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Composition design rule for energy harvesting devices in piezoelectric perovskite ceramics

Cheol-Woo Ahn*, Jong-Jin Choi, Jungho Ryu, Woon-Ha Yoon, Byung-Dong Hahn, Jong-Woo Kim, Joon-Hwan Choi, Dong-Soo Park

Functional Ceramics Department, Powder & Ceramics Division, Korea Institute of Materials Science (KIMS), Changwon, Gyeongnam 641-831, Republic of Korea

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ABSTRACT

A composition design rule is proposed for energy harvesting devices in piezoelectric perovskite ceramics. For energy harvesting devices, a piezoelectric voltage coefficient (g_{33}) as well as a piezoelectric distortion constant (d_{33}) must be considered, because a high $d_{33}xg_{33}$ value indicates a high energy density. It is suggested that a large $d_{33}xg_{33}$ value can be obtained by tuning the magnitude of atomic weight ratio between A and B site ($R_w=W_A/W_B$) in ABO_3 perovskite ceramics in this study. In addition, the various compositions were prepared in order to confirm the effect of crystal structure and R_W on $d_{33}xg_{33}$ value in piezoelectric perovskite materials.

$Pb(Zr,Ti)O_3$ (PZT)-based ceramics have been studied for long time owing to their excellent piezoelectric performance in morphotropic phase boundary (MPB) region [1–6]. In addition, recently, lead-free piezoelectric ceramics [such as $(Bi,Na)NbO_3$ (BNT) and $(K,Na)NbO_3$ (KNN) based solid solutions etc.] have received the considerable attention to replace PZT-based materials owing to the global interest about environment [7–12,14–21].

In general, in piezoelectric ceramics, it has been well-known that they have to show the coexistence of several phases for high piezoelectric response. Although this factor has been well-studied and can clarify the mechanism about high piezoelectric response in piezoelectric ceramics, that is limited to the story after the development of the compositions which show good piezoelectric response. Before the development, it cannot sufficiently assist the researchers who try to design a definitely new composition which nobody has studied. Hence, recently, we have proposed a rule for a high piezoelectric distortion constant (d_{33}) in the perovskite oxides [12]. It is "High d_{33} values can be obtained by tuning the magnitude of atomic weight ratio between A and B sites ($R_w=W_A/W_B$) in ABO_3 perovskite ceramics". In particular, it has been reported that a forbidden zone, which shows no piezoelectric response, is found at the range of $0.5 \le R_W \le 2.0$. However, it was limited to a d_{33} value, although a high piezoelectric voltage coefficient (g_{33}) is also required in an energy harvesting device because a high $d_{33}xg_{33}$ value indicates a high energy density [13]. Therefore, the variation of $d_{33}xg_{33}$ value with R_W was investigated in this study.

Table 1 lists the R_W, d_{33}, dielectric constant ($\varepsilon^T_{33}/\varepsilon_0$), g_{33}, and $d_{33}xg_{33}$ of piezoelectric perovskite compositions. It can be seen in this table that there is a specific trend in the variation of d_{33} with R_W. In PZT-based materials, R_W and d_{33} values are high (>2.5 and 157–740 pC/N respectively) except PT. On the contrary, BNT-based materials show the relatively low R_W and d_{33} values (<2.5 and 111–191 pC/N respectively). PT and BNT ceramics exhibit lower d_{33} values compared with the others, because they have one phase (PT: tetragonal phase, BNT: rhombohedral phase) while the others show the coexistence of tetragonal and rhombohedral [or pseudo-cubic at $(0.59-x)PbZrO_3$–$xPbTiO_3$–$0.41Pb(Ni_{1/3}Nb_{2/3})O_3$ (PZT-PNN)] phases. Hence, their dielectric and piezoelectric properties must be compared at the compositions which exhibit the coexistence of tetragonal and rhombohedral (or pseudo-cubic) phases as shown in Fig. 1.

Fig. 1 indicates the variations of dielectric and piezoelectric properties with R_W in piezoelectric perovskite ceramics which show the coexistence of the two phases (PZT-based and BNT-based materials: tetragonal and rhombohedral phases, KNN-based materials: tetragonal and orthorhombic phases). In PZT-PNN, the phases are tetragonal and pseudo-cubic structures. As seen in Fig. 1(a), the trend of d_{33} and $\varepsilon^T_{33}/\varepsilon_0$ are quite similar in A-site-heavy materials. A-site-heavy materials show high d_{33} and $\varepsilon^T_{33}/\varepsilon_0$ (higher than approximately 500 pC/N and 3000), when R_W is higher than 2.7. However, g_{33} is not varied significantly. It is because the trend of d_{33} and $\varepsilon^T_{33}/\varepsilon_0$ are quite similar in A-site-heavy materials ($g_{33}=d_{33}/\varepsilon^T_{33}$). Consequently, the $d_{33}xg_{33}$ value is dependent on d_{33} in A-site-heavy materials, because the variation

* Corresponding author. Tel.: +82 55 280 3406.
E-mail address: cheoruahn@kims.re.kr (C.-W. Ahn).

