PHYSICAL REVIEW B VOLUME 20, NUMBER 9 1 NOVEMBER 1979

# Valence change and phase stability of 3$d$-doped $BaTiO_3$ annealed in oxygen and hydrogen

Hans-Jürgen Hagemann and Holger Ihrig
*Philips GmbH Forschungslaboratorium Aachen, 5100 Aachen, Federal Republic of Germany*

(Received 20 December 1978)

$BaTiO_3$ ceramics doped with several iron-group elements up to 2.0 mole % were identically prepared and afterwards annealed at 700 °C in $O_2$ at 150 bar or in $H_2$-$H_2O$ with an oxygen partial pressure of $10^{-22}$ bar. The valence states of the dopants were determined by magnetic-susceptibility measurements, and the phase-transition temperatures were established by dielectric measurements. The transition temperatures and the charge of the Cr, Mn, and Co dopants were found to change reversibly upon annealing at different oxygen partial pressures whereas both remained constant for Fe, Ni, Zn, and Ga dopants. The change of the concentration of oxygen vacancies, which proved to be inherently connected with valence changes, was investigated gravimetrically.

## I. INTRODUCTION

The physical properties of the perovskite-type oxides are influenced in many ways by doping with transition-metal ions, in particular with those of the iron group. In the ferroelectric materials belonging to the $BaTiO_3$ family this opens a wide field for fundamental research of the ferroelectric phenomena as well as for technical applications. It is known, for example, that 3-$d$ doping ions affect the hysteresis and loss properties of ferroelectric materials[1–3] and improve the properties of ferroelectric switches based on semiconducting $BaTiO_3$ ceramics, known as PTC (positive-temperature characteristic) resistors.[4,5] Moreover, 3$d$-doped $BaTiO_3$ capacitor ceramic can be treated in reducing atmospheres which otherwise lead to conductivity due to conduction electrons provided by the creation of oxygen vacancies.[6]

All these effects are probably connected with the influence of the 3$d$ elements on the equilibrium defect distribution in these oxides in combination with the ambient oxygen partial pressure, temperature, and impurities present from the preparation.[7–9] This influence seems to be further sensitized by the ability of the 3$d$ ions to enter the crystal lattice in different valence states, depending on the particular thermodynamic conditions at high temperatures (see, e.g., Refs. 10–13). The dependence of the electrical and structural properties of the perovskites on their defect distributions opens the possibility of manipulating the conductivity, the structure stability, and the ferroelectric behavior of 3$d$-doped materials over a wide range by means of suitable preparation and aftertreatment.

Much experimental and theoretical work has been devoted to single crystals of the perovskite compound $SrTiO_3$. EPR and optical methods have been successfully applied to clarify the properties of transition-metal related centers (see, e.g., Refs. 14–16). Divalent to pentavalent states of iron-group ions substituting $Ti^{4+}$ have been identified. In some cases it has been found that ions with valencies smaller than 4 are in part charge compensated by nearest-neighbor oxygen vacancies.[17,18] Moreover, it has been described how oxidizing and reducing annealing treatments are changing the nature of the transition-metal related centers (see, e.g., Refs. 12, 16, and 18).

In the case of $BaTiO_3$ the knowledge is much less detailed, mainly because of the difficulty to obtain high-purity melt-grown single crystal.[11] We therefore attempted to analyze the valence states of transition-metal dopes in $BaTiO_3$ ceramic which has the advantage that it is comparatively easy to prepare by identical procedures well-defined samples with different doping ions over a wide range of doping concentrations. Whereas EPR and optical methods are difficult to apply for ceramic samples we obtained direct experimental knowledge about the valence states of the majority of the dopants by measuring the magnetic susceptibility.[19] It was observed that upon annealing treatments at high (150 bar) and low ($10^{-22}$ bar) oxygen partial pressures some of the dopants change their valence and others do not. A corresponding change of the oxygen vacancy concentration was determined gravimetrically which gave evidence that the charge deficiency of 3$d$ ions at $Ti^{4+}$ sites is compensated by doubly ionized oxygen vacancies. (We cannot decide from our measurements if or to what degree this compensation occurs locally.)

