



# Article Molecular Orbital Calculation of Lead-Free Perovskite Compounds for Efficient Use of Alkaline and Alkaline Earth Metals

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Received: 28 August 2020; Accepted: 20 October 2020; Published: 22 October 2020



**Abstract:** The effective ionic charges of lead-free perovskite dielectric complex compounds were investigated with molecular orbital calculation. The base model was a double perovskite cluster that consisted 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 the body center, corners, edge centers, or face centers of the cluster. The results showed significant covalent bonds between the transition metals and the oxygens, and the alkali metals, especially sodium and oxygen. On the other hand, the alkaline earth metals have weak covalency. Calculation was also performed with the replacement of some of the oxygens with chlorine or fluorine; such replacement enhances the covalency of the transition metals. These trends provide good guidelines for the design properties of lead-free perovskite piezoelectrics based on ubiquitous sodium use.

Keywords: perovskite; dielectrics; piezoelectrics; ferroelectrics; molecular orbital calculation

## 1. Introduction

Lead (Pb)-based piezoelectrics 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, which is denoted as ABO<sub>3</sub> in Figure 1, where A, B, and O are ionic species; A and B each corresponds to cations of lead and titanium, and O is an anion of oxygen that forms an octahedral cage with the five other O ions. The chemical bonding of lead titanate was studied with first-principles calculation by R. E. Cohen [8]. The results indicated that the lead (Pb) ion is significantly covalent with the oxygen (O) and titanium (Ti) ions. This feature suggests that the covalency forms a molecular orbital (i.e., electronic channels) through which valence electrons are transferred back and forth between the cations and anions in response to external fields. The response may be soft or hard, depending on the significance of the covalency. Thus, covalency plays an important role in causing the piezoelectric strain, which is a reason PT and other Pb-based systems have excellent properties. Therefore, other ionic species that cause covalency at the site of Pb can be substitutes for harmless, lead-free piezoelectrics and their promising application. One of the authors, N. Takesue [9], confirmed with molecular orbital calculation that (Bi<sub>1/2</sub>Na<sub>1/2</sub>)TiO<sub>3</sub> (BNT) [10,11] could be such a substitute. This substance is now widely recognized as a potential substitute and has been studied through many types of fabrication [11–13], long before N. Takesue's confirmation [9]. In addition to BNT, many excellent Pb-free piezoelectrics have been discovered [14–16].



Figure 1. Simple perovskite structure expressed as ABO<sub>3</sub>.

For piezoelectric perovskites, alkaline and alkaline-earth metals are traditionally regarded as representative ionic species occupying the site of Pb or A [17]. Although there are more modern systems such as BNT [10–13] and BNT-based solid solutions [18], we focused on traditional systems, namely, BiFeO<sub>3</sub> [19] and GaFeO<sub>3</sub> [20], since our work was on the efficient use of ubiquitous alkaline and alkaline-earth metals. Both species of traditional systems are ionic; their formal ionic charges are 1+ and 2+, respectively. However, this idea indicates only the valence charge of neutral atoms. A portion of the charge is transferred to neighboring atoms in substances consisting of more than one atom. Therefore, atoms—even those of alkaline and alkaline-earth metals—are not neutral in general. Rather, they are partially covalent and ionic, especially for metals with high-electronegativity atoms such as oxygen atoms as neighbors. This idea suggests that a table of effective ionic charges enables the control of the properties of lead-free piezoelectrics [8,21] and is considered compensative to tolerance factors [22,23], which is a well-established criterion for the stability of perovskite structures.

Among the representative species, alkaline metals (sodium [Na] and potassium [K]) and alkaline-earth metals (calcium [Ca] and barium [Ba]) are ubiquitous; in particular, sodium contained in marine resources is abundant. These are constituents of perovskite piezoelectrics such as NaNbO<sub>3</sub> (Nb Is niobium), KNbO<sub>3</sub>, CaTiO<sub>3</sub>, and BaTiO<sub>3</sub>, and they occupy the Pb site. We included BaZrO<sub>3</sub> (zirconium [Zr] is chemically similar to Ti) in this category despite its cubic crystal structure (i.e., nonpolar) because it is frequently used as a solute component for this kind of piezoelectrics for their solid solutions.

