Bond Valence Analysis of Tetragonal Zirconias

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In tetragonal zirconia, the cation is coordinated by two interpenetrating tetrahedra of oxygen ions, implying two different cation–oxygen bond lengths. On substituting the different tetravalent ions Ge, Ti, Sn, and Ce into tetragonal ZrO_2–2 mol% Y_2O_3, the mean value of the shorter cation–anion bond length varies linearly with the concentration of the substituent ion where the bond length increases or decreases depending on whether the substituted ion is larger or smaller than the zirconium ion it replaces. It is argued in this paper that the length of the longer bond is determined by the requirement that the bond valence sum remains constant. In each case the length of the longer bond calculated on this basis is in good agreement with the measured bond length (from neutron diffraction), and following small adjustments of the bond valence constants, excellent agreement is obtained. The requirement for the bond valence sum evidently accounts for the physics of the situation, and at the same time the available bond length data allow very precise determination of the bond valence constants of the different ions in the tetragonal zirconia environment. It is shown how these bond length considerations provide an explanation for the variation with composition of oxygen position and lattice parameters in all of the materials considered. Among the interesting features accounted for by this analysis are the increase in cell volume occurring when Zr is replaced by the smaller Sn ion, and slight departures from Vegard's law observed in the substitution of Zr by Ti. © 1999 Academic Press

INTRODUCTION

Zirconia and zirconia alloys find widespread application as engineering ceramics and have for this reason been extensively studied (1, 2). In this context the tetragonal form of zirconia attracts the greatest attention because it is the martensitic transformation from metastable tetragonal to monoclinic zirconia under applied stresses which confers the benefit of transformation toughening. Though the tetragonal phase is not the thermodynamically stable form of pure zirconia under ambient conditions, by alloying it with relatively small amounts of other oxide materials or by preparing it in fine particle form, it can be readily retained in ambient conditions.

The focus in this work is on tetragonal zirconia alloys in ternary oxide systems. Such materials have been the subject of several studies (3–13). The aim in most of these studies is to understand the factors influencing the stability (or conversely the transformability) of the tetragonal phase. The stability has been said to be influenced by the tetragonality (c/a ratio), the number and distribution of oxygen vacancies associated with aliovalent dopants, or the size of the dopant ions, but as yet no clear picture has emerged.

More specifically, we turn our attention to tetragonal ZrO_2–2 mol% Y_2O_3 doped with various amounts of CeO_2, SnO_2, TiO_2, or GeO_2, samples of which have been prepared and studied by Kim and his co-workers (12, 13). The samples were prepared by solid-state mixing of the oxides CeO_2, SnO_2, TiO_2, or GeO_2 with 2 mol% Y_2O_3 stabilized tetragonal zirconia (2Y–TZP) powder, followed by pressing and sintering (12). A laboratory X-ray diffractometer was used for lattice parameter determination, and a comprehensive Raman study was completed (12). The change in the frequency of a particular Raman mode gives an indication of the change in length with composition of the shorter cation–oxygen bond, but for the longer bond the frequency of the relevant Raman mode was dominated by other factors, so no comparable information was available. For Sn substituted materials, a particularly interesting ("anomalous") result was obtained from the X-ray and Raman study: though the Sn has a smaller ionic radius than the Zr ion and the Raman shift indicates that the mean length of the

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shorter cation–anion bond decreases as the concentration of Sn is increased, the unit-cell volume increases with increasing concentration of Sn. Subsequently, the variation of mean bond length with substituent concentration was established for both the shorter and longer cation–oxygen bonds using neutron diffraction (13), and in the case of the shorter bond the indications from the Raman scattering were confirmed. The case of Ti was interesting, in that substitution of Zr by the smaller Ti ion was accompanied by an increase in the c parameter, though, in line with expectation, the volume of the unit cell decreased. Slight departures from Vegard's law (linear dependence of lattice parameter on concentration) were noted in this case (13).

