Advances in Multifunctional Materials and Systems II
Contents

Preface vii

ADVANCES IN ELECTROCERAMICS

Pyroelectric Performances of Relaxor-Based Ferroelectric Single Crystals and their Applications in Infrared Detectors
Long Li, Haosu Luo, Xiangyong Zhao, Xiaobing Li, Bo Ren, Qing Xu, and Wenning Di

Formation of Tough Foundation Layer for Electrical Plating on Insulator using Aerosol Deposition Method of Cu-Al2O3 Mixed Powder
Naoki Seto, Shingo Hirose, Hiroki Tsuda and Jun Akedo

Formation and Electromagnetic Properties of 0.1BTO/0.9NZFO Ceramic Composite with High Density Prepared by Three-Step Sintering Method
Bin Xiao, Juncong Wang, Ning Ma, and Piyi Du

MICROWAVE MATERIALS AND THEIR APPLICATIONS

Thin Glass Characterization in the Radio Frequency Range
Alfred Ebberg, Jürgen Meggers, Kai Ratjen, Gerhard Fotheringham, Ivan Ndip, Florian Ohnimus, Christian Tschoban, Isa Pieper, Andreas Killian, Sebastian Methfessel, Martin Letz, and Ulrich Fotheringham

Formation of Silver Nano Particles in Percolative Ag-PbTiO₃ Composite Dielectric Thin Film
Tao Hu, Zongrong Wang, Liwen Tang, Ning Ma, and Piyi Du

Software for Calculating Permittivity of Resonators: HakCol & ErCalc
Rick Ubic
Effects of MgO Additive on Structural, Dielectric Properties and Breakdown Strength of Mg$_2$TiO$_4$ Ceramics Doped with ZnO-B$_2$O$_3$ Glass
Xiaohong Wang, Mengjie Wang, Zhaoqiang Li, and Wenzhong Lu

Design of Microwave Dielectrics Based on Crystallography
Hitoshi Ohsato

OXIDE MATERIALS FOR NONVOLATILE MEMORY TECHNOLOGY AND APPLICATIONS

Stable Resistive Switching Characteristics of Al$_2$O$_3$ Layers Inserted in HfO$_2$ Based RRAM Devices
Chun-Yang Huang, Jheng-Hong Jieng, and Tseung-Yuen Tseng

Improvement of Resistive Switching Properties of Ti/ZrO$_2$/Pt with Embedded Germanium
Chun-An Lin, Debashis Panda, and Tseung-Yuen Tseng

Nonvolatile Memories Using Single Electron Tunneling Effects in Si Quantum Dots Inside Tunnel Silicon Oxide
Ryuji Ohba

Resistive Switching and Rectification Characteristics with CoO/ZrO$_2$ Double Layers
Tsung-Ling Tsai, Jia-Woei Wu, and Tseng-Yuen Tseng

Research Of Nano-Scaled Transition Metal Oxide Resistive Non-Volatile Memory (R-RAM)
ChiaHua Ho, Cho-Lun Hsu, Chun-Chi Chen, Ming-Taou Lee, Hsin-Hau Huang, Kai-Shin Li, Lu-Mei Lu, Tung-Yen Lai, Wen-Cheng Chiu, Bo-Wei Wu, MeiYi Li, Min-Cheng Chen, Cheng-San Wu, Yi-Ping Hsieh, and Fu-Liang Yang

Author Index
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- Symposium 12: Advances in Electroceramics
- Symposium 13: Microwave Materials and Their Applications
- Symposium 14: Oxide Materials for Nonvolatile Memory Technology and Applications
- 2nd International Richard M. Fulrath Symposium on Frontiers of Ceramics for Sustainable Development

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Advances in Electroceramics
PYROELECTRIC PERFORMANCES OF RELAXOR-BASED FERROELECTRIC SINGLE CRYSTALS AND THEIR APPLICATIONS IN INFRARED DETECTORS

