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The influence of Yb and Nd substituents on high-power piezoelectric properties of PMS–PZT ceramics

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Abstract

This paper presents an investigation on the effect of Yb and Nd substituents on the piezoelectric properties and vibration velocity of $0.05Pb(Mn_{1/3}Sb_{2/3})O_3$–$0.95Pb(Zr_{0.52}Ti_{0.48})O_3$ piezoelectric ceramics. The X-ray diffraction (XRD) measurements were performed on the doped samples and the results indicate that all the Yb-doped samples exhibit a single phase of perovskite structures in tetragonal symmetry and pyrochlore phases are found in specimens with high Nd dopant. The ‘‘soft’’ characteristic is improved by adding small amount of Yb_2O_3 and the optimum properties of Yb-doped PMSZ5 ceramics are achieved at $x = 2$ mol% ($d_{33} = 390$ pC/N, $\varepsilon_r = 1380$, $K_p = 0.61$, $\tan\delta = 0.41\%$, $Q_m = 800$). Meanwhile, the piezoelectric properties of all Nd_2O_3-doped specimens are found deteriorating. Vibration velocity at $\Delta T = 20$ °C, one of the most important factors for high-power piezoelectric application, is found as high as 1100 mm/s for 2 mol% Yb-doped specimens, which is about 2.7 times higher than that of the conventional hard PZT ceramics.

Keywords: A. Powders: solid-state reaction; C. Piezoelectric properties; C. Dielectric properties; High-power properties

1. Introduction

In recent years, the applications of electroceramics have been extended from traditional sonar and ultrasound sections to almost every technological area. The most common electroceramic is $Pb(Zr,Ti)O_3$ (PZT), of which both compositional modifications and improved processes have been intensively investigated [1–3]. The piezoelectric ceramics used in transformers, ultrasonic motors and electromechanical transducers are usually driven under high-strain conditions and expected to have high mechanical quality factor (Q_m), large planar electromechanical coupling factor (K_p), low dielectric loss ($\tan\delta$) and high mechanical strength [4]. Previous research results [5–8] indicate that the $Pb(Mn_{1/3}Sb_{2/3})O_3$–$Pb(Zr,Ti)O_3$ (PMS–PZT) ternary solid solution near morphotropic phase boundary (MPB) shows both higher Q_m and K_p. In addition, it generates less heat when it is driven at large vibration velocity.

High-power piezoelectric devices are usually driven under a high-vibration velocity in order to obtain high deformation to transfer mechanical energy. Thus, usual measurements under low vibration level are not appropriate to evaluate the performance in high-vibration conditions. Therefore, many investigations have been focused on the high-power properties of the piezoelectric ceramics [9,10]. Recently, Gao et al. [11] reported that PMS–PZT ceramics doped with rare earth elements (Eu^{3+} and Yb^{3+}) caused a combination of ‘‘hard’’ and ‘‘soft’’ piezoelectric characteristics and resulted in significant increases in Q_m, d_{31}, and k_{31}. They also found that PMS–PZT modified with 2 at.% Yb had superior characteristics under high-power conditions suitable for acting as a new high-power material. Meanwhile, Ryu et al. [12] studied the effect of Yb substituent on $Pb(Zr,Ti)$–$Pb(Mn,Nb)O_3$ ceramics and found Yb substituent could reduce the Q_m and K_p but greatly improved the high-power piezoelectric property. The conclusions from

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the two investigations presented in refs. [11,12] disagree from each other on the effect of Yb substituent on the piezoelectric properties.

In this paper, a study of the effect of Yb_2O_3 and Nd_2O_3 additions on the piezoelectric properties and vibration velocity of PMS–PZT system is presented. It was carried out with the expectation that the contradictory conclusions mentioned above could be clarified. The PMS content was selected at $x = 0.05$ rather than $x = 0.10$ (Guo et al. report [11]) because the previous investigation showed that the PMSZ5 specimen had the optimized piezoelectric properties in xPMS − (1 − x)PZT systems [13].

