

Molecular orbital calculation on lead-free perovskite dielectrics for effective utilization of ubiquitous alkaline and alkaline-earth metals

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Abstract

Effective ionic charges of lead-free perovskite dielectric complex compounds have been investigated with molecular orbital calculation. The base model is of a doubled perovskite cluster; it consists of octahedral oxygen cages with a transition metal ion of titanium, niobium or zirconium located at each of their centers, and alkali and/or alkaline earth metal ions located at a body center of the cluster, and also the corners, edge centers, face centers. The results show significant covalent bonds between the transition metals and the oxygens, and also the alkali metal, especially sodium and the oxygen, while quite weak covalency of alkaline earth metals. The calculation has also been done with replacing some of the oxygens with chlorines or with fluorine, and the results show that this replacement enhances covalency of the transition metals. These trends provide good guidelines to design properties of lead-free perovskite piezoelectrics especially based on ubiquitous sodium use.

Keywords: Piezoelectrics, Ferroelectrics, Molecular orbital calculation

1. Introduction

Lead-based piezoelectrics have been considered to have exclusively high electric polarization and piezoelectricity[1-5]. The typical substance is lead titanate, designated as PbTiO_3 (PT)[6,7]. Its crystal structure is of a typical simple perovskite given in Fig.1 as ABO_3 , where A, B, O are ionic species; A and B each corresponds to cations of lead and titanium, and O an anion of oxygen which forms an octahedral cage with the other five. Chemical bonding of this substance was studied with first-principles calculation by R. E. Cohen[8]. The results indicate that the lead (Pb) ion is significantly covalent with the oxygen (O) ions and that the titanium (Ti) ion also. This feature suggested that the covalency plays an important role to cause piezoelectric strains; especially, the covalency of Pb is considered to provide the electronic channels for the strain stabilization and the soft response to external electric or mechanical fields, and furthermore to be a reason why PT and other Pb-based systems are excellent; therefore, it is expected that even other ionic species which cause the covalency at the site of Pb can be the substitutes for lead-free harmless piezoelectrics and their promising application. Previously,

one of the authors N. T. confirmed[9] with molecular orbital calculation that $(\text{Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_3$ (BNT)[10,11] is surely that kind. This substance is now widely recognized as potentially the good substitute, and has well been studied through many types of fabrication[11-13] since decades ago, much earlier than N. T.'s confirmation[9] done. It should be mentioned that BNT is not only one Pb-free but that also others excellent have been found so far[14-16].

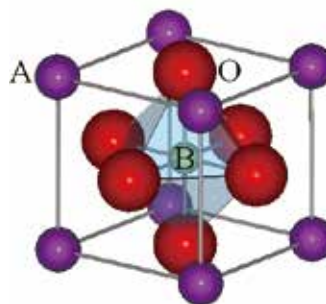


Fig. 1. Simple perovskite structure expressed as ABO_3 .

For the piezoelectric perovskites, representative ionic species occupying the site of Pb or A are alkaline and alkaline-earth metals. Both species have been considered quite ionic; the former has 1+ as the formal ionic charge,

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and the latter 2+. However, this idea indicates only the number of a valence charge of a neutral atom, and it has been known as common knowledge that a portion of the charge is transferred to neighboring atoms in substances consisting of more than one atom; therefore, the atoms, even alkaline and alkaline-earth metals are not neutral in general but partially covalent and also ionic, especially if those metals neighbor the high electronegatives such as oxygen. This idea suggests that a table of effective ionic charges provides us precious directions to control the properties of lead-free piezoelectrics[8,17].

Among the representative species, ubiquitous elements of alkaline metals are sodium (Na) and potassium (K), and alkaline-earth metals calcium (Ca) and barium (Ba); especially, sodium contained in marine resources is quite abundant. They are known to be constituents of perovskite piezoelectrics, e.g. NaNbO_3 , KNbO_3 , CaTiO_3 , BaTiO_3 , and occupy the Pb site, where Nb is niobium; we also line up BaZrO_3 (Zr, zirconium, is chemically similar to Ti) along this row, even if it has a cubic crystal structure, i.e. nonpolar, because it is frequently used as a solute component to this kind of piezoelectrics for their solid solutionization.

