A simple method for estimating of spontaneous polarization in perovskite-like nanocrystallites

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Abstract. The bond-valence sum approach to spontaneous valence polarization in perovskite-like nanocrystallites ABO₃ is presented. As the bond-valence method allows estimating the amount of valence charge distributed within the given bond according to bond length, the microscopic polarization in the ABO₃ structure may be directly derived from the valence deviation in two conjunctive bonding spheres A−O₁₂ and B−O₆. The concept was demonstrated on examples and a comparable agreement with data taken either from experiments or first principle calculation was seen. The bond-valence polarization appeared as one of the possible sources contributing to the final macroscopic polarization of the bulk materials.

Keywords: Perovskite, polarization, bond-valence, nanocrystallite.

1. Introduction

In the classical view [1, 2] the polarization of crystal is defined as the dipole moment per unit cell volume:

\[ P = \vec{P} = \frac{\sum q_i \vec{r}_i}{V}, \]

where \( q_i \) stands for charge and \( r_i \) position vector of the atom \( i \). The polarization \( P \) may also be decomposed into the product of atomic dipole moment \( p_i \) and concentration \( N_i \). The atomic dipole moment is again the product of atomic polarizability \( \alpha_i \) and local electrical field \( E_i \):

\[ P = \sum N_i p_i = \sum N_i \alpha_i E_i. \]

In this model the displacement of atoms from cubic positions may result in the separation of centers of positive and negative charges and accounts for the spontaneous polarization in absence of outer field. As an empirical rule, if the positive charge ions (e.g. Ba²⁺ and Ti³⁺ in BaTiO₃) were moved away from the negative O²⁻ ions by \( \delta \) Å then the dipole of a cell would be \( p \sim 6e\delta \). Therefore, a displacement of 0.1Å would imply a local polarization \( p \sim 1.2 \times 10^{-18} \text{Cm} \).
In contrast to this theory, recent developments consider the macroscopic polarization of crystal as a totally independent observable from the unit cell polarization. In quantum-mechanical approach, the center of negative charge is evaluated according to the value of position operator for the Berry’s phase of the Bloch wave function of the valence-band many-electron system \[3,4,5\]. So the polarization is described in terms of wave functions instead of real charge. Taken from \[10\] the polarization of a single electron is defined as:

\[
P_e = \lim_{L \to \infty} e \langle X \rangle / L ,
\]

where \(e\) is the electron charge, \(L\) the segment length along which the polarization is defined and \(\langle X \rangle\) the value of position operator for single-electron system. This position operator is defined as trivial

\[
\hat{X} = \sum_i x_i ,
\]

with the ground-state expectation value

\[
\langle X \rangle = \langle \Phi_0 \vert \hat{X} \vert \Phi_0 \rangle = \int dx x n(x) .
\]

In many-electron system the position operator takes form

\[
\hat{X} = \exp \left( i \frac{2 \pi}{L} \hat{X} / L \right) ,
\]

with ground-state value defined as

\[
\langle X \rangle = \frac{L}{2 \pi} \text{Im} \log \langle \Psi \vert \exp \left( i \frac{2 \pi}{L} \hat{X} \right) \vert \Psi \rangle .
\]

With this position operator the many-electron electronic polarization reads:

\[
P = \lim_{L \to \infty} \frac{e}{2 \pi} \text{Im} \log \langle \Psi_0 \vert e^{i \frac{2 \pi}{L} \hat{X}} \vert \Psi_0 \rangle .
\] (4)

The macroscopic polarization based on this electronic contribution will have unit of \[dipole per unit length\]. This short outline of the modern development was followed mainly Resta \[3, 4, 10, 11\] whereas the approaches from the other authors, e.g. King-Smith & Vanderbilt \[5\], Selloni \[6\] and Ortiz & Martin \[9\] were different. They all, however, originate in a common concept of the Berry’s phase of the Bloch wave function \[7\-8\]. To unify both classical and modern approaches we reformulate the macroscopic polarization as follows:

\[
P = \hat{P} P_{el} ,
\]

where \(\hat{P}\) is some operator acting on elementary contribution \(P_{el}\) and producing the final macroscopic polarization \(P\). Depending on either the classical or modern approach, this operator will take different forms and meanings. For classical approach \(\hat{P}\) is identity operator \(\hat{I}\) and \(P_{el}\) is the unit cell dipole moment

\[
P = \frac{e}{V} \sum_i q_i r_i / V .
\]

