Growth and pyroelectric property of 0.2 mol% Fe-doped Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$-0.38PbTiO$_3$ single crystals measured by a dynamic technique

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To develop a high-performance pyroelectric infrared detector, large-size and high-quality 0.2 mol% Fe-doped Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$-0.38PbTiO$_3$ single crystals have been grown by a modified Bridgman technique with a seed crystal. At 50 Hz, the doped single crystal showed a lower dielectric constant of 310 compared with the pure one. A low dielectric loss of 0.0067 was also obtained by doping with small concentration of iron ions. Piezoelectric coefficient (d_{33}) of $\langle 001 \rangle$ oriented sample was $\sim$260 pC/N. The pyroelectric properties and their temperature dependence were measured by the dynamic technique. At room temperature, the pyroelectric coefficient and calculated detectivity figure of merit F_D are 568 μC/m^2 K and 53 μPa$^{-1/2}$, respectively. The values of current response figure of merit F_i and voltage response figure of merit F_v are 227.2 pm/V and 0.083 m^2/C, respectively. These excellent pyroelectric properties as well as being able to produce large-size and high-quality single crystals make this kind of single crystal very promising for high-performance infrared detectors and other pyroelectric applications. © *2004 American Institute of Physics.*
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The pyroelectric effect in some materials has been known since ancient ages. This effect has been studied in many ferroelectric materials. $(1-x)$Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$ $-x$PbTiO$_3$ (PMN-PT) single crystals have been widely investigated due to their excellent dielectric, piezoelectric, and optical properties.[1–4] However, few investigations have reported on their pyroelectric performance. The properties of pyroelectric infrared detectors can be described by three major figures of merit (FOM), as current response FOM F_i, voltage response FOM F_v, and detectivity FOM F_D.[5] For high performance pyroelectric detectors, high FOMs are required, and they are related to the material parameters. Except for pyroelectric coefficient, dielectric constant and dielectric loss are of great importance. An effective way to improve the FOMs is to reduce the dielectric constant and dielectric loss by controlling the microstructure of the materials.

PMN-PT single crystals possess unusually large dielectric constants ($\epsilon_r \sim 5000$),[6] which is unfavorable for pyroelectric application. But in ferroelectric materials, small concentrations of substituents can dramatically influence their properties.[7] Recently, Fe-doped $(1-x)$Pb(Zn$_{1/3}$Nb$_{2/3}$)O$_3$ $-x$PbTiO$_3$ (PZN-PT) single crystals were grown and characterized.[8,9] It was found that in tetragonal phase, the

dielectric constant for Fe-doped PZN-PT single crystal is much lower than that of pure PZN-PT crystal. This may be related to the domain wall pinning by the dipolar defects due to the presence of the dopants, which will suppress the dielectric constants. This leads to the idea in this work to reduce the dielectric constants by doping Fe ions in tetragonal PMN-PT single crystals. PMN-0.38PT has been studied widely as a typical tetragonal single crystal.[10–12] The objectives of the present study are to investigate the pyroelectric properties of the Fe-doped PMN-0.38PT single crystals and to explore the possible application of this kind of crystal in high performance infrared detectors.

Single crystals of 0.2 mol% Fe-doped PMN-0.38PT were grown by a modified Bridgman technique.[6,13] The raw powders of Fe$_2$O$_3$, PbO, MgO, Nb$_2$O$_5$, and TiO$_2$ with purity more than 99.99% are used as the starting materials. B-site precursor synthesis method is used to prevent formation of the pyrochlore phase during crystal growth.[14] PMN-0.33PT single crystals were used as seed crystals. The crystal seeds had a key effect on restraining spontaneous nucleation and parasitic growth. The powders were put into a platinum crucible which was sealed to prevent the evaporation of lead. The growth temperature was raised to 1350 °C and soaked for about 10 h. The crucible was pulled down at a rate of 0.1–1.0 mm/h. Finally, the furnace temperature was decreased at a rate of 25 °C/h to room temperature. Usually high quality single crystals with a large size of about Φ48
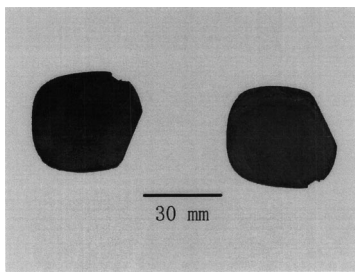
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FIG. 1. Single crystal slices of 0.2 mol % Fe-doped PMN-0.38PT.