The chemical bonding of BaTiO<sub>3</sub> was also studied by R. E. Cohen [8]. The results showed that an effective charge of Ba was about 2+ (i.e., ionic) and a strong covalency of Ti with O, similar to the case of PT, was observed. However, the other elements including those in the alkaline and alkaline-earth columns of the periodic table, have not been considerably investigated. Na and Ca may be covalent because of their higher electronegativity than that of Ba. If their effective charges show an evident systematic variation along the two columns, then the piezoelectricity of these kinds of substances can be controlled through the synthesis of solid solutions and/or heterogeneous structuralization such as coherent interfaces; the way(s) may be realized by matching the one base piezoelectric with the other piezoelectric component(s). The successful case leads us to certain achievements, after which lead-free substance(s) with properties are as good as, or better than, those of Pb-based systems will become obtainable. This scheme motivated us to investigate the effective charges of PT as the reference data through molecular orbital calculation. Then, we performed a calculation including the partial replacement of O with a 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 [24,25] was used throughout this study by using the SCAT code for calculating the electronic states. First, the covalency and ionicity of alkaline metals lithium (Li), Na, and K (designated as M<sub>A</sub>) were investigated based on a

fundamental compound cluster model  $(M_A)_2O$  with an antifluorite structure, as illustrated in Figure 2a. Previously reported lattice parameters [26] were used for these calculations. Second, the alkaline-earth metals magnesium (Mg), Ca, strontium (Sr), and Ba (designated as  $M_{AE}$ ) were investigated based on a cluster model ( $M_{AE}$ )O with a sodium chloride structure, as illustrated in Figure 2b. The same lattice parameters [26] were used for these calculations.

Model	Ion	Color
	Pb	green, blue
PT	Ti	gold, purple
	0	red, black
	M <sub>A</sub>	green, blue
M <sub>A</sub> NbO <sub>3</sub>	Nb	gold, purple
	0	red, black
	M <sub>AE</sub>	green, blue
M <sub>AE</sub> TiO <sub>3</sub>	Ti	gold, purple
	О	red, black
	Ва	green, blue
BaZrO <sub>3</sub>	Zr	gold, purple
	О	red, black
	Ba	green
	Na	blue
$(Ba, Na)(II, Nb)O_3$	Ti	gold
Ba-centered	Nb	purple
	О	red, black
	Na	green
	Ba	blue
$(Ba, Na)(11, Nb)O_3$	Ti	gold
Na-centered	Nb	purple
	О	red, black
	Ва	green
	Na	blue
$(Ba, Na) II(O, CI)_3$	Ti	gold, purple
Ba-centered	0	red
	Cl	black
	Na	green
$(\mathbf{P}_{\mathbf{r}}, \mathbf{N}_{\mathbf{r}}) \mathbf{T}_{\mathbf{r}}^{\dagger} (\mathbf{O}, \mathbf{C})$	Ba	blue
$(Da, Na) II(O, CI)_3$	Ti	gold, purple
Na-centered	0	red
	Cl	black
	Na	green, blue
	Ti	gold
Na(Ti, Nb)(O, Cl) <sub>3</sub>	Nb	purple
	0	red
	Cl	black
	Ba	green
	Na	blue
$(Ba, Na)Ti(O, F)_3$	Ti	gold. purple
Ba-centered	0	red
	F	black

 Table 1. Colors of the ions in each perovskite model.

Model	Ion	Color
	Na	green
$(\mathbf{P}_{2}, \mathbf{N}_{2}) \mathbf{T}_{1} (\mathbf{O}, \mathbf{F})$	Ba	blue
$(Da, Na) \Pi(O, F)_3$	Ti	gold, purple
Na-centereu	О	red
	F	black
	Na	green, blue
	Ti	gold
Na(Ti, Nb)(O, F) <sub>3</sub>	Nb	purple
	0	red
	F	black
	Ba	green
$(\mathbf{P}_{-}, \mathbf{N}_{-}) \times \mathbf{P}_{-} (\mathbf{O}, \mathbf{N}_{-})$	Na	blue
$(Ba, Na)Nb(O, N)_3$	Nb	gold, purple
ba-centered	0	red
	Ν	black
	Na	green
$(\mathbf{P}_{-}, \mathbf{N}_{-}) \times \mathbf{P}_{-} (\mathbf{O}, \mathbf{N}_{-})$	Ва	blue
$(Da, Na)ND(O, N)_3$	Nb	gold, purple
Na-centered	0	red
	Ν	black
	Ba	green, blue
	Ti	gold
Ba(Ti, Nb)(O, N) <sub>3</sub>	Nb	purple
	0	red
	Ν	black

