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Influence of Simultaneous Heterovalent Substitutions in Both Cationic Sites on the Ferroelectric Properties of PZT Type Ceramics

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Phenomena of conduction in an electric field and of ageing in PZT ceramics set severe limitations on the development of some industrial applications. Whereas it is well known how to suppress conduction with appropriate heterovalent substitutions, the ageing mechanism remains obscure. The purpose of the present study is to look experimentally for an ageing proof structure, and to document the privileged role of the couple (M^+, Nb^{5+}) (M^+ = K^+ and Na^+) in resistance to ageing. A structure model is proposed to interpret the possible mechanism of space charge compensation in polar material by imposition of a polarizable superstructure.

Introduction

Lead zircono-titanates of theoretical formula

$$Pb(Zr_{1-x}Ti_x)O_3 \qquad (\text{or } ABO_3)$$

constitute one of the most important series of ferroelectric materials used in the production of ceramics of industrial piezoelectric transducers. The cubic cell formed at higher temperatures, may be represented by ions A^{2+} at the apices, ions B^{4+} at the cube center, and ions O^{2-} at the face centers.

As is well known (*1*) such a structure permits considerable latitude in composition, by substitutions of A and/or of B ions by other ions of compatible ionic size (Table I). When the valence of the substituent ions differs from that of the host ions (i.e., +2 on sites A and +4 on sites B), compensation occurs by one or several of the following mechanisms:

(a) Change of lead on A sites from the +2 to the +4 state.

(b) Change of titanium on B sites from the +4 to the +3 state.

(c) Creation of vacancies.

These substitutions obviously influence the electrical conductivity, which, for ferroelectric applications, should remain as low as possible; they also affect resistance to ageing.

The ageing of piezoelectric ceramics results from progressive variations in time of their dielectric, elastic, and electromechanical characteristics. It occurs spontaneously during storage after polarization,

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TABLE I

SIZE OF IONS

Ion	Ionic radius (Å)
Pb^{2+}	1.32
Pb^{4+}	0.84
Na^{+}	0.98
K^{+}	1.33
Zr^{4+}	0.87
Ti^{4+}	0.64
Ti^{3+}	0.69
Nb^{5+}	0.69

or during usage, especially under heavy electrical or mechanical loads. Many authors (*1–3*) have attempted to analyze its causes and effects, without arriving at a precise solution.

Ageing is essentially due to the instability of domain walls which can move under the influence of defects, or of stress anisotropy produced by the presence of domains.

In attempting to lower the electrical conductivity and increase the resistance to ageing, we believed that vacancies were detrimental to both.

We therefore attempted to make up solid solutions containing as few vacancies as possible. The problem is essentially chemical in nature: it consists in finding a composition which corresponds to a desired structure and which is then actually obtained at the end of the preparation procedure (including sintering).

The usual dry process involving a reaction between solids does not meet these requirements due to the volatility of lead oxide at the high temperatures of reaction (900°C) and of sintering (1300°C). By contrast, it has been checked that in the coprecipitation method (*4–6*) all the cations initially used as reagents are actually present in the final solid.

To check the resistance of our samples to ageing, we adopted the igniter test, which consists in applying 10^4 to 10^5 electric strokes to a probe of 6.35 mm in diameter and 16 mm in height. Each stroke lasts 30 μsec and produces a voltage of about 20 kV. This test should not produce a variation greater than one percent for the electro mechanical coupling coefficient k_{33}, which is a very stringent and important requirement. Rather than repeat the experimental information which has already been published elsewhere (*7*, *8*), we limit ourselves to the presentation of original results and to their interpretation by a structural model.

I. Chemical Formulation of Non-substituted PZT Materials

We assume that at the end of the preparation process, the three mechanisms (a), (b), (c) described above have occurred (however without formation of oxygen vacancies), so that the cristallographic and chemical formula may be written

$$Pb^{2+}_{1-y_0-v_0}Pb^{4+}_{y_0}\square^{q_0}_{v_0}[Zr^{4+}_{1-x}Ti^{4+}_{x-z_0-w_0}Ti^{3+}_{z_0}\square^{q'_0}_{w_0}]O_3$$