2. Experimental

$Pb(Mn_{1/3}Sb_{2/3})_{0.05}(Zr_{0.52}Ti_{0.48})_{0.95}O_3$ (abbreviated as PMSZ5) + x mol% of Yb or y mol% Nd ($x = 0, 1, 2, 4, 6$; $y = 1, 2, 4, 6$; abbreviated as Y0, Y1, Y2, Y4, Y6; N1, N2, N4, N6, respectively) were fabricated using the conventional ceramic techniques. All samples were made in disk shape with 10 mm in diameter and 0.5 mm in thickness. They were sintered in a sealed alumina crucible at 1200–1300 °C for 2 h under a PbO-rich atmosphere to minimize the lead loss during sintering. More detail about the experiment could be found in ref. [6].

The bulk densities of the sintered specimens were measured based on the Archimedes method using distilled water as the medium. The density increased to the maximum at 2 mol% Yb (7.91 g/cm^3) and 1 mol% Nd (7.85 g/cm^3) before decreasing as more Yb and Nd substituents were added. However, the bulk densities of all doped PMSZ samples were high than 95% of the theoretical density (8.02 g/cm^3). The crystallite structure was examined using an X-ray diffraction with Cu Kα radiation (Rigaku D/max rB, Japan), and the microstructure was observed using a scanning electron microscope (HITACHI S-570, Japan). The dielectric constant and loss (tan δ) at room temperature and elevated temperature were measured using a precision impedance analyzer (Agilent 4294A, USA) with laboratory fabricated experimental setup in the frequency range of 1 –100 kHz. Piezoelectric properties were calculated from the resonance measurement method.

The observation and analysis of the vibration velocity at high-vibration levels were performed using a measuring circuit as shown in Fig. 1. Samples were driven under radial vibration mode (K_p mode) by a waveform generator (Agilent 33120A, USA) and a power amplifier (HSA 4011, Japan). The waveforms of the sample current and voltage were monitored using an ac current monitor (Hioki 3271, Japan) and an oscilloscope (Agilent 54662A, USA). A laser vibrometer (Polytec OFV-512, Germany) and a vibrometer controller (OFV-5000, Germany) with the accuracy of 0.01 nm were used to measure the vibration velocity. Sample temperatures were measured using a temperature Hitester (Hioki 3445, Japan) by laser radiation (semiconductor laser 670 nm, maximum 1 mW).

3. Results and discussion

3.1. Physical properties

The XRD patterns of the PMSZ5–xYb and PMSZ5–yNd (x, $y = 1, 2, 4, 6$ mol%) are shown in Fig. 2. The patterns are similar to the un-doped PMSZ5 samples which could be found in the literature [13]. The diffraction peaks have the distinct split, which indicates all the samples have the perovskite structure with tetragonal symmetry. The results also reveal that solid solution samples without any second impurity phases can be prepared in Yb-doped PMS–PZT system. But when the Nd dopant reaches 4 mol%, diffraction peaks occurred near $2\theta = \sim 29.6°$ (intrinsic peak of the pyrochlore phase), which indicates that high amount of Nd dopant could result in the occurrence of non-piezoelectric pyrochlore phase. The development of the pyrochlore phase $Nd_2Ti_2O_7$ or $Nd_2Zr_2O_7$ should be formed by excess Nd_2O_3 and TiO_2 or

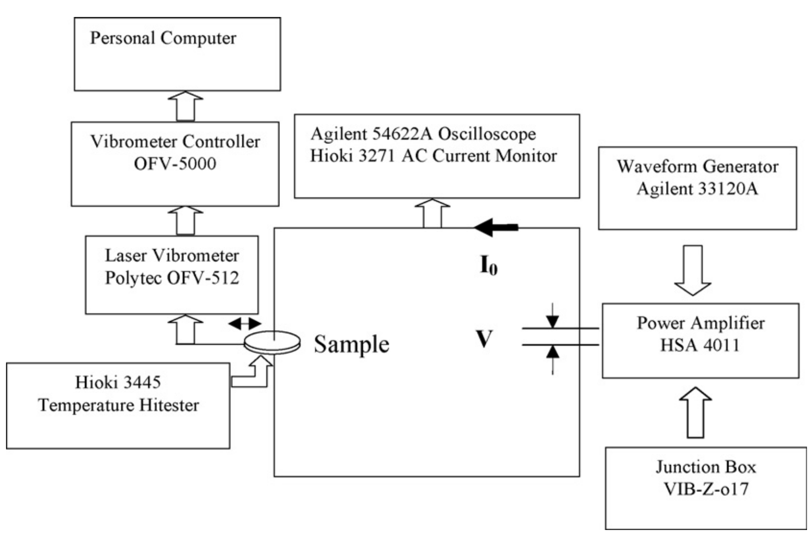

Fig. 1. Experimental setup for high-vibration measurement.

