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# A generalized rule for large piezoelectric response in perovskite oxide ceramics and its application for design of lead-free compositions

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We present a general rule for the perovskite oxide ceramics: “A large piezoelectric constant in  $ABO_3$  perovskite ceramics can be obtained by tuning the weight ratio of  $A$  and  $B$  sites,  $W_A/W_B$  or  $W_B/W_A$ , to 3. Piezoelectric constant decreases significantly when  $W_A/W_B$  or  $W_B/W_A$  is in the range of 0.5–2.0, termed as forbidden zone.” A comparative analysis was conducted for broad range of materials demonstrating the applicability of proposed rule. Further based on this rule optimized compositions in  $BaTiO_3$  and alkali niobate based systems were developed. Polycrystalline ceramics in modified  $BaTiO_3$  system were found to exhibit longitudinal piezoelectric coefficient ( $d_{33}$ ) of 330 pC/N, while alkali niobate ceramics showed  $d_{33}$  of 294 pC/N. © 2009 American Institute of Physics. [DOI: 10.1063/1.3142442]

## I. INTRODUCTION

Lead-free piezoelectric ceramics have been investigated for over a period of 40 years since the discovery of  $Pb(Zr,Ti)O_3$  (PZT) which is currently the state-of-the-art material. However, there is no known lead-free piezoelectric composition which can match the properties of PZT over the wide range of temperature. Modified compositions and solid solutions in the systems  $(Bi,Na)TiO_3$  (BNT),  $(Bi,K)TiO_3$  (BKT),  $BaTiO_3$  (BT), and  $(K,Na)NbO_3$  (KNN) have received considerable attention as the potential lead-free candidates but reported results are still inferior to that of PZT.<sup>1–14</sup> Design of new lead-free composition is challenging as formulations derived using structure maps, tolerance factor approach, electronegativity factor, and *ab initio* calculations have not resulted in any promising material. Naturally, the question that comes to mind is “how to design a lead-free composition and predict its approximate piezoelectric response?” Using perovskite formulation of  $A^{+2}B^{+4}O_3$  (as in  $SrTiO_3$ ), there can be many elemental variations on  $A$  and  $B$  sites given as  $(A_{1/2}^{+1}A_{1/2}^{+3})B^{+4}O_3$ ,  $A^{+1}B^{+5}O_3$ ,  $A^{+3}B^{+3}O_3$ ,  $A^{+3}(B_{2/3}^{+2}B_{1/3}^{+5})O_3$ ,  $A^{+3}(B_{1/2}^{+2}B_{1/2}^{+4})O_3$ ,  $(A_{1/2}^{+1}A_{1/2}^{+3}) \times (B_{1/2}^{+3}B_{1/2}^{+5})O_3$ ,  $A^{+1}(B_{1/2}^{+4}B_{1/2}^{+6})O_3$ ,  $A^{+3}(B_{3/5}^{+1}B_{2/5}^{+6})O_3$ ,  $A^{+2}(B_{1/4}^{+1}B_{3/4}^{+5})O_3$ ,  $A^{+1}(B_{1/3}^{+3}B_{2/3}^{+6})O_3$ , etc. However, without a guiding rule, narrowing the formulation that exhibits high piezoelectric response is a tedious task. We propose a simple but powerful rule to design piezoelectric compositions and predict their approximate electromechanical response. In doing so, we fully understand that piezoelectric response is dependent on multiple variables such as grain size, domain size, density, morphotropy, and defect structure. These factors have been well studied and can be used to further modify the magnitude of piezoelectric response once a proper formulation has been identified. It should be noted

here that these factors do not provide any guidance on the selection or design of a piezoelectric composition but can be only used to tailor the properties of known compositions.