Chemical bonding of BaTiO_3 was also studied by R. E. Cohen[8]. The results show that an effective charge of Ba is about 2+, meaning quite ionic, and that the strong covalency of Ti with O, similar to the case of PT, is seen. However, the other elements including those in the alkaline and alkaline-earth columns of a periodic table have not been investigated much. It may be possible that Na and Ca are covalent somehow because of their

larger electronegativity than that of Ba. If the effective charges show systematic variation along the two columns appreciably, piezoelectricities of this kind of substances can be controlled through solid-solutionization and/or heterogeneous structurization such as coherent interfaces based on the one with the other(s) so that the lead-free substance(s) with the properties, as excellent as the Pb-based systems or beyond, will become obtainable. This scheme has motivated us to investigate effective charges of the perovskites with alkaline and/or alkaline-earth metals located at the Pb site, including the charges of PT as the reference base data, through molecular orbital calculation. On top, the calculation was followed by that including partial replacement of O with halogen such as chlorine (Cl) and fluorine (F), or nitrogen (N) on the other side to investigate their electronegative effects on the effective charges of the cations.

2. Calculation

A discrete-variational (DV) $X\alpha$ method of molecular orbital calculation[18,19] was used throughout this study by using code SCAT for calculating electronic states. As the first step, covalency and ionicity of alkaline metals lithium (Li), Na, K (designated as M_A) was investigated based on fundamental compound cluster model $(M_A)_2\text{O}$ with a reverse fluoride structure, illustrated in Fig.2 (a). For these calculations, the lattice parameters previously reported[20] were used. As the second step, the investigation of alkaline-earth metals magnesium (Mg), Ca, strontium (Sr), Ba (designated as M_{AE}) was done based

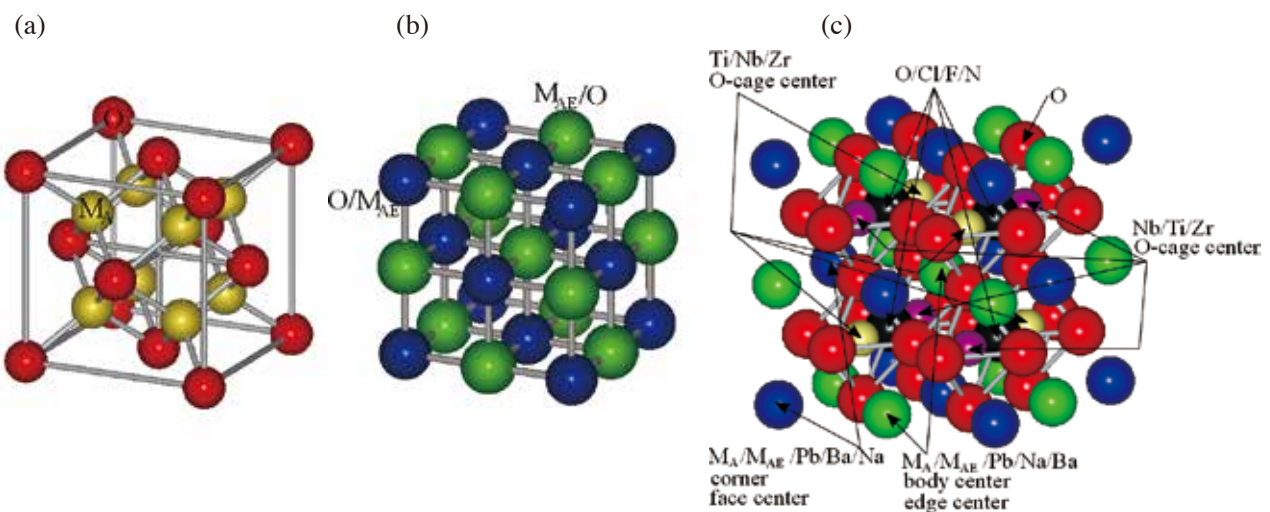


Fig.2. Cluster models for the calculation: (a) reverse fluoride structure $(M_A)_2\text{O}$, (b) sodium chloride structure $(M_{AE})\text{O}$, (c) double perovskite. There are oxygen sites unreplaceable and the others replaceable so that symmetry D2 is maintained.

on cluster model ($M_{AE}O$) with a sodium chloride structure, illustrated in Fig.2 (b). For these calculations, the lattice parameters reported[20] were also used.

