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PMN ceramics produced by a simplified columbite route

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Abstract

$Pb(Mg_{1/3}Nb_{2/3})O_3$ ceramics produced by a simplified columbite route were investigated. The second calcination and pulverization steps in the columbite route were omitted. Without calcining, a mixture of $MgNb_2O_6$ and PbO was pressed into pellets and sintered directly to form $Pb(Mg_{1/3}Nb_{2/3})O_3$ ceramics. PMN ceramics of 100% perovskite phase were produced by this simplified columbite route at 1100–1250 °C sintering temperatures, 1–5 h soak times, and 2–30 °C/min heating rates. $K_{max} > 17\,000$ at 1 kHz was obtained.
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1. Introduction

Lead magnesium niobate, $Pb(Mg_{1/3}Nb_{2/3})O_3$ (PMN), was first synthesized in the late 1950s [1]. Since that time, PMN has been extensively studied because of its naturally high dielectric constant and high electrostrictive coefficient [2–6]. The main feature of the dielectric properties of PMN is a broad and frequency-dependent dielectric constant maximum just below room temperature. The magnitude of the maximum decreases and the temperature for the maximum increases as frequency increases. This behavior is typical of relaxor ferroelectrics. PMN materials are useful in electrostrictive actuator applications because of their large electric-field-induced strains [7,8], and in capacitor applications because of their high dielectric constants [9]. However, the main problem in producing PMN ceramics has been the formation of parasite pyrochlore phase in the initial stages of reaction between mixed oxides [10,11]. Pyrochlore phase shows poor dielectric characteristics [12], and leads to low dielectric constant in PMN ceramics.

In order to avoid the formation of pyrochlore phase, many methods have been reported. Lejeune and Boilot [13] showed that the addition of excess PbO with an optimum sintering cycle could produce PMN ceramics with an almost pure perovskite phase by the conventional mixed oxide method. Guha and Anderson [14] prepared PMN ceramics by solid-state reaction between $Pb_3Nb_2O_8$ and MgO. Chaput et al. [15] reported a sol-gel route for the formation of PMN. MgO progressively was inserted into a B-site-deficient cubic pyrochlore that completely transformed into PMN at 700 °C. Addition of excess PbO [16,17] and MgO [17,18] can reduce and even eliminate the pyrochlore phase. Swartz and Shrout [19] developed a columbite route to fabricate PMN ceramics with better reproducibility. In the route, MgO and Nb_2O_5 was precalcined to form columbite $MgNb_2O_6$ and then reacted with PbO, this leads to PMN powder with a very low pyrochlore content. Liou et al. [20] developed a simplified wolframite route to obtain $Pb(Fe_{1/2}Nb_{1/2})O_3$ ceramics of 100% perovskite phase. Without calcining, the mixture of $FeNbO_4$ and PbO was pressed and sintered directly to form PFN ceramics. Han and Kim [21] proposed a method to prepare PMN powder with >99% perovskite phase by adding an aqueous $Mg(NO_3)_2$ solution rather than MgO to the alcoholic slurry of PbO and Nb_2O_5, followed by calcination at 950 °C for 2 h.

As the low reactivity problem of MgO is solved in the first calcination stage of columbite route. A simplified and effective process was developed to produce pyrochlore-free PMN ceramics in this study. In this simplified columbite route, a mixture of $MgNb_2O_6$ and PbO was pressed into pellets and sintered directly to form PMN ceramics.

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2. Experimental procedure

All samples in this work were prepared from reagent-grade oxides (E. Merck, Darmstadt, Germany): PbO (>99%), MgO (>97%) and Nb_2O_5 (99.9%). First, MgO and Nb_2O_5 with 5mol% excess MgO were ball-milled in distilled water with agate media for 8h and calcined at 1000 °C for 3 h in an alumina crucible to form the columbite precursor $MgNb_2O_6$. After reaction, the calcined powder was pulverized and the appropriate amount of PbO with 3 mol% excess was then added to the columbite and ball-milled in distilled water for 8 h. After drying, the pulverized mixture of $MgNb_2O_6$, PbO was pressed into pellets 12 mm in diameter and 2 mm thick. The pellets were heated to 850 °C for a period t_{850}°C = 0–5 h with a rate 5 °C/min, and then heated to sintering temperature of 1250 °C/2 h with a rate 10 °C/min in air. After sintering, the pellets were cooled with a rate 10 °C/min. The heating profile for pellets containing $MgNb_2O_6$ and PbO is illustrated in Fig. 1.