It was found from the neutron diffraction study (13) that the mean value of the cation–oxygen bond length, representing close cation–oxygen contact, depends linearly on the amount of substituent ion. This bond length increases or decreases depending on whether the substituted ion is larger or smaller than the zirconium ion it replaces. It is proposed in this paper that the length of the longer cation–oxygen bond is determined by a requirement that the bond valence sum remains constant. The bond lengths derived on this basis are in excellent agreement with those observed. It is shown how these bond length considerations provide an explanation for the variation with the composition of the oxygen position and the lattice parameters in all of the materials considered. As mentioned above, the substitution of Zr by the smaller Sn ion is an interesting case. There seems little prospect of explaining the increase in cell volume with increasing Sn concentration by purely geometrical arguments. However, using bond valence arguments, the "anomaly" is easily explained. As the shorter cation–anion bond gets shorter, the longer bond is driven to become longer, and an increase in cell volume results. The analysis also provides an explanation for the increase in the c parameter on substitution of Zr by Ti and, at least in part, for the slight departures from Vegard's law observed in the same case.

BOND VALENCE ANALYSIS

The bond valence sum (BVS) method (14, 15) is an empirical approach for predicting the valence of atoms given their local geometry, that is, the bonds they forms with neighboring atoms. Alternatively, the bond lengths around an atom might be predicted, given the valences of the atoms taking part in the bond. In the BVS method the valence of an atom is assumed to be distributed among its neighboring bonds, such that the total valence of an atom is the sum, v, of its bond valences. Thus, Brown and Altermatt (15) have written the total valence as

$$v = \sum_j s_j = \sum_j \exp\left(\frac{R_o - R_j}{B}\right), \qquad [1]$$

where s_j is the valence, R_j is the length of the jth bond, and R_o and B are experimentally determined parameters dependent on the types of atoms involved in the bond. This relationship has been found to be a good approximation of the bond valence for a large range of atoms.

In the case of tetragonal zirconia, the BVS method can be applied to predict the longer cation–anion bond length from the shorter cation–anion bond length and the valence. For ZrO_2–2mol% Y_2O_3, the valences of the Zr and Y ions are expected to be 4^+ and 3^+, respectively, in which case the average valence for the Zr/Y/M ion (M = tetravalent dopant) will be $+3.96$. For the shorter cation–anion bond length, d_s^{Zr-O}, we refer to the neutron diffraction study (13). In that study it was found that the bond length varied linearly with dopant content (Fig. 1); the slope, $d(d_s^{Zr-O})/dx$, (x = composition) is related to the ionic size of the dopant (see Table 1). The relationship between slope and ionic radius is roughly linear, as seen in Fig. 2, except that Ge, typically covalent, does not follow this trend.

From the knowledge of the way the shortest bond changes and assuming a fixed valence for the Zr/Y/M ion of $+3.96$, it is possible to predict the longer bond length, d_l^{Zr-O}, by solving Eq. [1]. Calculations of the longer bond distance using this simple model and tabulated R_o and B values were found to be in good agreement with the experimental bond length. An even better match, shown in Fig. 1, was obtained when the values of R_o were allowed to vary to fit the data. As previously published R_o values are averages taken from a number of differing systems, it is anticipated that the R_o values for these structures may vary a little from the average results. The values of R_o found by fitting experimental data are listed in Table 2. The R_o value for Zr was found by using the structural data of the starting ZrO_2–2% Y_2O_3 sample. The values obtained were within one standard deviation of the

TABLE 1
Effect of Substitution on the Short Bond Length, d_s^{Zr-O}, Compared with the Ionic Radii of the Substituting Ion. The Numbers in Parentheses Are Estimated Standard Deviations of the Last Significant Figures

