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Ferroelectricity and Antiferroelectricity in Pure and Nb_2O_5 Doped Lead Zirconate*

L. BENGUIGUI

Electronique Appliquee, 98 Rue Maurice Arnoux-Montrouge, France and
Department of Physics, Technion-Israel Institute of Technology,
Haifa, Israel†

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We have measured temperatures and heats of transition of pure and Nb_2O_5 doped $PbZrO_3$. The samples exhibit the following succession of phases: antiferroelectric (AF)–ferroelectric (FR)–paraelectric (PR). The Curie point (transition FR-PR) varies little with the percentage x of Nb_2O_5, but the temperature interval in which we can observe the FR phase increases rapidly as x increases (3°C at $x = 0$ and 58°C at $x = 1\%$). The heats of transition decrease as x increases, particularly the heat of the AF-FR transition, which is very low already at $x = 1\%$. We show that the atomic displacements in the AF and FR phases decrease as x increases. We believe that the lead vacancies are the origin of the appearance of the FR phase, but the particular properties of doped samples are due to Nb ions, probably located at interstitial positions and associated with Pb vacancies. We interpret the results concerning the FR phase by means of the Lambert–Comes theory and find that the length of the atomic chains of their model is increased by the doping.

1. Introduction

Lead zirconate is antiferroelectric (AF) at room temperature with an orthorhombic lattice (space group Pba2) (*1*), and becomes paraelectric (PR) (cubic lattice) at a temperature near 230°C. Depending on the impurities in the crystal, a third phase can exist, located between the AF and PR phases. This third phase can be ferroelectric (rhombic lattice) or antiferroelectric. We have shown (*2*) that doping with elements of valence five (such as Nb and Ta) increases the temperature interval in which the ferroelectric phase can be observed.

In a recent paper (*3*), the free energies of the AF (orthorhombic) and FR phases of pure and Nb_2O_5 doped samples of $PbZrO_3$ have been determined using a modification of Kittel's (*4*) development of the free energy. The main result is that adding Nb_2O_5 (0.5% by weight) modifies strongly the free energy of the AF phase and relatively little that of the FR phase.

In this paper we present results of measurements of temperatures and heats of transition at the AF-FR phase change for pure samples and for samples doped with 0.2, 0.5 and 1% (by weight) of Nb_2O_5. We analyze our results without the particular assumptions, made in Ref. (*3*), with regard to the form of the free energy and try to understand how the properties of $PbZrO_3$ are modified by Nb_2O_5.

2. Experimental Results

We determined the temperatures of transition by the discontinuities in the variation of the dielectric constant with the temperature. T_c' is the temperature at the FR-PR phase change (Curie point) and T_t is the transition temperature at the AF-FR phase change, as we increase the temperature. All the transitions exhibit thermal hysteresis and we conclude that they are of first order. In the case of FR-PR phase change, the thermal hysteresis interval is small (two or three degrees C), but it is large in the AF-FR transition. We have verified (*5*) that the Clapeyron relation giving the variation of T_t with the electrical field E, is satisfied:

$$\left(\frac{\partial T_t}{\partial E}\right) = -\frac{\Delta P}{\Delta S}$$

(ΔP is the difference of polarization, and ΔS is the difference of entropy between the AF and FR phases). T_t is very close to the true transition

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† Present address.

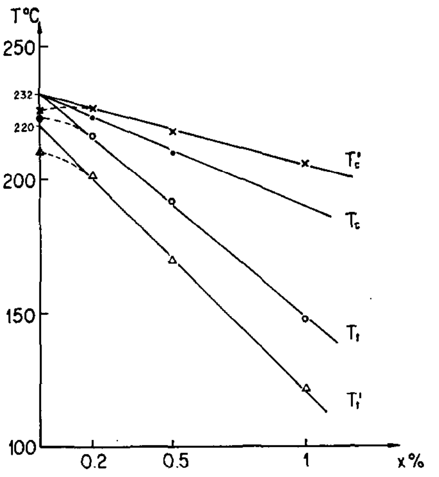

FIG. 1. Variation of the transition temperatures of $PbZrO_3$ with the Nb_2O_5 percentage: T_c' (FR-PR), T_t (AF → FR), T_t' (FR → AF). T_c is the temperature of the AF-PR transition if such a transition could be observed (see text, Section 3).

temperature, as defined by the temperature for which the free energies are equal. We, therefore, regard T_t as the true transition temperature.