It is well known that the phase-transition temperatures of $BaTiO_3$ are influenced by doping and by mixed crystal formation, and it has been found recently that the ferroelectric Curie temperature shows a pronounced dependence on the oxygen partial pressure in the case of Mn-doped $BaTiO_3$,[2,6] but not in the case of Fe-doped $BaTiO_3$.[2] In this paper we describe the correlation between the phase-transition temperatures and the number of electrons within the $3d$ shell of doping ions from the iron group. The number of electrons is different for different members of this group and for different valence states, but all doping ions are very similar otherwise, e.g., with respect to size and electronegativity. This equally holds for $Zn^{2+}$ and $Ga^{3+}$ dopants which differ from the iron-group ions mainly by the fact that their $3d$ shell is completely filled. Therefore they were included in the investigation.

We are suggesting that the phase stabilities of $3d$-doped $BaTiO_3$ are influenced by the symmetry properties of the $3d$ shell of the dopant in combination with the oxygen vacancies induced by the charge deficiency of the dope. In this sense the primary goal of this work on a large number of identically prepared samples is not to completely characterize the detailed structure of the transition-metal induced impurity centers but to sketch by comparing different doping ions and different annealing treatments a rough but consistent picture of the majority of the defects and their influence on the ferroelectric phase transitions.

## II. SAMPLE PREPARATION AND MEASUREMENTS

The preparation and measuring procedures have been described in detail in a previous paper.[19] The polycrystalline samples were synthesized from $BaCO_3$, $TiO_2$, and dopes by means of a conventional mixed-oxide technique.[20] The dopes were weighed-in substitutionally for titanium and added to the raw materials. Liquid phase sintering at 1400 °C in air was achieved by adding 3 mole% $TiO_2$ in excess of the stochiometric composition. The incorporation of the dopants was checked by semiquantitative microprobe analysis as previously stated.[19] This is backed up by Fig. 1 which clearly shows that the x-ray signal from arbitrarily chosen points of the polished samples corresponding to a particular $3d$ element is proportional to the weighed-in doping concentration up to 1.5 mole%. (Fe was investigated only up to 1.25 mole%.) The deviations at 2.0 mole% could indicate the formation of segregated phases. It was further proved that the x-ray intensities did not change from one grain to another nor within a grain. Thus an equal distribution of dopants within the ceramics can be assumed.

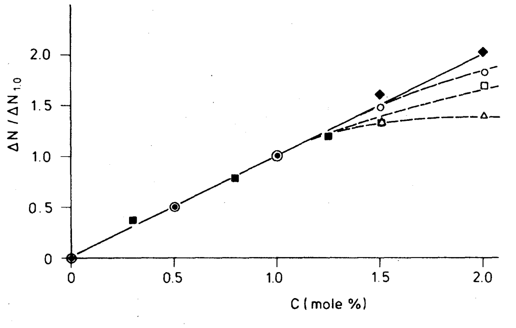

FIG. 1. Result of the x-ray microprobe analysis of the $3d$-doped $BaTiO_3$ ceramics. The relative x-ray intensities $\Delta N$ characteristic of a dopant are normalized by their 1-mole% value $\Delta N_{1.0}$ and plotted vs the weighed-in concentration. The intensities are obtained from the interior of the grains of the ceramic. ○Cr; ◆ Mn; ■ Fe; Δ Co; □ Ni; ◉ the intensities of all of the elements coincide.

From each batch several samples were taken for oxidizing and reducing treatments at elevated temperature. One fraction of the samples was annealed for 65 hours at 700 °C in pure oxygen at a pressure of 150 bar and cooled to room temperature at a rate of 5 K/min. These samples are indicated by $O_2$ in this paper. Another fraction (indicated by $H_2$—$H_2O$) was annealed in the same way but in a mixture of 95 vol% $N_2$ and 5 vol% $H_2$ which was saturated with $H_2O$ vapor at 15 °C. This provides a reducing atmosphere with an oxygen partial pressure of approximately $10^{-22}$ bar at 700 °C. The partial pressure was chosen such that the samples remained nonconducting after cooling. Room-temperature resistivities of $10^5$ to $10^{12}$ $\Omega$ cm were measured. Thus the concentration of charge carriers is at least some magnitudes smaller than the concentration of the $3d$ dopants. A third fraction (indicated by $O_2$—$N_2$) as sintered at 1400 °C in air has been investigated previously.[19] The annealing conditions guarantee that the microstructure of the ceramic and the concentration and distribution of the ionic defects except oxygen vacancies are not affected by the annealing.[8] The annealing was sufficient, however, to achieve the thermodynamic equilibrium in the oxygen sublattice and in the electronic subsystem of the materials.[21]

