DOI 10.5162/irs2013/i1.2

High Detectivity of Pyroelectric Detectors based on Relaxor-$PbTiO_3$ Single Crystals

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Abstract:
In this work the suitability of Mn-doped *lead* indium niobate-lead magnesium niobate-lead titanate (xPb($In_{1/2}Nb_{1/2}$)O_3-yPb($Mg_{1/3}Nb_{2/3}$)O_3-(1-x-y)$PbTiO_3$) single crystals in pyroelectric detectors was evaluated and compared with standard lithium tantalate ($LiTaO_3$). Pyroelectric and dielectric measurements confirmed an increased processing and operating temperature range due to higher phase transitions of 0.26Pb($In_{1/2}Nb_{1/2}$)O_3-0.42Pb($Mg_{1/3}Nb_{2/3}$)O_3-0.32$PbTiO_3$:Mn. Due to the high pyroelectric coefficient, relaxor-lead titanate based sensors perform an increase of the specific detectivity in relation to standard lithium tantalate based detectors. The evaluation shows good results in the design and fabrication of the detectors for long-range flame detection and high-resolution gas analysis.

Key words: Relaxor-PT, PIN-PMN-PT, Pyroelectric Detector, Responsivity, Specific Detectivity.

Introduction

Innovations in infrared systems continue to be the motivation for the development and exploration of new ferroelectric materials which are the core of pyroelectric sensors. Compared with bulk ceramic, thin films or polymers the single crystals with outstanding integrity and less defects offer many advantages, such as good electronic behaviours and in turn better device performance [1]. The goal of our work is to increase the specific detectivity by application of single crystals with improved pyroelectric properties.

Single crystalline Lithium Tantalate ($LiTaO_3$, LTO) is used as a preferred pyroelectric material for pyroelectric detectors more than 30 years. Since 2003, the superior pyroelectric performances of PMN-xPT single crystals (Pb($Mg_{1/3}Nb_{2/3}$)$_{1-x}$$Ti_xO_3$, PMNT) were first investigated in the group of Prof. Luo. The rhombohedral phase [111] oriented PMNT crystals with the orientation direction along spontaneous polarization perform ultra-high pyroelectric coefficient and relative low dielectric loss, especially for the composition near to the MPB about 0.26-0.29PT [2]. In our previous works was shown that PMN-26PT and PMN-29PT single crystals, doped with Mn, outperforms LTO in pyroelectric detectors by a 3 times higher specific detectivity [3-5]. Unfortunately, rhombohedral PMN-PT single crystals exhibit low phase transition temperatures (T_{RT}≈100°C), which limit the processing temperature during fabrication and also the operating temperature range. Therefore, more attention is focused on high Curie temperature relaxor-PT, particularly, the ternary solid solution system xPb($In_{1/2}Nb_{1/2}$)O_3-yPb($Mg_{1/3}Nb_{2/3}$)O_3-(1-x-y)$PbTiO_3$ (xPIN-yPMN-(1-x-y)PT, PIMNT) [6-7].

In the present work we focused on the investigation of composition and pyroelectric properties of PIN-PMT-PT:Mn for application in new generation high-performance pyroelectric detectors.

Material selection and detector design

Rhombohedral, [111] oriented, Mn-doped PIMNT crystals with different composition were supplied for this work as samples. EDX analysis was taken to define the composition of the as-grown crystalline. For the material characterization wafer with a thickness of about 300 µm were used with evaporated Cr/Au electrodes. The dielectric properties were measured with Novocontrol Alpha-A Impedance analyzer (with the phase accuracy of 0.002° and the tan(δ) accuracy of $3 \cdot 10^{-5}$) in the frequency range of 1 Hz to 10 kHz with a maximum AC field strength of 2 V/mm. The temperature dependences of dielectric permittivity were measured in the range 25 - 250°C with the LCR meters HP4284A (with 0.01% basic accuracy). The pyroelectric coefficient was measured with a sinusoidal driven thermo-electric cooler at an amplitude of about 0.5 K [8-9]. Very low frequencies of 30 mHz and 60 mHz, respectively, were applied to ensure a homogeneous temperature distribution of the pyroelectric samples and chips with a thickness of 300 µm and 30 µm, respectively.