The heats of transition have been measured by means of the calorimeter of Eyraud and Richard (*6*). We have also verified the nature of the lattice in each phase by means of X-ray diffraction. The samples were prepared by standard ceramic techniques by the firm "La Ceramique Ferroelectrique".

Above the Curie point the dielectric constant can be expressed by $\mathscr{E} = C(T-\theta_0)^{-1}$. We found the Curie constant $C = 1.4 . 10^5\,^\circ K$ practically independent of the percentage of Nb_2O_5. The variations of T_c' (FR-PR), T_t (AF-FR, rising temperature) and T_t' (FR-AF, decreasing temperature) with x are given in Fig. 1. In Fig. 2 we show the variation of θ_0 versus x. The variation of the entropy differences are given in Fig. 3. The entropy differences were calculated from the heats of transition and T_t (resp., T_c').

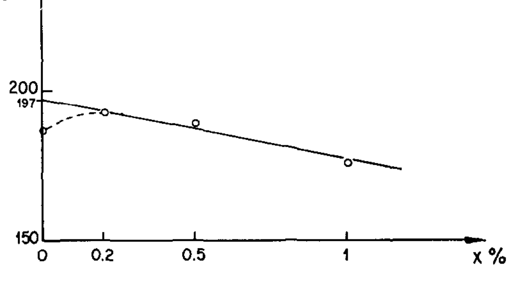

FIG. 2. Curie–Weiss temperature of $PbZrO_3 + xNb_2O_5$ versus x.

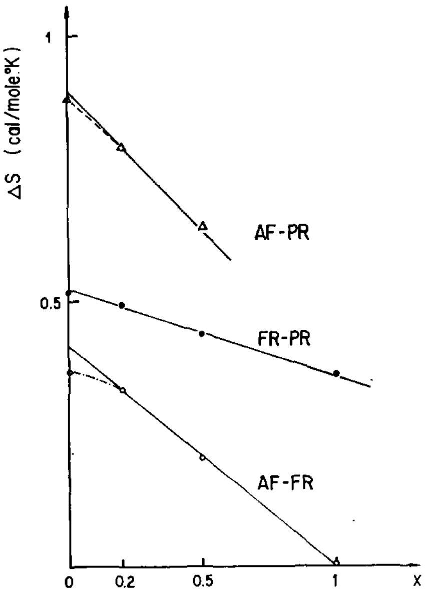

FIG. 3. Entropy differences of the AF-FR, AF-PR and FR-PR Transitions as a function of x.

We see that all the measured quantities (except T_c' and θ_0) decrease when x increases. T_c' and θ_0 show little variation with x, T_c' varies from 226° to 205°C and θ_0 from 186°C to 176°C. T_t varies faster with x than does T_c'. Therefore, the difference $T_c' - T_t$ increases fast with x, changing from 3°C for $x = 0$ to 58°C for $x = 1\%$.