The temperatures for the cubic-tetragonal, the tetragonal-orthorhombic, and the orthorhombic-rhombohedral phase transition were determined by measuring the dielectric constant $\epsilon$ in heating and cooling runs. The averages of the maxima for heating and cooling were taken as the transition temperatures. This gives by no means exact and absolute phase-transition temperatures, but our arguments will be based only on relative dependences which could be correctly measured because the shape of the $\epsilon$ curves of all samples is similar.

In order to determine the valence states of the incorporated dopants the magnetic susceptibility of the compounds was measured in a Faraday balance. Between 80 and 300 K the susceptibility after subtracting the diamagnetic portion shows a Curie-like behavior according to $\Delta\chi \propto c\, p_{\text{eff}}^2/T$ ($c$ is the doping concentration, $p_{\text{eff}}$ is the effective magnetic moment, and $T$ is the temperature) except for those Ni- and Co-doped compounds which were $H_2$—$H_2O$ annealed. This indicated that in all compounds, except the latter, the population of the magnetic levels remains constant in the temperature range of observation. Thus, level splitting of the order of $kT$ due to crystal fields (here greater $kT$) or spin-orbit coupling effects (probably smaller $kT$), which could have made the correlation to the valence states more difficult, are absent.[22]

The temperature dependence of $1/\chi$ of the samples doped with 0.6 mole% Ni or Co and annealed in $H_2$—$H_2O$ is depicted in Fig. 2. As can be seen, $1/\chi$ does not extrapolate to zero at 0 K for these samples; furthermore, the magnetic moment is about 5—6 times higher than expected for noninteracting ions. We cannot decide from these measurements whether this is an indication of ion-ion correlation in the matrix or simply the result of the appearance of a small amount of metallic Ni or Co formed in the second phase or at the grain boundaries by the reducing treatment. The latter explanation seems to be more probable to us. Gravimetric measurements were included in our investigations in order to detect possible weight losses caused by the creation of oxygen vacancies during the reduction process.[8] These investigations were carried out with ceramics possessing only 0.5 mole% titanium excess (weighed-in according to $BaTi_{1.005-x}M_xO_3$, where $M$ is the dopant) because we observed that the weight change was only reversible after a reoxidation if the titanium excess was less than 1 mole%. The other results did not depend on the Ti excess.

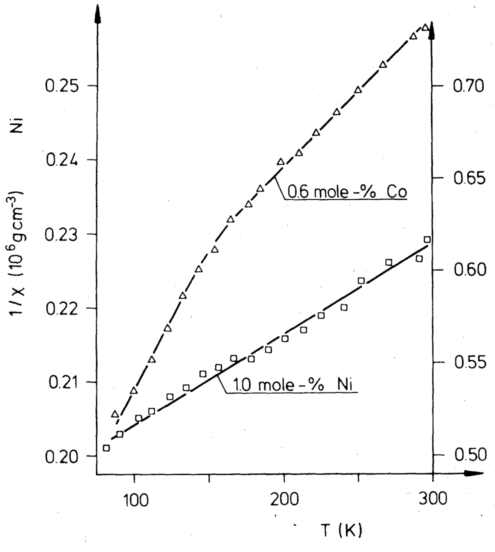

FIG. 2. Reciprocal magnetic susceptibility of polycrystalline $BaTiO_3$, doped with 0.6 mole% Co (Δ) and 1.0 mole% Ni (□). The samples were reduced in $H_2$—$H_2O$ at 700 °C at an oxygen partial pressure of approximately $10^{-22}$ bar. An experimental uncertainty of the actual sample temperature of ± 5 K must be taken into account.