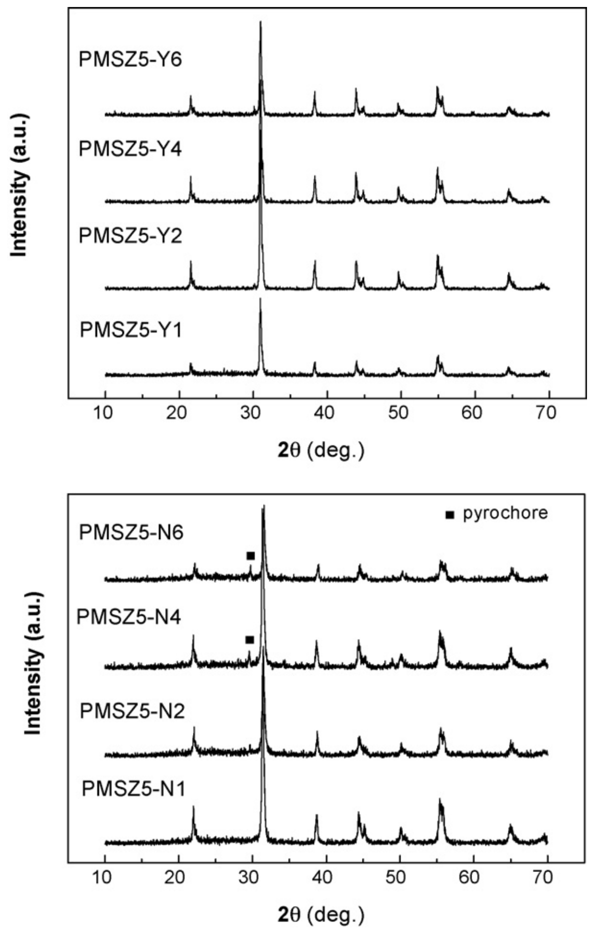

Fig. 2. XRD patterns of the PMSZ5 ceramics doped with x mol% Yb and y mol% Nd (x, y = 1, 2, 4, 6).

ZrO_2 during the sintering process. There is no intrinsic peak of the pyrochlore phase in all Yb-doped samples, which shows that Yb saturates in PMSZ5 samples at a higher dosage than Nd.

Fig. 3 shows the micrographs of the Yb and Nd-doped PMSZ5 samples taken under an SEM. All the structures are dense. It is observed that with the increase in the amount of Yb_2O_3 and Nd_2O_3, significantly changes in the grain size and grain boundary take place. The average grain size of Y2 is *ca.* 3–4 μm (Fig. 3a), which is similar to the un-doped PMSZ5 samples [13]. With further increase of Yb content to 4 mol%, the average grain size dramatically decreases to *ca.* 1.5–2 μm (Fig. 3b). Notably, with the addition of only 1 mol% Nd, the average grain size decreases to *ca.* 1.5 μm (Fig. 3c) as well, which shows that the average grain size is more sensitive to addition Nd than Yb. No significant change is observed in the average grain size by further increasing the Nd content, but microstructure morphology are significantly changed and many small particles are observed on the surface of grain or the grain boundary. These particles are likely to be pyrochlore phase, $Nd_2Ti_2O_7$ or $Nd_2Zr_2O_7$, which are in accord with the XRD pattern results. The occurrence of pyrochlore phase could contribute to the deterioration of piezoelectric properties of the PMS–PZT samples.

3.2. Dielectric and piezoelectric properties

In all the Yb-doped samples, the maximum of dielectric constant decreases as frequency increases, but permittivity maximum temperature (T_m) does not shift towards high temperature, which indicates that Yb substituent will not result in the ferroelectric relaxor behavior in the PMS5 ceramics. Curie temperature (T_c) of PMSZ5 ceramics is 290 °C, but the T_c of all Yb-doped samples is higher than PMSZ5 ceramics. The T_c slightly increases with the increase of Yb contents, which is beneficial to the thermal stability for the application of devices.

