect arises as a result of the change of this spontaneous polarisation with temperature [9]. If a pyroelectric material is connected to a sensitive ammeter as a Metal-Pyro Sample-Metal (M-PS-M) shown in Fig. 1, a pyroelectric current (I_p) flows between electrodes when this material is exposed to a temperature gradient through heating or cooling. This current is proportional to the rate of change of polarisation with respect to temperature as given below:

$$I=\Gamma A\frac{dT}{dt} \qquad (12)$$

where (dT/dt) is the rate change of the pyroelectric material’s temperature with time, (A) is the area of overlap of the two electrodes and (Γ) is the pyroelectric coefficient or the rate of change of polarisation with respect to temperature.

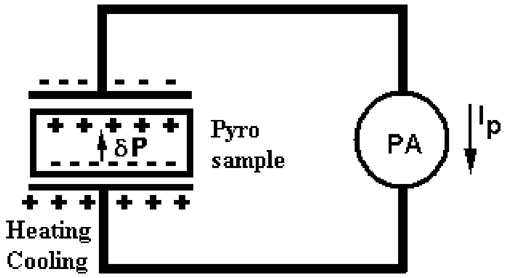

Fig. 1: A pyroelectric current flows between electrodes due to a temperature change

The pyroelectric coefficient, Γ, is thus dependent upon the change in the normal component (relative to the capacitor plates) of the electrical polarisation [10] and is a useful parameter with which to compare different materials and to understand the relationship between microscopic and macroscopic temperature-dependent electric polarisation behaviour.

2.2. *Dielectricity in the context of pyroelectric materials*

It is well known that if the space between the plates of the capacitor of value C_O under vacuum is filled with a dielectric material, the capacitance is increased to

$$C = \frac{\varepsilon'}{\varepsilon_O} C_0 = \varepsilon_r C_0 \qquad (13)$$

where ε' and ε_O are the permittivities of the dielectric and vacuum, respectively, and their ratio ε_r is the dielectric constant or relative permittivity of the material. The capacitance of a pyroelectric material as a function of thickness is given as:

$$C = \left(\frac{\varepsilon_r \varepsilon_0 A}{d} \right) \qquad (14)$$

where ε_r is the dielectric constant of pyroelectric sample, C is the capacitance, d is the thickness of the film, ε_o is the dielectric constant for free space and A is the effective electrode area.

2.3. *Figure of merit*

The Figure of Merit (FOM) is defined in the literature [11] and given in Equation 4 and 5. FOM is an important parameter when designing pyroelectric materials for their heat sensing applications [12]. A pyroelectric device requires high FOM values given below. To achieve maximum performance of the device, the pyroelectric material must have a high pyroelectric coefficient and a minimum dielectric constant.

$$FOM_1 = \frac{\Gamma}{\sqrt{\varepsilon_r}} \qquad (15)$$

where Γ is the pyroelectric coefficient and ε_r is the relative permittivity of the material. In some devices the dielectric loss tangent, tan δ, is the dominant noise source associated with the pyroelectric material. In this case a more useful FOM can be modified to

$$FOM_2 = \frac{\Gamma}{\sqrt{\varepsilon_r \tan\delta}} \qquad (16)$$

Thus FOM_2 can be increased by either i) high pyroelectric activity, ii) low dielectric constant or iii) low dielectric loss of the material.

Usually, single crystal materials have high values of FOM because of their high pyroelectric coefficients. However their relative permittivities are high as well. Unfortunately these materials are only available in bulk form [13]. Therefore it is difficult to make a device using single crystal materials. Ceramic materials have a large figure of merit because they also have high pyroelectric activity and low dielectric loss but their disadvantages are their large values of relative permittivity and their fabrication into thin films of optimum thickness is difficult. Polymers and thin film materials exhibit low dielectric loss over a wide frequency range and can be produced one monolayer thick at a time so that they yield the exact optimum thickness. Pyroelectric materials will be discussed in the next section.