For a modern, "à la Resta" approach, \(\hat{P}\) takes the form

\[
P_e = \lim_{L \to \infty} e \langle X \rangle / L .
\]

In this paper we explain the alternative approach to the elementary polarization \(P_{el}\) and show its direct association with the structure. This approach has its origin in the statistical evaluation of valence distribution in metal-to-oxygen bonding spheres \[13\-16\]. It was empirically so accurate that it was frequently used in the structural science to predict the positions of atoms. The resulting formulae, which will be clear in the next sections, can be given as follows:

\[
P_{el} = (\Delta \nu_A - \Delta \nu_B) r
\]

\[
P = \sum_{i=1}^N p_i \langle P_{el} \rangle_i
\] (7)
where $\Delta v_A$ and $\Delta v_B$ stand for the valence excess/deficit in the coordination spheres of positive ions $A$ and $B$ respectively, $r$ the position vector to the center of $A\ldots B$ and $p_i$ the probability of elementary contribution $P_{ei}$. The next section describes how can $P_{ei}$ be obtained from the unit cell parameters.

2. Nominal length and nominal valence

The bond-valence is originally defined as the atomic valence per bond [13, 14], i.e. it is a certain portion of valence charge distributed within a given bond. Evidently, the bond-valence distribution differs in each bond type.

![Diagram](attachment://diagram.png)

Figure 1. Nominal length $R_s$ shows the radius where the valence of cation is exactly equal its nominal value (oxidation state). Comparison of $R_s$ and ionic radii: cation with excessive negative charge ($a$); cation with excessive positive charge ($b$).

Table 1. Nominal length $R_s$ (Å) for some cations frequently encountered in perovskites.

| Cation | A–O$_{12}$ | A–O$_6$ | Cation | B–O$_{12}$ | B–O$_6$ |
|--------|------------|---------|--------|------------|---------|
| Ba$^{2+}$ | 2.948      | 2.691   | Cu$^+$ | 2.519      | 2.263   |
| Sr$^{2+}$ | 2.781      | 2.524   | Cu$^{3+}$ | 2.252      | 1.995   |
| Pb$^{2+}$ | 2.775      | 2.518   | Mn$^{2+}$ | 2.453      | 2.196   |
| Ag$^+$ | 2.761      | 2.505   | Mn$^{3+}$ | 2.273      | 2.016   |
| Na$^+$ | 2.722      | 2.466   | Mn$^{4+}$ | 2.159      | 1.903   |
| La$^{3+}$ | 2.685      | 2.428   | Co$^{3+}$ | 2.183      | 1.926   |
| Pr$^{3+}$ | 2.651      | 2.394   | Co$^{4+}$ | 2.046      | 1.790   |
| Hg$^2+*1$ | 2.635      | 2.378   | Pb$^{4+}$ | 2.448      | 2.192   |
| Ca$^{2+}$ | 2.630      | 2.373   | Ti$^{4+}$ | 2.221      | 1.965   |
| Nd$^{3+}$ | 2.618      | 2.361   | Fe$^{2+}$ | 2.397      | 2.140   |
| K$^+$ | 3.051      | 2.795   | Cr$^{6+}$ | 2.050      | 1.794   |
| Er$^{3+}$ | 2.501      | 2.244   | Fe$^{3+}$ | 2.272      | 2.015   |
| Eu$^{3+}$ | 2.587      | 2.330   | Fe$^{4+}$ | 2.186      | 1.930   |

Various studies [15, 16] showed that the bond-valence depends on bond length according to the simple relation

$$v_i = e^{(R_0 - R_i)/B}.$$  \(8\)

This relation holds well for the ionic compounds with erroneous level less than 5% (the $R_0$ was experimentally determined and $B$ was preset to 0.37). Mathematically read, $v_i$ is the Laplace transformation of $R_0/B$. In perovskites the only bond types of interest is the metal-to-oxygen bond in two bonding spheres A–O$_{12}$ and B–O$_6$. The total atomic valence of metal in each sphere is the sum over all bond-valences in the sphere. The detailed vector calculation for the perovskite-like structure
ABO₃ can be found in [17]. One aspect that comes straightforward from the relation (8) is that in symmetric coordination sphere of n bonds, the average bond-valence $v_s$ is exactly equal to the oxidation state $\nu$ dividing by $n$. This average bond-valence $v_s$ may be used to classify the coordination sphere since it refers to a nominal value of bond-length $R_s$ for which the atomic valence is equal to the oxidation state. This $R_s$ sets a balance level, for which when the bond contracts or stretches the coordination sphere becomes overcharged or discharged with respect to the cation oxidation state.

