JOURNAL OF SOLID STATE CHEMISTRY 47, 92–97 (1983)

Evaluation of the Valency of Fe, Cr, Cu, Sb Doping Ions in $Pb(Zr_{0.95}Ti_{0.05})O_3$ Ceramics

P. GONNARD AND M. TROCCAZ

Institut National des Sciences Appliquées Laboratoire de Génie Electrique & Ferroélectricité, Bâtiment 504, 20, Avenue Albert Einstein, 69621 Villeurbanne Cedex, France

Received July 1, 1982; in revised form November 5, 1982

The valency of the ions Fe, Cr, Cu, Sb, incorporated in PZT 95/5 ceramics, is evaluated from the viewpoint of a correlation between the mean radius of the ions at the octahedral site and the two parameters: the temperature of the antiferroelectric–ferroelectric phase transition, and the volume of the unit cubic cell. It is found that Fe and Cr enter as Fe^{2+} and Cr^{2+} at the *B* site. Experiments suggest that Cu is incorporated at the *B* site as Cu^+ and Cu^{2+} and that Sb enters partly at the *A* site as Sb^{3+} and mainly at the *B* site as Sb^{5+}.

1. Introduction

Some oxide additives acting as acceptors, such as Fe_2O_3, Cr_2O_3, . . . are added to $Pb(Zr\ Ti)O_3$ solid solutions to obtain hard or stabilized ceramics. A common characteristic of such metal ions is that they exhibit various valency states. The valency of these ions, when incorporated in the perovskite type structure ABO_3, has been evaluated by some authors using different methods of investigation: electron-spin Resonance and thermogravimetry (*1*), Mössbauer effect (*2*), molecular weight determination (*3*). In the case of Fe doping, a majority of papers assumes that it enters, as a trivalent ion, at the *B* site (*4–6*); however some authors suggest a possible incorporation of the Fe^{2+} ion at the *A* site (*7*) and also, in part, as Fe^{3+} at the *A* site in $PbTiO_3$ (*1*). A change of the Fe valency ($Fe^{3+} \rightarrow Fe^{2+}$ or $Fe^{3+} \rightarrow Fe^{4+}$) has also been reported in $BaTiO_3$ ceramics, according to the annealing treatments (*2*).

This work was undertaken to evaluate the valency of the ions Fe, Cr, Cu, Sb, when incorporated in $PbZr_{0.95}Ti_{0.05}O_3$ (PZT 95/5) from the viewpoint of a correlation, previously reported (*8, 9*), between the mean radius of the *B* ion and the two following parameters:

(a) the temperature of the antiferroelectric–ferroelectric (AF → F) phase transition.

(b) the volume of the unit cubic cell (*10*).

These previous studies allow certain conclusions to be drawn.

(i) If the doping ion decreases the average volume of the *A* (La^{3+}, Sr^{2+}) or *B* (Nb^{5+}, W^{6+}) ions, the unit cell volume is decreased; the reverse effect is also observed.

(ii) The dopants, such as rare earth oxides, whose ionic radii are greater than $R_{Zr^{4+}}$ are distributed in various proportions between the *A* and *B* sites. Such a distribution is favored because the *A* ion is ferroactive in the PZT 95/5 structure, the Goldschmidt factor $t = (R_A + R_O)/\sqrt{2}(R_B + R_O)$

0022-4596/83/040092-06$03.00/0

of this composition being smaller than unity.

(iii) The temperature of the $A\mathrm{F} \rightarrow \mathrm{F}$ transition increases when the factor t decreases (whether R_A diminishes or R_B increases).

Depending on the valency of the ion X incorporated at the B site, the more likely chemical equations may be written as

$$X^{6+} \quad \mathrm{Pb}_1\,\square_y(\mathrm{Zr}_x\mathrm{Ti}_{1-x}X_y)\mathrm{O}_{3(1+y)} \text{ (A vacancies hypothesis)} \tag{1}$$

$$X^{4+} \quad \mathrm{Pb}_{1+y}(\mathrm{Zr}_x\mathrm{Ti}_{1-x}X_y)\mathrm{O}_{3(1+y)} \tag{2}$$

$$X^{3+} \quad \mathrm{Pb}_{1+y}(\mathrm{Zr}_x\mathrm{Ti}_{1-x}X_y)\mathrm{O}_{3+5y/2}\square_{y/2} \tag{3}$$

$$X^{2+} \quad \mathrm{Pb}_{1+y}(\mathrm{Zr}_x\mathrm{Ti}_{1-x}X_y)\mathrm{O}_{3+2y}\square_{y} \tag{4}$$

$$X^{+} \quad \mathrm{Pb}_{1+y}(\mathrm{Zr}_x\mathrm{Ti}_{1-x}X_y)\mathrm{O}_{3+3y/2}\square_{3y/2}. \tag{5}$$