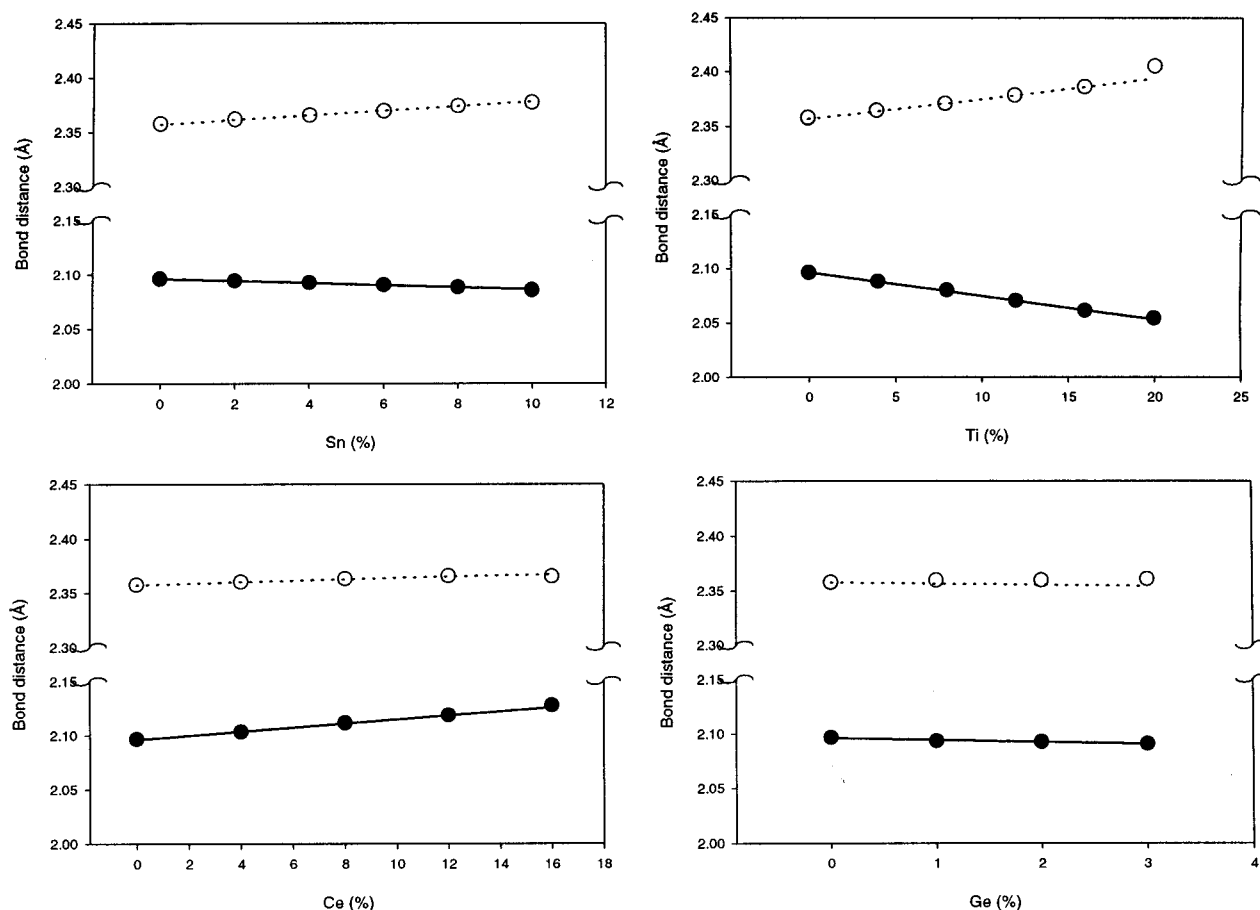| Element Ion	Ionic Radius[a] (Å)	$\dfrac{d(d_s^{Zr-O})}{dx}$ (Å mol%$^{-1}$)
Zr^{4+}	0.84	0.0
Ge^{4+}	0.66[b]	$-1.81(34) \times 10^{-3}$
Ti^{4+}	0.74	$-2.18(4) \times 10^{-3}$
Sn^{4+}	0.81	$-0.98(2) \times 10^{-3}$
Ce^{4+}	0.97	$1.84(6) \times 10^{-3}$

[a]Ref. 17.
[b]Refs. 12 and 17.

FIG. 1. The dependence of the short and longer Zr–O bond lengths in tetragonal ZrO$_2$–2 mol% Y$_2$O$_3$ on concentration for different substituents (a) Sn, (b) Ti, (c) Ce, and (d) Ge. The circle symbols represent values of the bond lengths obtained from neutron diffraction data. The solid continuous line is a linear fit to the data of the shorter bond length. The broken line has been calculated from BVS considerations.

tabulated values, except for the Ge series. This means that the simple BVS model adequately describes the bond length variations of the d_l^{Zr-O} bond, given the variation of the shorter bond, which itself depends simply on the ionic size of the dopant.

The simple physical interpretation of this is that if the short bond length decreases while the metal ion continues to have a fixed valence, the long bond length must increase (at a greater rate) to compensate for the increased contribution to the valence from the shorter bonds. Likewise, if the short bond length increases, as in Ce doping, then the bond valence sum would dictate that the longer bond length need not change significantly. Certainly the rate would be less than that of the short bond, as seen experimentally. The effects are precisely in accord with Brown's distortion theorem (18). In fact the stability of tetragonal zirconia relative to the cubic polymorph may also be explainable in terms of the distortion theorem since Zr is undersized in the cubic structure.

