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Image infrared converters based on ferroelectric-semiconductor thin-layer systems

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Abstract. Some questions concerning pyroelectric sensors application in microphotonics are considered. Data upon main characteristics of different pyroelectric materials (single crystals, ceramics, thin films) are summarized. Also represented are basic parameters of uncooled pyroelectric thermal vision image converters as a promising direction of the infrared engineering.

Keywords: thermal vision, infrared converter, ferroelectric, pyroelectric, thin-layer system, ceramics.

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Electromagnetic radiation of solids heated above absolute zero covers the range from visible light ($0.75 \mu\text{m}$) to microwave frequencies ($\sim 1000 \mu\text{m}$). Most of radiation in this range is absorbed by an ambient atmosphere, therefore, to ensure signal detection, «windows of transparency» in the interval $0.75\text{-}15 \mu\text{m}$ should be used. Detection of longwave IR radiation is of great interest when solving a wide circle of applied problems, namely: from absorption spectra registration in multicomponent gas mixtures to systems of indication, identification and tracking the heated objects. Herewith, two wavelength regions are of special interest: from 3 to $5 \mu\text{m}$ and 8 to $14 \mu\text{m}$. These are consistent with above «windows of transparency», moreover, the latter is the most interesting one as it corresponds to the radiation maximum of weakly heated bodies with temperature near 300 K (living beings, machinery, elements of buildings, technological equipment, etc.)

IR detectors convert energy into the form suitable for direct measurements, namely, an electrical signal. As to the mode of such conversion, these are of two types: the heat and photon ones. The majority of recently used serial devices providing sufficient temperature and spatial resolution as well as small time of response was based on photon detectors of IR radiation, for instance, the photovoltaic and photoconducting ones made of cadmium-mercury-telluride and other semiconductor materials. Unfortunately, up to date there exist some unovercome difficulties hindering application of these devices. These are technological complexities in mass production of such materials and devices based on it, and, of major importance, the necessity of operation at low temperatures ($\sim 77 \text{ K}$). As a consequence, it is necessary to use cooling systems,

which implies increased overall dimensions, weight, cost and considerable problems under operating conditions.

But in the number of practical applications, when demands to resolution and speed are not extremely high, it is acceptable to use thermal detectors, first of all, the pyroelectric ones. The pyroelectric radiation detectors (PRD) [1-3] are new fastdeveloping class of thermal detectors destined for revealing and measuring electromagnetic radiation in the wide range of wavelengths from 10^{-5} to $10^5 \mu\text{m}$. Although the pyroelectric effect was known for a long time, PRD began to develop much later than radiation thermocouples, bolometers and optical-acoustic detectors. Nowadays their field of applications is considerably extended in comparison with other thermal radiation detectors. PRDs are used in laser and microwave technique, IR radiometry, pyro- and spectrometry, ionizing radiation monitoring and in the fields of the measurement technology. According to the statistical review «USA market of military and commercial IR technology systems», the total output of IR sensors is expected to increase from 658 million dollars in 1994 up to 1400 million dollars in 2001 [4]. An essential part of this growth is associated with the development of pyroelectric instrument making (inspite of expected reduction in their production cost).

PRD development was especially promoted by rapid progress of laser technology metrological provision of which could not be satisfied with measuring means based on radiation detectors known earlier. With laser creation the range of measurable radiation fluxes was extended by more than 15 orders. It became necessary to study pulse radiation with powers up to tens of mega-

watts, generated within $10^{-6} \dots 10^{-12}$ s, current wave radiation with power densities from 1 to 10 kW/cm² and spatial radiation distribution. In view of optical heterodyning methods development, it became accessible to solve problems of measuring superweak spectral densities (from 10^{-14} down to 10^{-18} W/Hz) of light beams.

PRDs were developed mainly for middle and far IR spectral regions where application of profoelectronic radiation detectors is hindered because of needs to cool them, while other thermal radiation detectors are of slow response. PRDs can successfully compete with them in visible and UV spectral regions as well as in microwave ranges and in measurements of ionizing radiation.