3. Pyroelectric materials

Pyroelectric materials can be classified in four main areas as; single crystals, ceramics, polymers and thin film materials. General requirements of pyroelectric materials are a high pyroelectric coefficient, low relative permittivity, physical and chemical stability, low piezoelectric response, low cost, high quality, ease of processing and if ferroelectric, stability against depoling. A large number of pyroelectric materials have been extensively studied for their large potential applications and the pyroelectric coefficient, dielectric properties and the figure of merit for these materials will be given in here.

3.1. Single crystals

The most well known single crystal for pyroelectric applications is triglycine sulphate (TGS) or $((NH_2\ CH_2COOH)_3H_2SO_4)$ [14]. It is known that the ferroelectric nature of TGS is achieved by the rotation of polar groups. TGS has been extensively studied for thermal imaging applications and is well known for its use in infrared detectors where it is typically used in the form of a 10-30 μm thick disc cut from a solution grown single crystal [15]. TGS has a low Curie temperature (49°C) and high solubility in water. The low Curie temperature of TGS can be improved by deuteration to form DTGS. The pyroelectric coefficient of the crystal can also be increased slightly by replacing the sulphuric acid to form triglycine fluoroberyllate (TGFB). $LiTaO_3$ (Lithium Tantalate) [16], $LiNbO_3$ (Lithium Niobate) [17], and $Sr_{1-x}Ba_xNb_2O_6$ (Strontium Barium Niobate) [16] materials have also been studied for thermal imaging applications by several researchers. The figure of merit of some single crystal materials is given in Table 1. Single crystals materials usually have large pyroelectric coefficients and high values of dielectric constant. The difficulties of these materials are to prepare thin films and to bond to a substrate can prove rather difficult.

Table 1: The FOM values of single crystal materials

Material	Γ ($\mu Cm^{-2}K^{-1}$)	ε	tan δ	FOM_1 ($\mu Cm^{-2}K^{-1}$)	FOM_2 ($\mu Cm^{-2}K^{-1}$)	Reference
TGS	550	55	0.025	10	464	11
DTGS	550	43	0.020	12.8	593	18
$LiTaO_3$	230	47	<0.01	4.9	335	18
$LiNbO_3$	83	28	Not reported	3.0	---	18
$Pb_5Ge_3O_{11}$	110	40	0.0005	2.8	246	18
SBN-50 $Sr_{0.5}Ba_{0.5}Nb_2O_6$	550	400	0.003	1.4	502	7

3.2. Ceramics

Table 2 summarised some ceramic materials used in pyroelectricity studies. Ceramic materials are generally cheap, robust and easy to prepare.

Table 2: The FOM values of single ceramics materials

Material	Γ ($\mu Cm^{-2}K^{-1}$)	ε	tan δ	FOM_1 ($\mu Cm^{-2}K^{-1}$)	FOM_2 ($\mu Cm^{-2}K^{-1}$)	Reference
PPZT	60-500	300-3000	Not reported	0.02-1.67	---	18
PZFNTU	380	290	0.0027	1.31	429.44	18
$PbTiO_3$	180	190	0.01	0.95	130.59	7
$PbTiO_3$ PCWT4-24	380	220	0.01	1.73	256.20	7

They can be fabricated in a range of shapes and sizes thereby eliminating some of the more time-consuming and expensive processes of manufacture. Usually ceramic materials exhibit very high values of pyroelectric coefficient. However, they possess correspondingly high values of dielectric constants and the processing associated with producing thin films approaching optimum thickness (~ 5 - 10 μm) is difficult [19]. Perovskites are a large family of oxygen octahedra structures (ABO_3) which have been extensively investigated. A is a monovalent or divalent metal and B is a tetra- or pentavalent metal. After the discovery of barium titanate ($BaTiO_3$) in the late 1940s ceramic materials soon replaced TGS in most applications. Ferroelectric $BaTiO_3$ ceramics exhibits spontaneous electric polarisation and has a large dielectric constant [20]. Another important ceramic is lead zirconium titanate (PZT), which is well known as a perovskite ferroelectric, which possesses strong piezoelectric effects and can operate at higher temperatures. It is also possible to dope some other materials into ceramic composition. For example the pyroelectric properties of Mn-doped lead zirconate-lead-titanate-lead magnesium niobate ($Pb(Mg_{1/3}Nb_{2/3})O_3$-$PbTiO_3$-$PbZrO_3$) ceramics have been studied and the result showed that this ceramic composition has a large figure of merit which can compare with commercial ceramics in terms of their figure of merit values [21].