## III. EXPERIMENTAL RESULTS AND DISCUSSION

### A. Magnetic moments and valence states

Figure 3 shows the magnetic moments per doped ion as a function of the annealing treatment at the three different oxygen partial pressures. The results obtained for the $N_2$—$O_2$ treated samples have been already presented in detail[19] and we shall be using those results in this section without explicit reference. The Fe moment remains constant at all gas atmospheres, Co and Ni at $O_2$ and $O_2$—$N_2$ (no results could be obtained for these samples when treated by $H_2$—$H_2O$ because the susceptibilities did not follow the Curie law; see Fig. 2); the magnetic moments of Cr and Mn depend significantly on the gas atmosphere.

Figure 3 also gives the moments of the high-spin spin-only states because the magnetic moments of all $O_2$—$N_2$ treated samples, except the Co-doped ones, originate from spin-only states in the high-spin configuration.

Figure 4 shows the concentration dependence of the magnetic susceptibility of the Cr- and Mn-doped samples which were treated in $O_2$ and in $H_2$—$H_2O$. When these results are interpreted in terms of spin-only moments (negligible orbital contribution) the spin quantum number of Cr changes from about $S=1$ for the $O_2$-treated samples to $S=\frac{3}{2}$ for the re-

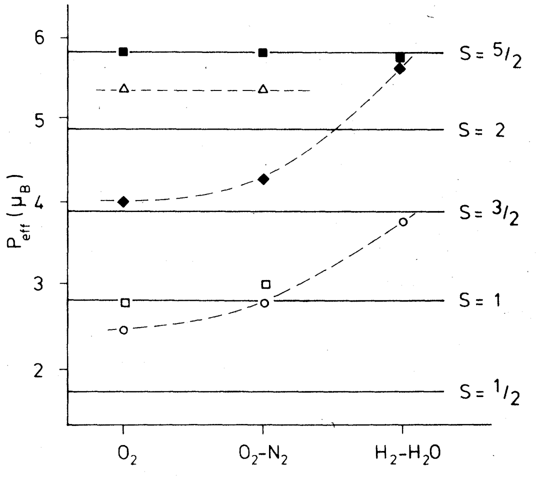

FIG. 3. Effective magnetic moment of $BaTiO_3$ ceramic doped with several iron-group elements. The doping concentrations are 0.17 to 2.0 mole% except for Fe (up to 1.25 mole%) and for Mn treated in $H_2$—$H_2O$ (up to 1.0 mole%). The horizontal lines are calculated for spin-only states. Pretreatment of the samples at 700 °C at different oxygen partial pressures $P_{O_2}$: $O_2$ means $P_{O_2}=150$ bar, $O_2$—$N_2$ means $P_{O_2}=0.2$ bar, and $H_2$—$H_2O$ means $P_{O_2}\approx 10^{-22}$ bar. ○Cr, ◆ Mn, ■ Fe, Δ Co, □ Ni.

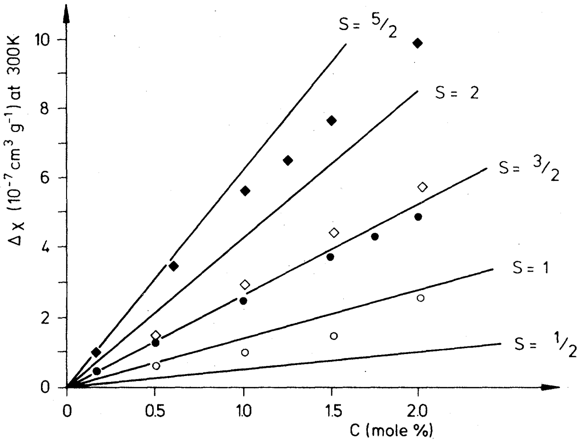

FIG. 4. Relative magnetic susceptibility of 300 K of Cr-(○, ●) and Mn-(◇, ◆) doped $BaTiO_3$. The diamagnetic contribution of the matrix has been subtracted. Open symbols: samples annealed in $O_2$; bold symbols: annealed in $H_2$—$H_2O$.

duced compounds. The spin quantum number of Mn changes from $S=\frac{3}{2}$ ($O_2$) to about $S=\frac{5}{2}$ ($H_2$—$H_2O$) for a Mn concentration up to about 1 mole%, whereas higher concentrations possess $S$ values between 2 and $\frac{5}{2}$.