Table 1. Cont.

In the third step, the perovskite was investigated based on double perovskite cluster models for PT,  $M_ANbO_3$ ,  $M_{AE}TiO_3$ ,  $BaZrO_3$ ,  $(Ba, Na)(Ti, Nb)O_3$ ,  $(Ba, Na)Ti(O, Cl)_3$ ,  $Na(Ti, Nb)(O, Cl)_3$ ,  $(Ba, 'Na)Ti(O, F)_3$ ,  $Na(Ti, Nb)(O, F)_3$ ,  $(Ba, Na)Nb(O, N)_3$ , and  $Ba(Ti, Nb)(O, N)_3$ , as illustrated in Figure 2c. The sites of ions in each model are indicated by colored spheres, and the correspondence of the colors to the ions is summarized in Table 1. Each model is a rectangular cluster and was given a nonpolar symmetry  $D_2$  (Schoenflies notation), common to all perovskite models employed; the reason is that the preliminary calculation with ferroelectric strains with a smaller symmetry than  $D_2$  indicated no essential effect on the bonds [9]. Furthermore, this simplified modeling reduced the time needed to complete the calculations while providing the essential chemical features. A typical value of the primitive cubic perovskite, 0.4 nm [7,17], was employed for the lattice parameters, so each of the three edge lengths of each model was given a value of 0.8 nm. The calculation on only PT was followed by a calculation based on its model, which incrementally provided an isotropic compression and expansion of 95%–105%; therefore, the above-mentioned effect of the electronic channels can be investigated [8,21].





**Figure 2.** Cluster models for the calculation. (a) is an antifluorite structure  $(M_A)_2O$  with oxygens colored red. (b) is a sodium chloride structure  $(M_{AE})O$  with  $M_{AE}$  body-centered;  $M_{AE}$  and O are each colored green and blue, and exchanging the colors provides the oxygen body-centered structure. (c) is a double perovskite structure. The green spheres and the blue spheres are  $M_A$ ,  $M_{AE}$ , Pb, Na, or Ba. The gold spheres and purple spheres are Ti, Nb, or Zr. The black spheres are O, Cl, F, or N. The red spheres are oxygens. Chemical species are located so that symmetry D<sub>2</sub> is maintained. The colors of ions in each model are summarized in Table 1.

All the above calculations were performed with the Madelung potential applied to each model, and Mulliken population analysis was conducted to determine the effective charges [24,25,27,28]. The lattice parameters used for modeling are listed in Table 2.

Model	Crystal System	Lattice Parameter (nm)
Li <sub>2</sub> O	cubic	a = 0.461
Na <sub>2</sub> O	cubic	a = 0.555
K <sub>2</sub> O	cubic	a = 0.644
MgO	cubic	a = 0.421
CaO	cubic	a = 0.480
SrO	cubic	a = 0.5144
BaO	cubic	a = 0.55391
Double perovskites	<i>a</i> , <i>b</i> , <i>c</i> orthogonal, $D_2$	$a = b = c = 0.4 \times 2 = 0.8$

Table 2.	Lattice	parameters	used for	modeling

#### 3. Results

The effective charges of the cations of each  $(M_A)_2O$  is listed in Table 3 in a downward sequence of the  $M_A$  column in the periodic table. The charges are shown as a histogram in Figure 3a. Each effective charge is the average of the eight  $M_A$  values in each model. The table and the figure indicate that the effective charges were noticeably below the formal charge of +1; in particular, the difference for sodium was significant. This evident charge transfer is considered to be caused by a large difference in electronegativity between neighboring  $M_A$  and O; this transfer can be used to control the covalency and ionicity of the perovskite A site.