As x increases, the entropy differences decrease faster at the AF-FR transition than at the FR-PR transition. At $x = 1\%$ ΔS(AF-FR) is apparently zero but since the transition is of first order, this means that the heat of transition is lower than the resolution of the calorimeter, i.e., at $x = 1\%$, $\Delta S < 0.02$ cal/mol°K. In Table I, we give the values Q and Q' of the heats of transition. We see, there-

TABLE I[a]

$x\,Nb_2O_5$ %	Q(Cal/mol) AF-FR transition	Q'(Cal/mol) FR-PR transition	P_s C/m^2
0	180	258	0.31
0.2	163	246	0.30
0.5	94	215	0.27
1	<10	173	0.25

[a] Q is heat of the transition AF → FR, Q' is heat of the transition FR → PR, and P_s is the spontaneous polarization of the FR phase at the Curie point.

fore, that when we add Nb_2O_5 to $PbZrO_3$, two main features can be observed (and we shall see below that they are related):

1. T_t moves toward low temperatures, increasing the temperature interval of the FR phase.
2. The decrease of the entropy difference at the AF-FR transition (–0.415 cal/mol°K per %).

3. Interpretation of the Influence of Nb_2O_5 Doping

We see in Figs. 1 and 3 that the transition temperatures and the entropy differences vary linearly with x, except near $x = 0$. The extrapolation of the straight lines till $x = 0$ does not correspond to the measured values for $PbZrO_3$. We note that the straight lines $T_c'(x)$ and $T_t(x)$ intersect on the temperature axis at 232°C.

We propose to interpret these results, assuming that the existence of the FR phase is due to the same mechanism in all cases (doped and pure samples). This assumption is justified by the fact that the temperature interval of the FR phase increases by doping also with elements other than Nb (*2*).

It is accepted that in $PbZrO_3$ there are lead vacancies which appear during the fabrication of the samples (*7*). When we add Nb_2O_5 to $PbZrO_3$ we can write the following possible reactions, where the PbO that is formed evaporates at the firing temperature 1200°C (*8*).

$$(1 - x)\,PbZrO_3 + xNb_2O_5 \rightarrow (Pb_{1-3x}\boxed{Pb}_{3x})Nb_x(Zr_{1-x}Nb_x)O_3 + 2xPbO. \quad (1)$$

or

$$(1 - x)PbZrO_3 + xNb_2O_5 \rightarrow (Pb_{1-3x}\boxed{Pb}_{2x}Nb_x)(Zr_{1-x}Nb_x)O_3 + 2xPbO. \quad (2)$$

In Eq. (1), we assume that there are $3x$ Pb vacancies, $\boxed{Pb}$, and x Nb ions in interstitial positions, while in Eq. (2) we assume that there are only $2x$ Pb vacancies with x Nb ions in substitution for Pb. In both cases x Nb ions are in substitution for Zr.

According to Nassau and Lines (*9*), it is unlikely that Nb ions substitute for Pb because of the large difference in the coordination numbers (12 for Pb and 6 for Nb). It seems more likely, also according to Nassau and Lines, that the Nb ions are in interstitial position but associated with a Pb vacancy and located in the [111] direction from the vacancy. We adopt, therefore, the first reaction, keeping in mind this particular position of the Nb ions. This would explain also the observation that the dielectric losses at 1 kHz increase for samples with Nb_2O_5. These losses can be due to the vibrations of the dipole Pb vacancy—Nb ion. The coercive field of the FR phase decreases by doping and this can also be understood by our model. The electrical field displaces first the Nb ions, which are interstitial (and we recall that in the FR phase the polarization is also along the [111] direction (*3*)), and this facilitates the displacement of the other ions of the lattice.

In all cases (pure and doped samples), the common defects in the samples are Pb vacancies, and we can assume that the Pb vacancies cause the appearance of the FR phase. In the case of pure samples the number of vacancies is not controlled, as in the case of doped samples, but depends on the conditions in firing the samples. This explains the fact that some researchers have observed the FR phase and others have not. Samara (*10*) notes that he observed the FR phase in one sample only.

If this interpretation is correct, the transition temperatures of Fig. 1 extrapolated to $x = 0$ will be those of stochiometric $PbZrO_3$. The Curie point will be at 232°C, a value very near that of Samara's samples which do not exhibit the FR phase. The FR phase will be observed for $x = 0$ with decreasing temperature as a metastable phase, since T_t' does not tend to T_c' when $x = 0$. At 232°C, we shall, in fact, have a triple point, at which the free energies of the three phases are equal.