At present PRDs are the most promising type of radiation detectors. It is associated with the fact that along with high sensitivity these possess fast response comparable to that of photodetectors, being simultaneously non-selective thermal detectors. PRDs are universal to some extent as their sensitivity and response can be tuned in wide limits with changing a load resistance. By their nature, PRDs are variable-capacitance transducers, which enables one to make their sensitive elements in the form of figures with arbitrary shapes of cone, wedge, sphere and so on, and receiving square dimensions from 10^{-4} to 10^6 mm². Besides, pyroelectric detectors need not special power supply and cryogenic facilities, are rather technological, stable, reliable and can withstand thermal, mechanical and radiation effects in various operation conditions.

Principle of PRD action is based on the pyroelectric effect consisting in the change of a crystal polarization value with temperature. Among 21 acentric crystal classes, 10 classes are characterized by a special polar axis, are pyroactive and referred to as pyroelectrics. Their main feature is spontaneous polarization in the absence of external fields that is the presence of dipole electric moment different from zero. An essential advantage of PRDs that determines their simplicity and convenience in operation is an anomalously high value of the pyroelectric effect itself in comparison with effects lying in an operational basis of other thermal radiation detectors: the change of sensitive element temperature by 1 K causes appearance of an electric field up to 10 kV/cm in it.

The list of main pyroelectric materials used at present time is represented in Table 1. It is seen that the vast majority of exhibited materials are ferroelectrics. Their high polarizability provides a large value of spontaneous polarization and high dielectric permeability, and, as a consequence, high induced polarization. Although such a great polarization is not an obligatory condition for a strong pyroelectric effect, it is a very useful property as, in the case, some domains with a strong temperature dependence, particularly near the temperature of a phase transition, can be easily found. High values of dielectric permeabilities are necessary in making multielement PRD arrays and matrices when small dimensions of sensitive elements prevent matching with a preamplifier input impedance.

Choosing any pyroelectric material is mainly determined by requirements placed to the facility as a whole.

Detector performances depend on the whole number of parameters: pyroelectric factor p , dielectric permeability ϵ , loss tangent of dielectric $tg\delta$, heat capacity per unit volume c' that, in their turn, depend on a difference between operating temperature and temperature of their phase transition T_c . Therefore, to estimate quality of any material and serviceability in solving specific problems, the number of quality criteria was proposed [2]; the following two them are the most important ones: $M_1 = p/c'$, that determines detector sensitivity in a mode of power measurements, and $M_2 = p/\epsilon c'$ as a factor controlling its sensitivity in a mode of energy measurements.

Tab. 2 shows abovementioned comparative characteristics of conventional pyroelectric materials operating without applying any external electric field at temperatures considerably lower than the Curie point. In most cases these values correspond to typical characteristics of given materials. Up to date, triglycinesulphate doped with alanine and arsenic as well as lead germanate doped with barium have the best characteristics among ferroelectric crystals. Unfortunately, reproducibility of doped crystal characteristics is not high, moreover, triglycinesulphate is sensitive to moisture exposure. It can explain increased interest to exploration and manufacturing ceramic materials as more technological and cheap. In chemical composition these can be distinguished as materials of barium titanate, lead zirconate-titanate, niobate and so on. Ceramic materials made of barium niobate and barium titanate possess high piezoelectric factors, but these materials have low temperature stability. Piezoceramic materials based on solid solutions of lead zirconate-titanate (PZT) are the most effective ones at present.

PZT solid solutions are formed in all interval of possible concentrations. Phase diagram of solid PZT comprises several domains: high-temperature (cubic), P_{∞} ; two low-temperature ferroelectric (rhombohedral, F_{∞} and tetragonal, F_{β}) as well as two anti-ferroelectric, A_{α} and A_{β} . A boundary between the tetragonal and rhombohedral ferroelectric phases (the so-called morphotropic boundary) does not practically depend on temperature. Compositions situated near to the morphotropic boundary have maximum values of a dielectric permeability, piezoelectric coupling factor, piezomodulus, while values of mechanical quality and frequency factor are minimum. Thermal expansion of PZT polarized ceramics in these compositions is anomalously low at temperatures below the Curie point and equal approximately $(1.5 \pm 0.5) 10^{-6} \text{ K}^{-1}$.