Model	Effective Charge of $M_A$
Li <sub>2</sub> O	0.601
Na <sub>2</sub> O	0.409
K <sub>2</sub> O	0.561

Table 3. Effective charges of M<sub>A</sub> of reverse fluoride structures.

The effective charges of the cations of each  $(M_{AE})O$  are listed in Table 4 in the same manner as those of  $(M_A)_2O$  and are drawn as a histogram in Figure 3b. Two types of sodium chloride cluster models, namely,  $M_{AE}$ - and O-body-centered, for each  $(M_{AE})O$  were employed. For the former model, the effective charge of  $M_{AE}$  at the body center, bonded with the six nearest neighbor oxygens, was employed.



**Figure 3.** Histograms of the effective charges of the cations of (**a**)  $(M_A)_2O$  and (**b**)  $(M_{AE})O$ . The values in Tables 3 and 4 were used.

Table 4. Effective charge of  $M_{AE}$  of the sodium chloride structures.

Model	Effective Charge of $M_{\mbox{\scriptsize AE}}$
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 the eight  $M_{AE}$  species at the corners was bonded with the three nearest neighbors, and each of the six at the face centers with the five; thus, the effective charges at these two non-body-centered locations were multiplied by 2 and 6/5, respectively, and the weighted values were averaged over each model.

The table and the figure indicate that the effective charges of  $M_{AE}$  increased downward along the column toward the formal charge of +2. This finding differed from those of  $M_A$  and was also related to the possible electronegativity of  $M_{AE}$  and O. Therefore, the results of  $M_{AE}$  may provide another aspect to control the chemical bonds of the perovskite A site.

The effective charges of the cations of the double perovskites of PT,  $M_ANbO_3$ ,  $M_{AE}TiO_3$ , and  $BaZrO_3$  are listed in Table 5 and drawn as a histogram in Figure 4. The effective charge of each of the A-site ions Pb,  $M_A$ , and  $M_{AE}$ , each located at the body center, was employed; that of each of the B-site ions in the cages was averaged over each model. The table and the figure showed variations in the effective charges of  $M_A$  and  $M_{AE}$  for the perovskite models, similar to those along the columns of the periodic table for  $(M_A)_2O$  and  $(M_{AE})O$ , respectively. For the effective charges of the B site, Nb showed a value of almost +3, regardless of the value of  $M_A$  in Table 5. Apart from PT, the values of Ti increased downward along the periodic column of  $M_{AE}$ . This variation of Ti is similar to that of  $M_{AE}$  and considered relevant to its electronegativity. The values of Zr of  $BaZrO_3$ , which lies immediately below Ti along the periodic column, were higher than those of Ti. This variation was the same as that of  $M_{AE}$ .



**Figure 4.** Histograms of the effective charges of the cations of double simple perovskites ABO<sub>3</sub>. The values in Table 5 were used.

Table 5. Effective charges of the cations of the ABO<sub>3</sub> double perovskites.

	Model	M <sub>A</sub> /M <sub>AE</sub> /Pb	Effective Charge of A	Ti/Zr/Nb	Effective Charge of B
]	LiNbO3	M <sub>A</sub>	0.703	Nb	3.020
1	NaNbO3	$M_A$	0.608	Nb	3.007
	KNbO3	$M_{A}$	0.791	Nb	3.032
	CaTiO <sub>3</sub>	$M_{AE}$	1.581	Ti	2.451
	SrTiO <sub>3</sub>	$M_{AE}$	1.838	Ti	2.480
	BaTiO <sub>3</sub>	$M_{AE}$	1.900	Ti	2.507
	BaZrO <sub>3</sub>	$M_{AE}$	1.910	Zr	2.823
	PbTiO <sub>3</sub>	Pb	1.302	Ti	2.369

The effective charges of Pb of PT were approximately in the middle of the  $M_A$  and  $M_{AE}$  levels, and this Ti showed a smaller value than those of Ti and Zr in the other models. If the value of Pb (1.302) and Ti (2.369) were both *magic numbers* for the excellent performance of Pb-based substances,

piezoelectricity may be designed or enhanced as a function of both the effective charges of the A and B sites averaged with respect to any arbitrarily modeled perovskite solid solution.

