

Fluoridated PZT Ceramics for Power Transducers

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PZT-type power ceramics are usually obtained by creating oxygen vacancies in the perovskite structure with the stoichiometric chemical formula ABO_3 . This is obtained by substituting lower valency for normal cations. The concomitant oxygen vacancies constitute large structural and electrical defects, which lower the vibrations of the domain walls and thereby limit the dielectric and mechanical losses. The present work concerns the introduction of fluoride ions in the anionic sublattice and its effects on the electromechanical properties of PZT-type power ceramics. This process leads to more stable compositions. © 1997

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INTRODUCTION

Lead zircono-titanates of the formula $Pb[Zr_{1-x}Ti_x]O_3$, or generally ABO_3 , constitute one of the most important families of ferroelectric materials used in the preparation of ceramic components of industrial piezoelectric transducers.

The cell, cubic at higher temperatures, can be represented by A^{2+} ions at the apices, a B^{4+} ion at the center, and O^{2-} ions at the face centers (Fig. 1).

It is well known that this structure permits large variations in composition by substitution on A or B sites by radius-compatible ions (1). When the valency of the substituent ions differs from that of the substituted ions, charge compensation results from the following mechanisms:

- (a) oxidation of lead ions on A sites from the +2 to the +3 or +4 valency state (14);
- (b) reduction of titanium ions on B sites from the +4 to the +3 valency state;
- (c) creation of neutral (or singly ionized) anionic vacancies.

These mechanisms affect the physical properties of the material.

PRESENT STATE OF THE PZT COMPOSITIONS

PZT-type solid solutions contain approximately 50% (by atom) Zr and 50% Ti. The substitution of Zr^{4+} for Ti^{4+} in $PbTiO_3$ reduces the tetragonal distortion and causes the appearance of another ferroelectric phase of rhombohedral

symmetry. The boundary between tetragonal and rhombohedral forms is nearly independent of temperature (morphotropism). This morphotropic phase boundary facilitates poling (Fig. 2).

According to the desired technical applications, the composition is modified by two main groups of substitutions.

– the the first group includes ions of a valency higher than that of the substituted ion, e.g., La^{3+} , Nd^{3+} on A sites and Nb^{5+} , Sb^{5+} on B sites. Such materials, used at low electrical fields, stresses, and strains, are termed “soft materials.” Dielectric losses at low electrical fields are about 2%.

– The second group includes substituent ions of a valency lower than that of the substituted ion, e.g., K^{1+} , Na^{1+} on A sites and Zn^{2+} , Mg^{2+} , Sc^{3+} , or Fe, Mn, Ni on B sites. In this second group, the transition ions with multiple valency (especially those of Mn) promote fixation of the domain configuration and are called “stabilizers” (4, 5, 10, 11). These substitutions result in “hard materials” with low losses ($tg \delta \cong 0.4\%$) and are mainly used as power transducers.

Some soft and hard compositions use dual substitutions (6). We have previously investigated the dual cationic substitution (M^{1+} , Nb^{5+}) to stabilize the soft ceramics used in stroke igniters (2).

Our present purpose is to study dual cationic–anionic substitutions for the improvement of hard materials (aging, hysteresis, dielectric losses, stability under strong uniaxial stress).

THE PREPARATION PROCESS

The process most widely used in industry is presently the “dry process” (5), starting from a mixture of oxides and carbonates with a solid state reaction at 900°C. This reaction is never complete and leads to vaporization of PbO during sintering at about 1300°C. The mixing process is generally not sufficient to lead to the uniformity of composition of the final product. The grain size is usually very disperse.

For all these reasons, and with a view to fundamental research, it is advisable to undertake the powder preparation by a wet process.

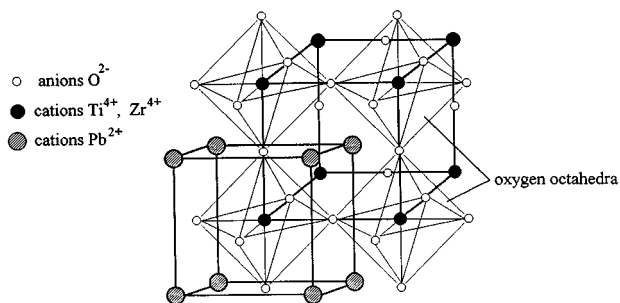


FIG. 1. Cubic cell ABO_3 .

