Structural effect of aliovalent doping in lead perovskites

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ABSTRACT

Composition–structure relationships are needed for various applications, including lattice-matching for heteroepitaxy; however, a general model to *predict* lattice constants in defective perovskites is not yet available because the exact nature of *A*-site vacancies in perovskites remains largely unknown. In this study, it has been shown experimentally via Le Bail refinements of x-ray diffraction data that such vacancies in $(Pb_{1-3x}La_{2x}\square_x)TiO_3$ and $(Pb_{1-3x}La_{2x}\square_x)(Zr_{0.6}Ti_{0.4})O_3$ have an *effective* size due to both Coulombic repulsion of coordinating oxygen ions and bond relaxation. For the first time, cell volume can be predicted in this system from stoichiometry and published ionic radii data alone to within 0.2% accuracy within $0 \leq x \leq \frac{1}{3}$ compositional range and $< 0.3\%$ accuracy all the way to $x = \frac{1}{3}$. The model may be applied to other perovskite systems and eventually provide tailored properties (magnetic, dielectric, and other) based on improved structure predictions.

1. Introduction

The perovskite E2₁ structure is central to many useful properties via defect engineering, for which a precise understanding of composition–structure relationships is needed. Lead zirconate titanate (PZT) perovskites are particularly attractive because of the optimal piezoelectric characteristics which are found close to the morphotropic phase boundary (MPB) (Zr/Ti ratio ~53/47).

Lead-containing perovskites continue to dominate the ever growing piezoelectric multi-billion dollar global market [1]. Lead zirconate titantate is low-cost, extremely reliable and the most common piezoelectric material in the market [1–2]. Donor doping is commonly used in PZT ceramics to control the effect of PbO volatilisation on sintering and enhance the relaxor properties [3]. The loss of PbO generally creates both Pb^{2+} and O^{2-} vacancies. The oxygen vacancies are particularly damaging to the dielectric properties, as they are highly mobile and result in ionic conduction and a large increase in dielectric loss. It is common to dope the *A*-site with La^{3+} (≈ 0.5–2 mol%) to allow the formation of lead vacancies without necessitating the creation of charge-compensating oxygen vacancies. Furthermore, such doping is very important in industry because of its additional beneficial effects which include: increased mechanical compliance, maximal electromechanical coupling coefficients, increased dielectric

constant, decreased coercive field, increased squareness of the hysteresis loop, and enhanced optical transparency [1–2], yet no attempt has been made to study the exact nature of vacancies in lead lanthanum zirconate titanate (PLZT), which remains problematic.

In 1993, Lal et al. [4] showed a decreasing shift in dielectric constant with increasing La^{3+} content between $(Pb_{0.925}La_{0.05})(Zr_{0.6}Ti_{0.4})O_3$ and $(Pb_{0.91}La_{0.06})(Zr_{0.6}Ti_{0.4})O_3$; however, in 2010, Thakur and Prakash [5] confirmed that the dielectric constant *increases* with increasing lanthanum concentrations in PLZT all the way through $(Pb_{0.88}La_{0.08})(Zr_{0.6}Ti_{0.4})O_3$. Moreover, lanthanum has relatively high solubility in PZT and is thus capable of producing a variety of solid-solution compositions with different lattice constants [5].

Lattice-parameter prediction is critical for various fields including lattice matching for heteroepitaxy and is a necessary first step in structure prediction. Lufaso and Woodward [6] developed the SPuDS program to predict perovskite structures and lattice parameters; however, SPuDS is unable to predict the lattice parameters for non-stoichiometric perovskite systems. An empirical equation relating the ionic radii to the cubic perovskite lattice constant was established with an average of 0.63% absolute relative error in 2006 by Jiang et al. [7]; however, they assumed a six-fold coordination for all ions. Although this assumption was problematic in that the perovskite *A*-site coordination is generally twelve-fold and the anion-site coordination should properly be two-fold (the anion is coordinated to two *B*-site cations; the nearest four *A*-site cations are ~41% further away), it yielded

highly accurate predictions. This model was later improved by Ubic [8–9] (Eqs. 1 and 2)

$$a_{pc} = 0.06741 + 0.49052(r_A + r_X) + 1.29212(r_B + r_X) \tag{1}$$

$$a_{pc} = 0.05444 + 0.467016(r_A + r_O) + 1.30838(r_B + r_O) \tag{2}$$

where a_{pc} is the pseudocubic lattice constant, r_A, r_B and r_x are the sizes of the A site, B site and anion, respectively, assuming six-fold coordination throughout.