The sintered PMN ceramics were analyzed by X-ray diffraction (XRD). The relative amounts of perovskite and pyrochlore phases were determined from XRD patterns of the samples by measuring the major peak intensities for the perovskite (110) and pyrochlore (222) phases. The following qualitative equation was used.

$$\%\ \text{perovskite} = 100 \times I_{\text{perov.}}/\left(I_{\text{perov.}} + I_{\text{pyro.}}\right) \quad (1)$$

Water immersion method was used to measure the density. Microstructures were analyzed by scanning electron microscopy (SEM). After polishing, the dimensions were measured before silver electrodes were formed on the pellets. Dielectric properties were measured with an HP4192A impedance analyzer in a temperature-controlled chamber from −35 °C to 40 °C at various frequencies between 100 Hz and 100 kHz.

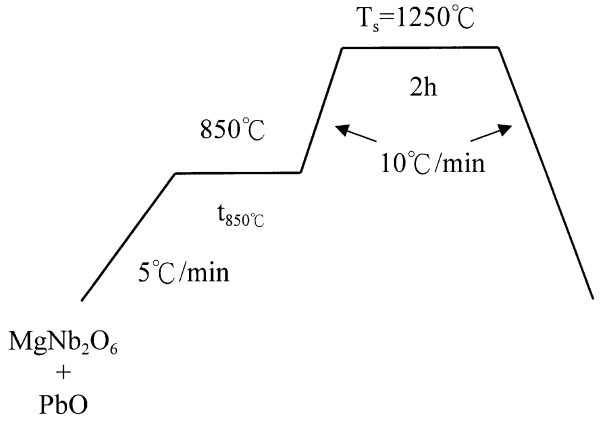

Fig. 1. Heating profile of PMN ceramics with calcining and sintering levels.

3. Results and discussion

The XRD profiles of as-fired surfaces of PMN ceramics sintered at 1250 °C/2 h with calcining level time $t_{850\ ^\circ C}$ = 0, 1, 3 and 5 h are shown in Fig. 2. The major peak (2 2 2) of pyrochlore phase at 2θ = 29.2 °C appears in these patterns due to PbO evaporation and resulting pyrochlore film on the surface. More than 90% of PMN perovskite phase is found on the as-fired surface of PMN ceramics. In Fig. 3, almost 100% perovskite phase PMN ceramics were obtained as shown in the XRD patterns of polished surfaces of pellets in Fig. 2. From the results in Fig. 3, $MgNb_2O_6$ can react with PbO and form almost pyrochlore-free PMN ceramics in a sintering profile which combines calcining level and sintering level. The pulverization procedure after $MgNb_2O_6$ and PbO calcining step in columbite route was omitted. Perovskite phase percentage and density of PMN ceramics sintered at 1250 °C/2 h with various $t_{850\ ^\circ C}$ are listed in Table 1. Density of PMN reaches 7.61 g/cm^3 as heated directly to 1250 °C without the 850 °C calcining level time, and decreases with increasing $t_{850\ ^\circ C}$. The pressed pellets of mixture of $MgNb_2O_6$ and PbO were calcined and became porous at 850 °C level time. These calcined pellets were then heated up to sintering temperature. Densification during the 1250 °C/2 h was not completed in the hard and porous pellets with long $t_{850\ ^\circ C}$. This could explain the results in Table 1.