Additives of doping elements, advanced technologies of ceramic making and a polarization process enable to satisfy different requirements of designers using this material. PZT ceramics are produced by methods of cold and hot compacting. Hot compacted materials compared to cold-compacted piezoceramics have better piezo- and dielectric properties, density close to a theoretical value, crystals more homogeneous in sizes. For instance, there exist information upon uncooled thermovision cameras operating with hybrid detectors based on modified PZT ($\text{PbZr}_{0.58}\text{Fe}_{0.2}\text{Nb}_{0.2}\text{Ti}_{0.02}\text{O}_3$:U) in service today and hav-

Table 1. Main pyroelectric materials

Abbreviation	Name of compound	Formula
TGS	Triglycinesulphate	$(\text{NH}_2\text{CH}_2\text{COOH})_3\text{H}_2\text{SO}_4$
DTGS	Deuteried triglycinesulphate	$(\text{ND}_2\text{CD}_2\text{COOD})_3\text{D}_2\text{SO}_4$
ATGSAs	Triglycinesulphate doped with arsenic and alanine	$(\text{NH}_2\text{CH}_2\text{COOH})_3\text{H}_2\text{SO}_4$: $\text{NH}_2\text{CH}_2\text{CH}_2\text{COOH};\text{H}_3\text{AsO}_4$
DTGFB	Deuteried triglycinefluorineberyllate	$(\text{ND}_2\text{CD}_2\text{COOD})_3\text{D}_2\text{BeF}_4$
KTN	Kalium tantalate-niobate	$\text{KTa}_{1-x}\text{Nb}_x\text{O}_3$
BST	Barium-strontium titanate	$\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$
BSCT	Barium-strontium-kalium titanate	$\text{Ba}_{1-x-y}\text{Sr}_x\text{Ca}_y\text{TiO}_3$
SBN	Strontium-barium niobate	$\text{Sr}_{0.5}\text{Ba}_{0.5}\text{Nb}_2\text{O}_6$
PT	Lead titanate	PbTiO_3
PCT	Calcium-lead titanate	$\text{Pb}_{1-x}\text{Ca}_x\text{TiO}_3$
PLT	Lanthanum-lead titanate	$\text{Pb}_{1-x}\text{La}_x\text{TiO}_3$
PLZT	Lanthanum-lead zirconate-titanate	$\text{Pb}_{1-x}\text{La}_x(\text{Zr}_{1-y}\text{Ti}_y)\text{O}_3$
PZT	Lead zirconate-titanate	$\text{Pb}_{1-x}\text{Zr}_{1-x}\text{Ti}_x\text{O}_3$
PZFTU	Zirconate-titanate modified with lead	$\text{PbZr}_{0.58}\text{Fe}_{0.2}\text{Nb}_{0.2}\text{Ti}_{0.02}\text{O}_3:\text{U}$
PSZFTNTU	Modified lead zirconate-titanate doped with strontium	$\text{Pb}_{1-x}\text{Sr}_x\text{Zr}_{0.58}\text{Fe}_{0.2}\text{Nb}_{0.2}\text{Ti}_{0.02}\text{O}_3:\text{U}$
PScT	Lead scandium-tantalate	$\text{PbSc}_{0.5}\text{Ta}_{0.5}\text{O}_3$
PMN	Magnesium-lead niobate	$\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3$
PZN	Lead zinc-niobate	$\text{PbZn}_{1/3}\text{Nb}_{2/3}\text{O}_3$
PNZT	Solid solution of lead zirconate-titanate and lead zinc-niobate	$\text{PbZr}_{1-x-y}\text{Zn}_{x/3}\text{Nb}_{2x/3}\text{Ti}_y\text{O}_3$
PcoW	Lead cobalt-tungstate	$\text{PbCo}_{0.5}\text{W}_{0.5}\text{O}_3$
PGO	Lead germanate	$\text{Pb}_5\text{Ge}_3\text{O}_{11}$
PVDF	Polyvinylidenfluoride	$(\text{CH}_2\text{CF}_2)_n$

ing not so bad characteristics: their equivalent noise temperature is 0.25 K in a matrix with 100×100 elements [5].