As the third step, the investigation of the perovskite was done based on double perovskite cluster models PT, $M_A NbO_3$, $M_{AE}TiO_3$, $BaZrO_3$, $(Ba, Na)(Ti, Nb)O_3$, $(Ba, Na)Ti(O, Cl)_3$, $Na(Ti, Nb)(O, Cl)_3$, $(Ba, Na)Ti(O, F)_3$, $Na(Ti, Nb)(O, F)_3$, $(Ba, Na)Nb(O, N)_3$, $Ba(Ti, Nb)(O, N)_3$, illustrated in Fig.2 (c). Each model is a rectangular-shaped cluster, and was given nonpolar symmetry D2 (Schoenflies notation), because the preliminary calculation with ferroelectric strains giving the much lower symmetry than D2 indicated no essential effect on the bonds[9]. Furthermore, this simplified modeling does not let us take much time to complete the calculations, while it provides the essential chemical features. For the lattice parameters, a typical value of the primitive cubic perovskite, 0.4 nm[7], was employed, so each of the three edge lengths of each model was given 0.8nm. The calculation on only PT was followed by that based on its model incrementally provided the isotropic compression and expansion of 95%-105% so that an effect of the electronic channels referred to the above as can be investigated[8,17].

All calculations mentioned above were each performed with Madelung potential applied to each model, and were followed by Mulliken's population analysis for obtaining the effective charges[18, 19, 21, 22].

3. Results

The effective charge of the cation of each $(M_A)_2O$ is listed in Table 1 in downward sequence of the M_A column in a periodic table, and is drawn as a histogram, shown in Fig.3 (a); the effective charge is of the averaged values over eight of M_A in each model. The table and the figure indicate the effective charges are way below the formal charge +1; especially, this is the significant case with sodium. This significant charge transfer is considered to be caused by a large difference in electronegativity between neighboring M_A and O, and to possibly be utilized for controlling covalency and ionicity of the perovskite A site.

Table 1. Effective charges of M_A of reverse fluoride structures.

Model	Effective charge of M_A
Li_2O	0.601
Na_2O	0.409
K_2O	0.561

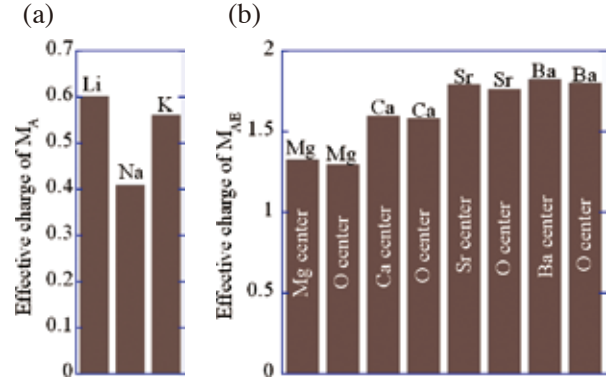


Fig. 3. Histograms of the effective charges of the cations of (a) $(M_A)_2O$ and (b) $(M_{AE})O$. The values in Tables 1 and 2 were used.

The effective charges of the cations of each $(M_{AE})O$ are listed in Table 2 in the same way as that of $(M_A)_2O$, and are also drawn as a histogram, shown in Fig.3 (b); two types of sodium chloride cluster models for each $(M_{AE})O$ were employed; the one is that M_{AE} -body-centered, and the other O-body-centered. For the former model, the effective charge of M_{AE} at the body center bonded with the six nearest neighbor oxygens was employed.

Table 2. Effective charge of M_{AE} of sodium chloride structures.