- The principle of this wet process (Fig. 3) lies in the formation of soluble oxalates, followed by complete coprecipitation of the main constituents in the form of insoluble oxalates and hydroxides. After filter-press filtration, washing, and drying, oxalates of cations soluble in the preceding steps or missing constituents are eventually added (K or Na oxalates, PbF_2 ...).

- A temperature of $600^\circ C$ is sufficient for the thermal decomposition of the very reactive oxalates, hydroxides,

and fluorides to ensure completeness of the reaction. A further heat treatment of about $800^\circ C$ finishes the process and yields the final PZT as a powder of specific surface area comprised between $0.5\text{ m}^2\text{ g}^{-1}$ and $2\text{ m}^2\text{ g}^{-1}$.

This powder can be used as the starting material in a customary industrial production line for a particular application.

The amount of lead introduced as PbF_2 is computed so as to ensure a B to A ratio of unity in the final product.

EXPERIMENTAL STUDY

(a) Materials Nonsubstituted on the B Site

The anionic lattice defects create an electric charge unbalance as well as a lattice strain. The oxygen vacancy produces a larger shrinkage of the perovskite lattice than the fluoride ion, but, the fluoride ion locks the average position of a domain wall more rigidly than does an oxygen vacancy, because of its smaller mobility. The maximum of electro-mechanical characteristics (Table 1) can be interpreted in the following manner: the nonfluoridated material naturally

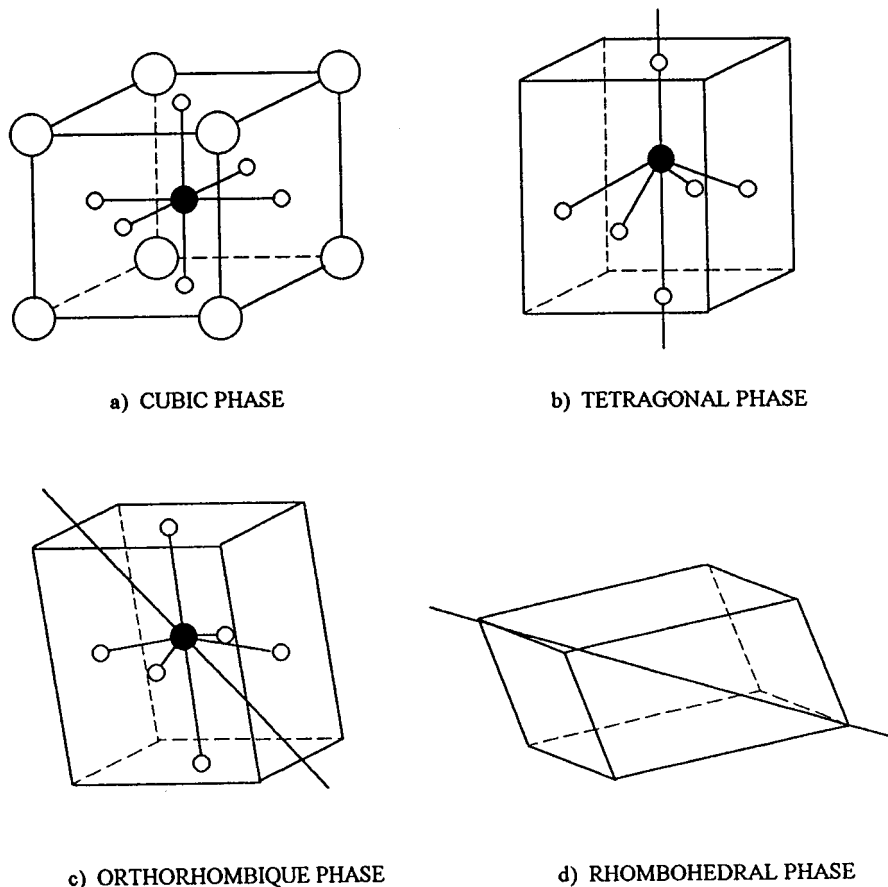


FIG. 2. Various structures of the ABO_3 cell.