The maximum dielectric constant for the un-doped PMSZ5 ceramic is *ca.* 14000. After a dope of 1 mol% Nd, the maximum dielectric constant dramatically decreased to *ca.* 8000. Then the maximum dielectric constant slightly decreased as more Nd content was added. In comparison with the un-doped PMSZ5 sample [13], the broadness of the dielectric response is found in all doped samples, but the T_m does not shift to high temperature as the measurement frequency increases, which also indicates that Nd dopant will not result in ferroelectric relaxor behavior in the PMS5 ceramics.

The significant decrease of the maximum dielectric constant in Nd-doped sample could be explained as follows: (i) small grain size causes high grain boundary ratio, which reduces the maximum dielectric constant [14]. This trend is in accord with Fig. 3c; (ii) After Pb^{2+} is substituted with Nd^{3+}, some PbO enters and stays on the grain boundary, which reduces the maximum dielectric constant. Another possible reason for the dielectric constant reduction in highly Nd-doped specimens is the occurrence of pyrochlore phase, which possesses low dielectric constant.

The Yb and Nd additives have significant influence on the piezoelectric properties of PMSZ5 ceramic. Fig. 4 illustrates the dielectric and piezoelectric properties of PMS–PZT ceramics as a function of Yb concentration. With the increase of Yb concentration, the piezoelectric constant (d_{33}) increases from 360 pC/N to 392 pC/N and the electromechanical coupling factor (K_p) from 0.58 to 0.61 before the both constants decrease slightly upon further increment of Yb concentrations. The dielectric constant ε_r reached its maximum when x is near 0.01, while mechanical quality factor (Q_m) decreases with the increase of the Yb concentration continuously over the range investigated. The increase of d_{33}, K_p and decrease of Q_m indicate that Yb addition increases the degree of the "soft" characteristic. The ion radius of Yb^{3+} (0.858 Å) is between Pb^{2+} (1.2 Å) and Ti^{4+} (0.68 Å). Therefore, Yb^{3+} could either enter the A-site of the perovskite structure to replace Pb^{2+} or B-site to replace Ti^{4+}. From the experimental results, it seems that Yb^{3+} ions tend to enter the A-site to act as donor dopants. A donor dopant reduces the concentration of the intrinsic oxygen vacancies created due to PbO evaporation during the sintering of PZT ceramics and introduces lead vacancies to maintain the charge neutrality [8]. Lead vacancies introduce the deformation of crystal structure, reduce the inner stress and increase the mobility of 90° domain wall, which increase the