## II. RELATIONSHIP BETWEEN WEIGHT RATIO AND PIEZOELECTRIC RESPONSE IN PEROVSKITES

Table I lists the tolerance factor ( $F_t$ ), atomic weight ratio of  $A$  to  $B$  sites ( $R_w = W_A/W_B$ ), and  $d_{33}$  for the commonly used piezoelectric perovskite compositions. It can be seen in this table that the magnitude of  $F_t$  is similar for most of the compositions; however, the atomic weight ratio of  $A$  site to  $B$  site ( $R_w = W_A/W_B$ ) was different and there is specific trend in the variation of  $d_{33}$  with  $R_w$  (or  $1/R_w$ ). This observation leads us to a generalized rule for achieving high piezoelectric response in oxide ceramics. It can be further noticed in this table that  $1/R_w$  for KNN ceramics (for Na/K ratio of 0.5) is quite similar to  $R_w$  for PZT ceramics at MPB composition. This is interesting as both of these compositions exhibit high piezoelectric response. All the piezoelectric compositions show large response when  $R_w$  for  $A$ -site heavy perovskites and  $1/R_w$  for  $B$ -site heavy perovskites was higher than 2.0.

Figure 1(a) shows the variation of  $d_{33}$  as a function of  $R_w$  for chemical formulations listed in Table I. It can be immediately noticed from Fig. 1(a) that there exists a forbidden zone in which the magnitude of piezoelectric constant remains significantly low. This zone is located in the range  $0.5 \leq R_w \leq 2.0$ , which implies that one of the cations in perovskite lattice must be approximately twice heavier than the other. This trend is further illustrated in Fig. 1(b) which shows the variation of  $d_{33}$  for various compositions in the same system. Lead-based systems exhibiting high piezoelectric response have heavier Pb-ion on  $A$ -site and lighter ion on  $B$ -site (such as Mg, Ti, Zn, Zr, etc.). In lead-free systems such as KNN, high piezoelectric response is obtained by

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TABLE I.  $R_W$  (or  $1/R_W$ ),  $F_t$ , and  $d_{33}$  in perovskite piezoelectric ceramics.

Mark	Abbreviation	Composition	$1/R_W$	$F_t$	$d_{33}$ (pC/N)
	KNN <sup>a</sup>	(K, Na)NbO <sub>3</sub>	2.99	1.01	97
T1	KNN-BT <sup>b</sup>	(K <sub>0.5</sub> Na <sub>0.5</sub> )NbO <sub>3</sub> -BaTiO <sub>3</sub>	2.49	1.01	225
T2	KNN-ST <sup>c</sup>	(K <sub>0.5</sub> Na <sub>0.5</sub> )NbO <sub>3</sub> -SrTiO <sub>3</sub>	2.68	1.01	220
T3	KNN-CT <sup>d</sup>	(K <sub>0.5</sub> Na <sub>0.5</sub> )NbO <sub>3</sub> -CaTiO <sub>3</sub>	2.88	1.01	241
L1	KNN-LN <sup>e</sup>	(K <sub>0.48</sub> Na <sub>0.535</sub> )NbO <sub>3</sub> -LiNbO <sub>3</sub>	3.13	1.00	314
L2	KNN-LS <sup>f</sup>	(K <sub>0.5</sub> Na <sub>0.5</sub> )NbO <sub>3</sub> -LiSbO <sub>3</sub>	3.17	1.00	286
L3	KNN-LNTS <sup>g</sup>	(K <sub>0.44</sub> Na <sub>0.52</sub> Li <sub>0.04</sub> )(Nb <sub>0.86</sub> Ta <sub>0.10</sub> Sb <sub>0.04</sub> )O <sub>3</sub>	3.49	1.00	308
L4	KNLNS-BT	0.99(K <sub>0.48</sub> Na <sub>0.48</sub> Li <sub>0.04</sub> )(Nb <sub>0.98</sub> Sb <sub>0.02</sub> )O <sub>3</sub> -0.01BaTiO <sub>3</sub>	2.99	1.00	294