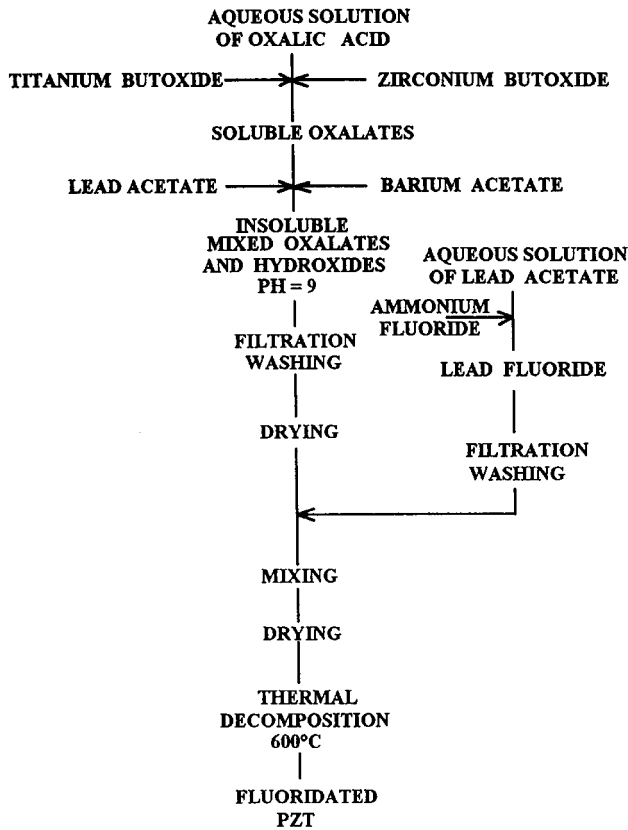


FIG. 3. Preparation of fluoridated PZT.

contains oxygen vacancies, the amount of which decreases as fluorination increases up to 0.5% of fluorine.

When all vacancies are filled with fluoride ions, further incorporation of these ions creates new defects ($Ti^{3+}-F^{1-}$) which depress the electromechanical properties. As shown in Fig. 4 which represents dielectric losses versus electric field, dielectric losses continually decrease with the addition of fluorine up to 1% fluorine.

Figure 5 represents evolution of the d_{33} piezoelectric coefficient of a cylindrical sample versus the uniaxial static stress applied. The rise of electromechanical characteristics up to 0.5% fluorine occurs without any reduction in stability under a high level of mechanical stress.

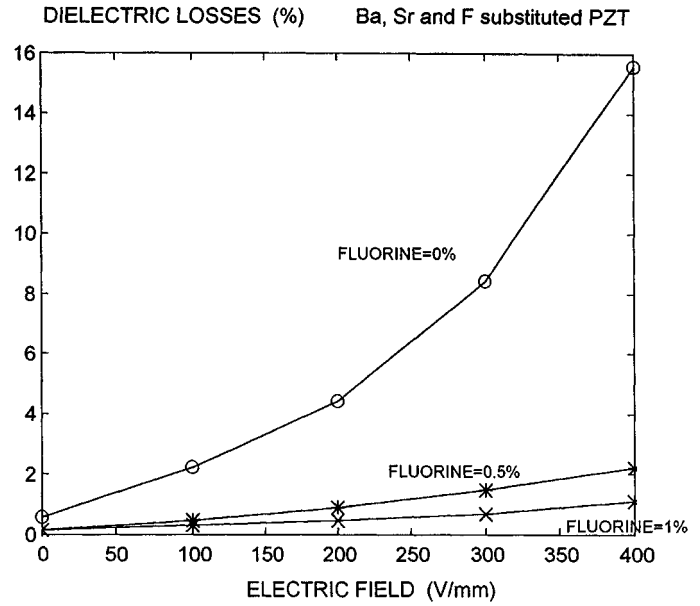


FIG. 4. Dielectric losses versus electric field.

(b) Fe Substituted Material

It is difficult to monitor the amount of Ti^{3+} during preparation. It is therefore recommended to intentionally introduce on the B sites an ion of valency lower than that of the substituted ion in order to increase the fluorination extent without modifying the electromechanical properties.