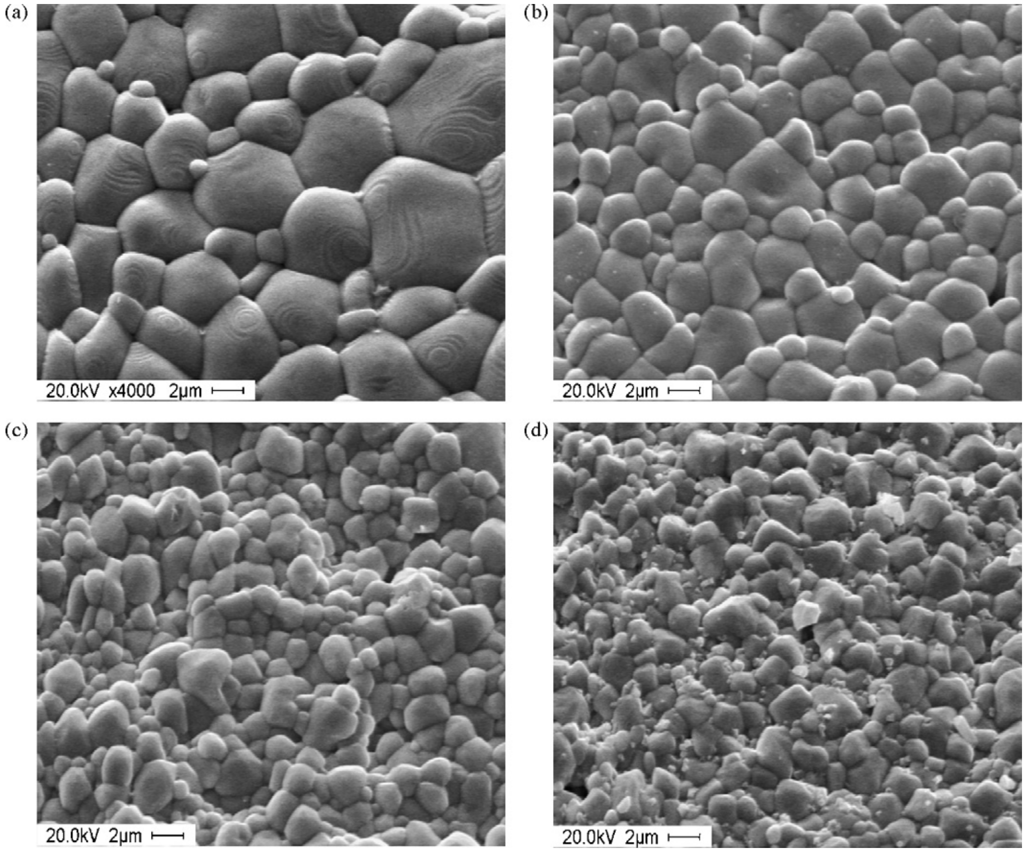

Fig. 3. Micrographs of Yb, Nd-doped PMSZ5 ceramics: (a) 2 mol% Yb, (b) 4 mol% Yb, (c) 1 mol% Nd, (d) 4 mol% Nd.

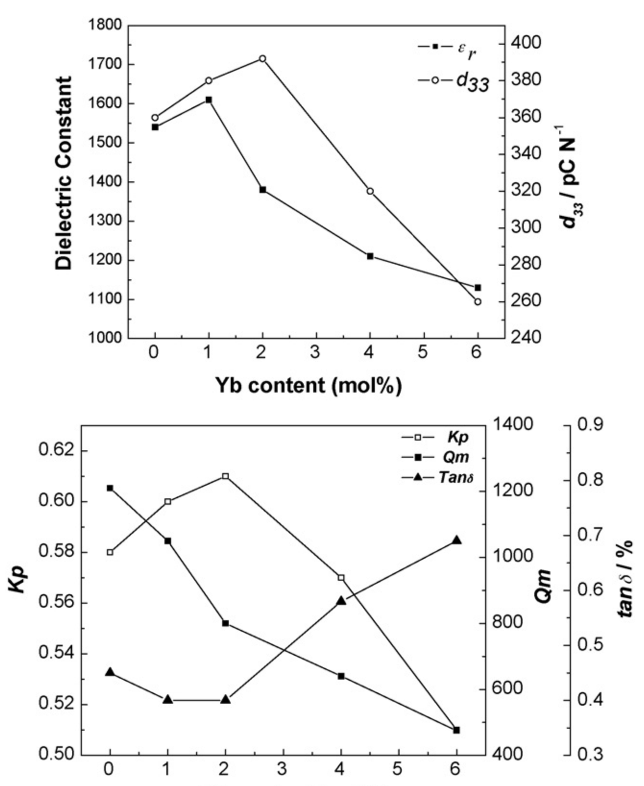

Fig. 4. Dielectric and piezoelectric properties change in Yb-doped PMSZ5 ceramics.

d_{33}, k_p and decrease the Q_m. This result is not in agreement with Gao et al.'s report [11], which found the addition of Yb introduced a combination of ''hard'' and ''soft'' piezoelectric properties, but in accordance with the results reported by Rye et al. [12].

The experiments show that when the Yb concentration increases further, all dielectric and piezoelectric properties deteriorate. When Yb doping concentration is higher than 4 mol% and beyond the saturation limit, more Yb ions will be deposited on the grain boundary as the second phase and cause reduction of the average grain size (Fig. 3b). The two likely causes for the deterioration of piezoelectric properties are the prevention of domain switching due to the second phases and domain clamping due to the reduction of the average grain size.