($\square$ designating a vacancy the charge of which is either q_0 or q'_0, and which may be either integral or nonintegral). The site availability dictates that for each type of cations, the summation of subscripts should be unity. From the electroneutrality condition one obtains the equation

$$2(1 - y_0 - v_0) + 4y_0 + q_0v_0 + 4(1 - x) + 4(x - z_0 - w_0) + 3z_0 + q'_0w_0 = 6$$

which, after some mathematical handling, yields

$$2y_0 - z_0 = 2v_0 + 4w_0 - q_0v_0 - q'_0w_0 \quad (1)$$

A further condition introduced by the preparation technique is that the number of *A* cations is always equal to the number of *B* cations (irrespective of their actual charge); this equality is maintained throughout the "wet" coprecipitation process. Hence,

$$1 - y_0 - v_0 + y_0 = 1 - x + x - z_0 - w_0 + z_0$$

or

$$v_0 = w_0 \qquad (2)$$

which shows that the number of vacancies on both sites is the same. It must be stressed that this condition is met only by the "wet" preparation method. Putting (*2*) into (1) yields the simple result:

$$2y_0 - z_0 = v_0(6 - q_0 - q_0') \qquad (3)$$

In the particular case where no vacancies occur,

$$v_0 = 0$$

$$2y_0 = z_0$$

which is an expression of the fact that the $2y_0$ electrons required to produce y_0Pb^{4+} ions have passed from the occupied *A* sites to the *B* sites thus transforming $2y_0Ti^{4+}$ ions into Ti^{3+} ions: Pb^{4+} ions behave as electron acceptors, and the Ti^{3+}, as electron donors.

II. Chemical Formulas of Substituted PZT Materials

As is well known, the introduction of heterovalent ions of compatible ionic radii permits control the defects and of their mobility.

Nb^{5+}-substituted PZT. Niobium ions occupy *B* sites. We shall assume (a) that their primary effect is to cancel out the occurrence of Pb^{4+} ions on *A* sites, (b) that there are no oxygen vacancies, (c) that the global number of *A* ions and of *B* ions remains the same. One of the formulas compatible with the hypotheses (a) and (b) is

$$Pb^{2+}_{1-v_1}\square^{q_1}_{v_1}[Zr^{4+}_{1-x_1}Ti^{4+}_{x_1-z_1-y_1-w_1}Ti^{3+}_{z_1}Nb^{5+}_{y_1}\square^{q_1'}_{w_1}]O_3$$

If now we take into account the condition (c) above, then

$$1 - v_1 = 1 - x_1 + x_1 - z_1 - y_1 - w_1 + z_1 + y_1$$

whence

$$v_1 = w_1 \qquad (4)$$

which means that in this case as well, the number of vacancies (if any) on both sites is the same.

The electroneutrality condition reads

$$2(1 - v_1) + q_1v_1 + 4(1 - x_1) + 4(x_1 - z_1 - y_1 - w_1) + 3z_1 + 5y_1 + q_1'w_1 = 6 \qquad (5)$$

which yields

$$v_1(q_1 + q_1' - 6) = z_1 - y_1 \qquad (6)$$

Experimentally, when y_1 approaches 0.02 the solid solution becomes insulating. Based on the interpretation of Jaffe *et al.* (*1*), this can be ascribed to non-charged vacancies:

$$q_1 = q_1' = 0 \qquad (7)$$

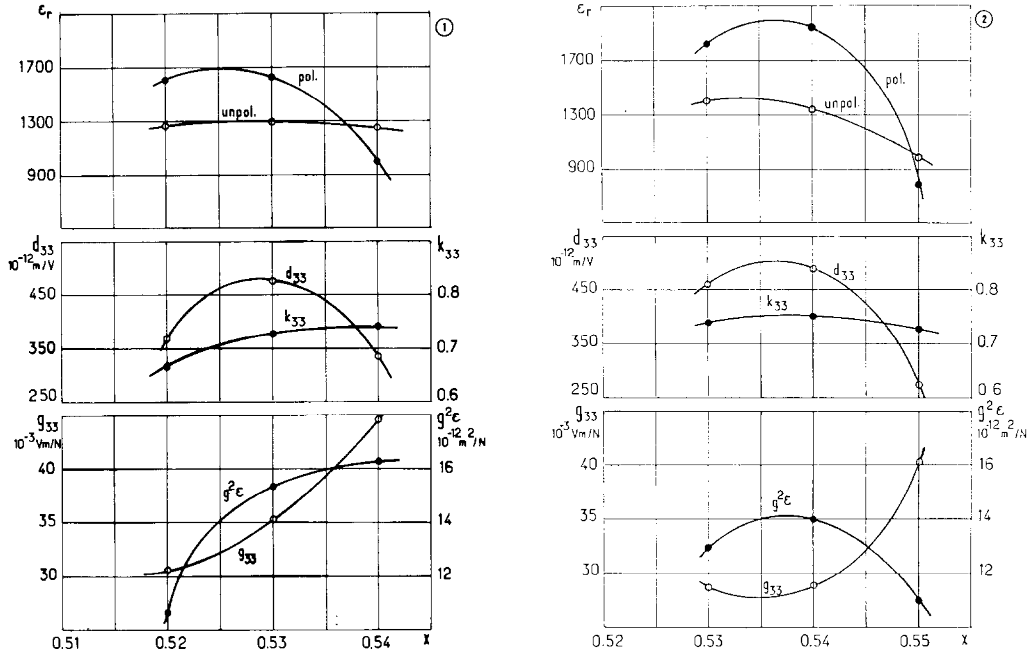
Equation (6) simplifies to

$$y_1 = z_1 + 6v_1 \qquad (8)$$

The physical significance of Eq. (8) is that Nb^{5+} ions counterbalance the Ti^{3+} and the lack of Pb^{2+} and Ti^{4+} ions replaced by uncharged vacancies.

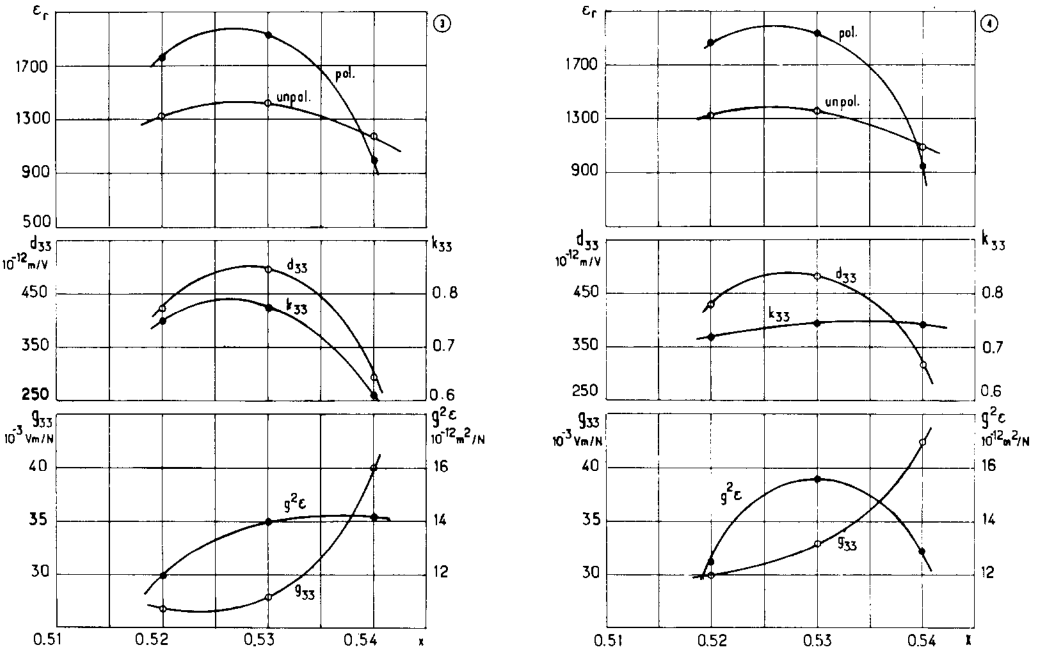
Alkaline and Nb^{5+}-substituted PZT. If we introduce alkali M^+ ions on *A* sites (in fact a mixture of Na^+ and K^+ for reasons of steric hindrance) they will again induce creation of Pb^{4+} (electron acceptors) on the same sites. If, simultaneously, Nb^{5+} ions are introduced on *B* sites, they will *solely* induce creation of Ti^{3+} (electron donors) on the same sites. We then obtain solid solutions containing very few vacancies (if any) and with acceptor centers Pb^{4+} on *A* sites and the donor centers Ti^{3+} on *B* sites.