Table 2 presents the characteristics of such a material as a function of the fluorination extent. Figure 6 shows a large decrease in dielectric losses under electric field with increasing fluorination.

Figure 7 shows the variations of the d_{33} charge coefficient versus the uniaxial stress for ceramics containing 1.6% iron and 1% fluorine and 3% iron and no fluorine. The dielectric losses of both materials are equivalent but the fluoridated materials have better electromechanical characteristics under a high level of mechanical stress.

TABLE 1
Data Sheet

Fluorine content (%)	d_{33} (pC/N) piezoelectric coefficient	ϵ_r permittivity	Q quality factor	s_{33}^E ($\times 10^{-12}$ Pa $^{-1}$) compliance	$tg \delta$ 5 v/mm (%) dielectric losses	$tg \delta$ 400 v/mm (%) dielectric losses
0	200	1250	550	14	0.6	16
0.5	260	1250	900	15	0.15	2.2
1	210	1170	600	13	0.15	1

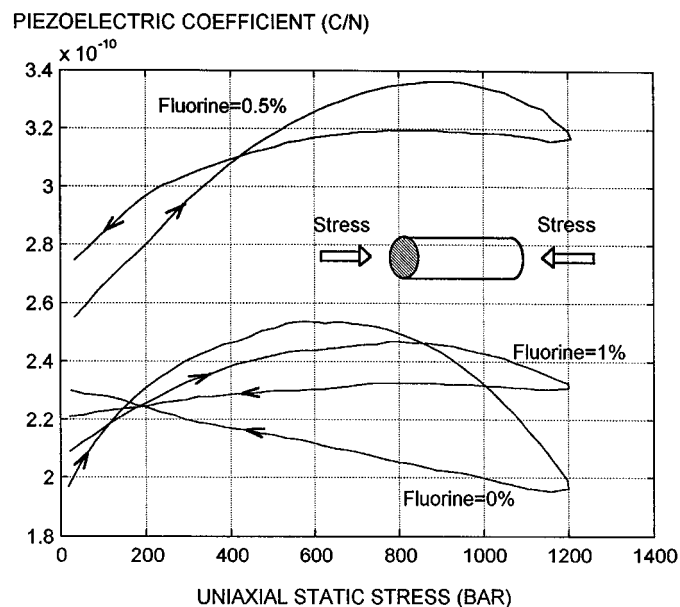
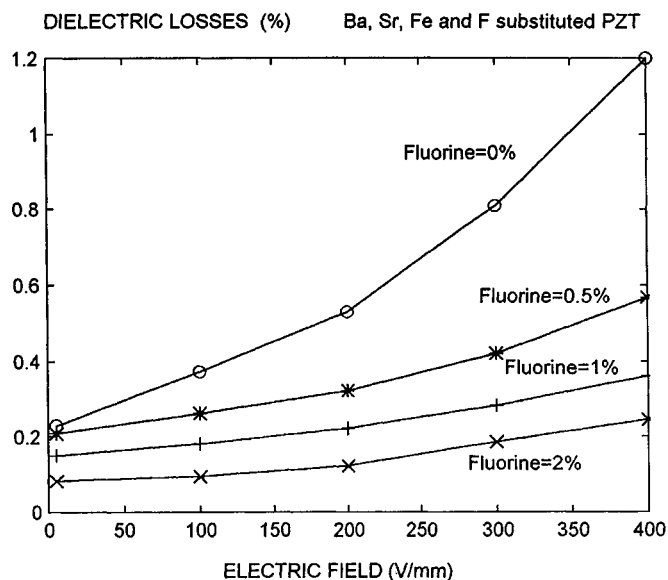
FIG. 5. d_{33} versus T3.

FIG. 6. Dielectric losses versus electric field.

CHEMICAL FORMULATION OF PZT TYPE CERAMICS

Table 3 lists the chemical formulations of some PZT materials.

Formula [1] is the basic theoretical formulation; formula [2] represents an alternate formulation without involving vacancies.