The effective charges of PT for each ratio of the isotropic deformation given for the model are listed in Table 6 and drawn as a histogram in Figure 5a. The effective charges were averaged as described above. The results show that the effective charges of Pb and Ti decreased with increasing expansion. Therefore, a compressed electronic state of the vacant 6s of Pb<sup>2+</sup> and fully occupied 2*p* of O<sup>2-</sup> benefits from their ionic nature. The reason is that these oppositely charged ions, which are closely located, decrease the electrostatic energy [21]. In contrast, a covalent nature is favorable for the expanded state. The reason is that they reduce energy through their orbital hybridization of the low energy states [21]. The whole trend is illustrated in Figure 5b and is similar to the case of  $3d^0$  of Ti<sup>4+</sup> [21]. Therefore, the effective charges can be utilized as a measure of covalency, similar to the Born effective charge [29].



**Figure 5.** Case similar to  $3d^0$  of Ti<sup>4+</sup>: (**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 6. *r*, *r*<sub>c</sub>, *r*<sub>e</sub> in (**b**) are the distance between the two ions in general meaning, the distance in the compressed state, that in the expanded state, respectively.

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

Table 6. Effective charges of PT (PbTiO<sub>3</sub>) for each ratio of the isotropic deformation.

An example of averaging the effective charges is given below. The effective charges of our solid solution model (Ba, Na)(Ti, Nb)O<sub>3</sub> are listed in Table 7 and drawn as a histogram in Figure 6. This case led us to assume two types of solid solution models, namely, Ba- and Na-body-centered. For the former model, the effective charge of Ba at the body center, bonded with the 12 nearest neighbor oxygens, was employed. For Na, each of the eight Na ions at the corners was bonded with the three nearest neighbors, and each of the six at the face centers with the eight. Thus, their charge transfers were multiplied by 4 and 12/8, respectively, to compute the effective charges at these two non-body-centered locations. These weighted transfers were each averaged over their equivalent locations of this model, and these averaged values were each subtracted from each formal charge to obtain each effective charge. Furthermore, the average effective charges of Ba and Na were further averaged in a manner we called the *cluster chemical mean field*. The further averaged value is also given in Table 7. In the same way, the effective charges of the latter model were obtained by reversing Ba and Na in the former model (reverse Na and Ba, respectively).



**Figure 6.** Histograms of the effective charges of the cations of the solid solution model (Ba, Na)(Ti, Nb)O<sub>3</sub>. A corresponds to (Ba, Na), and B (Ti, Nb). The values in Table 7 were used.

**Table 7.** Effective charges of the solid solution models (Ba, Na)(Ti, Nb)O<sub>3</sub>. Each of the detailed chemical notations of the models is given in parenthesis in each cell on the left.

Model	Ba/Na	A Averaged	Ti/Nb	B Averaged
(Ba, Na)(Ti, Nb)O <sub>3</sub> ((Ba <sub>1/2</sub> Na <sub>1/2</sub> )(Ti <sub>1/2</sub> Nb <sub>1/2</sub> )O <sub>3</sub> ) Ba-centered	Ba 1.900 Na 0.659	1.279	Ti 2.592 Nb 2.832	2.712
(Ba, Na)(Ti, Nb)O <sub>3</sub> ((Ba <sub>1/2</sub> Na <sub>1/2</sub> )(Ti <sub>1/2</sub> Nb <sub>1/2</sub> )O <sub>3</sub> ) Na-centered	Ba 1.914 Na 0.607	1.261	Ti 2.583 Nb 2.841	2.712

For the former and latter models, the effective charges of Ti were simply averaged over the four species, and the same was done for Nb. The averaged effective charges of Ti and Nb were further averaged, and this value is also given in Table 7.