**Figure 2.** a) The typical formulation of dipole in [A–O–B] chain; b) Coordination spheres of cations in the perovskite-type arrangement.

![Figure 2](image)

**Figure 3.** Values of $R_s = [R_{\text{cation}} + R(\text{O}_2^-)]$ for B-site and A-site cations.

In perovskites the calculated atomic valence for the cations usually differs from its oxidation state. For example, in LaCoO₃ the total valence over La³⁺–O₁₂ was found a little below +3 whereas the same over Co³⁺–O₆ was above. This situation can be explained using figure 1. In rigid bonding to oxygen, the metal ionic radius allows the closest contact but since the ionic radius is not equal to $R_s$ for the same atom, the metal will have different amounts of bonding electrons in comparison with its nominal oxidation number.

Table 1 lists some $R_s$ for the cations frequently encountered in perovskites. These values were calculated using the empirical valence-to-length values given in [15]. It shows that the right-side cations (e.g. Cu¹⁺, Ti⁴⁺, Fe³⁺, Cr⁶⁺, Mn⁷⁺) can hardly fall into the A-position (forcing B–O₁₂ coordination) since the average radius of the B–O₁₂ coordination spheres for these cations is around...
2.7Å which is too larger than their listed nominal lengths \( R_s \). So these cations will always be discharged if closely packed. Similarly, the left-side cations (e.g. Eu\(^{3+}\), K\(^+\), Ca\(^{2+}\), Hg\(^{2+}\), Nd\(^{3+}\)) can also hardly fall into the B-position (forcing A\(\text{—}O_6 \) coordination) because of a much smaller average radius of the A\(\text{—}O_6 \) coordination sphere (~1.9Å) in comparison with the nominal lengths. So these cations will be heavily overcharged if closely packed. In case such unlikely occupation happens, the structure is predicatively distorted with high local polarization being foreseen.

| Cation | Bonding domain | Bond-valence [b.v] |
|--------|----------------|-------------------|
| Cu\(^+\) | B—O\(_6\) | 0.17 |
| Cu\(^{3+}\) | B—O\(_6\) | 0.34 |
| Co\(^{4+}\) | B—O\(_6\) | -1.06 |
| Pb\(^{4+}\) | B—O\(_6\) | 1.10 |
| Pb\(^{2+}\) | A—O\(_{12}\) | -0.46 |
| Ca\(^{2+}\) | A—O\(_{12}\) | -0.49 |
| K\(^+\) | A—O\(_{12}\) | 0.24 |

3. Polarization of coordination domains
The incompatibility between ionic radii and nominal length \( R_s \) seems to have a strong impact on the microscopic polarization in perovskites. Figure 2 shows the possible formulation of dipole in the chain of two cation coordination spheres [A\(\text{—}O_{12}\)...[B-O\(_6\)].

For the cations listed in table 1, the figure 3 and table 2 demonstrate how possible is this polarization effect and its expected value. For the listed data, the \( R(O^2-) \) was preset to 1.21Å. In most of B-site cations, \( R_s(A—O_{12}) > [R_{cation}+R(O^2-)] \) so the difference between the two, \( \Delta R > 0 \), except for Co\(^{3+}\) and Co\(^{4+}\). Therefore, Co\(^{3+}\) and Co\(^{4+}\) can never reach their nominal oxidation states in perovskite-packed structures. The matching of oxidation state is adequate for Mn\(^{2+}\), Mn\(^{3+}\), Mn\(^{4+}\), Fe\(^{2+}\), Fe\(^{3+}\), Fe\(^{4+}\), Ti\(^{4+}\), Cr\(^{6+}\) (\( \Delta R < 0.05Å \)), but Cu\(^+\), Cu\(^{3+}\), Pb\(^{4+}\) (\( \Delta R > 0.05Å \)) show the excess in valence.