3.3. Polymers

Organic materials are greatly interesting in the study of pyroelectricity because of their easy preparation, low dielectric constant and dielectric loss. However they usually have a smaller pyroelectric coefficient that single crystals and ceramics. The other advantages of polymer materials over pyroelectric ceramics and crystals are simple handling and processing of devices, their low cost and the possibility of achieving their optimum thickness (~10 μm). Ferroelectric poly(vinylidene fluoride) [p(VdF), PVDF or PVF_2)] polymer has been extensively studied [19, 22-23]. In this material, the C-F bonds are highly polar with a large dipole moment, D = 6.4 x 10^{-30} Cm. Development of p(VdF) technology has enabled production of material which is cheap, with uniform and reproducible characteristics. Some figures of merit for polymeric materials are given in Table 3.

Table 3: Pyroelectric properties of polymer materials

Material	Γ ($\mu Cm^{-2}K^{-1}$)	ε	tan δ	FOM_1 ($\mu Cm^{-2}K^{-1}$)	FOM_2 ($\mu Cm^{-2}K^{-1}$)	Reference
P(VdF)	27	12	0.015	2.25	63.64	11
P(VdF/TrFE)60/40	50	9.5	0.015	5.26	132.45	18
P(VdF/TrFE) 50/50	40	18	0.03	2.22	54.43	7
P(VdF/TrFE) 80/20	31	7	0.015	4.43	95.67	7

3.4. Ultra-thin film materials

Many thin film technologies for example Langmuir-Blodgett, sol-gel, spin coating etc. have been employed to produce thin pyroelectric samples using organic or inorganic materials.

3.4.1. Langmuir-Blodgett thin films

The Langmuir-Blodgett film deposition technique [24-25] is a suitable method to produce non-centrosymmetric pyroelectric thin films using organic amphiphilic molecules which have a hydrophobic tail and a hydrophilic head group. There are several advantages of using LB films for pyroelectric devices; for example the LB film technique facilitates the production of a uniform, high quality organic film of precisely defined thickness and symmetry. LB films are organic assemblies which have low permittivities, ε_r, and low dielectric loss tangent, tanδ. The figure of merit for voltage responsivity, $\Gamma/(\varepsilon_r \tan\delta)^{1/2}$ is therefore expected to be large [26]. Richardson et al [27-28] measured the pyroelectric coefficient of 3.5 $\mu C\ K^{-1}\ m^{-2}$ (at 30°C) for an alternate layer LB film of an iridium complex of 4-alkoxystilbazole/tricosanoic acid. Some other examples of alternate layer LB films have been investigated by Kamata et al [29], Poulter et al [30], Tsibouklis et al [11, 31], Majid [32] and Jones et al [33]. Tsibouklis et al [31] suggested that the pyroelectric activity in acid/amine LB films was due to the temperature dependence of the head group orientational and/or packing changes and also the ionic interaction between adjacent headgroups. Poulter et al [2] suggested that the pyroelectric activity of the alternate layer system of ruthenium complexes with fatty acid arises from the temperature dependence of the tilting mechanism or the freedom of movement of the molecular chain. This tilting mechanism is confirmed using several organic materials by many researchers [34-35]. The mechanism of the pyroelectric effect in multilayer LB assemblies is likely to involve either ionic interaction between headgroups and/or the reorientation of polarised molecules or chemical groups [36-37].

It is also possible to add ions (Cd^{2+}, Mn^{2+}, Mg^{2+} etc.) into the LB film structure and these ions lead to improved thermal stability of the pyroelectric LB sample [38-39]. Some pyroelectric LB film materials are given in Table 4.