In every case the mean cubic radius R_B of the B ions is calculated from

$$(1 + y)R_B^3 = xR_{\mathrm{Zr}}^3 + (1 - x)R_{\mathrm{Ti}}^3 + yR_{\mathrm{X}}^3 \tag{6}$$

where

$$R_{\mathrm{Zr}^{4+}} = 0.87\ \text{Å} \qquad \text{and} \qquad R_{\mathrm{Ti}^{4+}} = 0.64\ \text{Å}. \tag{11}$$

2. Experimental Procedures

The preparation of the ceramic specimens was carried out by a conventional mixed oxide technique (9): mixing of the raw materials (PbO, $\mathrm{ZrO_2}$, $\mathrm{TiO_2}$, and the doping oxide), followed by calcination at 970°C for 3.5 hr in a closed alumina crucible under air with a PbO atmosphere, and grinding in an agate jar, and finally sintering for 3 hr at 1300°C under air with a PbO atmosphere in a covered $\mathrm{Al_2O_3}$ crucible. The $A\mathrm{F} \rightarrow \mathrm{F}$ transition temperature is measured as the temperature rises by recording the dielectric permittivity.

The X-ray determination of the lattice constants in the cubic phase at various temperatures is performed with a diffractometer, using a Co$K\alpha1$ radiation source.

3. Size Effects of *B* Ions and Vacancies

3.1 Shifting of the AF → F Phase Transition and of the Lattice Parameters with the Titanium Content

Figure 1a shows the variations of the measured AF → F phase transition temperature ($T_{\mathrm{AF}\rightarrow\mathrm{F}}$) as a function of the mean radius R_B, calculated according to Eq. (6) for various Zr/Ti ratios near 95/5: it is apparent that $T_{\mathrm{AF}\rightarrow\mathrm{F}}$ increases with increasing $R_B(\Delta T_{\mathrm{AF}} \neq 20°\mathrm{C}$ for $\Delta R_B = 0.0010$ Å).

The changes of the unit cell volume in the cubic phase are plotted as a function of temperature in Fig. 2 (dashed lines) for various Zr/Ti ratios. The values of the volume at 350°C (V_{350}) are used to draw the curve of the Fig. 1b: this curve shows a linear relation between the volume of the unit cell and the mean radius $R_B(\Delta V_{350} = 0.057$ Å^3 for $\Delta R_B = 0.001$ Å).