Model	Effective charge of M_{AE}
MgO Mg-centered	1.325
MgO O-centered	1.295
CaO Ca-centered	1.597
CaO O-centered	1.584
SrO Sr-centered	1.791
SrO O-centered	1.762
BaO Ba-centered	1.824
BaO O-centered	1.800

For the latter model, each of eight M_{AE} species at the corners is bonded with the three nearest neighbors, and each of the six at the face centers with the five, so the effective charges at these two nonbody-center locations were multiplied by 2 and 6/5, respectively, and the weighted values were averaged over each model.

The table and the figure indicate the effective charges are rather close to the formal charge +2, compared to the results of M_A , and the values are increased downward along the column. This feature is also related to possibly electronegativity of M_{AE} and O, but is quite different from the case with M_A , so the results of M_{AE} may provide us another aspect for controlling the chemical bonds of the perovskite A site.

The effective charges of the cations of the double

Table 3. Effective charges of the cations of the ABO₃ double perovskites.

Model	M _A /M _{AE} /Pb	Effective charge of A	Ti/Zr/Nb	Effective charge of B
LiNbO ₃	M _A	0.703	Nb	3.020
NaNbO ₃	M _A	0.608	Nb	3.007
KNbO ₃	M _A	0.791	Nb	3.032
CaTiO ₃	M _{AE}	1.581	Ti	2.451
SrTiO ₃	M _{AE}	1.838	Ti	2.480
BaTiO ₃	M _{AE}	1.900	Ti	2.507
BaZrO ₃	M _{AE}	1.910	Zr	2.823
PbTiO ₃	Pb	1.302	Ti	2.369

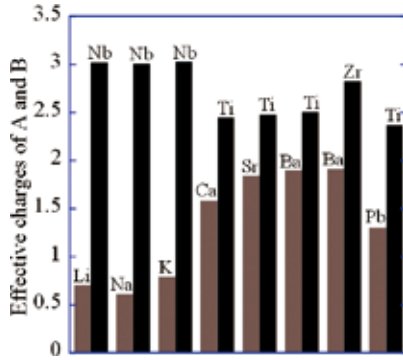


Fig. 4. Histograms of the effective charges of the cations of double simple perovskites ABO₃. The values in Table 3 were used.

perovskites of PT, M_ANbO₃, M_{AE}TiO₃, BaZrO₃ are listed in Table 3 and are also drawn as a histogram, shown in Fig.4. The effective charge of each of the A site ions Pb, M_A, M_{AE} each located at the body center was employed, and that of each of the B site ions in the cages was averaged over each model. The table and the figure both indicate features of the effective charges of M_A and M_{AE} similar to those of (M_A)₂O and (M_{AE})O, respectively. For the effective charges of the B site, Nb shows almost its value +3 whatever M_A is in the table, but besides PT, the values of Ti are increased downward along the column of M_{AE}. This variation of Ti

is similar to that of M_{AE} and is considered relevant to its electronegativity. The values of Zr of BaZrO₃, right below Ti along their periodic column, is larger than those of Ti. This is the same variation as that of M_{AE}.

On the other hand, the effective charges of Pb of PT are about in the middle of the M_A and M_{AE} levels, and this Ti shows the smaller value than Ti and Zr of the other models. If the value of Pb, 1.302, and of this Ti, 2.369, are both *magic numbers* for the high performance of the Pb-based substances, it may become able to design or enhance the piezoelectricity as a function of both effective charges of A and B sites averaged with respect to any perovskite solid solution arbitrarily modeled.

Results of the effective charges of PT for each ratio of the isotropic deformation given to the model are listed in

Table 4. Effective charges of PT for each ratio of the isotropic deformation.