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Table 1
R_W and dielectric/piezoelectric properties of piezoelectric perovskite compositions.

Abbreviation	Composition	R_W (or $1/R_W$)	d_{33} (pC/N)	$\varepsilon_{33}^T/\varepsilon_0$	g_{33} (10^{-3} Vm/N)	$d_{33}xg_{33}$ (10^{-15} m^2/N)
PT[1]	$PbTiO_3$	4.33	51	170	34	1734
PZT[2]	$Pb(Zr,Ti)O_3$	2.94	220	800	31	6820
Na-doped PZT[3]	$(Na,Pb)(Zr,Ti)O_3$	2.55	157	725	24	3768
La-doped PZT[4]	$(La,Pb)(Zr,Ti)O_3$	2.7	406	3480	13	5278
PZT-PZN[5]	$0.6Pb(Zr_{0.48}Ti_{0.52})O_3$-$0.4Pb(Zn_{1/3}Nb_{2/3})O_3$	2.74	460	1770	29	13,340
La, Ba, Sr, and Nb-doped PZT[6]	$(La,Ba,Sr,Pb)(Zr,Ti,Nb)O_3$	2.77	538	2377	26	13,988
PZT-PNN	*$0.24PbZrO_3$-$0.35PbTiO_3$-$0.41Pb(Ni_{1/3}Nb_{2/3})O_3$*	*2.88*	*460*	*2900*	*18*	*8241*
(0.59-x)PZ-xPT-0.41PNN	*$0.23PbZrO_3$-$0.36PbTiO_3$-$0.41Pb(Ni_{1/3}Nb_{2/3})O_3$*	*2.89*	*740*	*4400*	*19*	*14,056*
	$0.22PbZrO_3$-$0.37PbTiO_3$-$0.41Pb(Ni_{1/3}Nb_{2/3})O_3$	*2.91*	*610*	*4200*	*16*	*10,006*
PMN-PT[2]	$0.6Pb(Mg_{1/3}Nb_{2/3})O_3$-$0.4PbTiO_3$	3.39	690	5000	16	11,040
BNT[7]	$(Bi_{1/2}Na_{1/2})TiO_3$	2.42	66	300	25	1650
BNBT-KNN[8]	$0.94(Bi_{1/2}Na_{1/2})TiO_3$- $0.05BaTiO_3$-$0.01(K_{0.5}Na_{0.5})NbO_3$	2.4	118	600	22	2596
BNT-BT-CT	*$0.94(Bi_{1/2}Na_{1/2})TiO_3$- $0.05BaTiO_3$-$0.01CaTiO_3$*	*2.43*	*111*	*637*	*20*	*2220*
BKT-KNN[9]	$0.97Bi_{0.5}K_{0.5}TiO_3$–$0.03K_{0.5}Na_{0.5}NbO_3$	2.46	129	1500	10	1290
BNKT[10]	$(Bi_{1/2}Na_{1/2})TiO_3$-$(Bi_{1/2}K_{1/2})TiO_3$	2.46	151	1030	17	2567
BNKT-BT[10]	$(Bi_{1/2}Na_{1/2})TiO_3$-$(Bi_{1/2}K_{1/2})TiO_3$-$BaTiO_3$	2.46	191	1141	19	3629
KNN	*$(K,Na)NbO_3$*	*2.99*	*93*	*456*	*23*	*2139*
KNN-BT[15–16]	$(K_{0.5}Na_{0.5})NbO_3$-$BaTiO_3$	2.49	225	1058	24	5400
KNN-ST[17]	$(K_{0.5}Na_{0.5})NbO_3$-$SrTiO_3$	2.68	220	1447	17	3740
KNN-CT[18]	$(K_{0.5}Na_{0.5})NbO_3$-$CaTiO_3$	2.88	190	740	29	5510
KNLN-BT	*$0.99(K_{0.48}Na_{0.48}Li_{0.04})NbO_3$-$0.01BaTiO_3$*	*2.97*	*206*	*653*	*36*	*7416*
KNN-LN[19]	$(K_{0.5}Na_{0.5})NbO_3$-$LiNbO_3$	3.14	235	500	53	12,455
KNN-LNTS[20–21]	$(K_{0.44}Na_{0.52}Li_{0.04})(Nb_{0.86}Ta_{0.10}Sb_{0.04})O_3$	3.49	308	1009	34	10,472