The A-site cations, on the other hand, show the valence deficit for most of cases except for K\(^+\). The positive charge may be excessive as for Pb\(^{2+}\), Ca\(^{2+}\) (\( \Delta R < -0.05Å \)), or adequate as for Ba\(^{2+}\), Sr\(^{2+}\), Na\(^+\), La\(^{3+}\) (\( \Delta R \leq -0.025Å \)), or equilibrated as for Nd\(^{3+}\) (\( \Delta R = 0Å \)). Generally speaking, the cations Mn\(^{2+}\), Mn\(^{3+}\), Mn\(^{4+}\), Fe\(^{2+}\), Fe\(^{3+}\), Fe\(^{3+}\), Ti\(^{4+}\), Cr\(^{6+}\) (B—O\(_6\)) and Ba\(^{2+}\), Sr\(^{2+}\), Na\(^+\), La\(^{3+}\), Nd\(^{3+}\) (A—O\(_{12}\)) are the neutral cations with respect to the matching of their oxidation state, whereas the Cu\(^+\), Cu\(^{3+}\), Pb\(^{4+}\), Co\(^{4+}\) (B—O\(_6\)) and Pb\(^{2+}\), Ca\(^{2+}\), K\(^+\) (A—O\(_{12}\)) can be thought as the highly polarized cations.

According to this analysis the compounds like Pb\(^{2+}\)Co\(^{4+}\)O\(_3\) and Ca\(^{2+}\)Co\(^{4+}\)O\(_3\), which contain strongly polarized cations, are weakly polarized. This is because of the cancelation of the polarization effect by both cations. Similarly, the combination like K\(^+\)Pb\(^{4+}\)O\(_3\) can bring weak polarization effect. A weak effect is also expected for the compounds containing only neutral cations such as (Ba\(^{2+}\), Sr\(^{2+}\), Nd\(^{3+}\))(Ti\(^{4+}\), Fe\(^{2+}\), Fe\(^{3+}\), Cr\(^{3+}\))O\(_3\). For example, the polarization in BaTiO\(_3\) is not large, the calculation for closely-packed structure showed the dipole near \( p = 0.18e\times3.3Å = 0.59eÅ = 1.0\times10^{-29} \) Cm. The compounds that could lead to a strong polarization should contain the Pb\(^{2+}\), Pb\(^{4+}\), Co\(^{4+}\) or Ca\(^{2+}\) cations. This claim agrees well with experiments. For the numeric calculation of valence polarization we adopt the following definition.

**Definition.** The coordination domain ABO\(_3\) is referred to as polarized if the decline of the cation bond-valence from its nominal oxidation state differs in two bonding spheres A—O\(_{12}\) and B—O\(_6\), i.e. the differences in matching oxidation states for both cations cause the atomic valence imbalance:

\[
\Delta v = (v - v_S)_A - (v - v_S)_B \neq 0 ,
\]
where \((v - v_S)_A\) and \((v - v_S)_B\) are the declines of the cation bond-valences from their proper nominal values. The unit of \(\Delta v\) is evidently [valence/domain]. The dipole of domain is understood as common as for the general case:

\[ P_{el} = \Delta v \times r , \]

where \(r\) is the distance from cation A (or B) to the A...B center, the direction of \(r\) is chosen so that \(\Delta v\) is positive. In the next section we compare this dipole with some other concepts that were obtained from the experiments or first principle calculation.

### Table 3. Born effective charges (1st row) versus bond-valence charge (2nd row) for BaTiO₃.

| \(a(\text{Å})\) | \(Z(\text{Ba})\) | \(Z(\text{Ti})\) | \(Z(\text{O})\) | \(\Delta v\) | \(p(\text{eÅ})\) |
|-----------------|----------------|----------------|----------------|-------------|-------------|
| 3.64            | 2.95           | 7.23           | -3.95          | 1.02        |
|                 | 5.19           | 5.68           | -3.80          | 0.52        | 1.64        |
| 3.94            | 2.77           | 7.25           | -3.93          | 1.00        |
|                 | 3.10           | 3.95           | -2.35          | 0.45        | 1.54        |
| 4.00            | 2.74           | 7.29           | -3.94          | 1.00        |
|                 | 2.76           | 3.64           | -2.13          | 0.44        | 1.53        |
| 4.40            | 2.60           | 7.78           | -4.17          | 1.04        |
|                 | 1.29           | 2.12           | -1.14          | 0.42        | 1.57        |