LATTICE PARAMETERS AND STRUCTURE

The bond lengths derived from the neutron diffraction data are accounted for very well by assuming that the shorter bond length varies linearly with dopant concentration and then using the BVS method to calculate the length of the longer bond (Fig. 1). It is of interest to explore whether the lattice parameters and oxygen position might be derived from the bond lengths.

The length of the short and longer bonds are (16)

$$d_s^{Zr-O} = \sqrt{\frac{a^2}{8} + c^2\left(\frac{1}{4} - \delta\right)^2} \qquad [2]$$

and

$$d_l^{Zr-O} = \sqrt{\frac{a^2}{8} + c^2\left(\frac{1}{4} + \delta\right)^2}, \qquad [3]$$
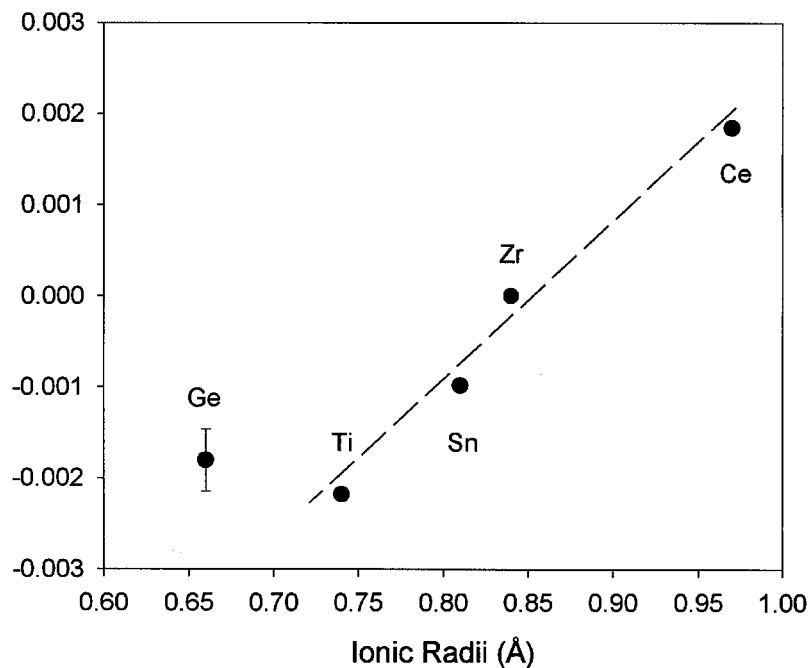
FIG. 2. The slopes from the linear fit of the shorter bond length as a function of ionic radius (17). The estimated error is shown explicitly for Ge—in other cases the error is comparable to the size of the symbols. The line is a guide to the eye.

where a and c are the lattice parameters and δ measures the deviation of the oxygen position from the position it would have in the ideal fluorite structure.

From the lengths of these two bonds, it is evidently not possible to derive accurate values for a, c, and δ. An approximate value of δ can be obtained, however, by neglecting
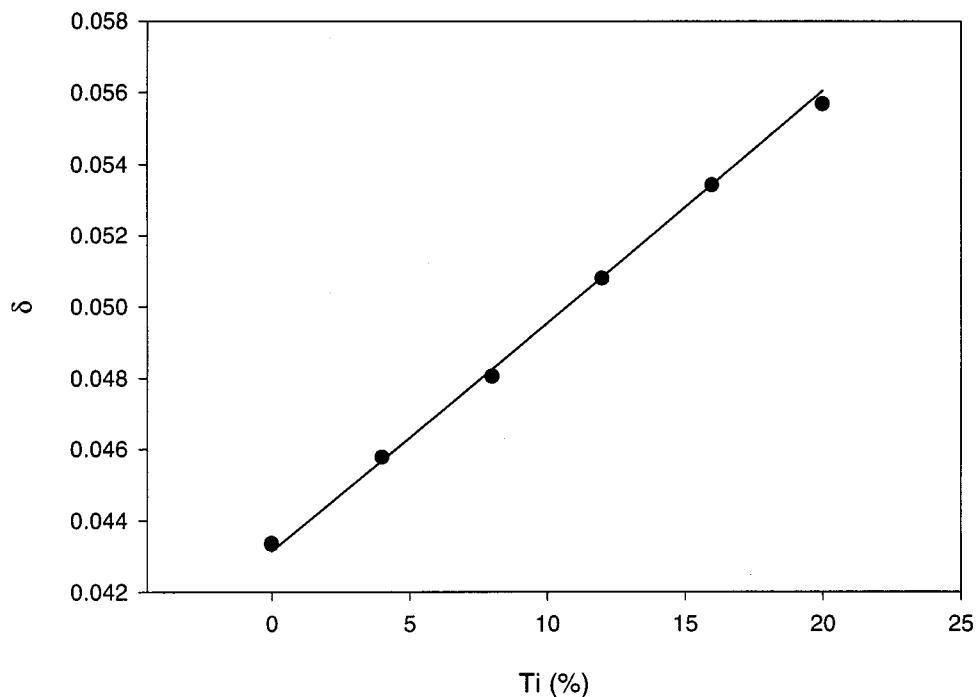
FIG. 3. The parameter δ, describing the oxygen position, as found from the bond lengths and Eq. [4] for the Ti-substituted material. Values of δ determined from neutron diffraction are shown as circle symbols for comparison.