Table 4: Pyroelectric properties of Langmuir-Blodgett thin film materials.

Material	Γ ($\mu Cm^{-2}K^{-1}$)	ε	tan δ	FOM_1 ($\mu Cm^{-2}K^{-1}$)	FOM_2 ($\mu Cm^{-2}K^{-1}$)	Reference
$[Ru(PPh_2biP)_2]PhOC_{16}$/behenic acid	1.07	3.4	0.004	0.31	9.18	18
Z-type Liquid crystal LB film	1.0	5.8	Not reported	0.17	------	18
WTA/Docosylamine superlatice	1.9	2.7	Not reported	0.70	------	18
Hexadec-1-ene-maleic anhydride alternating polymer/1-docosylamine	0.8	3.8-2.9	0.114-0.020	0.21-0.27	3.32-1.22	11
Linear polysiloxane /eicosylamine	9.6	2.6	0.011	3.69	56.77	39
Linear polysiloxane /eicosylamine with $CdCl_2$	12.2	2.4	0.012	5.08	71.89	39
Copolymer of fluorinated alkylmethacrylate and methacrylic acid/p-(p-octadecylaminophenyl-azo) benzensulfamide	0.0025	2.2-3.0	Not reported	0.0008-0.001	------	40
1H,$1H_1$,$2H_1$,2H-per fluorodeconoylmonoitaconate monomer / eicosylamine	4.9	2.8	0.011	1.75	27.92	41
1H,$1H_1$,$2H_1$,2H-per fluorodeconoylmonoitaconate polmer/eicosylamine	3.9	2.8	0.012	1.39	21.28	41
A mixed polysiloxane /eicosylamine	5.6	4.8	0.008	1.17	28.57	42
Polysiloxane/eicosylamine	12		0.016	3.61	52.06	18
T-butyl calix[4]arene acid/amine	1.5	Not reported	Not reported	Not repoted	6.8	43
T-octyl calix[8]arene acid/amine	6.9	Not reported	Not reported	Not reported	26.1	43
T-butyl calix[8]arene acid/amine	14.33	Not reported	Not reported	Not reported	75.2	43
Z-type azobenzene derivative LB film	22	Not reported	Not reported	Not reported	------	44

3.4.2. Sol-gel technique

The sol-gel thin film deposition technique is an interesting method that can be used to prepare nanocrystalline and large-area homogeneous thin films which can be used for pyroelectric studies. Table 5 summarises pyroelectric properties of some sol-gel thin film materials.

Table 5: Pyroelectric properties of sol-gel thin film materials

Material	Γ ($\mu Cm^{-2}K^{-1}$)	ε	$\tan\delta$	FOM_1 ($\mu Cm^{-2}K^{-1}$)	FOM_2 ($\mu Cm^{-2}K^{-1}$)	Reference
PZT	400	558	0.011	0.72	161.45	45
PZT/PT	380	389	0.012	0.98	175.88	45
PZT 30/70	300	380	0.008	0.79	172.06	46
PZT 25/75	220	350	0.008	0.63	131.48	46
PZT 20/80	180	260	0.011	0.69	106.44	46
PZT 15/85	220	210	0.015	1.05	123.95	46
$Ba_{0.64}Sr_{0.36}TiO_3$	1860	592	0.028	3.14	456.85	47
$KTa_{1-x}Nb_xO_3$ (x=0.45, 0.5, 0.55)	2.7	1100	0.012	0.002	0.73	48
P(VdF-TrFE)	43	10	0.018	4.30	101.35	49
PCLT-P(VdF-TrFE)	58	13.2	0.019	4.39	115.81	49
Pt/Si	490	700	0.008	0.70	207.06	7
NPAH4 and Ta(V) [organic-inorganic hybrid]	1.6	4.2	0.0046	0.38	11.51	50