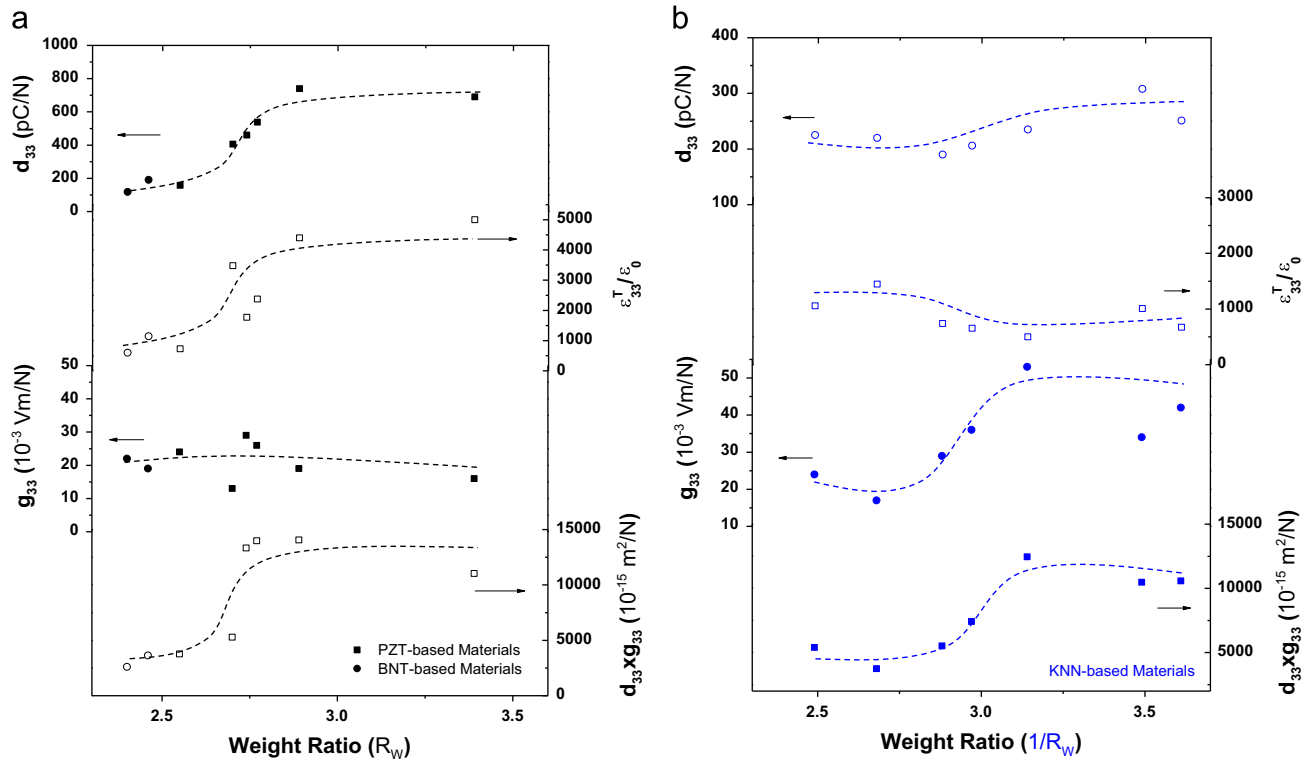

Fig. 1. Variation of dielectric and piezoelectric properties with R_W (or $1/R_W$) in piezoelectric perovskite ceramics: (a) A-site-heavy and (b) B-site-heavy materials.

of g_{33} is not significant. On the contrary, in B-site-heavy materials, the variation of d_{33} and $\varepsilon_{33}^T/\varepsilon_0$ is not significant but they show the opposite trend each other as seen in Fig. 1(b). Because of this trend, the variation of g_{33} is considerable. Therefore, the $d_{33}xg_{33}$ values are dependent on the g_{33} in B-site-heavy materials which are KNN-based materials. It was not identified in this study why A-site-heavy and B-site-heavy materials show different trends in $\varepsilon_{33}^T/\varepsilon_0$ as seen in Fig. 1. It is interesting that the compositions had better be designed to have high R_W in order to obtain high $d_{33}xg_{33}$ values in piezoelectric perovskite ceramics. On the contrary, at the range of $0.5 \le R_W \le 2.0$, the $d_{33}xg_{33}$ value cannot be observed because the perovskite materials do not show the piezoelectric response at the forbidden zone.[12] There are several related questions which were not identified in this study such as: "How is weight ratio related to phase transitions or polymorphism?", "How is weight ratio related to intrinsic piezoelectric response?", and "What kind of multiple phases is good for energy harvesting devices?". The answers to these questions are under investigation.