From the earlier results, the 850 °C calcining level can be omitted in the sintering profile. The process to produce PMN ceramics with high perovskite phase content and high density was simplified as follows: the mixed $MgNb_2O_6$ and PbO powders were pressed to pellets and then heated to the sintering temperature directly. The XRD patterns of polished surfaces of PMN ceramics produced by simplified columbite route and sintered at

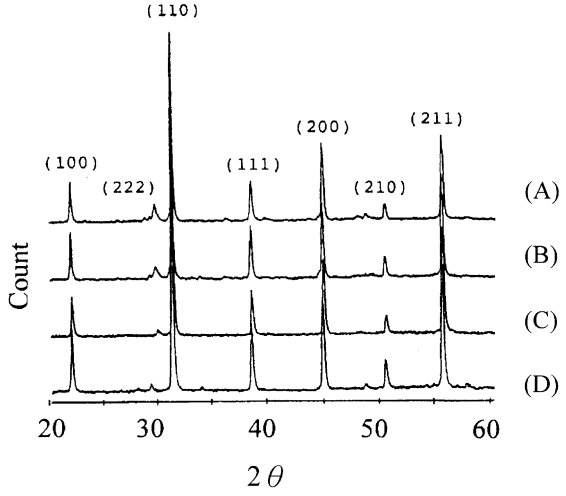

Fig. 2. The XRD patterns of as-fired surfaces of PMN ceramics sintered at 1250 °C/2 h with calcining level time $t_{850\ ^\circ C}$ = (A) 5, (B) 3, (C) 1 and (D) 0 h.

temperatures from 1100 to 1250 °C for 2 h are illustrated in Fig. 4. There is no peak (2 2 2) of pyrochlore phase at $2\theta = 29.2°$. Therefore, all pellets are pyrochlore-free. Good reproducibility for pure perovskite PMN ceramics at various sintering temperatures is proved in this simplified route. The second calcining step of $MgNb_2O_6$ and PbO in the columbite route of Swartz and Shrout is proved unnecessary in producing dense and pyrochlore-free PMN ceramics. Density of the PMN ceramics increases with sintering temperature and reaches 7.61g/cm^3 at 1250 °C as shown in Fig. 5. In the study of Swartz et al. [18], density of PMN ceramics decreased as sintering temperature increased from 1200 to 1300 °C. The influence of sintering temperature on density of PMN ceramics is quite different in columbite route and simplified columbite route in this study. In Fig. 6, microstructures of PMN ceramics produced by simplified columbite route show that the grain size increases with sintering temperature. There are sub-micrometer particles isolated in the perovskite PMN grains. These are MgO particles originating from the excess MgO that was added to eliminate the pyrochlore phase [22,23]. The maximum dielectric constant (K_{max}) at 1 kHz, temperature related to K_{max} (T_{max}) and average grain size of PMN ceramics sintered at various temperatures are listed in Table 2. K_{max} increases with sintering temperature and reaches 17,100 at 1250 °C. Grain size also increased with sintering temperature and was smaller than 4 μm at temperatures 1100 and 1150 °C. Grains larger than 4 μm were formed in PMN ceramics sintered at 1200 and 1250 °C. Grains of PMN ceramics produced in this study are smaller than those in the study of Swartz et al. [18]. Grains of 6 and 8.9 μm were obtained in PMN ceramics sintered at 1200 and 1270 °C/1 h by columbite route.

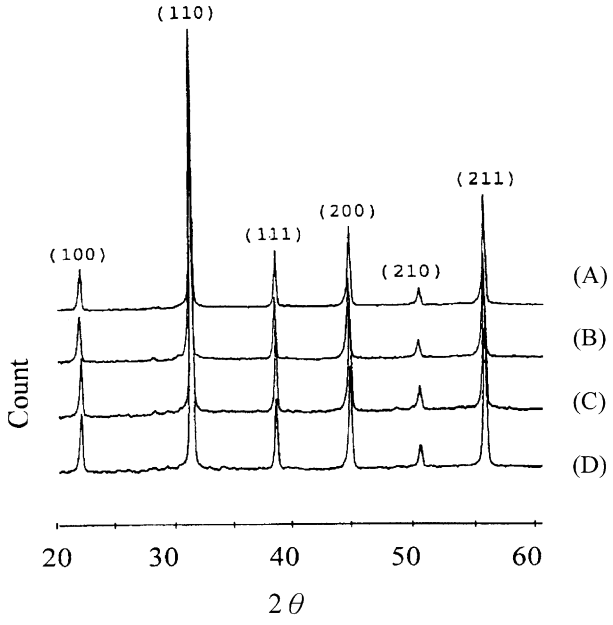

Fig. 3. The XRD patterns of polished surfaces of PMN ceramics sintered at 1250 °C/2 h with calcining level time $t_{850\,°C}$ = (A) 5, (B) 3, (C) 1 and (D) 0 h.

