Pyroelectric Ceramics with Low Resistivity

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Abstract--- According to the requirement of pyroelectric ceramics used for commercial IR detector without FET gate resistor , $PbZrO_3$-$PbMnSbO_3$-$PbTiO_3$ pyroelectric ceramics with high figure of merit and low resistivity were studied. The resistivity ρ of above system can be adjusted in the range of 0.8-5x10^{11}Ωcm by further Mn doping. The signal to noise ratio of the detector without gate resistor made by this ceramics can reach the same level of the detector with FET gate resistor. The large size ceramic blocks with good mechanical processing property can be manufactured by pressureless sintering.

INTRODUCTION

A single element IR detector compacted in TO5 case usually consists of four parts: sensitive element, optical filter, FET and FET gate resistor.[1] The idea of eliminating the FET gate resistor by adjusting the sensitive element resistance has been proposed for a long time. The condition is that the resistivity ρ of pyroelectric ceramics is in the desired range. The input resistance of current FET is about 1x10^{11}Ω. The resistivity ρ of pyroelectric ceramics is usually larger than 1x10^{12}Ωcm. The element resistance for standard sensitive size (1x2x0.08mm) is equal to 0.4(cm^{-1})ρ. In order to eliminate the FET gate resistor and keep good match with FET, it is necessary to decrease the resistivity of pyroelectric ceramics and keep a high figure of merit of pyroelectric ceramics at the same time. The required resistivity for above application is in the range of 1-3x10^{11}Ωcm, and the minium voltage figure of merit Fv=p/c'ε should be 0.07m^2C^{-1}.

Where : p is the pyroelectric coefficient ; c' is the specific heat capacity; ε is the permittivity.

U_3O_8 doping is an effective way to decrease the resistivity of PZT ceramics. [2] [3] [4] But there are still problems when this system used for single element detector without gate resistor:(1) temperature stability of detector is not good; (2) the radiative property of U_3O_8 raw material is not proper for mass production.[5]

The basic composition of pyroelectric ceramics for commercial single element IR detector is $PbZrO_3$-$PbNbFeO_3$-$PbTiO_3$ (PZNFT). But the resistivity of this system is larger than 1x10^{12}Ωcm and hot-pressing sintering is needed to get high density and good mechanical processing property, which increase the cost and needs complicated equipments.

In this paper, We studied the $PbZrO_3$-$PbMnSbO_3$-$PbTiO_3$ (PMSZT) system ceramics ,which was used as piezoelectric filter ceramics.[6] High figure of merit was got and the resistivity can be adjusted in the range of 0.8-5x10^{11}Ωcm by further Mn doping. The single element IR detector without gate resistor made of PMSZT can reach the high signal to noise ratio. Large ceramic blocks(36x36x18mm) with good mechanical processing property were produced by pressureless sintering.

EXPERIMENTS AND RESULTS

The basic composition is $APb(Mn_{1/3}Sb_{2/3})O_3$-$B(PbZrO_3)$-$C(PbTiO_3)$. The ranges of A,B,C coefficient are: A=0.03-0.15; B=0.75-0.95; C=0.05-0.20. First we got the composition range with the relative permittivity ε_r below 300 shown in table 1. we choosed PMSZT-2 as the middle experiment composition because the resistivity of which is relatively low and the F_{l-h} phase transition temperature is relatively high. And then we added dopants Fe_2O_3, Cr_2O_3 and $MnCO_3$ to adjust resistivity. The resistivity can be changed in the range of 0.8-5x10^{11}Ωcm. We fixed one composition PMSZTA with the resistivity 2x10^{11}Ωcm. The property can be repeated in mass production. The properties of which and the comparision with other pyroelectric ceramics are listed in table 2.

The ceramic powders were prepared by ordinary processing procedure. The samples were sintered by pressureless sintering. The pyroelectric coefficient was measured by charge integral method.

Table 1 Dielectric properties of PMSZT system

Samples	p $10^{-4}Cm^{-2}K^{-1}$	ε_r	ρ $10^{11}\Omega cm$	F_{l-h} °C	Tc °C
PMSZT-1	2.38	280	>10	78.5	210
PMSZT-2	3.14	210	5-8	71	194
PMSZT-3	3.58	280	>10	63	170
PMSZT-4	4.88	265	>10	50	153

Table 2 Pyroelectric properties of PMSZTA and comparision with other ceramics

Samples	p $10^{-4}Cm^{-2}K^{-1}$	ε_r	ρ $10^{11}\Omega cm$	tanδ %	Fv=p/c'ε m^2C^{-1}
PMSZTA	3.8	205	2-2.5	0.3	0.083
PZNFT	4.2	250	>10	0.5	0.075
Japan low ρ	3.5	190	1-3	0.5	0.083
Japan high ρ	4.0	330	>10	0.5	0.054

The single element IR detectors without FET gate resistor were made by PMSZTA material . The properties of detector are shown in table 3.

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Table 3 Detector properties made by different ceramics

	No gate resistor		With gate resistor
	PMSZTA	Japan low ρ	PZNFT high ρ
Signal (V)	3.6-4.0	4.0	3.5-3.7
Noise (mV)	80-85	80	70-75
S/N	45-50	50	47-52

DISCUSSION

The sensitive area size is different for diffrent applications. From the single element IR detector $2mm^2$ to the forcal plane arrays $0.01mm^2$. So for the moment FET input resistance , We need the resistivity of materials changing in the range $10^9\Omega cm$ to $10^{11}\Omega cm$.

In our experiment, pressureless sintering were successfully used to sinter large blocks of ceramics . The dielectric loss and mechanical processing property can reach the same level of hot-pressing sintered PZNFT ceramics. This would be very helpful for mass production.

Decreasing of resistivity by Mn doping in $PbZrO_3$-$PbMnSbO_3$-$PbTiO_3$ system is resulted from the aliovalent substituents.[7] Lower charge Mn^{3+} ions replacing the Zr^{4+} and Ti^{4+} sites would provide more holes in p-type conductive PZT ceramics, which increases the total conductivity of the ceramics. This is only a simple and direct explanation. A detail study would be carried out in the following work.

SUMMARY

Extra Mn doping $PbZrO_3$-$PbMnSbO_3$-$PbTiO_3$ system is a very good pyroelectric ceramics used for production of single element IR detector without FET gate resistor by following reasons: (1) They possess high figure of merit and the required low resistivity; (2) High quality large size ceramic block can be produced by pressureless sintering.

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