FIG. 3. Temperature dependence of pyroelectric properties for 0.2 mol % Fe-doped PMN-0.38PT single crystal.

mm×80 mm could be obtained. To confirm the presence of a pure perovskite phase, x-ray diffraction analysis was performed.

It is known that for tetragonal PMN-PT single crystals, the spontaneous polarization is along the $\langle 001 \rangle$ direction. In this work, all the samples were oriented and cut along the $\langle 001 \rangle$ direction as confirmed by x-ray diffractometer. Figure 1 shows some crystal slices of 0.2 mol % Fe-doped PMN-0.38PT. They are light black in color. There are still some cracks in the crystals presumably caused by stress brought about by the lattice deformation during phase transition and by the thermal gradient during crystal growth. But the size and quality of the crystals are good enough for various applications. Rectangular-shaped specimens (6×6×0.6 mm) were prepared for property measurements. Silver paste was painted on the sample surfaces and sintered at 580 °C for 30 min. Then, the samples were poled along the $\langle 001 \rangle$ direction under an electric field of 10 kV/cm for 15 min near their T_m (~180 °C) in silicone oil and then slowly cooled to room temperature while maintaining half of the applied electric field.

The dielectric properties of poled samples were measured using an Agilent 4294A precision impedance analyzer at room temperature and in the frequency range of 50 Hz to 1 kHz. Figure 2 shows the dielectric constant and the dielectric loss versus frequency for a 0.2 mol % Fe-doped PMN-0.38PT single crystal. At 50 Hz, the dielectric constant and constant loss are about 310 and 0.0067, respectively. They are almost invariable until 1 kHz. The dielectric constant reported at 1 kHz for pure PMN-0.38PT single crystal is ~700,[10] which is much higher than the Fe-doped sample. No value of the dielectric loss for pure PMN-0.38PT single crystal has been reported. According to the principles of crystal chemistry, metallic ions prefer to enter sites with equal valence and similar radii. When iron ions were doped into
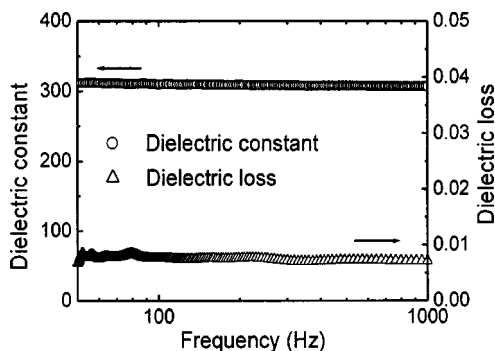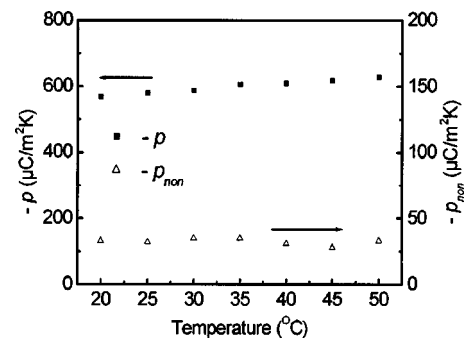
PMN-0.38PT single crystal, it will substitute Ti^{4+} and oxygen vacancies will be produced, forming a $2Fe_{Ti}^{\times} - V_O^{\bullet\bullet}$ defect dipole pair.[9] The domain walls will presumably be pinned by the dopant dipolar defects and the dielectric constants are suppressed. By doping with small concentration of iron ions, the dielectric constant of pure PMN-0.38PT single crystal was reduced while keeping a low loss. Piezoelectric coefficient (d_{33}) of the single crystal was also measured by a Berlincourt-type quasistatic d_{33} meter and the value is ~260 pC/N at room temperature.