In conclusion, the optimum dielectric and piezoelectric properties of Yb-doped PMSZ5 ceramics are achieved at $x = 2$ mol% and the resultant properties are $d_{33} = 390$ pC/N, $\varepsilon_r = 1380$, $K_p = 0.61$, $\tan\delta = 0.41\%$ and $Q_m = 800$. Dielectric and piezoelectric properties of all doped specimens decrease significantly and Q_m reaches the maximum with 2 mol% substituent (the figure is not shown here). According to Figs. 2 and 3, the Nd substituent saturates at a lower dosage than Yb. When 1 mol% Nd was added, the average grain size was greatly reduced and then lots of pyroclore phase occurred with further increment of Nd. The deterioration of piezoelectric properties is due to the reduction of the average grain size and the occurrence of large quantities of pyroclore phase.

3.3. High-power properties

For a circular sample driven under the K_p mode, Li et al. [4] describe the function of maximum vibration velocity (v_m) as follows:

$$v_m = \sqrt{\frac{\varepsilon_{33}^T}{2\rho(1+\sigma)}}\frac{BK_pQ_mV_m}{T} \quad (1)$$

where ε_{33}^T is the relative permittivity, σ the Poission ratio, ρ the density of sample, B the constant with the value of 2.065, K_p the radial coupling coefficient, Q_m the mechanical quality factor, V_m the maximum value of ac applied voltage and T the thickness of the sample.

From Eq. (1), it can be seen that v_m is linearly proportional to the product $\sqrt{\varepsilon_{33}^T}k_pQ_m$. Accordingly, it is essential to have a combination of high K_p, Q_m and ε_{33}^T to achieve the highest vibration velocity. Since the addition of Nd causes significantly deterioration in the piezoelectric properties, only the high-powder properties of Yb-doped PMSZ5 specimens were measured in the investigation.

Fig. 5 shows the relationship between vibration velocity and the electric field (E) of PMSZ5 ceramics doped with Yb of different percentage. At a given electric field (10 kV/m), vibration velocity increases with the increase of Yb concentration and reaches the maximum with $x = 0.02$ mol. Further increase in Yb concentration causes the vibration velocity decreasing and possibly reaching the level even lower than un-doped PMSZ5 ceramics. Under a relatively low driving field ($E \leq 8$ kV/m), vibration velocity is nearly proportional to the electric field. With the increase in E, the saturation in the value of vibration velocity starts to become evident. The saturation was due to the considerable decrease in Q_m with the increasing electric field above a critical vibration level as well as heat generation [11]. For un-doped PMSZ5 ceramic, the maximum vibration velocity (v_m) is 670 mm/s achieved at $E = 10$ kV/m, similar to the value 620 mm/s reported by Takahashi et al. [15]. At $E = 12$ kV/m, v_m was found to be as high as 1150 mm/s for 2 mol% Yb. It was the highest value observed in the whole study and is 2.7 times higher than that of the conventional hard PZT ceramic which has a typical value of 0.40 m/s [16].

Above a certain vibration level, the increase in temperature under electric drive is significant, as a partial depoling begins to occur under reverse bias with increasing electric field. This restricts the practical upper limit for v_m. The desired performance characteristics for a high-power device application need a high v_m and a low heat generation (ΔT). This is because the operation conditions to reach higher v_m values must be restricted in order to maintain thermal stability. From a practical perspective, the maximum vibration velocity can be defined as the v_m at $\Delta T = 20$ °C [11].

The relationship between temperature rise and vibration velocity for Yb substituted PMSZ5 ceramics is shown in Fig. 6. The result indicates that Y2 specimen produces much less heat than any other specimens when they work under a given vibration frequency. The maximum vibration velocity ($\Delta T = 20$ °C) was found on 2 mol% Yb substituted PMSZ5 ceramic and the value can reach as high as 1100 mm/s, higher than that of PMnN–PZT system [4]. It is expected that this exceptionally high-vibration velocity can generate more power and covert electric energy. PMSZ5 doped with 2 mol% Yb could be utilized for high-power piezoelectric devices such as piezoelectric transformers and ultrasonic motors.