The general assessment parameters of pyroelectric materials are three FMOs:

$$F_R = \frac{p}{c'_p} \qquad (1)$$

$$F_D = \frac{p}{c'_p(\varepsilon_p \tan\delta)^{1/2}} \qquad (2)$$

$$F_V = \frac{p}{c'_p \varepsilon_p} \qquad (3)$$

In eq. (1-3) p, c_p, ε_p, and tanδ are the pyroelectric coefficient, volume specific heat, relative dielectric constant and dielectric loss, respectively. The common wisdom concerning the selection of materials for pyroelectric devices is to maximize the FOMs.

The results of the material qualifying measurements are shown in table 1. The small variation in the composition leads to a shift of the phase temperatures and to change the values of the pyroelectric coefficient and dielectric permittivity. Within the selected relations of xPIN-yPMN-zPT we can see an increase of T_{RT} with decreasing PT content value. The reduction of the p/ε ratio can be caused by an increase of the PIN content. For the use in pyroelectric detectors sample number 1, 3 and 4 were selected which have a high temperature T_{RT} and the highest FOMs. The average values of an optimum composition of x/y/z was chosen as x=0.25±0.01, y=0.43±0.02, z=0.32±0.02.

Table. 1: Influence of the composition of PIN-PMN-PT:Mn crystals on the material properties

No	xPIN-yPMN-zPT			T_{RT}	T_c	p	ε (1kHz)	tanδ (1kHz)	F_R	F_D	F_V
	x	y	z	(°C)	(°C)	µC/m²/K		10^{-4}	10^{-12} m/V	10^{-12} m/V	10^{-10} m/V
1	0.244	0.455	0.302	126	173	778	553	3.0	311	764	56
2	0.244	0.443	0.313	126	172	751	566	5.3	300	548	53
3	0.237	0.445	0.318	125	181	739	518	3.0	296	750	57
4	0.257	0.418	0.325	125	183	738	529	4.0	295	642	56
5	0.249	0.423	0.328	124	184	729	561	5.6	292	520	52
6	0.246	0.403	0.352	118	191	722	529	3.6	289	662	55

For the detector characterization wafers were lapped and polished to a thickness of about 30 µm. NiCr/Au electrodes were evaporated on both sides. After that the wafers were coated with a black absorbing layer, and cut into pyroelectric chips of 2 mm x 2 mm. The processing temperatures for the fabrication of the detectors did not exceed 80°C. For easy comparison, LTO detectors were also fabricated. InfraTec's simplest detector design LIE-300 was used for the evaluation (fig.1, 2).

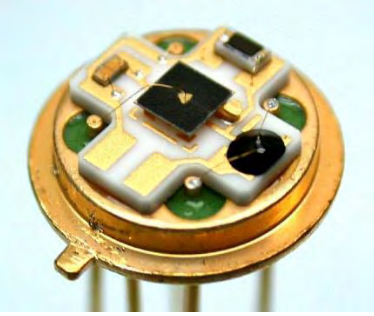

Fig. 1. Pyroelectric PIMNT detector (LME-300)

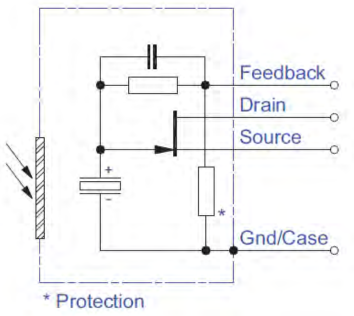

Fig. 2. Circuitry of a LME-300 pyroelectric detector.

It is equipped with a JFET and can be operated alternatively in both voltage and current modes. The feedback resistor R_{fb}=100 GOhm and the feedback capacitor C_{fb}=10 fF were used.

Detector measurements

The detector responsivity was measured with a blackbody, running at 500 K. As a second method, especially for measurements in a broad frequency range, an infrared super-luminescent diode was used.

A comparison of the response of detectors based on PIMNT and LTO is shown in fig. 3.