TABLE 2
Bond Valence Constants

Element Ion	Tabulated B^a	Tabulated R_o^a	R_o Used in This Work
Zr^{4+}	0.326	1.962	1.968
Y^{3+}	0.340	2.047	As tabulated
Ge^{4+}	0.37	1.748	1.850
Ti^{4+}	0.37	1.815	1.814
Sn^{4+}	0.37	1.905	1.938
Ce^{4+}	0.326	2.117	2.096

^{a}Refs. 14 and 15.

terms in the small quantities δ^2 and $1 - a^2/c^2$,

$$\delta = \frac{3}{8} \frac{d_1^2 - d_s^2}{d_1^2 + d_s^2},$$

and by incorporating the relationship between oxygen displacement and tetragonality proposed by Howard *et al.* (16),

an even better approximation,

$$\delta = \frac{3}{8} \frac{d_1^2 - d_s^2}{d_1^2 + d_s^2} \left[1 - 0.88 \left(\frac{d_1^2 - d_s^2}{d_1^2 + d_s^2} \right)^2 \right] \qquad [4]$$

is obtained. The comparison of δ estimated from the bond lengths with the δ determined from neutron diffraction (13), shown in Fig. 3 for the Ti-substituted material, confirms that this approximation is very good indeed. Once δ has been estimated in this way, extraction of the correspondingly approximate lattice parameters a and c from Eqs. [2] and [3] is straightforward.