The corresponding valence changes are then from $Cr^{4+}$ ($S=1, 3d^2$) to $Cr^{3+}$ ($S=\frac{3}{2}, 3d^3$) and from $Mn^{4+}$ ($S=\frac{3}{2}$, $3d^3$) to $Mn^{2+}$ ($S=\frac{5}{2}$, $3d^5$); at Mn concentrations higher than 1 mole% the reduction is most probably incomplete and we obtain a mixture of $Mn^{3+}$ ($S=2, 3d^4$) and $Mn^{2+}$ ions. Our result for Cr confirms earlier observations by Ariya *et al.*[23] obtained from EPR and magnetic-susceptibility measurements.

The assumption of vanishing orbital contributions to the magnetic moments is justified in all of these cases because $Mn^{4+}$ ($3d^3$, $A_{2g}$ symmetry at the substituted Ti octahedron site), $Mn^{3+}$ ($3d^4$, $E_g$), $Mn^{2+}$ ($3d^5$, $A_{1g}$) as well as $Cr^{3+}$ ($3d^3$, $A_{2g}$) possess spin-only moments if or if not the $O_h$ symmetry of the $3d$-substituted Ti site is further lowered.

The magnetic moments of the strongly oxidized Cr compounds are somewhat below the $S=1$ line in Fig. 4. These smaller moments may indicate either the presence of some higher-valent chromium ions or the existence of a small orbital moment contribution of $Cr^{4+}$.[24]

The magnetic moment of Fe does not change by annealing in $O_2$ and in $H_2$—$H_2O$ and we conclude that the majority of the Fe ions is trivalent as in the case of $N_2$—$O_2$-treated samples.

Unfortunately no information is obtained about the reduced samples doped with Co and Ni. Thus we tried to learn something about the valence states of these ions by means of gravimetric measurements.

Valence changes of ions caused by treatments under different thermodynamic conditions require charge compensation in order to maintain the neutrality of the compounds.[7,8,25] Therefore, the valence changes to smaller values resulting from the reduction treatment have to be connected with the creation of extra oxygen vacancies which are positively charged with respect to the lattice. The density of the additionally created oxygen vacancies can directly be detected from the weight loss of the compounds due to oxygen evaporation.

The reversible weight changes of several samples doped with 0.5 mole% $3d$ ions (the total $TiO_2$ excess was 0.5 mole% for the reasons mentioned in Sec. II) are given in Table I. We see from this table that the reduction treatment causes the smallest weight changes, and hence the smallest amount of additional oxygen vacancies for Fe, Ni, Zn, and Ga. This is as expected, because these ions are known to have very stable valencies ($Ni^{2+}$, $Zn^{2+}$, and $Ga^{3+}$). The small weight change of the Fe-doped samples confirms the conclusion from the magnetic measurements that Fe is in the trivalent state, independent of the oxygen partial pressure during annealing.

The small weight changes found in these samples, which correspond to an oxygen vacancy content of about 10% of the $3d$-dopant concentration (0.5 mole%: $7.8\times10^{19}$ cm$^{-3}$) could arise from a small fraction of the doped ions or impurities that change their valence state. We think, however, that these weight losses most probably reflect the change of the oxygen vacancy concentration due to the thermodynamic equilibrium between the oxygen partial pressure of the surrounding atmosphere at 700 °C and the oxygen of the $BaTiO_3$ lattice.[8]

Large weight losses were found for the Cr-, Mn-, and Co-doped samples which, in the case of Cr and Mn, directly correspond to the magnetically deter-

TABLE I. Reversible relative weight change $\Delta m/m$ of $3d$-doped $BaTiO_3$ due to vacancy formation or annihilation $\Delta V_0$ in the oxygen sublattice by alternating $N_2$—$O_2$ and $H_2$—$H_2O$ treatments.

| Dope (0.5 mole %) | $\pm10^6\Delta m/m$ | $\pm10^{-19}\Delta V_0$(cm$^{-3}$) |
|---|---|---|
| Cr | 151 ± 10 | 3.4 ± 0.2 |
| Mn | 276 ± 30 | 6.2 ± 0.7 |
| Fe | 26 ± 7 | 0.6 ± 0.2 |
| Co | 170 ± 16 | 3.8 ± 0.4 |
| Ni | 30 ± 6 | 0.7 ± 0.2 |
| Zn | 15 ± 5 | 0.3 ± 0.1 |
| Ga | 29 ± 6 | 0.7 ± 0.2 |

mined valence changes. For a valence reduction of 1, which was magnetically derived for Cr ($Cr^{4+}$ to $Cr^{3+}$), it is necessary to have $3.9\times10^{19}$ $cm^{-3}$ doubly ionized oxygen vacancies (oxygen vacancies not occupied by electrons which are twofold positive with respect to the oxygen lattice sites); this is close to the value obtained gravimetrically for Cr [$(3.4\pm0.2)\times10^{19}$ $cm^{-3}$].