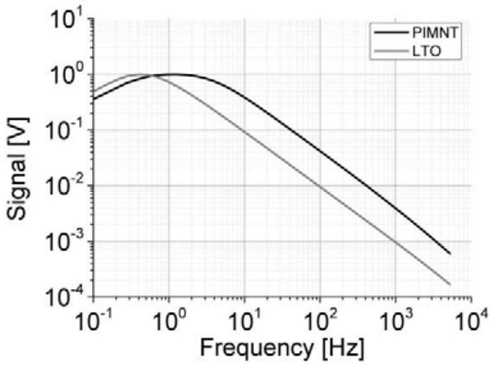

Fig. 3. Responsivity of PINMT and LTO detectors (LME-300, Current Mode).

The highest response of detectors based on PIMNT was obtained at higher frequency (1,23 Hz) compared to detectors based on LTO (f=0,4 Hz). The signal of the detectors decreases with a -20 dB/decade slope above the electrical corner frequency.

The noise measurements were performed with a PXI based data acquisition system using a FFT algorithm in the frequency range of 0.3 Hz to 15 kHz (fig.4).

The low frequency noise (<10 Hz) is dominated by the Johnson noise of the feedback resistance. In the medium frequency range of about 10 to 1000 Hz the most important noise source is the dielectric loss tanδ of the pyroelectric chip. At high frequencies above 1000 Hz the input voltage noise of the preamplifier is the dominant noise source.

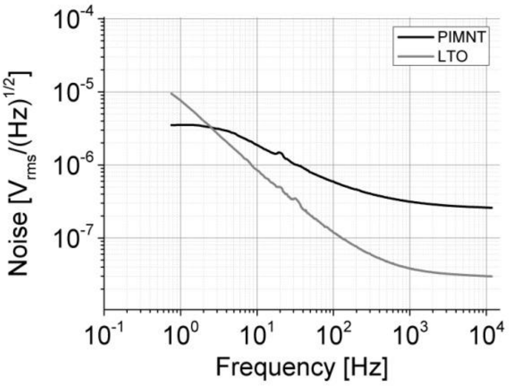

Fig. 4. Noise density of PINMT and LTO detectors (LME-300, Current Mode).

An outstanding specific detectivity of $1.18\cdot10^9$ cmHz$^{1/2}$/W was achieved at a frequency of 2 Hz with PIMNT in LME-300 detectors. The frequency dependence of the specific detectivity is depicted in fig. 5.

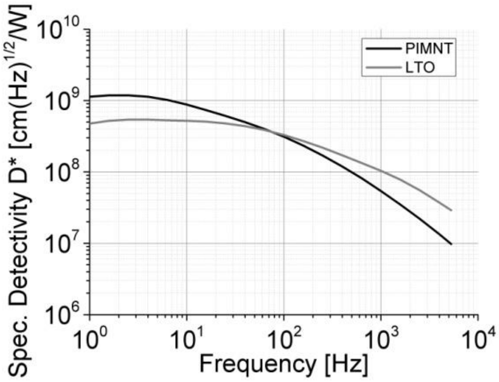

Fig. 5. Specific detectivity D of PINMT and LTO detectors (LME-300, Current Mode).*

The results of detector measurements were summaries in table 2.

Table. 2: Parameter and Specification of pyroelectric LME-300 detectors based on PIMNT and LTO

Parameter @ 10Hz	LME-300	
	PINMT	LTO
Thickness [µm]	33	24
Feedback resistance [GOhm]	100	100
Feedback capacitance [pF]	10	10
Signal [mV]	263	68
Responsivity [V/W]	8454	2387
Noise voltage [µV/Hz$^{1/2}$]	1.88	0.85
Spec. Detectivity [10^8 cmHz$^{1/2}$/W]	9	5.6

Conclusion

The evaluation has shown that rhombohedral [111] oriented Mn-doped 0.26PIN-0.42PMN-0.32PT is well suited for the fabrication of pyroelectric detectors. Due to the high figures of merit F_R and F_D of the chosen single crystals the PIMNT-based detectors are featured by a much higher specific detectivity at frequencies below around 100 Hz in relation to standard LTO-based detectors. This fact confirms that relaxor-$PbTiO_3$ crystals are well suited for high-performance pyroelectric detectors.

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