Model	Pb	Ti
PbTiO ₃ 95%	1.381	2.584
PbTiO ₃ 97.5%	1.337	2.471
PbTiO ₃ 100%	1.302	2.369
PbTiO ₃ 102.5%	1.275	2.274
PbTiO ₃ 105%	1.254	2.188

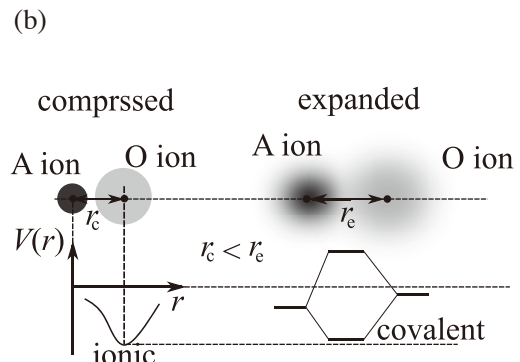
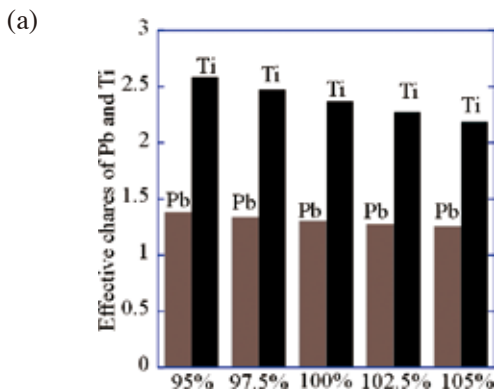


Fig. 5. Case similar to 3d⁰ of Ti⁴⁺: (a) histogram of the effective charges of the cations of strained and unstrained PT, (b) physical and chemical image of energy gain and loss with respect to strain. (a) was drawn by using the values in Table 4. r , r_c , r_e in (b) are a distance between the two ions in general meaning, the distance in the compressed state, that in the expanded state, respectively.

Table 5. Effective charges of solid solution models (Ba, Na)(Ti, Nb)O₃. Each of the detailed chemical notations of the models is given in a parenthesis in each cell on the left.

Model	Ba/Na	A averaged	Ti/Nb	B averaged
(Ba, Na)(Ti, Nb)O ₃ ((Ba _{1/2} Na _{1/2})(Ti _{1/2} Nb _{1/2})O ₃) Ba-centered	Ba 1.900 Na 0.659	1.279	Ti 2.592 Nb 2.832	2.712
(Ba, Na)(Ti, Nb)O ₃ ((Ba _{1/2} Na _{1/2})(Ti _{1/2} Nb _{1/2})O ₃) Na-centered	Ba 1.914 Na 0.607	1.261	Ti 2.583 Nb 2.841	2.712

Table 4 and are also drawn as a histogram, shown in Fig.5 (a); the effective charges are averaged as described above. The results show the effective charges of both Pb and Ti are decreased with increasing expansion. This feature means that a compressed electronic state of vacant 6s of Pb²⁺ and fully-occupied 2p of O²⁻ prefers their being ionic. The reason is that these oppositely charged ions closely located lower the electrostatic energy[17]. On the other hand, the expanded state prefers covalent. The reason is that they reduce the energy through their orbital hybridization of the low energy states[17]. The whole trend is illustrated in Fig. 5 (b), and is known as the case similar to 3d⁰ of Ti⁴⁺[17]; therefore, the effective charges can be utilized as a measure of covalency, similar to Born's effective charge[23].

An example of averaging the effective charges are given below. Those of our solid solution model (Ba, Na)(Ti, Nb)O₃ are listed in Table 5 and are also drawn as a histogram, shown in Fig.6; this case also leads us to assume two types of solid solution model; the one is that Ba-body-centered, and the other Na-body-centered. For the former model, the effective charge of Ba at the body center bonded with the twelve nearest neighbor oxygens was employed. For Na, each of eight Na ions at the corners is bonded with the three nearest neighbors, and each of the six at the face

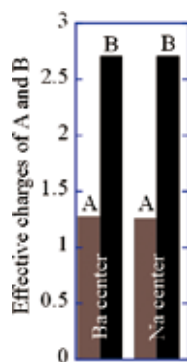


Fig. 6. Histograms of the effective charges of the cations of solid solution model (Ba, Na)(Ti, Nb)O₃. The values in Table 5 were used.

centers with the eight, so to compute the effective charges at these two nonbody-center locations, their charge transfers are multiplied by 4 and 12/8, respectively; these weighted transfers are each averaged over their equivalent locations of this model, and these averaged values are each subtracted from each formal charge to obtain each effective charge. Furthermore, averaging the averaged effective charges of Ba and Na was taken; we would like to call this way *cluster chemical mean field*. The further averaged value is also given in the table. In the same way, the effective charges of the latter model were obtained by exchanging Ba and Na in the former model with reversely Na and Ba, respectively.