Thereshold sensitivity of all thermal radiation detectors can be improved by decreasing thickness of a sensitive element. However, though diminishing a film thickness can decrease its specific heat, reaching maximum possible characteristics of pyroelectric detectors is restrained by the fact that, starting from definite thickness, one has aggravation of ferroelectric film parameters as compared to properties of respective bulk materials. It can be explained by violation of grating periodicity near a ferroelectric boundary and associated with it arising mechanical strains and electric fields as well as by carrier diffusion from an electrode material into the contact region. Therefore, as the greatest success in the field of ferroelectric materials science, one could take elaboration of manufacturing technology for thin micron and submicron films. This technology is compatible with standard semiconductor microelectronic technologies including operations in surface treatment, thinning, polishing, sectioning, metallization and thermal insulation

of systems consisting of 10^4 elements (aligned with respective elements of multichannel integrated circuit) and combining such inconsistent properties as a low noise level and superhigh input impedance (up to 10^{12} Ohm). Nowadays, thin films of lead titanate, both pure and lanthanum doped ones, possess properties approaching to those of the best ceramics based on solid solutions of lead zirconate-titanate.

Taking into account that electrical characteristics of ferroelectrics, including spontaneous polarization, effectively depend on external electric fields, one can control parameters of pyroelectric detectors. As a rule, this way is also used in the case when a phase transition temperature T_c lies within the range of detector operation temperatures. In this case, polarization induced by an electric field both above and below T_c can exceed the spontaneous one. Therefore, devices of this type are often referred to as dielectric bolometers in literature. An analogous operation mode can be also realized without application of any external electric field when the direction of material polarization in a sensitive element prepared,

Table 2. Normal pyroelectrics ($T < T_c$)

Material	T_c °C	c' J/cm ³ K	p μCoul/cm ³ K	\hat{a}	$tg\delta$	M_1 cm ² /Coul	M_2 Vcm ² /J	References
Single crystals								
TGS	49	2.3	0.028	38	0.01	3620	0.066	[6]
DTGS	60	2.4	0.055	43	0.02	6020	0.083	[7]
ATGSAs	51	2.5	0.07	32	0.008	9900	0.19	[8]
LiTaO ₃	665	3.2	0.18	43	0.003	1440	0.051	[9]
LiNbO ₃	1210	3.0	0.083	28	0.005	1140	0.025	[9]
SBN 46/54	132	2.1	0.043	380	0.003	610	0.065	[9]
PGO:Ba	70	2.0	0.032	81	0.001	2200	0.19	[10]
Ceramics								
PLZT 7/65/35	150	2.6	0.13	1900	0.015	300	0.032	[11]
PLZT 8/65/35	105	2.6	0.18	4000	0.003	190	0.066	[12]
PZNFUTU	230	2.7	0.039	290	0.0031	570	0.052	[13]
PSZNFUTU	170	2.7	0.049	400	0.0028	520	0.058	[13]
PGO	178	2.6	0.002	25	0.003	350	0.009	[14]
Polymers								
PVDF	—	2.4	0.0027	12	0.015	1040	0.009	[10]
Thin films								
PbTiO ₃	490	2.9	0.095	200	0.02	1870	0.056	[15]
PLT 90/10	330	3.2	0.065	200	0.006	1150	0.062	[16]
PCT 70/30	270	3.3	0.05	390	0.015	440	0.021	[17]
PZT 54/46	380	3.1	0.07	950	0.016	260	0.019	[15]

for instance, in the form of an epitaxial film, is determined by its preliminary orientation.

Among mass applications of pyroelectric detectors one should separate protective signalling facilities, power saving devices, i.e. «automatic switches», and pyroelectric thermo-vision cameras. The former two types of devices are based on operation of an executive element under action of a pyroelectric signal arising due to temperature field changes in controlled apartments. These are widely used all over the world for last two decades, and their output have reached several million units per year.