3.2 Shifting of the AF → F Phase Transition Temperature and of the Lattice Parameters with the Vacancies Content

To ascertain the vacancies effect, some of the compositions with nearly the same

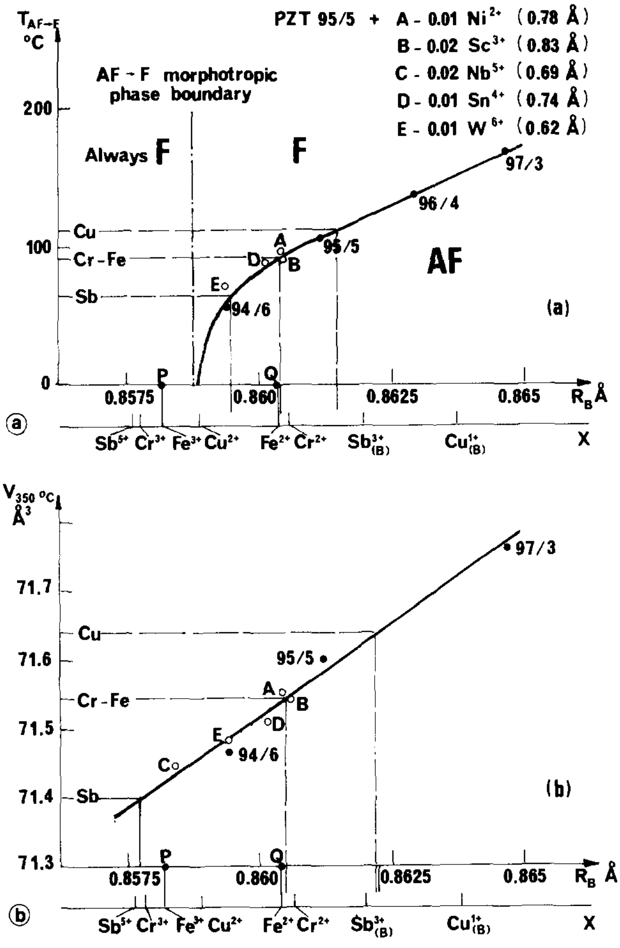

FIG. 1. (a) Temperature of the $AF \rightarrow$ F phase transition as a function of the mean radius R_B at B site. (b) Volume of the unit cubic cell at 350°C as a function of the mean radius R_B.

mean ionic radius R_B, but with different vacancy states, were investigated.

- PbO nonstoichiometry

A PbO deficiency is obtained by annealing the ceramics for 2 hr at 1000°C in air. The loss of PbO is measured by gravimetry.

	R_B Å	Molar PbO deficiency	$T_{AF \rightarrow F}$°C	V_{350} Å^3
PZT 94/6	0.8594	0	58	71.465
PZT 94/6 annealed	0.8594	2.6%	69	71.445

The small decrease of the unit cell volume is similar to the one observed by Takahashi (*12*) on PbTiO$_3$ with Pb and O defects.

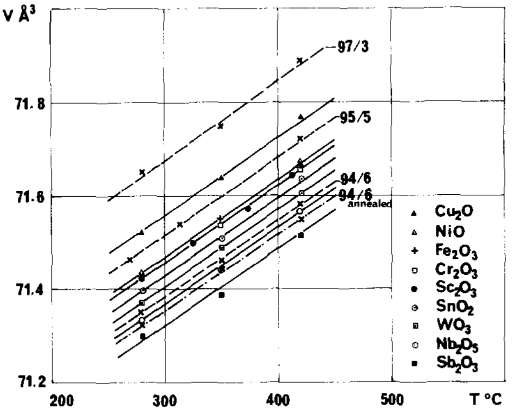

FIG. 2. Temperature dependence of the unit cubic cell, V, of PZT 95/5 specimens doped with different additive oxides (2 at.%)

· *A* site vacancy composition

The PZT 94/6 undoped composition is compared with the PZT 95/5 + 1% WO_3 composition containing 1% A site vacancies (Eq. (1)).

	R_B Å	Vacancy content	$T_{AF\to F}$°C	V_{350} Å^3
PZT 94/6	0.85940	0	59	71.465
PZT 95/5 + 1% WO_3	0.85946	1%	71	71.495

The *A* vacancies produce a small increase of $T_{AF\to F}$ but do not significantly alter the volume of the unit cell.

· O site vacancy composition.

A PZT 95/5 + 1% SnO_2 is compared with a PZT 95/5 + 1% NiO having nearly the same R_B value, but containing 1% O site vacancies (Eq. (4)).

	R_B Å	Vacancy content	$T_{AF\to F}$°C	V_{350} Å^3
PZT 95/5 + 1% SnO_2	0.8601	0	88	71.510
PZT 95/5 + 1% NiO	0.8605	1%	95	71.545

The slight increase in $T_{AF\to F}$ and in V_{350} is probably due to the small difference between the R_B values of the two compositions, rather than to the O site vacancies which generally produce a small shrinkage of the lattice (according to the results of Section 3.1, $\Delta R_B = 0.0004$ Å leads to $\Delta T_{AF\to F} = 8$°C and $\Delta V_{350} = 0.023$ Å^3).

Jaffe *et al.* (*4*) reports a volume contraction of 0.04 Å^3 for 4% Sc^{3+} introduced in $BaZrO_3$. This variation of the unit cell may be due to the 2% O site vacancies, and also to the size of the Sc^{3+} ion, which should be a little smaller than the Zr^{4+} ion, according to the Goldschmidt values.

In conclusion it can be seen from Fig. 1 that the points *A* to *E*, corresponding to various doped PZT 95/5, are close to the curves drawn for the undoped compositions, taking into account the uncertainty of the volume measurements ($\Delta V = \pm 0.02$ Å^3). Therefore it appears that the vacancies present a smaller disturbance with respect to $T_{AF\to T}$ and to the lattice than a doping ion, incorporated on the *B* site, with a radius sufficiently far from the one of the undoped composition.