A dynamic method was used to measure the pyroelectric coefficient p.[15–18] In the traditional method, such as the Byer–Roundy method,[19] the pyroelectric coefficients consist of the contributions of nonpyroelectric current. Using the dynamic technique, we can separate the real pyroelectric response from thermally stimulated discharge and obtain the pure pyroelectric coefficients. In the measurement, temperature of the sample was controlled by a Peltier heater and modulated sinusoidal with amplitude of 1 °C at a frequency of 5 mHz. The pyroelectric current was amplified with an electrometer and the 90° out-of-phase component of the current with respect to the temperature modulation was measured with a digital lock-in amplifier. After setting to a new temperature, the sample was kept for 15 min for the signal to become stable before the pyroelectric measurement was performed.[20]

At room temperature, the measured pyroelectric coefficient $-p$ for a 0.2 mol % Fe-doped PMN-0.38PT single crystal is 568 $\mu C/m^2 K$. (The signs of pyroelectric coefficients are defined according to the IRE standard.) The large value implies that the crystal is a very promising pyroelectric material. The unidirectional nonpyroelectric current due to space charge relaxation or the leakage current which is the component of the current in-phase with the temperature modulation has been separated from the true pyroelectric current. The coefficient due to nonpyroelectric effect ($-p_{non}$) is 33 $\mu C/m^2 K$, which is smaller than one tenth of $-p$. This indicates the nonpyroelectric current only amounts to a very small part in the poled single crystals. The temperature dependence of the pyroelectric properties was also characterized and shown in Fig. 3. From 20 to 50 °C, the pyroelectric coefficient increases from 568 to 628 $\mu C/m^2 K$, while $-p_{non}$ remains almost constant. The temperature stability is also an important property when the crystal is used as pyroelectric detectors. Table I gives the summary of pyroelectric coefficients, dielectric properties, and various

FIG. 2. Frequency dependence of dielectric constant and dielectric loss of 0.2 mol % Fe-doped PMN-0.38PT single crystal at room temperature.

TABLE I. The values of pyroelectric coefficient, dielectric properties, and various FOMs at room temperature for 0.2 mol % Fe-doped PMN-0.38PT single crystal.

$-p$ (μC/m^2 K)	ϵ_r (50 Hz)	tan δ (50 Hz)	d_{33} (pC/N)	F_i (pm/V)	F_v (m^2/C)	F_D (μPa$^{-1/2}$)
568	310	0.0067	260	227.2	0.083	53

FOMs at room temperature. FOMs are useful parameters for judging a pyroelectric material and are defined as follows: current response FOM $F_i = p/c_p$, voltage response FOM $F_v = p/(c_p \epsilon_0 \epsilon_r)$, and detectivity FOM $F_D = p/(c_p(\epsilon_0 \epsilon_r \tan \delta)^{1/2})$. Here, c_p is the heat capacity per unit volume ($\sim 2.5 \times 10^6$ J/m^3 K).[5,21] $\epsilon_0 = 8.85 \times 10^{-12}$ F/m is the permittivity of free space. ϵ_r is the dielectric constant and tan δ is dielectric loss. At 50 Hz, the values of $-p$ and F_D are 568 μC/m^2 K and 53 μPa$^{-1/2}$, respectively. They are higher than those of widely used pyroelectric single crystal LiTaO$_3$ (230 μC/m^2 K and 49 μPa$^{-1/2}$).[22] These excellent pyroelectric properties, as well as being able to obtain large-size and high-quality single crystals, make this 0.2 mol % Fe-doped PMN-0.38PT single crystal a promising candidate for uncooled infrared detectors and thermal imaging applications.

In summary, large-size and high-quality 0.2 mol % Fe-doped PMN-0.38PT single crystals have been grown by a modified Bridgman technique with a seed crystal. The dielectric constant was controlled successfully by doping with a small concentration of iron ions. The pyroelectric properties and their temperature dependence are measured by the dynamic technique. The pyroelectric coefficient is 568 μC/m^2 K and figures of merit F_i, F_v, F_D are 227.2 pm/V, 0.083 m^2/C, 53 μPa$^{-1/2}$, respectively. These outstanding pyroelectric properties make this kind of single crystal very promising for infrared detectors and other pyroelectric applications.

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