Mark	Abbreviation	Composition	$R_W$	$F_t$	$d_{33}$ (pC/N)
	PT <sup>h</sup>	PbTiO <sub>3</sub>	4.33	1.02	51
	PZT <sup>i</sup>	Pb(Zr, Ti)O <sub>3</sub>	2.94	0.99	223
P1	Na-doped PZT <sup>j</sup>	(Na, Pb)(Zr, Ti)O <sub>3</sub>	2.55	0.99	157
P2	La, Li, Na, and K-doped PZT <sup>k</sup>	(La, Li, Na, K, Pb)(Zr, Ti)O <sub>3</sub>	2.65	0.98	200
P3	La-doped PZT <sup>k</sup>	(La, Pb)(Zr, Ti)O <sub>3</sub>	2.70	0.99	406
P4	La, Ba, Sr, and Nb-doped PZT <sup>k</sup>	(La, Ba, Sr, Pb)(Zr, Ti, Nb)O <sub>3</sub>	2.77	0.99	538
	PZT-PZN <sup>l</sup>	0.6Pb(Zr <sub>0.48</sub> Ti <sub>0.52</sub> )O <sub>3</sub> -0.4Pb(Zn <sub>1/3</sub> Nb <sub>2/3</sub> )O <sub>3</sub>	2.74	0.99	460
P5	PZT-PNN <sup>m</sup>	0.59Pb(Zr <sub>0.39</sub> Ti <sub>0.61</sub> )O <sub>3</sub> -0.41Pb(Ni <sub>1/3</sub> Nb <sub>2/3</sub> )O <sub>3</sub>	2.89	1.00	740
P6	PMN-PT <sup>i</sup>	0.6Pb(Mg <sub>1/3</sub> Nb <sub>2/3</sub> )O <sub>3</sub> -0.4PbTiO <sub>3</sub>	3.39	1.00	690
	BT <sup>i</sup>	BaTiO <sub>3</sub>	2.87	1.06	190
BT1	BT-BCuN	0.975BaTiO <sub>3</sub> -0.025Ba(Cu <sub>1/3</sub> Nb <sub>2/3</sub> )O <sub>3</sub>	2.82	1.06	330
	BCuN	Ba(Cu <sub>1/3</sub> Nb <sub>2/3</sub> )O <sub>3</sub>	1.65	1.03	0
	ST	SrTiO <sub>3</sub>	1.83	1.00	0
	CT	CaTiO <sub>3</sub>	1.19	0.97	0
	BNT <sup>n</sup>	(Bi <sub>1/2</sub> Na <sub>1/2</sub> )TiO <sub>3</sub>	2.42	0.99	66
	BNKT <sup>o</sup>	(Bi <sub>1/2</sub> Na <sub>1/2</sub> )TiO <sub>3</sub> -(Bi <sub>1/2</sub> K <sub>1/2</sub> )TiO <sub>3</sub>	2.46	0.99	151
	BNKT-BT <sup>o</sup>	(Bi <sub>1/2</sub> Na <sub>1/2</sub> )TiO <sub>3</sub> -(Bi <sub>1/2</sub> K <sub>1/2</sub> )TiO <sub>3</sub> -BaTiO <sub>3</sub>	2.46	1.00	191
	BNBT-KNN <sup>p</sup>	(Bi <sub>1/2</sub> Na <sub>1/2</sub> )TiO <sub>3</sub> -BaTiO <sub>3</sub> -(K <sub>0.5</sub> Na <sub>0.5</sub> )NbO <sub>3</sub>	2.24	0.99	140

<sup>a</sup>Reference 10.<sup>b</sup>References 3 and 6.<sup>c</sup>Reference 5.<sup>d</sup>Reference 12.<sup>e</sup>References 10 and 19.<sup>f</sup>References 14 and 20.<sup>g</sup>References 1 and 11.<sup>h</sup>Reference 21.<sup>i</sup>Reference 22.<sup>j</sup>Reference 23.<sup>k</sup>Reference 24.<sup>l</sup>Reference 25.<sup>m</sup>Reference 26.<sup>n</sup>Reference 27.<sup>o</sup>Reference 28.<sup>p</sup>Reference 29.

selecting heavier *B*-site ion (such as Nb and Ta) and lighter *A*-site ion (such as Li). The materials with mixed distribution of heavier and lighter ions such as BNT have averaging effect. The variation of  $d_{33}$  with  $R_W$  in PZT-based ceramics is shown in Fig. 1(c). A large  $d_{33}$  magnitude in the range of 600 pC/N was observed when  $R_W$  was higher than 2.89. A similar trend was found for lead-free materials as shown in Fig. 1(d), where excellent  $d_{33}$  was observed for compositions in the range of  $1/R_W \geq 2.9$ . It should be mentioned here that additional factors such as domain size and domain orientation were not considered but their effect is already included in the chemical formulations of the compositions listed in Table I. The variation of  $d_{33}$  by phase, microstructure, and weight

ratio is shown for compositions P5 and BT1 in Fig. 1(c) and L4 in Fig. 1(d).