For this work, lattice constants were both measured via x-ray diffraction (XRD) and calculated (Eq. (1)). Pseudocubic lattice constants were derived from experimental XRD data, which provided the means to back-calculate the average sizes of the anions (Eq. (3)), from which the average sizes of the A site could be derived (Eq. (4)).

$$\bar{r}_O = \frac{a_{pc,\text{exptl}}}{2} - r_B \tag{3}$$

$$\bar{r}_A = \frac{a_{pc,\text{exptl}}}{\sqrt{2}} - r_O \tag{4}$$

$$\bar{r}_A = (1 - 3x)r_{Pb} + 2xr_{La} + xr$$
$$= \bar{r}_{A(ideal)} + xr_\square \tag{5}$$

$$\bar{r}_\square = \frac{\bar{r}_A - (1-3x)r_{Pb} - (2x)r_{La}}{x} = \frac{\bar{r}_A - \bar{r}_{A(ideal)}}{x} \tag{6}$$

The average A-site size can be calculated from stoichiometry (Eq. (5)), from which the effective size of the extrinsic vacancies could be derived (Eq. (6)). The value of $\bar{r}_{A(ideal)}$ corresponds to the A-site size not considering the effect of vacancies (i.e., setting $r_\square$ to zero).

In many cases the oxygen octahedra have a certain distortion associated with them, which is also related to the stability of the perovskite structure. The tolerance factor, t, is a relative measure of the perovskite stability and was first introduced by Goldschmidt [10] (Eq. (7)).

$$t = \frac{r_A + r_X}{\sqrt{2}(r_X + r_B)} \tag{7}$$

In 2001, Lufaso and Woodward [6] derived a tolerance factor based on bond-valence which predicts the tilt system of perovskites more accurately than Eq. (7), and Ubic [9] later developed an equally accurate model based on peudocubic lattice constant and B–X bond length (Eq. (8)).

$$t = \frac{a_{pc} - 0.05444}{0.660460(r_B + r_X)} - 1.981012 \tag{8}$$

Lanthanum-modified lead titanate (PLT) and lead zirconate titanate (PLZT) systems synthesized with a saturated PbO environment (i.e., muffling) are not expected to generate B-site vacancies; [5,11–13] rather, charge compensation causes A-site vacancy formation exclusively as follows:

$$La_2O_3 \xrightarrow{3Pb(Zr_yTi_{1-y})O_3} 2La_{Pb}^\bullet + V''_{Pb} + 3O_o^x$$
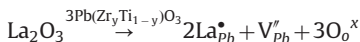
resulting in $Pb_{1-3x}La_{2x}\square_x(Zr_yTi_{1-y})O_3$. This formulation is convenient, as x is then directly equivalent to the vacancy concentration, $x=[\square]$. A total of 25 compositions (six of which were previously reported) were studied to investigate the effective size of A-site vacancies. Each composition had a known concentration of A-site vacancies due to supervalent charge compensation. Effective vacancy size as a function of supervalent dopant concentration has not before been reported for this system.

Table 1
Site distribution according to nominal A-site vacancy concentration in $(Pb_{1-3x}La_{2x}\square_x)(Zr_yTi_{1-y})O_3$.