## 4. Discussion and Guidelines for Designing Lead-Free Piezoelectrics

We checked the uniqueness of the above-mentioned magic numbers of PT and other Pb-based systems such as relaxor Pb( $Mg_{1/3}Nb_{2/3}$ )O<sub>3</sub>, called PMN [30], which is a good component for high piezoelectric performance. Since there is no adequate symmetry for modeling the PMN cluster, we believed that the calculation of PMN would consume a long time. Thus, the calculation was not conducted; instead, the charges of Pb and Nb in Table 5 and that of Mg in Table 4 were employed to obtain the charges. The obtained values of A and B were approximately 1.3 and about 2.4, respectively, and these values for PMN were close to those for PT. Therefore, the magic numbers are likely true, although they must be verified through the fabrication of Pb-free substances, at least indirectly.

We also checked the relaxor PbZn<sub>1/3</sub>Nb<sub>2/3</sub>O<sub>3</sub>, called PZN [31], which is also a good component. The Zn contained in this substance did not belong to the related columns of the periodic table, so the effective charge was not calculated. However, the Zn of its oxide is expected to have a charge that is considerably less than the formal charge of +2 because Zn is a relatively highly electronegative metal. Let us assume that the effective charge of Zn in its oxide is +2, which is the maximum value. An estimated value of the effective charge of this B site, designated as B<sub>avereged</sub>, given by averaging the formal charge of Zn with the charge of Nb of about +3 in Table 5, was about 2.7, which was evidently beyond the proposed magic number, but the inherent electronegativity of Zn causes B<sub>avereged</sub> to be reduced in reality.

We also examined the well-known, excellent piezoelectric Pb( $Zr_xTi_{1-x}$ )O<sub>3</sub> (*x*~0.5) called PZT [32]. This B<sub>avereged</sub> averaged with the charges of Ti and Zr in Table 5 was approximately 2.6, which was also

considerably higher than the proposed magic number. Thus, the good property is considered purely as the morphotropic effect of PT with PbZrO<sub>3</sub>, which is the case with BT–BZ solid solutions [14–16].

A check of the uniqueness of the magic numbers did not reveal any morphotropic effect, piezoelectric coefficient, or electromechanical coupling coefficient, but it confirmed whether the effective charges of the modeled perovskites were close to the magic numbers. It also suggests the fabrication target systems that may have Pb–O-type covalency.

We set up two orthogonal axes so that they both lay on one plane. We assumed that one of the two axes indicated the averaged effective charges of either A or B ions for each model; the other axis, the other charge of B or A. In this way, both charges for each model give a coordinate in the plane. We marked, with a dot, each coordinate determined from the charges in Tables 5–7 including those of the BNT of the Na-centered model employed in a previous study [9]. The dots are given in Figure 7, which shows the following features.

- 1. The one circled dot is at the coordinate of the unstrained PT.
- 2. The three dots of M<sub>A</sub>NbO<sub>3</sub> are in the region where the effective charges of A and B are relatively low and high, respectively.
- 3. The three dots of M<sub>AE</sub>TiO<sub>3</sub> are 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<sub>3</sub> are about in the middle of the regions of M<sub>A</sub>NbO<sub>3</sub> and M<sub>AE</sub>TiO<sub>3</sub>.
- 5. The one dot of BaZrO<sub>3</sub> is where the charges of A and B are both high.
- 6. The one dot of BNT is in the vicinity of PT.



**Figure 7.** Map of the values in Tables 5–7 including those of BNT (Bi<sub>1/2</sub>Na<sub>1/2</sub>TiO<sub>3</sub>) of the Na-centered model. LN, NN, KN are LiNbO<sub>3</sub>, NaNbO<sub>3</sub>, KNbO<sub>3</sub>. CT, ST, BT are CaTiO<sub>3</sub>, SrTiO<sub>3</sub>, and BaTiO<sub>3</sub>.

From the above features, the solid solutions of  $M_ANbO_3$  and  $M_{AE}TiO_3$  formed a narrow band from one region to the other, as shown in the figure. This band includes the locations of (Ba, Na)(Ti, Nb)O\_3, but not PT, so the lead-free property improvement through this synthesis of solid solutions is chemically limited. Moreover, BaZrO<sub>3</sub> is not effective in the property improvement according to this idea. Nonetheless, this substance solely has a morphotropic effect with BT [14–16].