The lattice parameters, a and c, estimated from the bond lengths via the approximation just explained, are shown in Fig. 4. The cube root of the unit-cell volume, $\sqrt[3]{a^2 c}$, is also shown. The values for a, c, and $\sqrt[3]{a^2 c}$ obtained in this way are seen to be in remarkably good agreement with the results obtained from the neutron diffraction experiment.
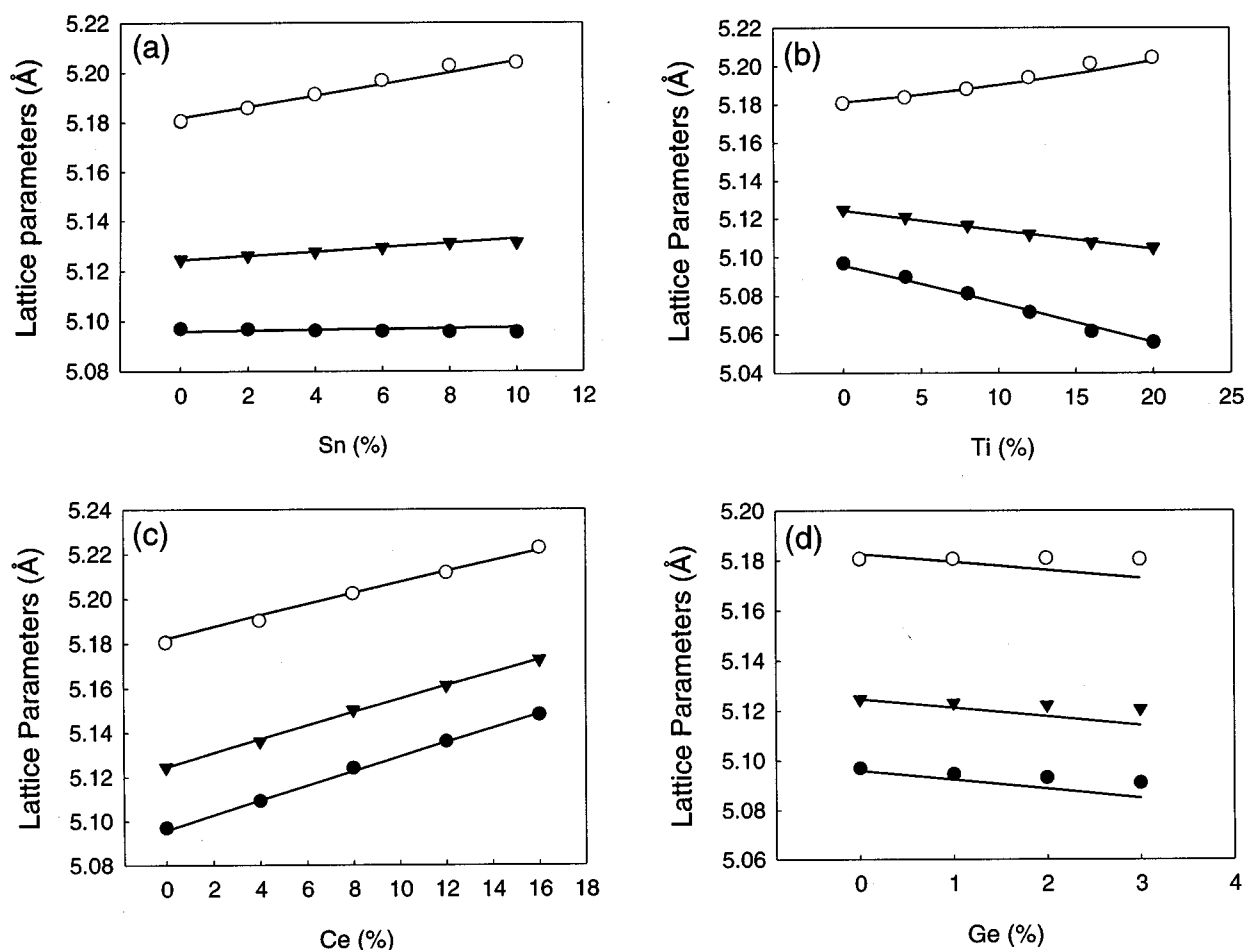
FIG. 4. Lattice parameters a and c and the cube root of the cell volume $\sqrt[3]{a^2 c}$ for the different tetragonal zirconias examined in this work: (a) Sn, (b) Ti, (c) Ce, and (d) Ge. The points are experimental data, ($\bullet$) a lattice parameter, ($\circ$) c lattice parameter, ($\blacktriangledown$) cube root of the unit-cell volume, and the lines have been calculated as explained in the text.

It is gratifying to note that in Sn substitution, the calculation gives a slight increase in the unit-cell volume in the face of a slight decrease in the shorter cation–anion bond distance, thus explaining the "anomaly" noted in both the Raman (12) and neutron studies (13). In Ti substitution, the calculation accounts naturally[2] for both the increase in the c parameter and the associated decrease in cell volume with increasing concentration of Ti. The calculation for Ti also leads to some nonlinearity in the variation of the lattice parameter with concentration in Ti substitution, thereby providing at least a partial explanation of the departure from Vegard's law evident in this case. There are some slight discrepancies at the highest concentrations in the Ce, Sn, and Ti systems, attributable to small amounts of second phases detected in these heavily doped systems.

SUMMARY

A comprehensive description of the structures of tetragonal zirconias incorporating tetravalent substituents has been developed by using the bond valence sum method for calculating bond lengths. The method gives results in excellent agreement with the experimental data and in particular accounts for apparent anomalous behavior of the Sn- and Ti-doped systems.

The concern in this paper, as well as in previous Raman (12) and neutron studies (13), has been the mean cation–anion bond length and its dependence on the concentration and type of dopant. Investigation of local bonding in these now well-characterized materials by a technique, such as EXAFS, would seem to be worthwhile.

It is anticipated that the methodology developed here might be used to study the structures in related systems, such as tetragonal zirconias stabilized by different trivalent dopants.

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[2]The simplicity of the bond valence sum explanation is in marked contrast to the complexity of explanations offered elsewhere (5).

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