4. Evaluation of the Valency State of Fe

To clarify the valency of the Fe ion, the two methods of investigation previously mentioned Section 1(a,b) have been used. The Fe ion is introduced as Fe^{3+} by means of the ferric oxide Fe_2O_3. The solubility limit of iron in PZT is about 3 mole% (*7*).

(a) The mean radii R_B are calculated in the case of a 2 at.% Fe addition, with respect to the two following cases and are designated on Fig. 1a as.

Fe^{3+} $R_{Fe_{3+}} = 0.67$ Å *P* point, corresponding to a ferroelectric material
Fe^{2+} $R_{Fe_{2+}} = 0.82$ Å *Q* point, corresponding to $T_{AF\to F} = 90$°C.

Since the measured value of $T_{AF\to F}$ is 92°C, it may be concluded that the Fe ion is divalent. The comparison with some of the $T_{AF\to F}$ reference values observed for PZT 95/5 compositions doped with ions having only one valency state confirms this result (Table I).

(b) The volume at 350°C of the composition PZT 95/5 + 0.02 Fe, reported in Fig. 1b, yields a value of R_B closely related to the one calculated assuming Fe^{2+} to be

TABLE I

PZT 95/5 Composition +	R_X (Å)	R_B (Å) Calculated from Eq. (6)	$T_{AF\to F}$ (°C) Measured
Undoped		0.8612	105
0.02 Nb^{5+}	0.69	0.8584	Always F
0.02 Fe^{3+}	0.67	0.8582	92
$2+$	0.82	0.8604	
0.02 Sc^{3+}	0.83	0.8606	90

present, but far from the one calculated using the Fe^{3+} model.

In summarizing, these two methods of investigation confirm that the iron is incorporated at the *B* site as a divalent ion under the present experimental conditions of ceramic preparation.

5. Evaluation of the Valency of Other Ions (Cr, Cu, Sb)

PZT 95/5 Doped with Chromium

Chromium is introduced as Cr^{3+} by means of the oxide Cr_2O_3. The solubility limit of chromium in the PZT is about 1.1 mole% (*13, 14*). Experimental investigations show that the Cr doped PZT 95/5 ceramics have the same temperature $T_{AF\rightarrow F}$ and the same unit cell volume as the Fe doped specimens (Figs. 1, 2). Taking into account the ionic radii ($R_{Cr^{2+}} = 0.83$ Å $\approx R_{Fe^{2+}}$ and $R_{Cr^{3+}} = 0.64$ Å), it may therefore be concluded that the chromium enters the *B* site as a divalent ion.

PZT 95/5 Doped with Copper

Copper is introduced as Cu^+, by means of the oxide Cu_2O. The $T_{AF\rightarrow F}$ and the unit cell volume measurements lead to a mean radius $R_B \approx 0.8620$ Å, intermediate between the radii calculated with the extreme hypothesis:

(i) Cu^+ at 100% at the *B* site ($R_{Cu^+} = 0.96$ Å)
$R_B = 0.8638$ Å
(ii) Cu^{2+} at 100% at the *B* site ($R_{Cu^{2+}} = 0.72$ Å)
$R_B = 0.8588$ Å

The most likely assumption is that the copper ion enters the *B* site with both valencies +1 and +2, because a distribution of the Cu^+ ion between the *A* and *B* sites would raise $T_{AF\rightarrow F}$ and decrease the unit cell volume with respect to the undoped PZT 95/5 (this behavior being similar to the one observed with Tb^{3+} or Ho^{3+} ions having radii close to that of Cu^+ (*9*)).

PZT 95/5 Doped with Antimony

Antimony is introduced as Sb^{3+} by means of the oxide Sb_2O_3. The experimental observations (Fig. 1, 2), lead to the following conclusions.

(i) The hypothesis concerning the presence of Sb^{3+} ($R_{Sb^{3+}} = 0.90$ Å) at the *B* site is ruled out.

(ii) The hypothesis that Sb exists solely as Sb^{5+} ($R_{Sb^{5+}} = 0.62$ Å) at the *B* site, agrees well with respect to the volume of the unit cell, but conflicts with the value of $T_{AF\rightarrow F}$ (64°C), since the composition should have remained ferroelectric.