In order to compare the region on left and right sides of forbidden zone, Figs. 1(c) and 1(d) were merged together as shown in Fig. 1(e). For the region on left side, the data are plotted as  $d_{33}$  versus  $1/R_W$ , while for region on the right side, the data are plotted as  $d_{33}$  versus  $R_W$ . This figure clearly illustrates the unified nature of correlation between the weight ratio of *A*- and *B*-site atoms in perovskite lattice. A large  $d_{33}$  response is obtained when  $R_W$  (or  $1/R_W$ ) is higher than 2.9 in perovskite piezoelectric ceramics.

Thus, a general rule for perovskite oxide ceramics can be proposed as following: "A large piezoelectric constant in

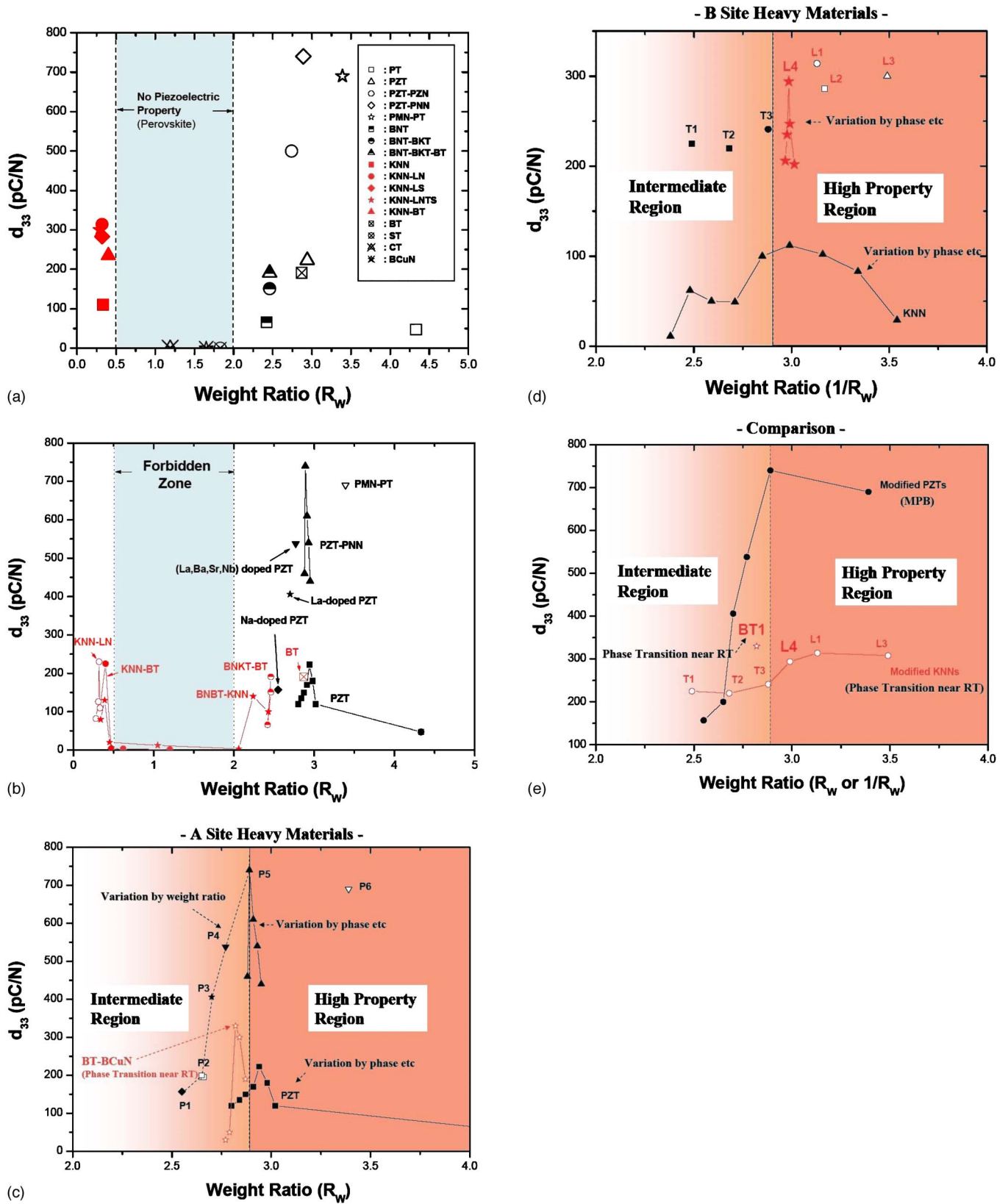


FIG. 1. (Color online) Variation of  $d_{33}$  as a function of  $R_w$  or  $1/R_w$  in perovskite piezoelectric ceramics: (a) MPB compositions in PZT and BNT based compositions, two-phase-polymorphic compositions in KNN and BT based ceramics, and pure perovskite ceramics; (b) various compositions in perovskite piezoelectric ceramics; (c) A-site heavy region; (d) B-site heavy region; (e) merged graph of (c) and (d) (Refs. 1–15 and 18–29). Abbreviations are indicated in Table I.