BNT is close to PT; BNT, which has been noteworthy for decades, is a successful case of solid solutions [10–13]. However, the bismuth (Bi) contained in BNT is volatile at high temperatures for sintering [33–35], which often deteriorates the quality during fabrication. Therefore, Bi may be an unwanted element from a fabrication point of view. Furthermore, the hardness of BNT is high compared

with those of Pb-based systems. Therefore, an ultimate enhancement of the piezoelectricity may be naturally difficult, although BNT is a good piezoelectric, and solid solutions are promising because they can be fabricated at relatively low sintering temperatures [18], thereby suppressing vaporization.

Figure 7 shows that reducing the effective charge of the B site of (Ba, Na)(Ti, Nb)O<sub>3</sub> improved its properties. The reduction can be done by replacing O with halogens such as F and Cl, which are more electronegative than O. The replacement is performed to enhance the covalency and reduce the charge of B, thus effectively mitigating the limitation of the property improvement. According to this idea, the replacement with N is the opposite case because N is less electronegative than O.

The results of the replacement are listed in Table 8 and drawn as a histogram in Figure 8. The four oxygens marked in Figure 2c were replaced with Cl, F, and N. Since their formal charges are different from that of O, the simple replacement causes the total charges, as the double perovskite unit cell, to be nonzero. Therefore, the zero charge was maintained by further replacing Ba with Na or the opposite, and Ti with Nb or the reverse, depending on each model given by replacing with Cl, F, and N. We marked at each coordinate with a dot as determined from the charges in Table 8. The table and figure indicate an expected reduction in the effective charges. The dots of the coordinates of the charges in the table are given in Figure 9. The dots of PT and (Ba, Na)(Ti, Nb)O<sub>3</sub> in Figure 7 were also given to confirm any effect of the replacement. Figure 9 shows the two dots of (Ba, Na)Ti(O, Cl)<sub>3</sub> and the two dots of (Ba, Na)Ti(O, F)<sub>3</sub>. Their locations were very close to PT, which means that the replacement with halogens is effective. Furthermore, Nb is not necessary in these substances; otherwise, the opposite effect is expected, since the charge of Nb is relatively high compared with that of Ti. The figure also shows the data of the other halogen-replaced models, namely, Na(Ti, Nb)(O, Cl)<sub>3</sub>, and Na(Ti, Nb)(O, F)<sub>3</sub>. The data indicate that the charges of A were excessively low because there was no Ba included, and B was also excessively high because Nb was included. Therefore, Ba is also effective for the design of piezoelectrics as well as halogens. Finally, as expected, the calculation based on the N-replaced models, namely, (Ba, Na)Nb(O, N)3 and Ba(Ti, Nb)(O, N)3, showed the reverse effect.



**Figure 8.** Histogram of the effective charges of A and B of cluster model (Ba, Na)(Ti, Nb)O<sub>3</sub> replaced with Cl, F, N, respectively. The values in Table 8 were used. The values of PT in Table 5 and (Ba, Na)(Ti, Nb)O<sub>3</sub> in Table 7 were also used for comparison.



**Figure 9.** Map of the values in Table 8. The dots of PT and (Ba, Na)(Ti, Nb)O<sub>3</sub> in Figure 7 are given for comparison.

**Table 8.** Effective charges of solid solution models (Ba, Na)(Ti, Nb)O<sub>3</sub>; O ions were partially replaced with halogen Cl or F, or not halogen N. Each of the detailed chemical notations of the models is given in parenthesis in each cell on the left.