In the case of Mn too, which, due to the magnetic measurement, changes from a mixture of $Mn^{4+}$–$Mn^{3+}$ ($O_2$–$N_2$) to $Mn^{2+}$ ($H_2$–$H_2O$), the weight loss agrees with the postulate of a charge compensation by doubly ionized vacancies; the value of $6.1\times10^{19}$ $cm^{-3}$ (Table I) is in between the values required for the compensation of a valence change of 1 ($3.9\times10^{19}$ $cm^{-3}$) and 2 ($7.8\times10^{19}$ $cm^{-3}$).

The weight loss of the Co compounds indicates a valence change of 1. Taking into consideration that the magnetic moments of the $O_2$- and $O_2$–$N_2$-treated samples had to leave it undecided whether Co is incorporated in the divalent or trivalent state, the gravimetrically determined valence change of 1 clearly favors the postulate that Co is divalent in the hydrogen-treated samples and trivalent in the oxygen- and air-treated samples.

Corresponding weight changes which show the same one-to-one relation to valence changes were detected for compounds with doping concentrations different from 0.5 mole%.

Summing up, magnetic susceptibility measurements assisted by weight-change investigation revealed that in $BaTiO_3$ some 3*d* dopants change their valence when treated in different gas atmospheres, whereas others do not (Table II). The valence change is always connected with the creation or annihilation of doubly ionized oxygen vacancies required for charge compensation. We conclude that 3*d* ions substituted at titanium sites with valencies smaller than four are predominantly compensated by doubly ionized oxygen vacancies.

TABLE II. Predominant valence states of 3*d* ions as a function of annealing in gas atmospheres of different oxygen partial pressures $P_{O_2}$.

| $O_2$ | $O_2$–$N_2$ | $H_2$–$H_2O$ |
|---|---|---|
| $P_{O_2}=150$ bar | 0.2 bar | $10^{-22}$ bar |
| $Cr^{4+}$ | $Cr^{4+}$ | $Cr^{3+}$ |
| $Mn^{4+}$ | $Mn^{4+}$–$Mn^{3+}$ | $Mn^{2+}$ |
| $Fe^{3+}$ | $Fe^{3+}$ | $Fe^{3+}$ |
| $Co^{3+}$ | $Co^{3+}$ | $Co^{2+}$ |
| $Ni^{2+}$ | $Ni^{2+}$ | $Ni^{2+}$ |
| $Zn^{2+}$ | $Zn^{2+}$ | $Zn^{2+}$ |
| $Ga^{3+}$ | $Ga^{3+}$ | $Ga^{3+}$ |

At this point we should note that the experimental uncertainties of the results obtained from the magnetic and gravimetric measurements only allow information about the majority of the doped ions; a smaller fraction of the ions may nevertheless be in other valence states, and for thermodynamic reasons and because of occupation probabilities of the electrons,[8] this cannot even be avoided. Indeed, more sensitive methods like EPR detect a large variety of different valence states of 3*d* ions in perovskite compounds.[18,26] The valence of the majority of the dopants, however, is dominating the defect chemistry of the compounds and is important for macroscopic effects like dielectric properties and conductivity and for collective phenomena like phase transitions.

### B. Phase-transition temperatures

The phase-transition temperatures of the three structure transformations of $BaTiO_3$ doped with Fe, Ni, Zn, or Ga do not depend on the oxygen partial pressure during annealing. However, the three transition temperatures of the Cr-, Mn-, and Co-doped compounds are drastically altered upon annealing; this is shown for the cubic-tetragonal transition in Fig. 5(a) and for orthorhombic-rhombohedral transition in Fig. 5(b). Hence the phase stability is affected by annealing in the case of precisely those ions that change their valencies and that cause changes of the oxygen vacancy concentration. The temperatures of the tetragonal-orthorhombic transitions are not presented here because we wish to limit the discussion to transformations between a distorted (tetragonal, orthorhombic) and an undistorted oxygen sublattice (cubic, rhombohedral—which can be regarded as quasicubic[19]).