Lead titanate, $PbTiO_3$, lanthanum-modified lead titanate, $Pb_{1-x}La_xTi_1\text{-}x/4O_3$ (abbreviated to PLT) and calcium modified lead titanate, $Pb_{1-x}Ca_xTiO_3$ (abbreviated to PCT) have been promising candidates for the pyroelectric applications [51]. Imai et al [51] have studied the pyroelectric properties of PbTiO3, $Pb(La)TiO_3$ and $Pb(Ca)TiO_3$ pyroelectric materials using sol-gel deposition technique. This research shows that a PCT 10 ($Pb_{1-x}Ca_xTiO_3$, x=0.1) sample exhibits a large pyroelectric coefficient and that it is useful for commercial pyroelectric applications. Samarium doped PZT (4:55:45) [52], $Pb(Zr_{0.3}Ti_{0.7})O_3$ and $Pb(Zr_{0.3}Ti_{0.7})O_3/PbTiO_3$ [53] sol-gel thin film yield a high pyroelectric coefficient. Some other pyroelectric studies using sol-gel thin film deposition technique can be found in the literature [54-60].

3.4.3. Spin coating and sputtering methods

Spin coating and sputtering thin film techniques are not used in the pyroelectric research as much as sol-gel and Langmuir-Blodgett thin film techniques. In some studies these spin coating and sputtering methods have been used with other thin film methods to fabricate pyroelectric samples. Poyato et al [61] employed multiple deposition using spin coating and Rapid Thermal Processing (RTP) crystallisation to produce a pyroelectric thin film of $Pb_{0.88}La_{0.08}TiO_3$ onto two types of substrates: Ti/Pt/Ti/(100)Si and $Pt/TiO_2/(100)Si$ His research showed that a higher value of pyroelectric coefficient was measured for the film deposited onto Ti/Pt/Ti substrate. Lithium Tantalate ($LiTaO_3$) thin film has been deposited by RF sputtering [62] and the pyroelectric activity is significantly improved after the poling of the sample. Pyroelectric properties of some spin-coated or sputtered thin films are given in Table 6.

Table 6: Pyroelectric properties of spin coating and sputtering thin film materials

Material	Γ ($\mu Cm^{-2}K^{-1}$)	ε	tan δ	FOM_1 ($\mu Cm^{-2}K^{-1}$)	FOM_2 ($\mu Cm^{-2}K^{-1}$)	Reference
P(VdF-TrFE) (Spin coating)	41.2	11	0.018	3.75	92.59	63
PCLT/P(VdF-TrFE) (Spin coating)	56.5	15.1	0.0165	3.74	113.20	63
$PbTiO_3$/(001)Pt/MgO (Sputtering)	250	97	0.006	2.58	327.70	7
PLT 5-15/(001)Pt/MgO (Sputtering)	400-1300	100-350	0.006-0.01	1.14-13	400-1678	7
PLZT 7.5/8/92-20/80/(001)/Pt/MgO (Sputtering)	360-820	193-260	0.013-0.017	1.38-4.25	171.23-518.68	7

4. Applications of pyroelectric materials

The efficient conversion of thermal energy into electrical energy using pyroelectric materials is of considerable importance in their applications and these materials can be used to develop temperature-sensing devices [64-65]. They have a great interest due to their potential applications in many areas. In this paper we will give some applications of these materials. It is well known that pyroelectric materials react to changes in detectable radiation intensity. As a result they may be used in a wide variety of applications such as spectrometry, radiometry, pyrometry, thermometry, direction sensing, remote temperature measurement, solar energy conversion, laser diagnostics, infrared imaging pollution monitoring [6, 8, 18, 66-71]. Pyroelectric detectors are used in intruder/burglar and fire alarm security systems [72]. Intruder alarms are designed to operate in the 8 - 14 μm infrared region and an electrical signal is generated as the intruder moves in and out of area covered by the mirror(s) which is focused onto the detector. Pyroelectric fire alarms operate at shorter wavelengths than intruder alarms and detect the flicker frequency of the flames in the region of 3-5 μm.