From the basic formulation of the PZT ceramics, the physics of the material combined with the fabrication process conditions leads to alternate formulations:

- formula [3] with charged vacancies,
- formula [4] with neutral vacancies.

In formula [2], it is seen that some *A* sites act as "electron acceptors" and some *B* sites act as "electron donors."

There are many possibilities for representing deviations from the ideal formula. These deviations are more likely to occur at higher temperatures of the preparation process and change during cooling, both in concentration and electrical charge.

In order to maintain the stability of donor and acceptor sites, various substitutions have been examined.

As we have shown for "soft materials" (2) an optimal distribution of Pb^{4+} (or Pb^{3+}) (14) and Ti^{3+} can be maintained by using a dual heterovalent substitution technique (formula [5]).

Fluorination also is a stabilizing factor by filling the oxygen vacancies indicated in formula [6].

The advantage of fluorination (even partial) of the oxygen vacancies (3) is to improve the stabilization of the poled ceramics using heterovalent substituted cations smaller than those used in the customary power ceramics (5, 10, 11) (formulas [7] and [8]).

AGING IN PIEZOCERAMICS OF PZT TYPE AND MODELIZATION

Aging of poled piezoelectric ceramics can be considered as due to variations of the electrical, mechanical, and

TABLE 2
Data Sheet

Fluorine content (%)	d_{33} (pC/N)	ϵ_r	s_{33}^E ($\times 10^{-12}$ Pa $^{-1}$)	Q	$tg \delta$ 5 v/mm (%)	$tg \delta$ 400 v/mm (%)
0	230	1200	12	1200	0.25	1.2
0.5	220	1100	12.5	1300	0.15	0.60
1	220	1000	13	2100	0.15	0.40
2	200	850	15.5	1700	0.10	0.25

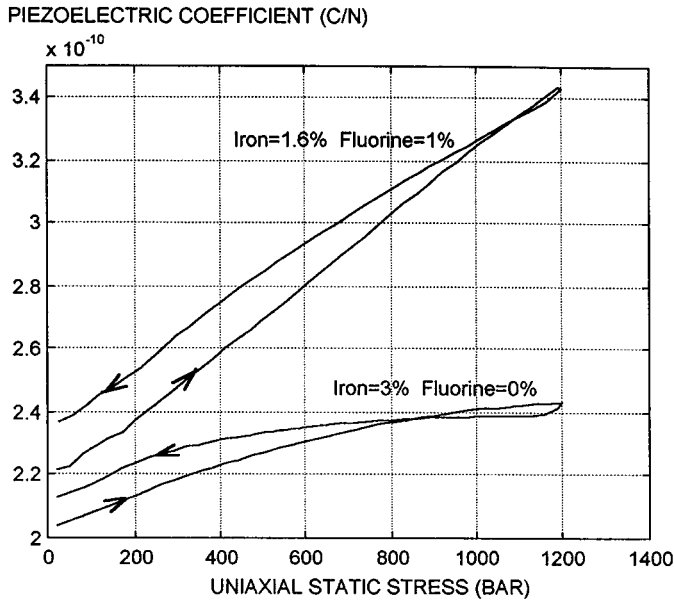


FIG. 7. d_{33} versus T3.

electromechanical characteristics (7–9) with time. Essentially, this arises from an instability of the domain walls which may shift under the action of mobile electrical charge carriers or of a stress anisotropy generated by the orientation of domains during the poling process.

The great difference between ferroelectricity and ferromagnetism is that in the latter case there are no “monopoles.” In the former, there may be free electric charges which participate in the cancellation of the density of the bound charges $\rho = -\text{div } \mathbf{P}$. These free charges derive mainly from the above mentioned “acceptor” and “donor” sites. Every electrical or mechanical stress can change the local electrical equilibrium which induces an irreversible motion of these charges. This creates “aging” if these charge carriers (ions, vacancies, and electrons) do not revert to their initial position leading to the irreversible motion of domain walls.