According to Eq. (1), the v_m of all doped specimens should decrease because of the low Q_m value. However, Y2 specimen achieved the highest vibration velocity. The origin of such effect could be explained as follows. When the materials vibrate on the high-power condition, the decrease of vibration velocity is due to the deterioration of the Q_m. Li et al. found the reduction magnitudes of Q_m disaccord for different materials [4] and Xiang et al. found rare earth substitution could greatly improve the mechanical strength [17]. Ryu et al. also found the Yb substituent could improve the mechanical properties, such as fracture strength and fracture toughness [12]. The improvement of mechanical properties may decrease the reduction magnitude of Q_m driven at the high-vibration condition, which makes the Y2 specimen achieve

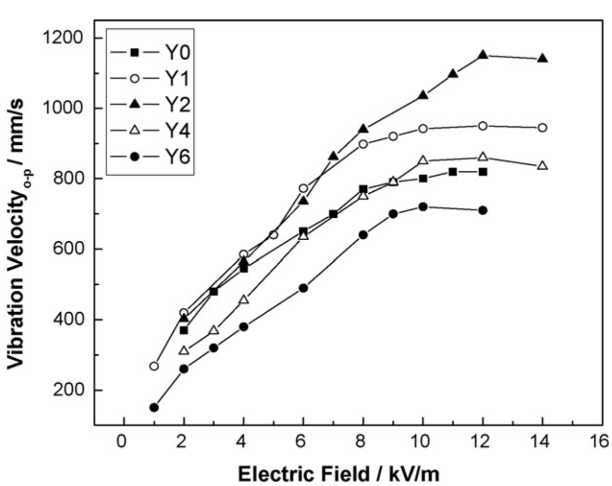

Fig. 5. Vibration velocity vs. electric field for PMSZ5 ceramics doped with different Yb contents.

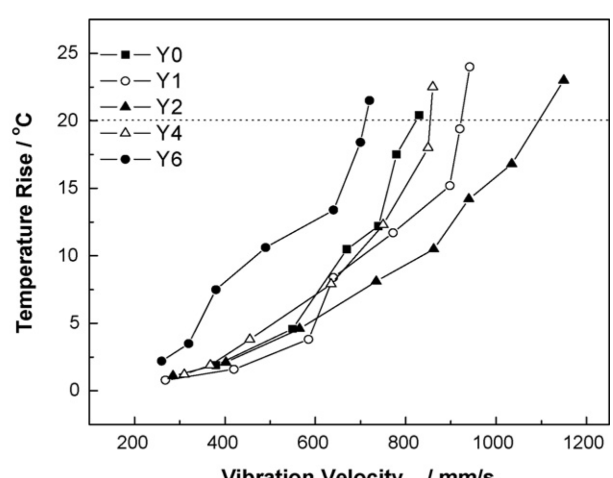

Fig. 6. Temperature rise vs. vibration velocity of PMSZ5 ceramics doped with different Yb contents.

the highest vibration velocity. More experimental and theoretical studies will be carried out on the improvement of high piezoelectric properties for 2 mol% Yb-doped PMSZ5 ceramic in the future.

4. Conclusions

Rare earth (Yb_2O_3, Nd_2O_3) doped PMSZ5 piezoelectric ceramics were prepared in a conventional ceramic process. The XRD results indicate that Yb-doped samples exhibit a single phase of perovskite structure with tetragonal symmetry. Curie temperature (T_c) of 2 mol% Yb-doped specimen is *ca.* 304, which is higher than un-doped PMSZ5 ceramic (290 °C). Yb^{3+} substituent tends to enter the A-site to act as a donor dopant and increases the degree of ''soft'' characteristic of PMSZ5 ceramics, which results in the increase of d_{33}, K_p and decrease of Q_m. PMSZ5 modified with 2 mol% Yb has the optimum piezoelectric properties ($d_{33} = 390$ pC/N, $\varepsilon_r = 1380$, $K_p = 0.61$, $\tan\delta = 0.41\%$, $Q_m = 800$). Meanwhile, Vibration velocity ($\Delta T = 20$ °C) could be reached as high as 1100 mm/s, which is *ca.* 2.7 times higher than commercial hard Pb(Zr, Ti)O_3 piezoelectric ceramics. It is expected that this piezoelectric materials can be utilized in high-power piezoelectric devices, such as piezoelectric transformers and ultrasonic motors.

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