Once we have assumed that the appearance of the FR phase must be related to the Pb vacancies, we must ask whether the variation of properties of doped samples is related to the Pb vacancies or to the Nb ions. We shall explain below why we think that the second possibility is the most probable one (see Section 5).

4. Thermodynamic Analysis

In Ref. (*3*) it is shown that the curves of the free energies of pure and Nb_2O_5 doped $PbZrO_3$ as a function of T have a low curvature. We assume, therefore, that the curves $G_{FR}(T)$ and $G_{AF}(T)$ (free energies of the FR and AF phases, respectively) are straight lines, at least in a small temperature interval.

We have then simply

$$G_{FR}(T) = \Delta S(\text{FR-PR})(T - T_c')$$

(we take here $G_{PR} = 0$).

The curve G_{AF} passes through the point defined by $G_{AF}(T_t) = G_{FR}(T_t)$ and $T = T_t$, and we have to determine its slope. The quantity $\Delta S(\text{AF-FR})$ is equal (in absolute value) to the difference of the slopes of G_{AF} and G_{FR} and, therefore, the slope of G_{AF} is equal to $\Delta S(\text{AF-FR}) + \Delta S(\text{FR-PR})$.

It follows that

$$G_{AF}(T) = G_{FR}(T_t) + (T - T_t) \times$$
$$\times [\Delta S(\text{AF-FR}) + \Delta S(\text{FR-PR})],$$

which can be written as

$$G_{AF}(T) = (T - T_c) \times$$
$$\times [\Delta S(\text{AF-FR}) + \Delta S(\text{FR-PR})],$$

where we have defined

$$T_c = T_t - G_{FR}(T_t) \times$$
$$\times [\Delta S(\text{AF-FR}) + \Delta S(\text{FR-PR})]^{-1},$$

T_c, the temperature at which the line $G_{AF}(T)$ intersects the temperature axis, can be viewed as the temperature of AF-PR transition, if the FR phase does not exist, and the sum $\Delta S(\text{AF-FR}) + \Delta S(\text{FR-PR})$ as the entropy difference at this transition. In Fig. 4, we have drawn the curves $G_{FR}(T)$ and $G_{AF}(T)$ for $x = 0$, 0.2 and 0.5%. The variation of $\Delta S(\text{AF-PR})$ as a function of x is given in Fig. 3, and that of T_c in Fig. 1. As $x \to 0$, T_c tends toward the same temperature as T'_c and T_t.

When we add Nb_2O_5, the angles made by G_{FR} and G_{AF} with the temperature axis decrease, but the angle made by G_{AF} decreases faster than that made by G_{FR} (sec Fig. 4). The tangents of these angles are nothing other than $\Delta S(\text{AF-PR})$ and $\Delta S(\text{FR-PR})$ and their relative change is related to the fact that $T'_c - T_t$ increases as x increases.

In the ferroelectric phase, we can apply the results of the Devonshire theory (*11*) and calculate the spontaneous polarization P_s at the Curie point

$$\Delta S(\text{FR} - \text{PR}) = \frac{1}{2}\frac{P_s^2}{C} \tag{3}$$

The values of P_s are given in Table 1. P_s decreases from 0.31 C/m^2 for $x = 0$ to 0.25 C/m^2 for $x = 1$%.

Recently Abrahams et al. (*12*) proposed an empirical relation between P_s and δz (displacement from the centrosymmetric position of the "homopolar" atom: in our case Zr) valid for some displacive ferroelectrics:

$$P_s = (258 \pm 9)\,\delta z \tag{4}$$

(P_s in $\mu c/cm^2$, δz in Å). In our opinion, such a relation is certainly more precise if it is applied to materials with the same structure. The proposed relation is obeyed very well by $LiTaO_3$ and $LiNbO_3$ (*12*). In the case of perovskites, it is preferable to take a coefficient equal to 200, as is shown by calculation of the ratios $P_s/\delta z$ of $BaTiO_3$, $KNbO_3$ and $PbTiO_3$ (*12*). We obtain 189, 187 and 221, respectively. Using the value 200, we get for $PbZrO_3 + x\,Nb_2O_5$ values of δz from 0.155 Å ($x = 0$) to 0.125 Å ($x = 1$%), i.e., the atomic displacement is decreased by doping.