TABLE 3

[1]	$\text{Pb}^{2+} [\text{Zr}_{1-x}^{4+} \text{Ti}_x^{4+}] \text{O}_3^{2-}$
[2]	$\text{Pb}_{1-z}^{2+} \text{Pb}_z^{4+} [\text{Zr}_{1-x}^{4+} \text{Ti}_{x-2z}^{4+} \text{Ti}_{2z}^{3+}] \text{O}_3^{2-}$
[3]	$\text{Pb}_{1-z}^{2+} \square_z^{2+} [\text{Zr}_{1-x}^{4+} \text{Ti}_x^{4+}] \text{O}_{3-2z}^{2-} \square_z^{2-}$
[4]	$\text{Pb}_{1-2z}^{2+} \text{Pb}_{2z}^{4+} \square_z^{0+} [\text{Zr}_{1-x}^{4+} \text{Ti}_{x-2z}^{4+} \text{Ti}_{2z}^{3+}] \text{O}_{3-z}^{2-} \square_z^0$
[5]	$\text{Pb}_{1-z-u}^{2+} \text{Pb}_z^{4+} \text{M}_u^{1+} [\text{Zr}_{1-x-v}^{4+} \text{Ti}_{x-2z+u-v}^{4+} \text{Ti}_{2z-u+v}^{3+} \text{Nb}_v^{5+}] \text{O}_3^{2-}$
[6]	$\text{Pb}_{1-z}^{2+} \text{Pb}_z^{4+} [\text{Zr}_{1-x-2y-t}^{4+} \text{Ti}_x^{4+} \text{Ti}_{2y}^{3+} \text{B}_t^{2+}] \text{O}_{3-w_1}^{2-} \square_{w_2}^0$
[7]	$\text{Pb}_{1-z}^{2+} \text{Pb}_z^{4+} [\text{Zr}_{1-x}^{4+} \text{Ti}_{x-2y}^{4+} \text{Ti}_{2y}^{3+}] \text{O}_{3-w_1}^{2-} \text{F}_{w_1}^{1-}$
[8]	$\text{Pb}_{1-z}^{2+} \text{Pb}_z^{4+} [\text{Zr}_{1-x-2y-r'}^{4+} \text{Ti}_x^{4+} \text{Ti}_{2y}^{3+} \text{B}_{r'}^{2+}] \text{O}_{3-w_3}^{2-} \text{F}_{w_3}^{1-}$

To prevent aging, it is necessary to lock the average position of these charge carriers.

Figure 8 is a model of poled ceramic where θ is the average spontaneous oriented polarization angle.

Domain wall 1 leads to a $\text{div } \mathbf{P} = 0$, resulting in a null charge. Domain wall 2 leads to a $\text{div } \mathbf{P} > 0$ resulting in a negative charge $\rho < 0$. Domain wall 3 leads to a $\text{div } \mathbf{P} < 0$ resulting in a positive charge $\rho > 0$.

A method to cancel this distribution of charges is to superimpose on the spontaneous polarization an induced polarization p_i , created by electronic commutation between two sites.

The degree of electronic compensation can be tailored by a convenient choice of substitutions.

The requisite induced polarization can be derived from the following approach: for a spontaneous polarization $P_s = 50 \times 10^{-2} \text{ C m}^{-2}$ and $\cos \theta = 0.83$ in tetragonal structure, this induced polarization should be $p_i = 4.6 \times 10^{-2} \text{ C m}^{-2}$.

Figure 9 represents a model of soft material showing the electronic exchange between two sites in a polarized configuration for given substitutions. These dual substitutions arise from the introduction of Nb^{5+} in B sites and of (K, Na) in A sites.

For hard materials, the dual substitutions arise from the introduction of Fe^{3+} in B sites and F^{1-} in anionic sites (Fig. 10).