Pyroelectric materials are very useful for detecting a small change in a relatively large background level of incident energy and these detectors can be used to detect radiation of any wavelength, usually in the infra-red region of the spectrum. In recent years more research using different materials and many fabrication techniques have been directed towards room-temperature-operated infrared sensors. There are two types of infrared detectors which are of particular significance when considering possible applications: photon detectors (they are not pyroelectric) and thermal detectors (pyroelectric). Thermal detectors are slightly less sensitive than photon detectors but they operate at room temperature without requiring cooling and have very wide spectral response. Our focus will concentrate on thermal detectors which have an important place in military, industrial and space applications. Thermal detectors absorb incident radiation and as a result there occurs a change in some macroscopic physical property which is usually detected electrically. Pyroelectric detectors can be configured for thermal imaging of a scene in three different ways.

Firstly, a two dimensional scan is made with a single detector over which the image is scanned, allowing a picture to be built up. The second way is that a reduction in the detector bandwidth required is obtained and a line of detectors is used corresponding to a picture line. Finally, mechanical scanning is avoided using a two-dimensional array of detectors enabling the picture to be mapped point by point. The pyroelectric vidicon tube [73-77] and the detector array [78-81] are good examples of thermal imaging devices. Fig. 2 shows a schematic diagram of a simple pyroelectric vidicon or pyricon tube. The basic principle of operation of this pyroelectric vidicon tube is that it has a pyroelectric target which consists of a disc of pyroelectric material, with a transparent electrode on the front surface.

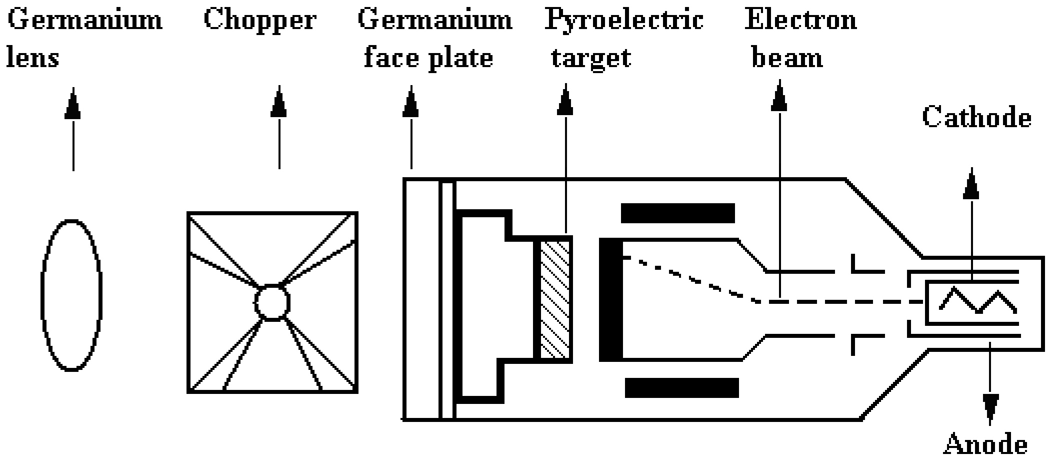

Fig. 2: The schematic diagram of a simple pyroelectric vidicon tube

A thermal image is produced by the infrared lens on the pyroelectric target and the resulting charge distribution can be read off the back surface by a scanning electron beam. Today, the most common pyroelectric target materials used are TGS, TGFB, $LiTaO_3$, PBZT and P(VdF) because these materials usually have large pyroelectric activity. There is still much research in progress using different materials to produce a pyroelectric target which has a better performance at room temperature.

The second type of thermal imaging device is the detector array shown in Fig. 3. The image can be built up by scanning over all the pixels using the pyroelectric linear or two-dimensional array.