Table 1
Perovskite phase percentage and density of PMN ceramics sintered at 1250 °C/2 h with various $t_{850\,°C}$

$t_{850\,°C}$ (h)	0	1	3	5
Perov.%	100	99.8	99.6	99.6
ρ(g/cm^3)	7.61	7.18	6.96	6.72

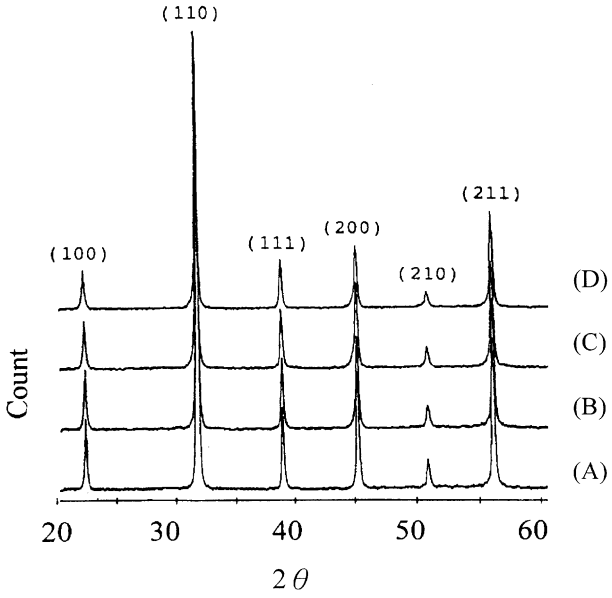

Fig. 4. The XRD patterns of polished surfaces of PMN ceramics produced by simplified columbite route and sintered at (A) 1100 °C, (B) 1150 °C, (C) 1200 °C and (D) 1250 °C for 2 h.

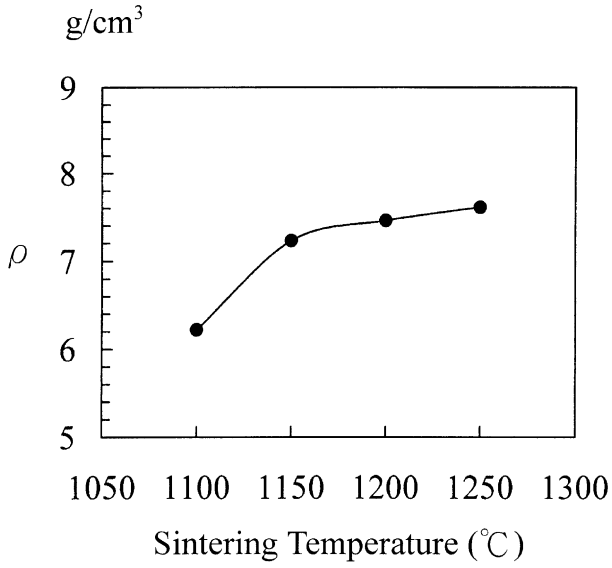

Fig. 5. Variation of density with sintering temperature for PMN ceramics produced by simplified columbite route.