### 4. Test examples and comparison

Table 3 lists the results from the first principle calculations of dynamic charge and associated dipole for BaTiO₃ [12] and compares them with our values (we used \(p = \Delta v (a\sqrt{3})/2\) where \(a\) is the cubic lattice constant; the authors in [12] did not list dipoles, so we recalculated according to the given charges). The samples were under isotropic compression and in cubic phase. The bond valence seems to be more sensitive. Note that the charge associated with bond valence is the static charge, whereas the Born effective charge (BEC) is the dynamic charge, i.e. the charge observed by dipole and contains certain amount of electrons from the inner core. The BEC is not the valence charge and it is evident that this charge depends only a little on pressure, reflecting a small change on final dipole.

How well do the bond-valences reflect the reality of valence charge distribution within the BaTiO₃ structure, this can be estimated by comparing them with other concepts of static charge. For Ba⁺², the empirical models gave 2.00 and 1.86; the first principle calculation gave 2.00, 2.12 and 1.39, whereas the bond-valence gave its best estimation near 2.56 for the cell constant approaching 4.041Å. For the larger cell, the bond valence might drop to 1.29 as seen in table 3.

For Ti⁴⁺ the situation was similar, the empirical models gave 1.88 and 3.18; the first principle calculation gave 2.89, 2.43 and 2.79, whereas the bond-valence developed from 2.12 to 5.68 and gave the best estimation near 3.44 for the same cell around 4.041Å. The situation for oxygen was different since none of the calculations either based on empirical or first principle models gave values below \(-2.0\). The bond-valence model, on the other hand, developed from -1.14 to -3.62 reflecting the core theoretical presumption about its elasticity. This means, for the BaTiO₃, that under certain circumstances the oxygen might accept more than 2 valence electrons.

In Table 4 we summarized the measured spontaneous polarizations of various samples taken from the classical literature [2] and compared them with our results. The listed \(P_s\) is equal \(p/V\), where \(p\) is dipole and \(V\) is unit cell volume. For the cited compounds the structural data were retrieved from the Powder Diffraction Database [18]. When many samples existed then the one with lowest profile-weighted \(R_p\) factor has been chosen. For all compounds the cations were assumed to occur only in one oxidation state, e.g. Ti⁴⁺, Ba⁺², Sr⁺², Pb⁺², Nb⁵⁺, Ta⁵⁺ and Li⁺. The mix valence state was omitted. The
structural models were simple for these cases. As seen, the observed and calculated values are quite close to each other, although the absolute agreement is not expected, since the listed polarizations belong to two different concepts. However, we might certainly conclude that the bond valence polarization should be considered as one of the local sources that contribute to the final macroscopic polarization.

Table 4. The spontaneous polarization $P_s$ at room temperature for several classical perovskites.

| Compound   | $P_s$ (C/m²) | Reference [2] | This work |
|------------|--------------|---------------|-----------|
| BaTiO₃     | 0.26         | 0.22          |
| SrTiO₃     | 0.20         | 0.17          |
| PbTiO₃     | 0.50         | 0.65          |
| LiNbO₃     | 0.71         | 0.87          |
| LiTaO₃     | 0.50         | 0.53          |

Figure 4 compares the calculated bond-valence polarization with the experimental data. As seen, the agreement is good for many cases and the erroneous level holds below 15% for all cases. At the first guess, this is an excellent result. It demonstrates the applicability of the bond-valence method to the study of polarization effect in perovskite-like materials. The method may be used as guidance for content selection when preparing the new piezoelectric materials.

5. Conclusion
The polarization effect was the main aspect in many studies concerning the perovskites and perovskite-like compounds. However, we found that there was no attempt to discuss the polarization in terms of the classical bond-valences sum concept, although it appeared simple and straightforward to derive the microscopic polarization from the bond-valence model. This investigation, though given in the primary stage, revealed that the bond-valence approach provided the results that are comparable to those of the experiments or quantum-mechanical models. Furthermore, it gave a clear classification of cations according to their tendency to form the polarized structures. This method, however, might...
produce mismatched valence configuration if the crystal structure was not modelled correctly. The main difficulty was that with the substitution of foreign elements, the correct location for each of the substituted elements could not be exactly determined. So many structural models must be taken into account to avoid the possible misconstruction. Despite this difficulty the ease of using this method in many common cases persuades its usefulness and applicability in the study of perovskites and perovskite-like compounds.

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