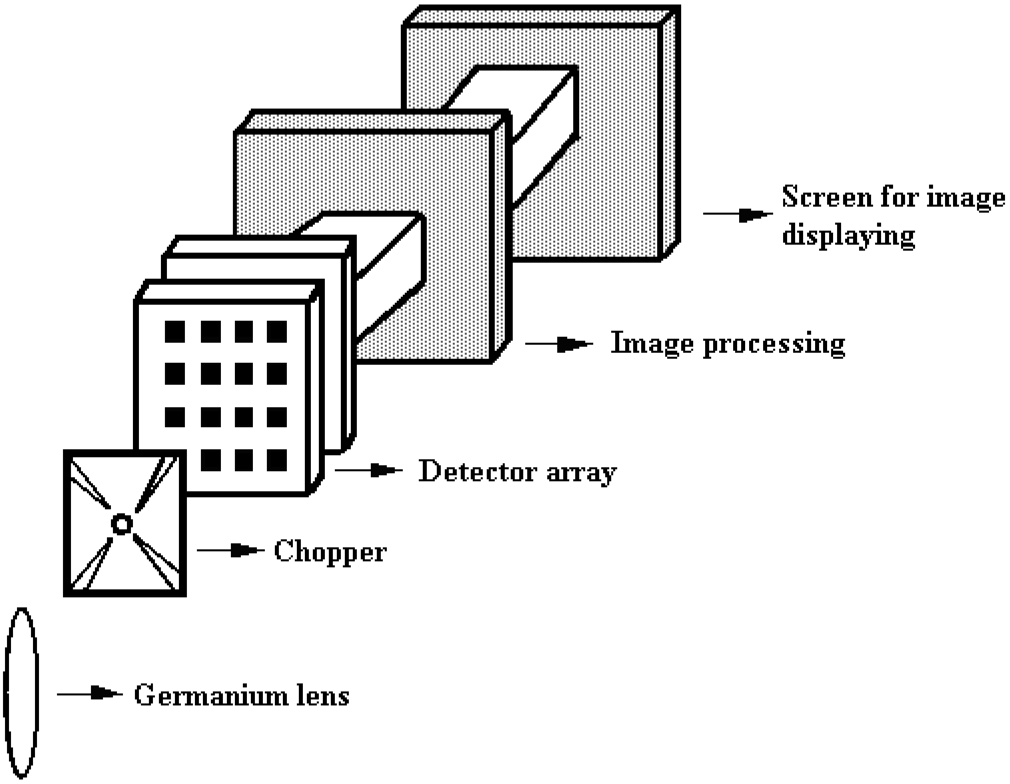

Fig. 3: A diagram of the detector array

A linear array of pyroelectric detectors for thermal imaging has been developed in which the electrical current produced in an external circuit is amplified and processed electronically to produce the picture point by point. Pyroelectric polyvinyl fluoride (PVF_2) has been used for the detector array of 40 thin membranes (0.5-0.8 μm thick) [8].

One of other applications for pyroelectric materials is radiometry [82]. A radiometer is designed to measure the power generated by a radiation source and is used to calibrate UV, visible and infrared radiation sources [8] because the pyroelectric detector has a fast response and a flat spectral sensitivity. These specifications allow us to build a calibrated radiometer used as a standard. Pyroelectric detectors are used as very sensitive thermometers to detect small temperature changes. A novel radiometer is applied by Yokoo [83] to the measurement of food temperatures in a microwave oven.
Pyroelectric detectors also have become a popular in medicine because they are used to sense cells which are warmer than usual that can show the disease of rhuematoid arthritis or malignant tumours [43]. A sensitive pyroelectric sensor without direct thermal contact onto the sample is used in biological materials to extend the investigation field of the pyroelectric method [84]. A new application of IR sensors for the detection and protection of wildlife is reported in 1996 [85]. Pyroelectric IR device can detect wild animals and their movements by using the difference of IR radiation in the environment and can be used to save the life of animals when they need protection.

5. Conclusions

Pyroelectric materials have a wide range of potential application in many areas. Most of the studies show that inorganic materials have a larger pyroelectric coefficient than organic materials. The advantages of organic materials however over inorganic materials are low dielectric constant and low dielectric loss. Pyroelectric materials are still worthy of research due to their potential applications in a wide range of areas.

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