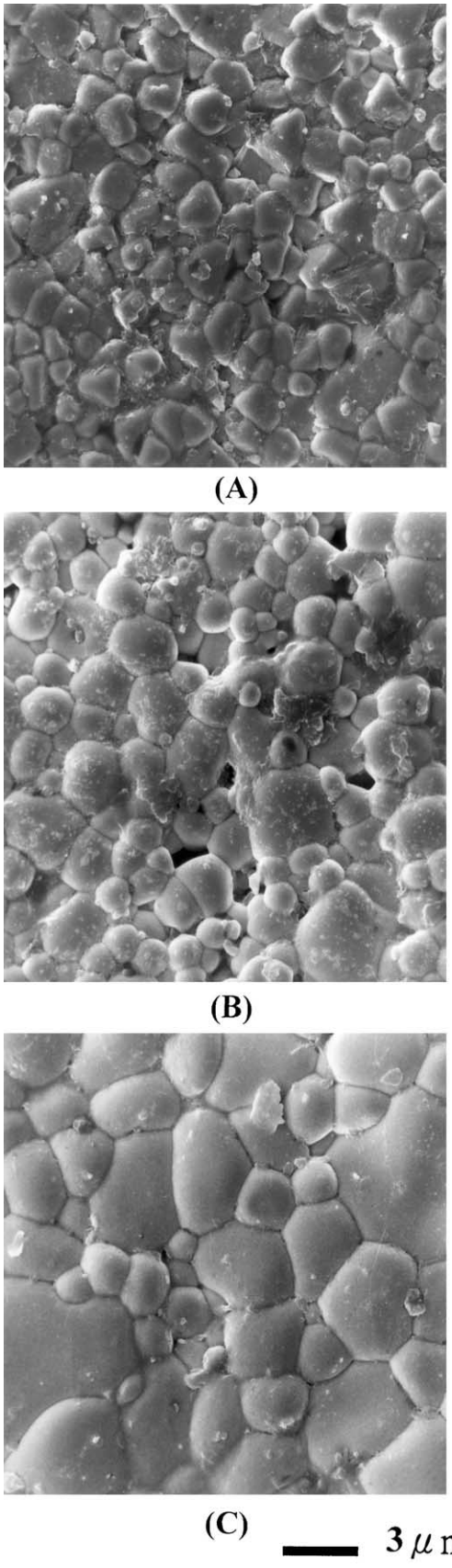

Fig. 6. SEM photographs of PMN ceramics sintered by simplified columbite route at (A) 1100 °C, (B) 1150 °C and (C) 1250 °C for 2 h.

Density and perovskite phase percentage of PMN ceramics sintered at 1250 °C/2 h with various heating rates are listed in Table 3. Pyrochlore-free PMN ceramics were produced by simplified columbite route with heating rates from 2 to 30 °C/min. Density increases obviously with heating rate from 2 to 10 °C/min. There are two possible reasons for these results. Landin and Schulze [23] reported that fast heating leads to densification in Zn-modified PMN due to increasing grain-boundary and lattice diffusion. This may be one reason why density of PMN ceramics sintered at 1250 °C/2 h increases with heating rate from 2 to 10 °C/min. The other reason is that the PbO volatilization decreases at fast heating rate and more PbO were remained to cause liquid phase sintering. Weight loss of PMN ceramics during sintering procedure can be thought of as a measure of the degree of PbO volatilization. This was analyzed by recording the weight before and after sintering procedure. Data for weight loss of samples sintered with various heating rates at 1250 °C/2 h are also listed in Table 3. Note that $MgNb_2O_6$ and PbO in the pellets is only mixture without calcining reaction. If the heating rate is too fast (15 and 30 °C/min), the reaction of $MgNb_2O_6$ and PbO will not be completed before 1250 °C sintering level. Meanwhile, the non-reacted PbO increases with the heating rate. Therefore, the volatilization of PbO increased during the sintering level time at faster heating rate. As a result, density decreased at heating rate 15 and 30 °C/min. The maximum dielectric constant (K_{max}) at 1 kHz of PMN ceramics sintered at 1250 °C/2h with various heating rates are shown in Fig. 7. K_{max} increases with heating rate from 2 to 10 °C/min and decreases at heating rate 15 and 30 °C/min. As sintered at same temperature and soak time, the effect of grain size on K_{max} is not obvious. Therefore,

Table 2
The maximum dielectric constant (K_{max}), temperature related to K_{max} (T_{max}) and average grain size of PMN ceramics sintered at various temperatures

Sintering temperature (°C)	K_{max} (1kHz)	T_{max} (°C)	Grain size(μm)
1100	13 500	−9	3.2
1150	16 000	−9	3.6
1200	16 500	−9	4.6
1250	17 100	−9	5.5

Table 3
Perovskite phase percentage, density, and weight loss of PMN ceramics sintered at 1250 °C/2 h with various heating rates

heating rate (°C/min)	2	5	10	15	30
Perov.%	100	100	100	100	100
ρ(g/cm^3)	6.67	7.19	7.61	7.52	7.46
Weight loss(%)	3.44	2.91	2.35	2.42	2.54

density affects K_{max} mostly in 100% perovskite PMN ceramics sintered with various heating rates.