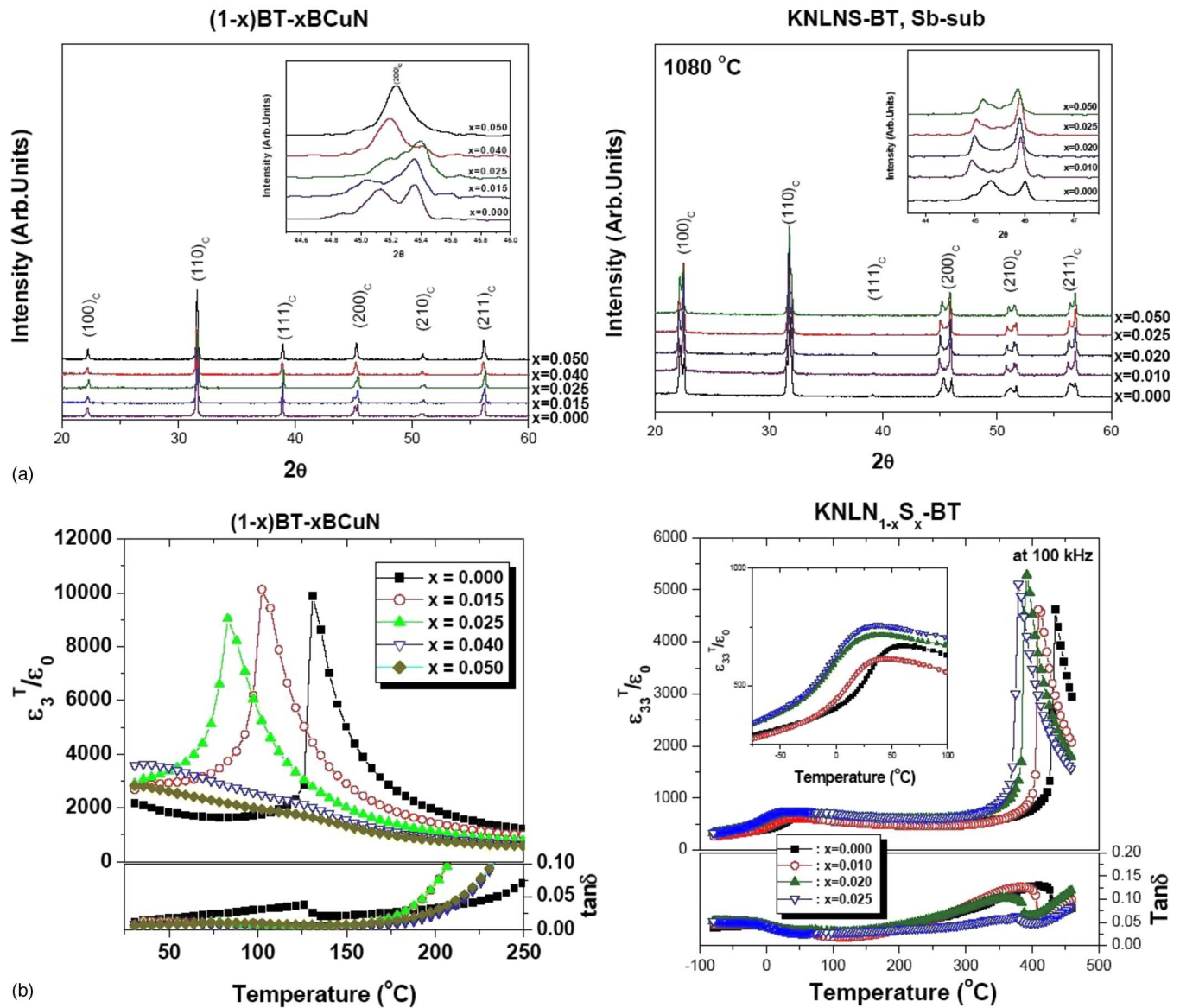


FIG. 2. (Color online) (a) XRD patterns and (b) dielectric constant as a function of temperature for  $(1-x)\text{BT}-x\text{BCuN}$  and  $0.99\text{KNLN}_{1-x}\text{S}_x-0.01\text{BT}$  ceramics.

$\text{ABO}_3$  perovskite ceramics can be obtained by tuning  $W_A/W_B$  or  $W_B/W_A$  to 3. Piezoelectric constant decreases significantly when  $W_A/W_B$  or  $W_B/W_A$  is in the range of 0.5–2.0 termed as forbidden zone.”

Our experimental observations in Fig. 1 have empirical resemblance to Birch’s law, commonly used in geophysical research that states “compressional wave velocity ( $V_p$ ) is linearly related to mean atomic weight and density” as follows:<sup>16</sup>

$$V_p = aM + b\rho, \quad (1)$$

where  $M$  is the mean atomic weight and  $\rho$  is the density. Using this relationship and noting that elastic stiffness constant is related to velocity of sound which in turn is related to piezoelectric coefficient, an empirical factor for piezoelectric coefficient outside of the “forbidden zone” can be written as

$$d \propto \frac{1}{1 + n/R_w} \quad (\text{PZT based}),$$

$$\propto \frac{1}{mR_w + 1} \quad (\text{KNN based}), \quad (2)$$