As the amount of Ti^{3+} initially present or induced by Nb^{5+} is not known, the composition which balances the acceptor–donor centers has to be found by trial and error. Figures 1 to 4 show how the usual ferroelectric parameters vary as functions of the



$Pb_{0.985}Sr_{0.015}Ba_{0.005}Na_{0.0075}K_{0.0075}(Zr_x\ Ti_{1-x}Nb_{0.02})O_{3(1+0.02)}$

$Pb_{0.99}Sr_{0.015}Ba_{0.005}Na_{0.005}K_{0.005}(Zr_x\ Ti_{1-x}Nb_{0.02})O_{3(1+0.02)}$



$Pb_{0.995}Sr_{0.015}Ba_{0.005}Na_{0.0025}K_{0.0025}(Zr_x\ Ti_{1-x}Nb_{0.02})O_{3(1+0.02)}$

$Pb_{1.00}Sr_{0.015}Ba_{0.005}(Zr_x\ Ti_{1-x}Nb_{0.02})O_{3(1+0.02)}$

FIGS. 1–4. Variations of the parameters ε_r, d, g, and k vs Zr/Ti ratio. ε_r = relative permittivity. $d = P/T$ = variation of polarization/variation of stress (in short circuit). $g = -E/T$ = variation of electrical field/variation of stress (in open circuit). k = electromechanical coupling coefficient.

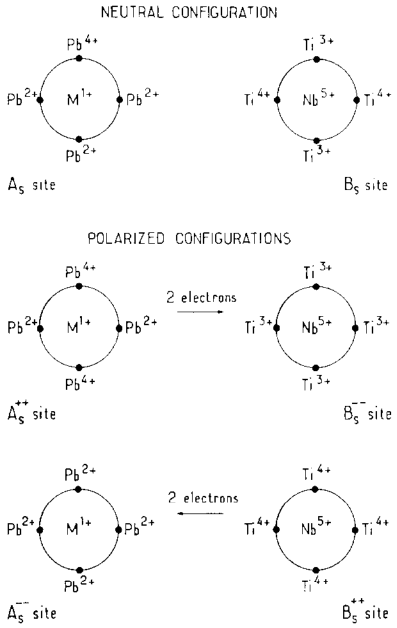


FIG. 5. Mechanism of superposed polarization.

ratio Zr/Ti for different values of the occupancy of A sites by M^+ cations (comprised between 5×10^{-3} and 15×10^{-3}). The best global composition may be written (without regard to the crystal formula)

$$\mathrm{Pb_{0.995}Sr_{0.015}Ba_{0.005}Na_{0.0025}}$$
$$\mathrm{K_{0.0025}(Zr_{0.53}Ti_{0.47}Nb_{0.02})O_{3(1+0.02)}}$$

Generally, the chemical formula of such phases may be written as

$$\mathrm{Pb}^{2+}_{1-u-v}\mathrm{Pb}^{4+}_{u}M^{+}_{v}$$
$$(\mathrm{Zr}_{1-x-w}\mathrm{Ti}^{4+}_{x-2u+v-w}\mathrm{Ti}^{3+}_{2u-v+w}\mathrm{Nb}^{5+}_{w})\mathrm{O}_3$$

(assuming no vacancies of either type).

III. Theoretical Interpretation

It is seen that ageing-proof solid solutions present the following characteristics: the cationic sites may be simultaneously electron donors and electron acceptors, owing to the simultaneous occurrence of Pb^{2+} and Pb^{4+} on A sites and of Ti^{4+} and Ti^{3+} on B sites.

It then may be assumed that for a given amount of K^+ and Nb^{5+}, a polarizable compensation superstructure forms which superposes its polarization on the spontaneous polarization, so as to minimize the space charge $\rho_v = -\operatorname{div} P$, and therefore to stabilize the material. The compensation mechanism could be the following: the monovalent M^+ ions in A positions may form a superstructure the unit cell of which Δ_O is derived from the unit cell of the host lattice via:

$$\Delta_O = \frac{a_0}{\sqrt[3]{5 \times 10^{-3}}} = 23\ \text{Å}$$

Let us denote these particular A sites as A_s. With each A_s site can be associated alternatively one Pb^{4+} ion and one Pb^{2+} ion, since two M^+ ions are required to create one Pb^{4+} ion. The A_{s1} sites associated with one Pb^{4+} ion are electron acceptors, the A_{s2} sites associated with one Pb^{2+} ion are electron donors. The Nb^{5+} ions which are spread on B sites in a titanium environment may be regarded as B_s sites, these are electron donors when a Ti^{3+} ion is associated with Nb^{5+} and electron acceptors when a Ti^{4+} ion is associated with Nb^{5+} (Fig. 5). There are many ways of partitioning B_s sites amidst A_s sites. According to the formula their number is higher by a factor of four. Thus, a tentative model could be consistent with a body-centered and face-centered cubic structure (Fig. 6). Transfer of two electrons from one site A_{s2} to two neighboring B_s sites (or con-