The third direction is comparatively new. Despite that the first pilot samples of uncooled portable thermo-vision cameras came into being near the boundary between 80s and 90s, these have already attracted interest of reliable producers. The most important fields of applications for such facilities are the following: night vision, reconnaissance, objective recognition, car driving, protective systems, process monitoring and so on.

During 70-80s most attention was concentrated on developing and applying pyroelectric vidicons, that is cathode-ray tubes based on pyroelectric materials [28-34]. From the early 90s the new direction using matrix hybrid pyroelectric-semiconductor structures is effectively developed [35, 36]. One of the first acting device based on modified lead zirconate-titanate made in the form of an PRD matrix placed on multichannel silicon integrated circuit was described by Shorrocks and Edwards [5] in 1990. As a result, quite competitive portable pyroelectric infrared cameras were developed. These are capable to provide television quality of an image. Costs of the cameras are an order of magnitude less than that of traditional cooled systems. In this sense, the Texas Instruments experience in development of pyroelectric converters [18, 37] is rather instructive. Pioneer works at uncooled heat converters were begun there in the middle 70s. Considerable results were achieved in 1987 when a demonstrative sample was capable to provide tempera-

Table 3. Pyroelectric materials for PRD operating in the vicinity of a phase transition temperature point

Material	Bias kV/cm	T_c °C	c' J/cm ³ K	p μCoul/cm ³ K	\hat{a}	$tg\delta$	M_1 cm ² /Coul	M_2 Vcm ² /J	References
Single crystals									
DTGFB	0	74	2.0	1.4	2400	0.02	3300	0.34	[18]
KTN 67/33	2.5	4	3.7	8.0	25000	0.002	1000	0.46	[19]
BST 67/33	5	5	2.5	0.3	20000	0.007	170	0.034	[10]
Ceramics									
BST 67/33	1	21	3.2	23.0	31000	0.028	2700	0.84	[18]
BST 67/33	2	22	3.2	6.3	33000	0.021	670	0.25	[18]
BST 67/33	6	24	3.2	0.70	8800	0.004	280	0.12	[18]
BST 65/35	40	29	2.5	0.10	1200	0.0013	380	0.11	[10]
PMN:La	90	40	3.0	0.085	1200	0.0008	800	0.10	[10]
PScT	53	40	2.7	0.38	2900	0.0027	550	0.17	[19]
PZT 94/6*	0	50	2.6	0.37	300	0.02	5300	0.19	[20]
PZT 90/8/2*	0	30	2.6	0.185	290	0.019	2800	0.10	[21]
PCT 70/30:PCoW 96/4	0	106	3.3	3.07	400	0.037	1380	0.18	[22]
PZN/BT/PT 80/10/10**	0	12	2.7	5.93	4670	0.01	5310	1.08	[23]
PZN/BT/PT 80/10/10	0	85	2.7	2.9	18300	0.018	660	0.20	[23]
Thin films									
PScT (deposition)	40	40	2.7	0.52	6000	0.012	360	0.076	[24]
PScT (sol-gel)	—	40	2.7	0.30	7000	0.002	180	0.10	[25]
PScT	20	40	2.7	0.08	1000	0.002	330	0.07	[26]
KTN	30	40	3.7	20.0	1200	0.01	50000	5.0	[27]***

* transition between two rhombohedral phases

** transition between rhombohedral and tetragonal phases

*** data are doubtful

ture resolution close to 0.5 K. For next stages this work was included into the number of state programs and got some considerable financial support. As a result, a set of devices for military and civil purposes was produced. In Fig. 1 shown schematically are a fragment of the pyroelectric structure consisting of 80.000 (245×328) elements and lying in the basis of portable infrared thermal-vision camera «Night Sight» mounted on a patrol police car [37]. A matrix of sensitive elements 1 is made of a barium-strontium titanate plate using laser scribing.