For each of the former and latter models, the effective charge of Ti was simply averaged over the four species and Nb also, and further averaging the averaged effective charges of Ti and Nb was also taken, and the value is also given in the table.

4. Discussion and Guidelines of Designing Lead-free Piezoelectrics

Let us set up orthogonal two axes so that both lie in one plane, and assume that the one of the two axes indicates the averaged effective charges of either A or B ion for each model and that the other axis the other charge. In this way,

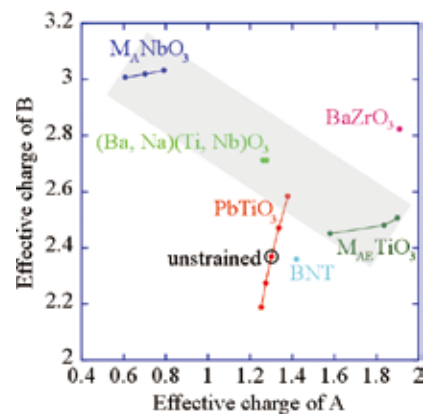


Fig. 7. Map of the values in Table 3, 4, 5 including those of BNT of the Na-centered model.

both charges for each model gives a coordinate in the plane. Also let us mark with a dot at each coordinate determined from the charges in Table 3, 4, 5 including those of BNT of the Na-centered model employed in the previous study[9]. The dots are given in Fig.7 and the figure shows the following features:

1. The one dot circled is at the coordinate of unstrained PT.
2. The three dots of $M_A NbO_3$ are located in the region where the effective charges of A and B are relatively low and high, respectively.
3. The three dots of $M_{AE} TiO_3$ are located in the region where the charges of A and B are high and low, respectively.
4. The two dots of $(Ba, Na)(Ti, Nb)O_3$ are about in the middle of the regions of $M_A NbO_3$ and $M_{AE} TiO_3$.
5. The one dot of $BaZrO_3$ is where A and of B are both high.
6. The one dot of BNT is in the vicinity of PT.

Based on the above features, it is expected that solid solutionization of $M_A NbO_3$ and $M_{AE} TiO_3$ draws a narrow band from one of their regions to the other as shown in the figure. This band includes the locations of $(Ba, Na)(Ti, Nb)O_3$ but does not PT, so the lead-free property improvement through this solid solutionization is considered to chemically be limited.

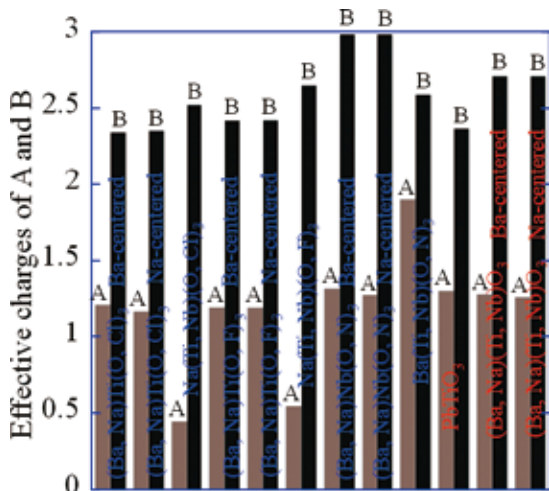


Fig. 8. Histogram of the effective charges of A and B of cluster model $(Ba, Na)(Ti, Nb)O_3$ replaced with Cl, F, N, respectively. The values in Table 6 were used. The values of PT in Table 3 and $(Ba, Na)(Ti, Nb)O_3$ in Table 5 are also used for comparison.