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ABSTRACT

In this work the pyroelectric performances of relaxor-based ferroelectric single crystals (PMN-PT, Mn-doped PMN-PT, ternary PIN-PMN-PT and Mn-doped PIN-PMN-PT) are reported. The crystals show high pyroelectric coefficients (p), especially for PMN-0.26PT and Mn-doped PMN-0.26PT with values as high as 15.3×10−4 C/m²K and 17.2×10−4 C/m²K respectively. A co-design methodology of the macroscopic symmetry constraint controlling spontaneous polarization order parameter and dipole defects pinning controlling dynamic loss was established to control growth of crystals and reveal the physical mechanism of low dielectric loss for Mn-doped crystals. Dielectric losses of binary and ternary relaxor-based single crystals are depressed to 0.05 %, enhancing the detectivity figure of merit (F_d) up to 40.2×10−5 Pa1/2 for Mn-doped PMN-0.26PT. The simulations were carried out for the performances of relaxor-based single crystal detectors in order to fabricate high performance detectors. The results show that relaxor-based ferroelectric single crystals have great advantages compared with the conventional LiTaO3 and DTGS in the low frequency range. By using Mn-doped PMNT single crystals as sensitive element and the multi-walled carbon nanotubes as absorbing layer, the outstanding infrared detectors were achieved. The specific detectivity (D*) of Mn-doped PMNT-based detector is up to 3.01×109 cmHz1/2/W (at 2 Hz) and 2.21×109 cmHz1/2/W (10 Hz, 500 K, 25 °C) respectively, four times higher than that of LiTaO3-based detectors.

INTRODUCTION

Pyroelectric infrared detectors exhibit advantages for the wide wavelength response, uncooled, high sensitivity, compacted structures and low cost, which are enable a variety of applications such as body detectors, flame and fire detectors, IR spectrometry, gas analyzers, night vision, thermal imaging and IR camera.1, 2 Nowadays traditional pyroelectric bulk materials, such as triglycine sulfate (TGS), lithium tantalate (LiTaO3), barium strontium titanate (BST), and lead scandium tantalate (PST) have been widely utilized for fabricating single-element infrared (IR) sensors and portable uncooled IR focal plane arrays (UFPAs) in military, paramilitary and commercial imaging applications.3, 4 To enhance the performances of the IR detectors, much attention has been paid on the novel pyroelectric materials with high pyroelectric coefficient, high figure of merits (FOMs), low dielectric loss and high temperature stability.1, 5

In 1996, large-size single crystals of PMNT were fabricated and then reported.6, 7 In 2002, Zhao discovered their high pyroelectric coefficients along the spontaneous polarization direction of [111] in rhombohedral phase.8 From then on, related researches on structure, composition, orientation and performances of the crystals have been carried out in detail.9–17 All these results
show that relaxor-based ferroelectric single crystals are promising for the next-generation high performance pyroelectric materials used for IR detection applications.

In this paper, we present our recent work and progresses on the fabrication and properties of these novel pyroelectric materials of pure PMNT, PIMNT, Mn-doped PMNT and Mn-doped PIMNT. More important is that we report our main progress in the fabrication of high performance IR detectors using Mn-doped PMNT single crystals.

EXPERIMENTS AND RESULTS

(1) Growth and Properties of Single Crystals

Relaxor-based ferroelectric single crystals PMNT, Mn-doped PMNT, PIMNT and Mn-doped PIMNT (Figure 1) were all grown by the modified Bridgman technique. The crystals were oriented along [001], [110] and [111] directions using an x-ray diffractometer. For the characterization, the crystals were cut into specimens with dimensions of $4 \times 4 \times 0.5$ mm$^3$, coated with silver paste and sintered at 700 °C. Then, the samples were poled under an electric field of $4 \times E_c$ for 15 min at a high temperature in silicone oil. The pyroelectric coefficient was measured by a dynamic technique using sinusoidal temperature change at very low frequency of 45 mHz.

The dielectric properties were performed with a HP4294 impedance analyzer while the hysteresis loops were measured with a TF1000.