Interelement space and distance between element centers are equal to 10 and 48.5 μm, respectively. After scribing, the plates are etched for skimming slugs, then these are annealed in oxygen atmosphere to recover stoichiometry. Deposition of the absorbing cover 4 consisting of the parylene film 6, semitransparent 5 and opaque common to all elements 7 electrodes as well as recovering flatness of the scribed surface accomplish treatment of the side receiving infrared emission. The film-electrodes

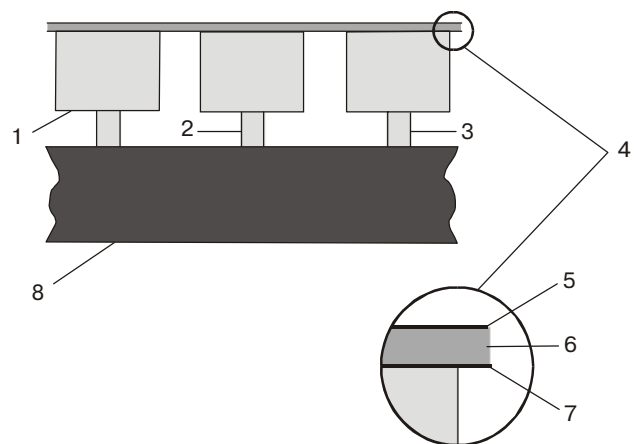


Fig. 1. Schematic view of a pyroelectric matrix fragment: 1 – sensitive element; 2 – basis; 3 – conductive coating; 4 – absorbing coating; 5 – parylene; 6 – semitransparent electrode; 7 – opaque electrode; 8 – integrated circuit.



Fig. 2. Infrared image of a car obtained by using a detector with equivalent temperature 0.2°C and optics of $f/1.0$ type [18].

system forms some resonance cavity that provides absorption coefficient not worse than 90% in the range of 7.5 to $13\mu\text{m}$. To reduce heat losses from the rear side, each sensitive element is placed on the tiny base 2, surface of which is covered by conducting layer 3 providing an electrical contact with an input of respective channel of the matching integrated circuit 8. Preamplifiers are inverting stages with feedback resistances of the order of 10^{11} – 10^{12} Ohm. Outputs of each amplifier are gated in such manner that the matrix output is compatible with standard television facilities. The matrix is mounted on mono-stage thermoelectric cooler and placed into standard case with dimensions $25\times 24\times 6\text{ mm}^3$ having 40 leads. This device provides an image uniformity not worse than 1.5%. Obtained data are acceptable for representing them both on indoor displays and on the outdoor ones. An example of infrared image is shown in Fig. 2. Main technical performances of the camera are summarized in Tab. 4.

The cost of this device in batch production is equal approximately to \$6,000. Since 2000 the company Raytheon plans to equip Cadillac cars with similar thermovision cameras developed in Texas Instruments [14]. In experts' opinion, it will be one of essential stages in the development of automatic control systems in car transportation that should be one of the main spheres of IR-sensors application by 2010–2015 years.

Table 4. Performances of the thermal-vision camera "Nightsight"

Field of view angle	28×18
Depth of field	From 6 m to infinity (at fixed focus)
Type of videointerface	RS170/NTSC
Automatical functions	Contrast and brightness
Image polarity	Arbitrary
Readiness time	< 30 s
Temperature range	From -20°C to $+50^{\circ}\text{C}$
Maximum temperature of ambient air	105°C
Power consumption	6 W
Supply voltage	$12\text{ V} = /24\text{ V} \sim$ (on choice)
Case type	Waterproof
Dimensions	$20.4\text{ cm}\times 15.2\text{ cm}\times 15.2\text{ cm}$
Weight	< 2.25 kgf
Equivalent noise temperature	< 0.12°C
Angle resolution	5'

Thus, uncooled sensors that up to date were of a most limited application become a basis for a new branch of photoelectronics, namely, uncooled thermal vision. The following progress in the field of pyroelectric detectors should be associated with searching new effective materials, elaborating methods of making thin ferroelectric films and improving technologies of manufacturing hybrid structures based on ferroelectric-semiconductor systems.

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