where  $m$  and  $n$  are the system dependent constants.

Recently, Yamashita *et al.*<sup>17</sup> hypothesized that by adjusting the difference in atomic weight of  $A$  and  $B$  sites ( $W_A - W_B$ ) in compositions given by formula  $\text{Pb}(B'B'')\text{O}_3 - \text{PbTiO}_3$ , a large electromechanical coupling factor ( $k_p$ ) can be obtained. However, this empirical observation did not fit for piezoelectric constant in whole range of ceramics shown in Table I. Yan *et al.*<sup>18</sup> proposed a dimensionless number given as  $F(w) = |M| + |R| + 100|X|$ , where  $M$  is atomic weight,  $R$  is ionic size, and  $X$  is electronegativity, for variation of coupling factor. It was shown for BNT ceramics that large magnitude of  $F(w)$  corresponds to large magnitude of coupling factors. However, this correspondence is very specific to a selected set of material systems with proper density, phase, and microstructure. In comparison to these prior stud-

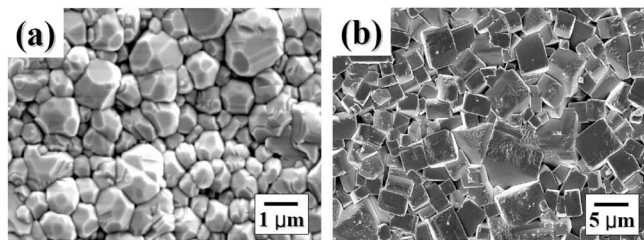


FIG. 3. SEM images of BT1 and L4 ceramics sintered at 1350 and 1080 °C for 2 h, respectively.

ies, the results of Fig. 1 conclusively demonstrate the change in piezoelectric constant with  $R_W$  for wide range of ceramic systems.