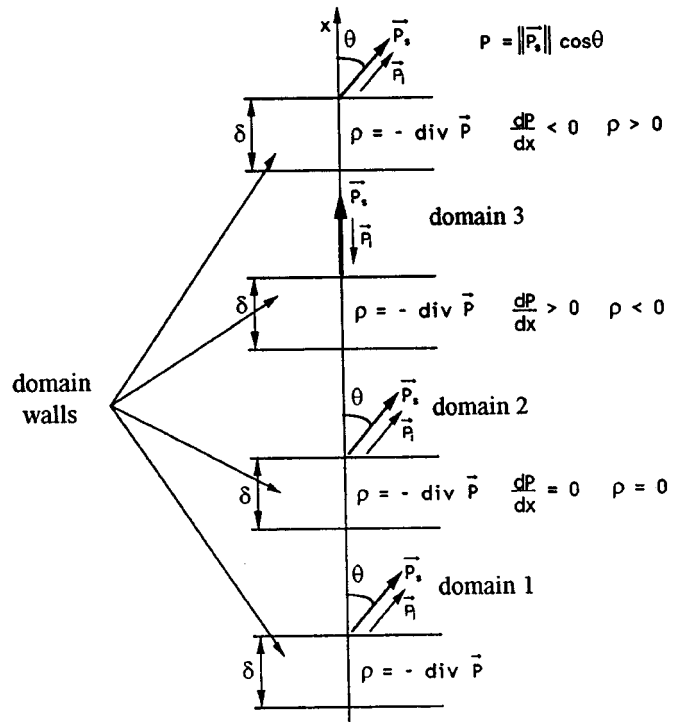


FIG. 8. Tentative model of poled ceramic.

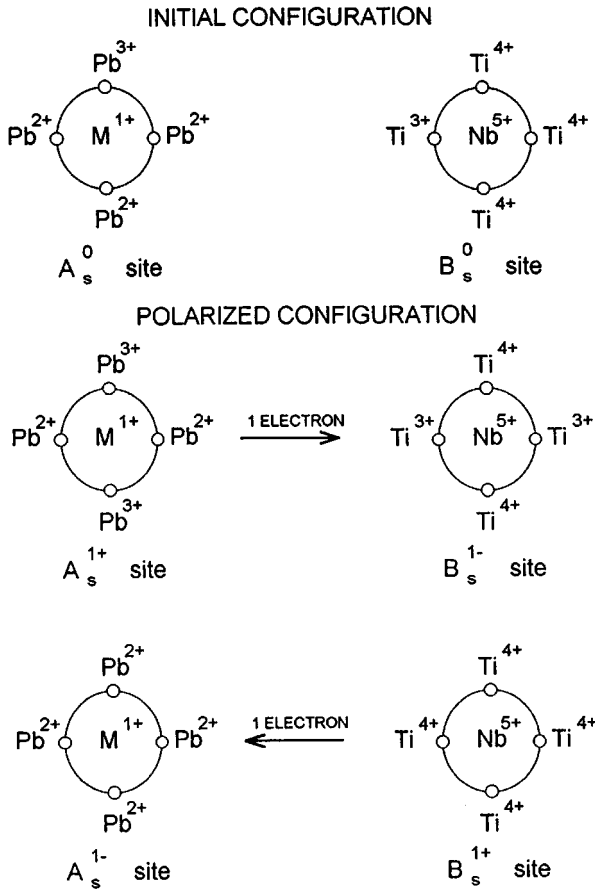


FIG. 9. Tentative model of a soft material.

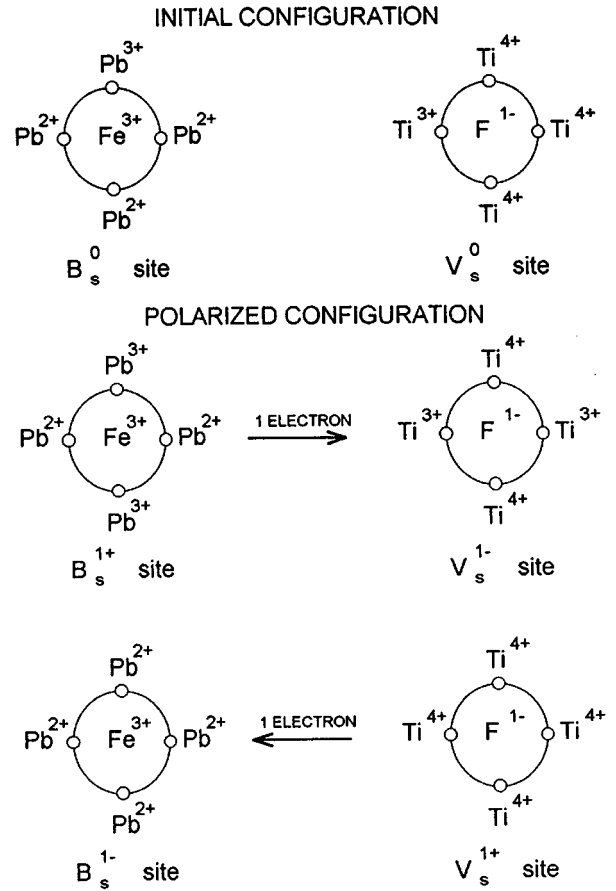


FIG. 10. Tentative model of fluoridated material.