The results derived from the measurements of the cubic-tetragonal and orthorhombic-rhombohedral phase-transition temperatures are summarized in Figs. 6(a) and 6(b). These figures show $dT/dc$ for $O_2$, $O_2$–$N_2$, and $H_2$–$H_2O$ treatment ($T$ is the transition temperature and $c$ is the nominal doping concentration). The $dT/dc$ values are obtained by approximating the concentration dependence of the transition temperatures by straight lines for concentrations smaller than 1 mole%.[27]

It should be borne in mind that the absolute values of $dT/dc$ might be strictly valid only for compounds with 3 mole% Ti excess and the preparation conditions chosen. It has been checked in some representative cases, however, that the relations for different dopes and annealing conditions are qualitatively maintained with different amounts of Ti excess. The discussion that follows is therefore based only on the qualitative features of the phase-transition temperatures.

The investigations of the Ga- and Zn-doped compounds were included in order to study the influence on the phase stability[28] arising from the presence of divalent and trivalent closed electron shell ions with a size and electronegativity comparable to those of the iron-group ions. The shift of their phase-transition temperatures may thus be considered as a reference for the divalent and trivalent $3d$ ions with unfilled shells.[29]

When comparing the phase-transition temperatures of compounds doped with different $3d$ ions being in the same valence state and treated under the same

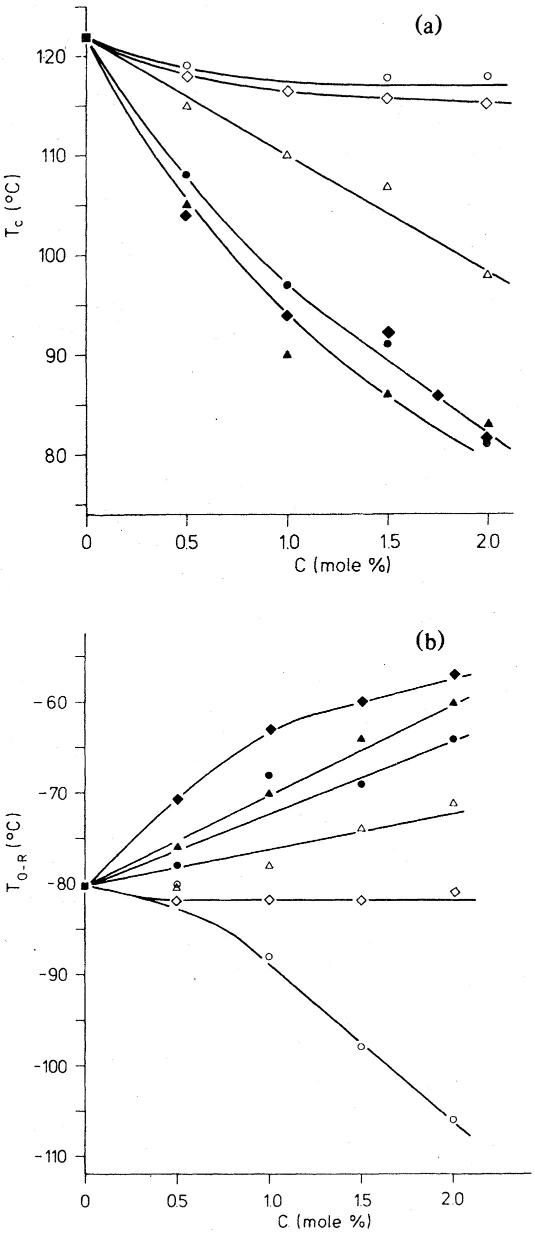

FIG. 5. Phase-transition temperatures of Cr- (○, ●), Mn- (◇, ◆), and Co- (Δ, ▲) doped $BaTiO_3$ polycrystals vs the nominal doping concentration. (a) Cubic-to-tetragonal transition (Curie point). (b) Orthorhombic-to-rhombohedral transition. Open symbols: samples annealed in $O_2$; bold symbols: annealed in $H_2$–$H_2O$.