The effect of soak time on density and perovskite phase percentage of PMN ceramics sintered at 1250 °C with a heating rate 10 °C/min are listed in Table 4. Pyrochlore-free PMN ceramics were produced by simplified columbite route with soak time from 1 to 5 h. Maximum density occurred at 2 h soak time. With 1 h soak time, it is not enough for densification. For longer soak time, the increased volatilization of PbO resulted in decreased density. Data for weight loss of PMN samples sintered for various soak times at 1250 °C with a heating rate 10 °C/min are listed in Table 4. The maximum dielectric constant (K_{max}) at 1 kHz of PMN ceramics sintered for various soak times at 1250 °C with a rate 10 °C/min are shown in Fig. 8. K_{max} increases with soak time from 1 to 2 h and decreases at 3 and 5 h. As sintered at same temperature and heating rate, the effect of grain size on K_{max} is not obvious. Therefore, density affects K_{max} mostly in 100% perovskite PMN ceramics sintered with various soak times.

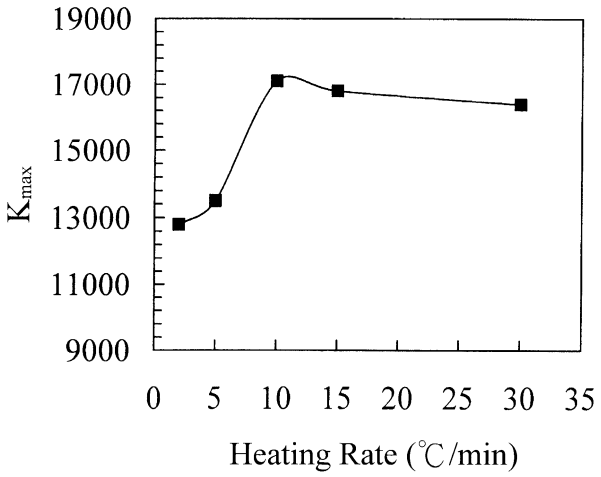

Fig. 7. Variation of K_{max} at 1 kHz with heating rate for PMN ceramics sintered at 1250 °C/2 h.

Table 4
Perovskite phase percentage, density, and weight loss of PMN ceramics sintered at 1250 °C with a rate 10 °C/min for various soak times

Soak time (h)	1	2	3	5
Perov.%	100	100	100	100
ρ (g/cm^3)	7.25	7.61	7.42	7.39
Weight loss (%)	2.23	2.35	2.46	2.67

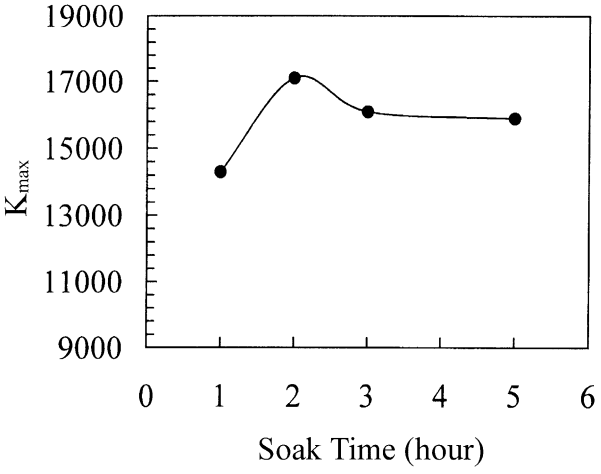

Fig. 8. Variation of K_{max} at 1 kHz with soak time for PMN ceramics sintered at 1250 °C.

4. Conclusions

The second calcining step to react $MgNb_2O_6$ with PbO in the columbite route can be omitted. Without calcining, the pressed pellets of mixed $MgNb_2O_6$ and PbO were sintered to $Pb(Mg_{1/3}Nb_{2/3})O_3$ ceramics. PMN ceramics produced by this simplified columbite route are 100% perovskite phase at 1100–1250 °C sintering temperatures, 1–5 h soak times, and 2–30 °C/min heating rates. $K_{max} > 17\,000$ at 1 kHz was obtained.

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