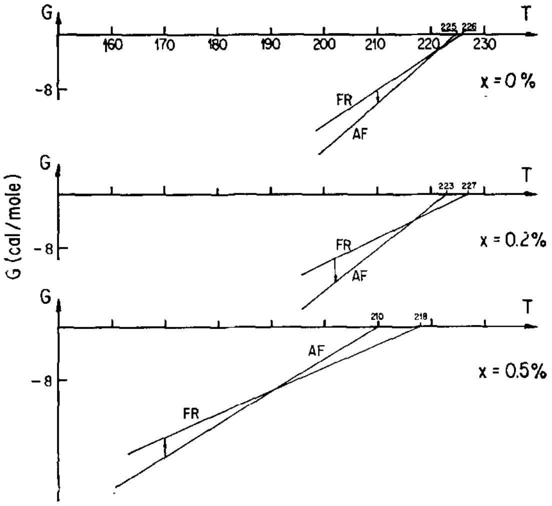

FIG. 4. Free energy curves of the AF and FR phases as a function of T, for $x = 0$, 0.2 and 0.5%. The arrow indicates the temperature of the transition FR → AF.

We shall now show that the effect of doping in the AF phase is the same as in the FR phase, namely, the diminuation of the atomic displacements. The structure of the AF phase is complicated and cannot be described by one order parameter (*1*). The free energy can be viewed as a function of several order parameters. These can be, as shown by Kwock and Miller (*13*), linear combinations of the atomic displacements. However, Boccara (*14*) has shown that we can use a new expression for the free energy G_{AF} which depends only on T and one order parameter (arbitrarily chosen). Let y be the order parameter which is an increasing function of the atomic displacements. The equilibrium value y_0, which minimizes G, is determined by $\partial G/\partial y = 0$. From the equation $S_{AF} = -\partial G_{AF}/\partial T$ and the fact that G_{AF} increases with T, it follows that S_{AF} is negative. The quantity $\Delta S(\text{AF-PR})$ is the absolute value of the difference of the entropies of the AF and PR phases. We have taken $G_{PR} = 0$, so $S_{PR} = 0$, and, therefore,

$$\Delta S(\text{AF-PR}) = |S_{AF} - S_{PR}| = |S_{AF}| = -S_{AF}. \tag{5}$$

Boccara (*14*) proved the following relation

$$\frac{dy_0}{dt} = -\frac{\dfrac{\partial S_{AF}}{\partial y}}{\dfrac{\partial^2 G_{AF}}{\partial y^2}}.$$

As the AF phase is stable, we have $\partial^2 G/\partial y^2 > 0$. The order parameter decreases if T increases; that means that $dy_0/dT < 0$ and therefore $\partial S_{AF}/\partial y < 0$. Therefore, using (5), we have

$$\frac{\partial[\Delta S(\text{AF-PR})]}{\partial y} > 0.$$

This shows that ΔS(AF-PR) is an increasing function of the order parameter y. Since y is an increasing function (*13*) of the atomic displacements, we can say that ΔS(AF-PR) is also an increasing function of the atomic displacements. We have seen above the decrease of ΔS(AF-PR) when we add Nb_2O_5, and we conclude that doping $PbZrO_3$ with Nb_2O_5 decreases the atomic displacements also in the AF phase.