On the other hand, $BaZrO_3$ is not effective in the property improvement according to this idea. What is important of this substance has solely been a morphotropic effect with BT[14-16]. It should be noted that BNT is quite close to PT; BNT, which became noteworthy decades ago, has been really a successful case of the solid solutionization[10-13]. However, bismuth (Bi) contained in BNT is volatile at high temperature for sintering[24-26], which often causes a problem of deterioration of the quality on the fabrication. Furthermore, hardness of BNT is high compared with those of Pb-based systems, so ultimate enhancement of the piezoelectricity may be naturally difficult and Bi may be an unwanted element from a fabrication point of view (though a good piezoelectric currently).

Fig.7 tells us that reduction of the effective charge of the B site of $(Ba, Na)(Ti, Nb)O_3$ realizes the property improvement. The reduction can be done by replacing O with halogens such as F or Cl which are more electronegative than O. The replacement is considered to enhance the covalency and to reduce the charge of B so that the limitation of the property improvement is eased effectively. According to this idea, the replacement with N is the reverse case, because N is less electronegative than O.

The results of the replacement are listed in Table 6 and are also drawn as a histogram, shown in Fig.8; the replacement was done so that four oxygens marked in Fig. 2 (c) were replaced with Cl, F, N, respectively. Since their formal charges are different from that of O, the simple replacement causes the total charges as the double

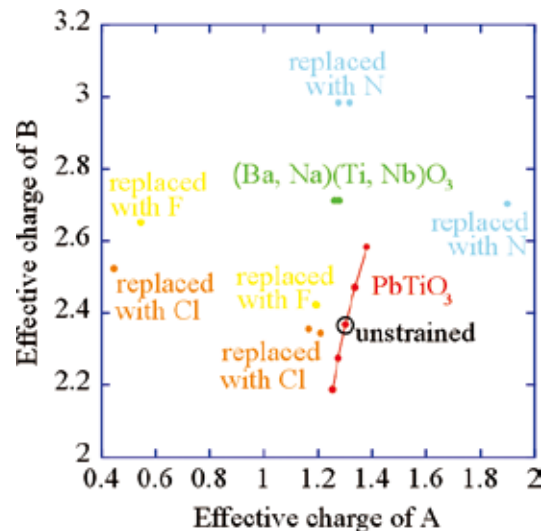


Fig. 9. Map of the values in Table 6. The dots of PT and $(Ba, Na)(Ti, Nb)O_3$ in Fig. 7 are given for comparison.

perovskite unit cell to be nonzero; therefore, the zero charge was maintained by further replacing Ba with Na or the reverse, and Ti with Nb or the reverse, depending on each model given by replacing with each of Cl, F, N. Let us mark with a dot at each coordinate determined from the charges in Table 6. The table and figure indicate reduction of the effective charges as expected. Dots of the coordinates of the charges in the table are given in Fig.9; the dots of PT and (Ba, Na)(Ti, Nb)O₃ in Fig. 7 are also given to confirm any effect of the replacement. Fig. 9 shows the two dots of (Ba, Na)Ti(O, Cl)₃ and the two dots of (Ba, Na)Ti(O, F)₃. Their locations are very close to PT, which means that we have found through this simulation the replacement with halogens effective. Furthermore, we have found that Nb is not necessary in these substances; otherwise, the reverse effect is expected, since the charge of Nb is relatively high compared to that of Ti. The figure also shows the data of the other halogen-replaced models, Na(Ti, Nb)(O, Cl)₃ and

Na(Ti, Nb)(O, F)₃. The data indicate the charges of A are excessively low because of no Ba included, and B high because of Nb included; therefore, Ba is also effective in designing the piezoelectrics as well as halogens. On the other hand, the calculation based on the N-replaced models, (Ba, Na)Nb(O, N)₃ and Ba(Ti, Nb)(O, N)₃ shows the reverse effect as expected.