### III. EXPERIMENTAL VERIFICATION

Using the above mentioned rule, we attempted to design lead-free compositions in KNN and BT systems which exhibit high piezoelectric coefficient. In order to design BT based ceramics, lighter ions on  $B$  site such as Cu and Nb were selected to adjust the  $R_W$ . In the case of KNN based ceramics, lighter Li ion was selected for  $A$  site, Sb for  $B$  site, and solid solution with BT was formed in order to adjust the atomic weight ratio as  $2.9 < 1/R_W < 3.0$ . The phase and microstructures of synthesized modified-BT and KNN compositions are shown in Figs. 2 and 3. Ceramics were synthesized by mixed oxide route and calcination/sintering temperatures were 950/1080 °C for  $0.99(\text{K}_{0.48}\text{Na}_{0.48}\text{Li}_{0.04})(\text{Nb}_{1-x}\text{Sb}_x)\text{O}_3 - 0.01\text{BaTiO}_3$  ( $0.99\text{KNNLN}_{1-x}\text{S}_x - 0.01\text{BT}$ ) and 950/1350 °C for  $(1-x)\text{BT} - x\text{BCuN}$ . It can be seen in Fig. 2(a) that  $(1-x)\text{BT} - x\text{BCuN}$  ceramics exhibited coexistence of tetragonal/cubic phases while  $0.99\text{KNNLN}_{1-x}\text{S}_x - 0.01\text{BT}$  ceramics showed the coexistence of orthorhombic/tetragonal phases at RT. In the case of  $(1-x)\text{BT} - x\text{BCuN}$  ceramics, the phase variation from tetragonal to cubic was found to occur in the range of  $x=0.025$  and  $x=0.040$ . In the case of  $0.99\text{KNNLN}_{1-x}\text{S}_x - 0.01\text{BT}$  ceramics, the coexistence of orthorhombic and tetragonal phases was observed for entire range of Sb doping investigated in this study. The orthorhombic-rich phase was found to occur at  $x=0.000$  and all the other compositions exhibited tetragonal-rich phases as shown in Fig. 2(a). The optimized compositions, BT1 and L4, exhibited phase transition near RT as shown in Figs. 2(a) and 2(b). Figure 3 shows that these ceramics had dense microstructure and large grain size ( $\sim 1 \mu\text{m}$  for BT1 and  $> 3 \mu\text{m}$  for L4).

Our compositions, BT1 and L4, had  $R_W$  of 2.82 and  $1/R_W$  of 2.99, respectively, and were found to exhibit excellent  $d_{33}$  magnitudes of 330 and 294 pC/N as shown in Fig. 1(e). Interestingly, BT1 ( $A$ -site heavier region) had higher  $d_{33}$  magnitude than L4 ( $B$ -site heavier region) although both are located in intermediate region of Fig. 1(e). KNN based ceramics exhibited  $d_{33}$  of 240 pC/N in the region similar to that of BT based ceramics ( $1/R_W \sim 2.8$ ). The  $d_{33}$  magnitude of BT1 is lower than that of PZT based ceramics which are located in similar weight ratio range. This can be explained by taking into account the existence of MPB in PZT based ceramics. There are several related questions which were not answered in this study such as: “How is weight ratio related

to phase transitions or polymorphism?” and “How is weight ratio related to intrinsic piezoelectric response?.” The answers to these questions are under investigation and will be reported elsewhere. However, one can easily apply the rule presented here to tune the piezoelectric composition with weight ratio higher than 3 without considering any additional factors and expect to achieve high piezoelectric response.

### IV. SUMMARY

In summary, we demonstrate a generalized rule for designing perovskite piezoelectric ceramic compositions for achieving high response. The rule is given as: “a large piezoelectric constant in  $\text{ABO}_3$  perovskite ceramics can be obtained by tuning the weight ratio of  $A$  and  $B$  sites,  $W_A/W_B$  or  $W_B/W_A$ , to 3. Piezoelectric constant decreases significantly when  $W_A/W_B$  or  $W_B/W_A$  is in the range of 0.5–2.0, termed as forbidden zone.” Using this rule, modified BT and KNN based compositions were designed which were found to exhibit high  $d_{33}$  of 330 and 294 pC/N, respectively.

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