(iii) The hypothesis that Sb^{3+} is distributed between the *A* and *B* sites (a behavior similar to the one obtained with PZT 95/5 + 0.02 Yb^{3+} ($R_{Yb^{3+}} = 0.92$ Å) (9)), would involve $T_{AF\rightarrow F} = 115$°C.

It is therefore probable that Sb ion enters the *B* site mainly as Sb^{5+} and that the last portion enters the *A* site as Sb^{3+}. Some experimental data provide support to this assumption.

First, the PZT 95/5 + 0.02 Sb_2O_3 composition presents a lowered Curie temperature ($T_c = 208$°C), while the other doped PZT 95/5 (Ni, Sc, Sn, Fe, Cr, Cu) have nearly the same value of T_c (232 ± 3°C) as the undoped material. Such a shift of T_c is characteristic of PZT doped with cations on the *A* site having a smaller radius than Pb^{2+}(4), (9), (15).

Second, the properties of the Sb doped samples are typical of cationic vacancy ceramics (yellow color, high electrical resistivity $\geq 10^{10}$ Ω cm at 280°C). On the other hand, the Fe, Cr, or Cu doped compositions present all the experimental features of O position vacancy ceramics (dark color, low electrical resistivity $\leq 10^7$ Ω cm at 280°C).

6. Discussion and Conclusion

The formation of Fe^{2+}, Cr^{2+}, and Cu^+ at octahedral sites is surprising in the sense that the number of oxygen vacancies is increased in spite of the sintering conditions under a PbO atmosphere. Such a formation may be explained by taking into account the small amount of doping ion incorporated and assuming a preponderance of the size effects over the electrical effects which are balanced with lattice vacancies. Fe and Cr are in a divalent state because the radius of the divalent ion is close to the radius R_{OB} of the undoped composition (R_{OB} = 0.86 Å). Copper enters the *B* site as a mixture of divalent and monovalent ions so that the mean radius is close to R_{OB}. With such an hypothesis, antimony would enter the *B* site mainly as trivalent ion, but this conflicts with experimental results. It is then proposed that the Sb^{5+} ions at the *B* site create *A* vacancies, which facilitate the incorporation of Sb^{3+} ions at the *A* site.

Further investigations might involve two studies.

(i) The study of the valence changes as a function of the preparation procedures or after an annealing treatment, in a wide range of O_2 partial pressure.

(ii) The study of the valency and the distribution of the doping ions between the *A* and *B* sites as a function of the mean radius R_{OB}, as, for example, near the morphotropic phase boundary in PZT and near Pb TiO_3. However, the lack of the antiferroelectric–ferroelectric phase transition, as an element of comparison, would involve a more complex investigation.

References

1. D. Hennings and H. Pomplun, *J. Amer. Ceram. Soc.* **57,** 527 (1974).
2. H. J. Hagemann, A. Hero, and U. Gonser, *Phys. Status Solidi* **61,** 63 (1980).
3. K. H. Hardtl, *J. Amer. Ceram. Soc.* **64,** 283 (1981).
4. B. Jaffe, W. R. Cook, and H. Jaffe, "Piezoelectric Ceramics," Academic Press, New York (1971).
5. T. B. Weston, A. H. Webster, and V. M. McNamara, *J. Amer. Ceram. Soc.* **52,** 257 (1969).
6. K. Tanaka, Y. Hamakawa, K. Wakiwo, and M. Murata, *J. Amer. Ceram. Soc.* **59,** 465 (1976).
7. K. Carl and K. H. Hardtl, *Ferroelectrics* **17,** 473 (1978).
8. M. Troccaz, P. Gonnard, Y. Fetiveau, L. Eyraud, and G. Grange, *Ferroelectrics* **14,** 679 (1976).
9. P. Gonnard and M. Troccaz, *J. Solid State Chem.* **23,** 321 (1978).
10. R. D. Shannon and C. T. Prewitt, *Acta Crystallogr.* **25,** 925 (1969).
11. J. Zeeman, "Chimie Cristalline," Dunod, Paris (1970).
12. K. Takahashi, S. I. Shirasaki, and K. Kakegawa, *J. Amer. Ceram. Soc.* **56,** 430 (1973).
13. H. Thomann, *Ferroelectrics* **4,** 141 (1972).
14. N. Uchida and T. Ikeda, *Jap. J. Appl. Phys.* **6,** 1292 (1967).
15. G. H. Haertling and C. E. Land, *J. Amer. Ceram. Soc.* **54,** 1 (1971).