Model	А	A Averaged	В	<b>B</b> Averaged
(Ba, Na)Ti(O, Cl) <sub>3</sub> ((Ba <sub>4</sub> Na <sub>4</sub> )Ti <sub>8</sub> (O <sub>20</sub> Cl <sub>4</sub> )) Ba-centered	Ba 1.920 Na 0.500	1.210	Ti 2.344	2.344
(Ba, Na)Ti(O, Cl) <sub>3</sub> ((Ba <sub>4</sub> Na <sub>4</sub> )Ti <sub>8</sub> O <sub>20</sub> Cl <sub>4</sub> ) Na-centered	Ba 1.873 Na 0.459	1.166	Ti 2.355	2.355
Na(Ti, Nb)(O, Cl) <sub>3</sub> (Na <sub>8</sub> (Ti <sub>4</sub> Nb <sub>4</sub> )(O <sub>20</sub> Cl <sub>4</sub> ))	Na 0.445	0.445	Ti 2.434 Nb 2.611	2.523
(Ba, Na)Ti(O, F) <sub>3</sub> ((Ba <sub>4</sub> Na <sub>4</sub> )Ti <sub>8</sub> (O <sub>20</sub> F <sub>4</sub> )) Ba-centered	Ba 1.865 Na 0.523	1.194	Ti 2.422	2.422
(Ba, Na)Ti(O, F) <sub>3</sub> ((Ba <sub>4</sub> Na <sub>4</sub> )Ti <sub>8</sub> (O <sub>20</sub> F <sub>4</sub> )) Na-centered	Ba 1.856 Na 0.528	1.192	Ti 2.423	2.423
$\begin{tabular}{ c c c c c c c c c c c c c c c c c c c$	Na 0.545	0.545	Ti 2.542 Nb 2.761	2.651
(Ba, Na)Nb(O, N) <sub>3</sub> ((Ba <sub>4</sub> Na <sub>4</sub> )Nb <sub>8</sub> (O <sub>20</sub> N <sub>4</sub> )) Ba-centered	Ba 1.912 Na 0.724	1.318	Nb 2.983	2.983
(Ba, Na)Nb(O, N) <sub>3</sub> ((Ba <sub>4</sub> Na <sub>4</sub> )Nb <sub>8</sub> (O <sub>20</sub> N <sub>4</sub> )) Na-centered	Ba 1.943 Na 0.609	1.276	Nb 2.983	2.983
Ba(Ti, Nb)(O, N) <sub>3</sub> (Ba <sub>8</sub> (Ti <sub>4</sub> Nb <sub>4</sub> )(O <sub>20</sub> N <sub>4</sub> ))	Ba 1.899	1.899	Ti 2.589 Nb 2.817	2.703

#### 5. Conclusions

The effective ionic charges of perovskite dielectric complex compounds were investigated with molecular orbital calculation. Aside from PT, the results showed remarkable covalency for almost all cations and systematic variations in the effective charges of the A-site ions along their column in the periodic table. This variation corresponded to their electronegativity, and this was also the case with Ti and Zr, which belong to the same column. However, the charge of Pb for PT, which is an important

component of good piezoelectrics, was a stand-alone value. Therefore, both charges of Pb and Ti may be *magic numbers*. In fact, the calculation results for the good piezoelectrics BNT and PMN were close to the proposed numbers. Hence, they may provide us with good guidelines for the design properties of lead-free piezoelectrics that will lead to excellent performance. Through the *cluster chemical mean field*, the calculation of (Ba, Na)(Ti, Nb)O<sub>3</sub> indicates values close to those of PT, but this improvement was limited by the excessively high charge of B. Thus, the O in the model was replaced with the halogen Cl or F, which was more electronegative. The obtained charges were very close to that of PT, and Ba, Na, Ti, O, Cl, or F was necessary for the simplified synthesis of the perovskite substances. This idea does not explain the morphotropic effect, but may support it in terms of obtaining good Pb-free substances from a chemical point of view. This finding may also be very useful for the efficient use of ubiquitous alkaline metals and alkaline-earth metals, especially sodium.

**Author Contributions:** Conceptualization, N.T.; Methodology, N.T.; Validation, N.T. and J.-i.S.; Investigation, N.T. and J.-i.S.; Writing—original draft preparation, N.T.; Writing—review and editing, N.T. and J.-i.S. All authors have read and agreed to the published version of the manuscript.

Funding: This work was funded by the research team of science and technology of Fukuoka University.

**Acknowledgments:** N. T. thanks H. Zhang and S. Park for extending this work to the next fabrication stage. Figures 1 and 2 in this text were partially drawn with graphic software VENUS developed by R. A. Dilanian and F. Izumi.

Conflicts of Interest: The authors declare no conflict of interest.

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