If we assume that the fraction of fluoride sites V_s , as well as that of the B_s^{3+} sites, is about 1/100, the $B_s - V_s$ couples constitute a set of dipoles; the moment per unit volume can be readily calculated.

If we assume that B_s and V_s are at the apices of two interpenetrating cubic lattices (Fig. 11), the dimension of the dipolar unit cell (with $a_0 = 0.4$ nm) will be

$$\Delta_0 = \frac{a_0}{\sqrt[3]{10^{-2}}} = 4.7 \times 4 = 19 \text{ \AA}.$$

The distance between a V_s site and the nearest B_s site in this configuration will be

$$l = \Delta_0 \frac{\sqrt{3}}{2}.$$

Assuming that the transfer of one electron can be used to cancel the space charge density ($\rho = -\text{div } \mathbf{P}$) the resulting dipolar moment would be

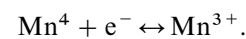
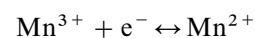
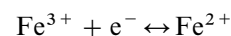
$$\mu_1 = el = \frac{e\Delta_0 \sqrt{3}}{2} = 26 \times 10^{-29} \text{ C m},$$

that is per unit volume,

$$p_i = \frac{\mu_1}{(\Delta_0)^3} = 38 \times 10^{-3} \text{ C m m}^{-3}$$

$$p_i = 3.8 \mu\text{C cm}^{-2}.$$

This value is of the same order of magnitude of the calculated induced polarization. The preceding scheme is based on use of a transition element (Fe). It remains valid with other lower valency cations on the B site. The use of a transition element renders possible another type of electronic exchange between two valency states of this element, e.g.,



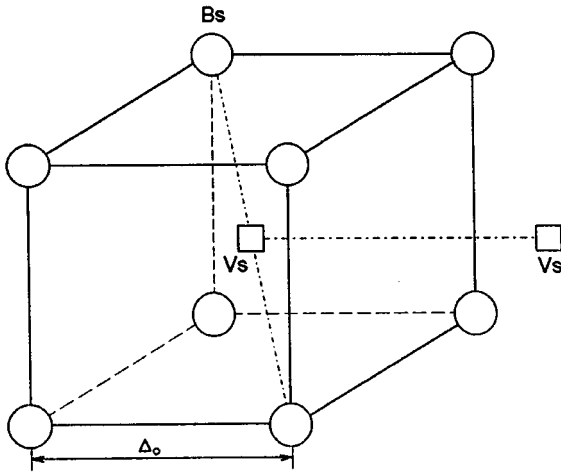


FIG. 11. Geometrical distribution of defects.

CONCLUSION

The fluoridation of anionic sites in the perovskite lattice of PZT-type ABO_3 , with or without oxygen vacancies, can greatly stabilize the remnant polarization under high stress and field levels. Dielectric losses are smaller than for oxygen deficient materials. The stabilization mechanism is ascribed to sites which act either as electron donors or cancel the distribution of bound charges $\rho = -\text{div} \mathbf{P}$ in the poled phase. The (B, F) couples (Table 3, formulas [9] and [10] of substituted ions constitute dipoles which have a greater stability than the $[B, \square]$ couples (Table 3, formula [8]) which are only present in perovskite ceramics with oxygen vacancies.

This study demonstrates the advantage of fluoridating PZT ceramics for use as power transducers. There are still many open questions. One is the optimization of the composition of industrial ceramics. The second, linked with the first, is to explain why the multiple valence substitutions with transition elements like Fe, Ni, and Mn seem most appropriate. A third practical question involves the possibility of carrying out by a dry preparation process what has been reported above with the wet process.

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