$x=[\square_A]$	y	Pb^{2+}	La^{3+}	Zr^{4+}	Ti^{4+}	O^{2-}
0.00	0.6	1.000	0.00	0.6	0.4	3
0.00[a]	0.0	1.000	0.00	0.0	1.0	3
0.0010	0.6	0.997	0.002	0.6	0.4	3
0.0015	0.6	0.9955	0.003	0.6	0.4	3
0.0025	0.6	0.9925	0.005	0.6	0.4	3
0.0035	0.6	0.9895	0.007	0.6	0.4	3
0.005	0.6	0.985	0.01	0.6	0.4	3
0.010	0.6	0.970	0.02	0.6	0.4	3
0.015	0.6	0.955	0.03	0.6	0.4	3
0.020	0.6	0.940	0.04	0.6	0.4	3
0.025	0.6	0.925	0.05	0.6	0.4	3
0.025[b]	0.0	0.925	0.05	0.0	1.0	3
0.03	0.6	0.91	0.06	0.6	0.4	3
0.04	0.6	0.88	0.08	0.6	0.4	3
0.05[b]	0.0	0.85	0.10	0.0	1.0	3
0.05	0.6	0.85	0.10	0.6	0.4	3
0.06	0.0	0.82	0.12	0.0	1.0	3
0.06	0.6	0.82	0.12	0.6	0.4	3
0.07	0.6	0.79	0.14	0.6	0.4	3
0.075[b]	0.0	0.775	0.15	0.0	1.0	3
0.08	0.6	0.76	0.16	0.6	0.4	3
0.10	0.0	0.70	0.20	0.0	1.0	3
0.10	0.6	0.70	0.20	0.6	0.4	3
0.125[b]	0.0	0.625	0.25	0.0	1.0	3
0.15[b]	0.0	0.55	0.30	0.0	1.0	3
0.333[c]	0.0	0.0	0.667	0.0	1.0	3

References a[14], b[15] and c[22]

2. Materials and methods

Table 1 lists 25 compositions in the system $Pb_{1-3x}La_{2x}\square_x(Zr_yTi_{1-y})O_3$ which were synthesized via the solid-state mixed-oxide route. No excess lead was added to the compositions, but a $PbZrO_3$ sacrificial powder bed was used to induce and control a lead-rich closed environment. [11] Additionally, calcination and sintering were conducted in a pre-contaminated crucible to inhibit lead-loss due to the crucible walls.

Nine of the compositions, described in this paper, were in the system $(Pb_{1-3x}La_{2x}\square_x)TiO_3$ $(0 \leq x \leq 0.15)$ (PLT). Two of the nine PLT compositions were synthesized for this work and the remaining seven compositions were previously reported [14–15]. Stoichiometric amounts of PbO (99.9%, Thermo Fisher Scientific Inc., Pittsburgh, PA), TiO_2 (99.9%, Aldrich Chemical Co., Milwaukee, WI), and La_2O_3 (99.9%, Alfa-Aesar, Ward Hill, MA) were ball milled with yttria-stabilized ZrO_2 (YSZ) media in deionized water for $\sim$24 h in a high-density nylon pot. Powders were then dried overnight in an atmospheric drying oven at 80–100 °C until the water was evaporated. Calcination was conducted at 900 °C for three hours in a box furnace (1807FL, CM Furnaces Inc., Bloomfield, NJ) in an inverted Al_2O_3 pre-contaminated crucible and 4 wt% $PbZrO_3$ sacrificial powder bed. After calcination the powders were milled and sieved to under 250 μm. Cylindrical green compacts were formed of about 6–8 mm in height and 20 mm in diameter by applying a pressure of $\sim$63 MPa. Compacts were sintered in a pre-contaminated crucible for two hours at 1250 °C in a lead-rich atmosphere (4 wt% $PbZrO_3$ sacrificial powder bed) using an inverted crucible.

Another 17 compositions were synthesized in the system $(Pb_{1-3x}La_{2x}\square_x)(Zr_{0.6}Ti_{0.4})O_3$ $(0 \leq x \leq 0.1)$ (PLZT). The lanthanum oxide was heated to 700 °C for 1 h and weighed after cooling. The oxides PbO ($>$99%, Liebau), ZrO_2 ($>$99%, SEPR), TiO_2 ($>$99%, Tronox), and La_2O_3 ($>$99%, Merck) were homogenized via attrition milling with 2 mm YSZ media in isopropanol with a polyamide crucible and rotors. After drying in a roto-evaporator the compounds were stored in an oven for several days, after which they were sieved (160 μm mesh) and calcined in an Al_2O_3