Let us check uniqueness of the magic numbers proposed above on PT with the other Pb-based system, for example, relaxor Pb(Mg_{1/3}Nb_{2/3})O₃, called PMN[27]; it has been considered a good component for the high piezoelectric performance. Since there was no adequate symmetry for modeling the PMN cluster, it was considered that the calculation of PMN would take tremendously long time. So the calculation was not carried out, but instead, the charges of Pb and Nb in Table 3 and that of Mg in Table 2 were employed to obtain the charges. The obtained value of A is just that given in the table, about 1.3, and B, about 2.4,

Table 6. Effective charges of solid solution models (Ba, Na)(Ti, Nb)O₃; O ions are partially replaced with halogen Cl or F, or not halogen N. Each of the detailed chemical notations of the models is given in a parenthesis in each cell on the left.

Model	A	A averaged	B ave	B averaged
(Ba, Na)Ti(O, Cl) ₃ ((Ba ₄ Na ₄)Ti ₈ (O ₂₀ Cl ₄)) Ba-centered	Ba 1.920 Na 0.500	1.210	Ti 2.344	2.344
(Ba, Na)Ti(O, Cl) ₃ ((Ba ₄ Na ₄)Ti ₈ O ₂₀ Cl ₄) Na-centered	Ba 1.873 Na 0.459	1.166	Ti 2.355	2.355
Na(Ti, Nb)(O, Cl) ₃ (Na ₈ (Ti ₄ Nb ₄)(O ₂₀ Cl ₄))	Na 0.445	0.445	Ti 2.434 Nb 2.611	2.523
(Ba, Na)Ti(O, F) ₃ ((Ba ₄ Na ₄)Ti ₈ (O ₂₀ F ₄)) Ba-centered	Ba 1.865 Na 0.523	1.194	Ti 2.422	2.422
(Ba, Na)Ti(O, F) ₃ ((Ba ₄ Na ₄)Ti ₈ (O ₂₀ F ₄)) Na-centered	Ba 1.856 Na 0.528	1.192	Ti 2.423	2.423
Na(Ti, Nb)(O, F) ₃ (Na ₈ (Ti ₄ Nb ₄)(O ₂₀ F ₄))	Na 0.545	0.545	Ti 2.542 Nb 2.761	2.651
(Ba, Na)Nb(O, N) ₃ ((Ba ₄ Na ₄)Nb ₈ (O ₂₀ N ₄)) Ba-centered	Ba 1.912 Na 0.724	1.318	Nb 2.983	2.983
(Ba, Na)Nb(O, N) ₃ ((Ba ₄ Na ₄)Nb ₈ (O ₂₀ N ₄)) Na-centered	Ba 1.943 Na 0.609	1.276	Nb 2.983	2.983
Ba(Ti, Nb)(O, N) ₃ (Ba ₈ (Ti ₄ Nb ₄)(O ₂₀ N ₄))	Ba 1.899	1.899	Ti 2.589 Nb 2.817	2.703

and these two values for PMN provide the location close to PT. The magic numbers are maybe true, though they must be proved through fabrication of Pb-free substances at least indirectly.

5. Conclusion

Effective ionic charges of perovskite dielectric complex compounds have been investigated with molecular orbital calculation. Besides PT, the results show remarkable covalency for almost all cations and systematic variation of the effective charges of the A site ions along their column in a periodic table; the variation quite corresponds to their electronegativity, and this is also the case with Ti and Zr, both belonging to the same column. But the charge of Pb for PT, an important component of good piezoelectrics, indicates the stand-alone value; therefore, both charges of Pb and Ti may be *magic numbers*. In fact, the calculation of good piezoelectrics BNT and PMN gives the values close to the proposed numbers. So they may provide us good guidelines to design properties of lead-free piezoelectrics for the high performance. In a way of *cluster chemical mean field*, the calculation of (Ba, Na)(Ti, Nb)O₃ indicates the values closer to PT. But this improvement is limited by the charge of B, excessively high. So O in the model was replaced with halogen Cl or F, more electronegative. The obtained charges are very close to PT, and Ba, Na, Ti, O, Cl or F are considered necessary for simplified synthesis of the perovskite substances. This idea is for obtaining the good Pb-free substances, and also very useful for efficient use of ubiquitous alkaline metals and alkaline-earth metals, especially sodium.

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