This result is in agreement with those obtained in (*3*). In this paper, it is assumed that the main contribution to the free energy of the AF phase comes from the displacements of atoms in the [110] directions, which then form two sublattices. Therefore, the free energy is a function of P_a and P_b, the polarizations of the two sublattices. P_a is calculated in (*3*) and is equal to 0.43 C/m^2 for $x = 0$, and to 0.26 C/m^2 for $x = 0.5\%$. As P_a is a linear and increasing function of the atomic displacements, these results show also the drastic influence of the doping on the atomic displacements.

Briefly, we can say that the main effect of the doping is to decrease the atomic displacements in the AF phase as well as in the FR phase. But in the former, the consequences of this effect are more accentuated than in the latter, resulting in the fast decrease of $\Delta S(\text{AF} - \text{PR})$ and the impossibility to observe the AF phase when the Nb_2O_5 amount is increased.

5. Relation with the Comes–Lambert Theory

In the present state of theories of ferroelectrics and of antiferroelectrics, it seems very difficult to interpret the results obtained in the preceding section on a microscopic model. However, we can consider the relation between our results for the FR phase and the recent theory of $BaTiO_3$ type ferroelectrics, proposed by Comes and Lambert (*15, 16*).

In their theory, the cubic phase is considered as a disordered phase, the atoms being displaced along one of the [111] directions; but several neighboring atoms have their displacement in the same direction and thus form a chain. The rhombic phase is completely ordered, and all the atoms have their displacement in the same [111] direction. On the other hand, the tetragonal and orthorhombic phases are partially ordered.

The entropy difference between the rhombic and the cubic phases (per unit cell) is (*16*)

$$\Delta S(\text{FR-PR}) = \frac{k \log 8}{n} \tag{6}$$

(n is the mean number of atom in a chain in the cubic phase, and k is the Boltzmann constant). We can compute n from Eq. (6) and find that the mean number n increases with x, from 35 to 50 atoms per chain as x increases from 0 to 1 %. This result seems surprising since we should expect that increasing the number of defects will decrease the mean length. But we have assumed that the interstitial Nb ions are located along the [111] direction, which is the polarization direction. We can suppose that the Nb ions interact with the other lattice ions and this interaction increases the mean length. If this interpretation is correct, the particular properties of the doped samples must be attributed to the Nb ions located in interstitial positions and not to the Pb vacancies.

We have seen that as x increases, the mean length increases, but the atomic displacements decrease. This can be understood in the Comes–Lambert theory, by the following argument. If n increases indefinitely, the paraelectric crystal tends to become perfectly ordered. But as it is nonferroelectric, this can only be if $\delta z \to 0$.

We can also see the opposite dependence of n and δz with x in another way. It is possible to show that, in the Comes–Lambert model, the Curie constant C is proportional to $n(\delta z)^2$. In our case, C is independent of x and since n increases with x, this can be only if δz decreases. The proportionality of C with $n(\delta z)^2$ can be seen also by using Eqs. (*3, 4* and *6*).

The Comes–Lambert theory has been formulated only for the ferroelectric case, and we cannot use it in the AF phase.

5. Conclusion

The consequences of doping $PbZrO_3$ with Nb_2O_5 are the decrease of the entropy differences at the AF-FR and FR-PR transitions, and the extension of the temperature interval of the FR phase. We have shown that these effects are related to the decrease of the atomic displacements in the AF and FR phases.

We have used the Comes–Lambert theory and shown that the Nb_2O_5 doping increases the mean length of the chains in the cubic phase.

We have proposed relating the appearance of the FR phase (i.e., the fact that $T_c' > T_c$) to the Pb vacancies. In the pure sample, they appear during the sample preparation in an incontrolled manner. But in the doped samples, the Pb vacancies are valence controlled, since the Nb ions have a valency of five. There are also other defects: Nb in substitution for Zr and Nb in an interstitial position but associated with a Pb vacancy. It seems reasonable to assume that some of the new properties of the doped samples (increase of dielectric losses, decrease of the coercive field, increase of the mean length of the chains) are due essentially to the Nb ions in the interstitial position.

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