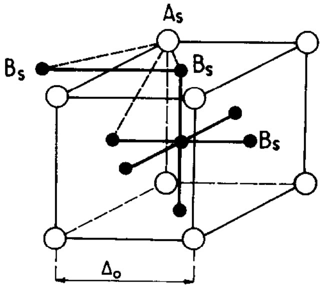


FIG. 6. Model for distribution of doping cations.

versely) gives rise to two dipoles separated by an angle ϕ (30 or 45°), so that the resulting moment is $\mu = 2el \cos \phi$, with $l = A_sB_s$. This distance may be readily evaluated from the model:

$$l = \frac{\Delta_O\sqrt{2}}{2} \text{ or } \frac{\Delta_O\sqrt{3}}{2}$$

The smallest distance is, of course, the most likely, and corresponds to $\phi = 45°$. We thus set

$$\mu = 2el \times \frac{\sqrt{2}}{2} = e\Delta_O = 37 \times 10^{-29}\ \mathrm{C \cdot m}$$

As every A_s site contains one Pb ion able of producing one dipole of moment μ per superstructure cell of edge Δ_O, the dipole moment created per unit volume will be

$$\frac{\mu}{(\Delta_O)^3} = \frac{37 \times 10^{-29}}{(23)^3 \times 10^{-30}} = 3 \times 10^{-2}\ \mathrm{C \cdot m^{-2}}$$

We now show that such an induced superstructure polarization, superimposed on the spontaneous domain polarization, may suffice to annul the overall space charge

$$\rho_v = -\operatorname{div} \mathbf{P}$$

Let us note that, in the absence of compensation,

$$\operatorname{div} \mathbf{P} \simeq \frac{\partial P_x}{\partial x}$$

Defining δ as the thickness of a domain wall, on an average (Fig. 7), we find

$$(\operatorname{div} \mathbf{P})_{\mathrm{av}} = \frac{P_s}{\delta}(1 - \cos \theta_{\mathrm{av}})$$

If P_i is the average induced polarization imposed on P_s as indicated by Fig. 7, the condition that div $\vec{\mathrm{P}}$ vanish in the presence of compensation may be written as

$$P_s - P_i = (P_s + P_i)\cos \theta_{\mathrm{av}}$$

Hence,

$$P_i = P_s \frac{1 - \cos \theta_{\mathrm{av}}}{1 + \cos \theta_{\mathrm{av}}}$$

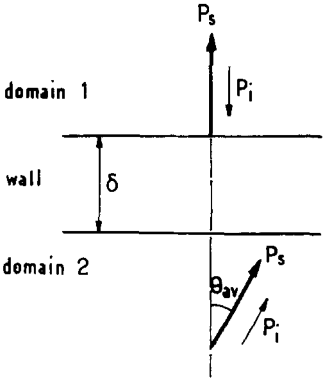


FIG. 7. Vector composition of spontaneous and induced polarizations in neighboring domains.

Now set

$$P_s = 50 \times 10^{-2}\ \mathrm{C \cdot m^{-2}}$$

and

$$\left.\begin{array}{l} \cos \theta_{\mathrm{av}} = 0.8313 \\ \quad \text{for the tetragonal structure} \\ \cos \theta_{\mathrm{av}} = 0.866 \\ \quad \text{for the trigonal structure} \\ \cos \theta_{\mathrm{av}} = 0.9122 \\ \quad \text{for the orthorhombic structure} \end{array}\right\} \qquad (9)$$

The following values for P_i are then found:

$$\begin{aligned} P_i &= 4.6 \times 10^{-2}\ \mathrm{C \cdot m/m^3} \\ &= 3.6 \times 10^{-2}\ \mathrm{C \cdot m/m^3} \\ &= 2.28 \times 10^{-2}\ \mathrm{C \cdot m/m^3} \end{aligned}$$

which are of the same order of magnitude as the polarization originating from the scheme:

$$\mathrm{Pb^{2+}\text{-}2Ti^{4+}} \qquad \mathrm{Pb^{4+}\text{-}2Ti^{3+}}$$

where one should recall that usually the PZT material is a mixture of the three phases.

To conclude, the proposed model of a superstructure polarizable through electron transfer between cationic sites explains the space charge compensation in polarized ceramics, and therefore the stability of these ferroelectrics. Of course, a lead vacancy could also induce the creation of a Pb^{4+} ion. However, in that case, both vacancy and Pb^{4+} ion can move under stress, which decreases the stability of polarized phases.

Acknowledgment

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