![Figure 1. (a) PMNT crystal, (b) Mn-doped PMNT crystal, (c) PIMNT crystal and (d) Mn-doped PIMNT crystal.](image)

By analysis of relation between pyroelectric properties and compositions, phase structures and crystallographic directions optimization of compositions and structures, growth technology of high performance and large-size relaxor-based ferroelectric single crystals was established and optimized. The PT-content ($x$) dependence of pyroelectric coefficients ($p$) for the crystals at room temperature is shown in Figure 2 (a). The pyroelectric coefficients increase intensively with the decrease of $x$ and exhibit their largest values along spontaneous polarization directions where the structures of the crystals are rhombohedral ([111]), morphotropic phase boundary ([110]) and tetragonal ([001]) for $x \leq 0.30$, $0.30 < x < 0.35$ and $x \geq 0.35$, respectively. Temperature dependence of the pyroelectric coefficient for the crystals is given in Figure 2 (b). The values of
Pyroelectric Performances of Relaxor-Based Ferroelectric Single Crystals

$p$ for PMN-0.26PT, Mn-PMN-0.26PT, PIMNT (41/17/42) and Mn-PIMNT (23/47/30) crystals at room temperature are $15.3 \times 10^{-4} \text{ C/m}^2\text{K}$, $17.2 \times 10^{-4} \text{ C/m}^2\text{K}$, $5.7 \times 10^{-4} \text{ C/m}^2\text{K}$ and $7.37 \times 10^{-4} \text{ C/m}^2\text{K}$, respectively, much higher than those of traditional pyroelectric materials (LiTaO$_3$ and PZT). As the temperature increases, the pyroelectric coefficients increase slightly.

Figure 2. (a) Composition dependence of the pyroelectric coefficient for PMN-xPT crystals at room temperature.\textsuperscript{15} (b) Temperature dependence of pyroelectric coefficients for pure PMN-0.26PT,\textsuperscript{15} Mn-doped PMN-0.26PT,\textsuperscript{11} PIMNT (41/17/42)\textsuperscript{12} and Mn-doped PIMNT (23/47/30) crystals along their spontaneous polarization directions.

To select pyroelectric materials for practical devices, three major figures of merits (FOMs) are introduced: current responsivity ($F_c$), voltage responsivity ($F_v$) and detectivity ($F_d$),\textsuperscript{1} where the detectivity FOM ($F_d$) can be defined as:

$$F_d = p/[C_b(e_0s, \tan \delta)^{1/2}]$$

Here, $p / e_0^{1/2}$ is associated with the intrinsic parameters of the pyroelectric materials. For the crystals having the same structure and orientation, $p / e_0^{1/2}$ has little change,\textsuperscript{21-24} shown in Figure 3 (a), demonstrating that the detectivity FOM ($F_d$) can’t be enhanced by improving the $p / e_0^{1/2}$. So a co-design methodology was established, consisting of the macroscopic symmetry constraint controlling spontaneous polarization order parameter and dipole defects pinning controlling dynamic loss. In this work, Mn ions, occupying the B-site of perovskite structure, were introduced. The generated ($Mn_z^{2+}$) - $V_o^{**}$ dipole defects can pinning the domain walls and suppress the transport of vacancy conductance,\textsuperscript{26} revealing the physical mechanism of low dielectric loss for Mn-doped PMNT single crystals. The frequency dependence of dielectric properties in the range of 50 Hz to 10 kHz for pure and Mn-doped crystals is shown in Figure 3 (b). Very low dielectric losses of 0.05% and 0.049% at 1 kHz were observed for Mn-doped PMN-0.26PT and Mn-doped PIMNT (23/47/30), respectively. It is obvious that Mn-doping is an effective solution to decrease the dielectric losses for both PMNT and PIMNT crystals.

To extend the processing and operating temperature range, ternary PIN-PMN-PT single crystals were grown, announcing not only high Curie temperature but also good pyroelectric properties. The temperature dependence of dielectric constants is measured in Figure 4 for pure PMN-0.26PT, PIMNT (41/17/42), Mn-doped PMN-0.26PT and Mn-doped PIMNT (23/47/30)