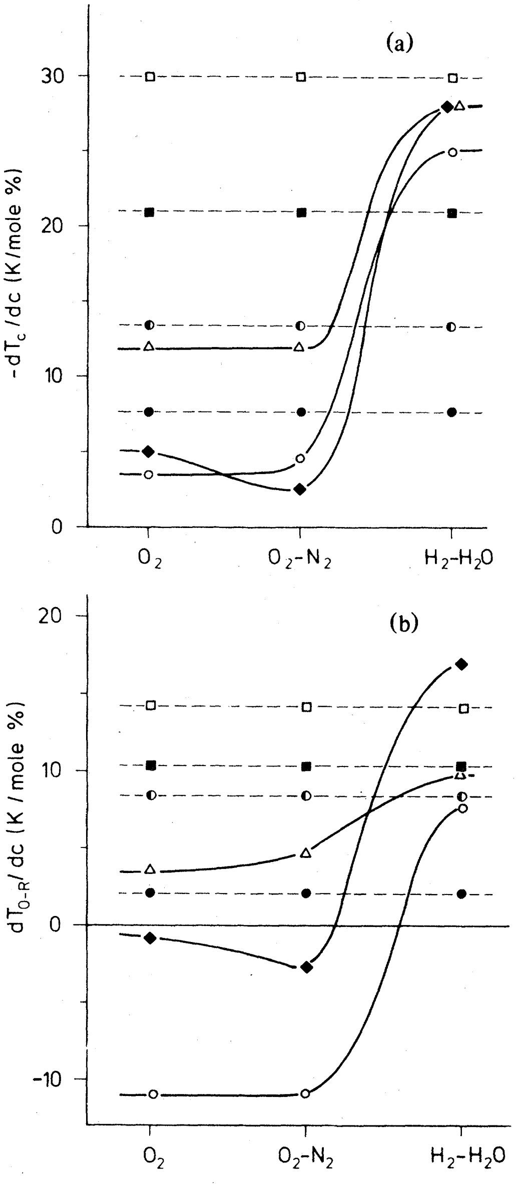

FIG. 6. Shift per doping concentration of (a) the cubic-to-tetragonal and of (b) the orthorhombic-to-rhombohedral transition temperatures of $BaTiO_3$ doped with Cr to Ni, Zn, and Ga at the oxygen partial pressures of 150 bar ($O_2$), 0.2 bar ($O_2$–$N_2$), and $10^{-22}$ bar ($H_2$–$H_2O$). The $dT/dc$ values were obtained from a straight-line approximation of the concentration dependence of the transition temperatures up to 1 mole% of the nominal concentration; only the Co value for $O_2$–$N_2$ is an approximation of the whole concentration range. ○Cr, ◆ Mn, ■ Fe, Δ Co, □ Ni, ●Ga, ◐Zn.

atmospheric conditions, one observes significant differences: e.g., the orthorhombic-rhombohedral transition of $Cr^{4+}$ and $Mn^{4+}$ ($O_2$), both transitions of $Co^{3+}$ and $Fe^{3+}$ ($O_2$ and $O_2-N_2$). On the other hand, $Co^{2+}$, $Ni^{2+}$, and $Mn^{2+}$ treated in $H_2-H_2O$ show more or less the same behavior. In connection with the results for the $Ga^{3+}$- and $Zn^{2+}$-doped samples this points out that the phase stability depends neither on the specific kind of dopant only (e.g., number of $d$ electrons) nor on its particular valence state or the concentration of oxygen vacancies only, but also on the symmetry properties of their electronic wave functions.

The tetravalent ions ($Cr^{4+}$, $Mn^{4+}$ in $O_2$) which are enclosed by complete oxygen octahedra do not influence very much the cubic-tetragonal phase-transition temperature. Neither the $A_{2g}$ ground state of $Mn^{4+}$ nor the $T_{1g}$ state of $Cr^{4+}$ additionally resist the tetragonal distortion of the cubic cell; the singlet $A_{2g}$ state obviously has no special preference for either one of the structures (this is a correction of the previously stated assumption[19] that the singlet $A_{2g}$ state favored the cubic phase) and the $T_{1g}$ state couples only little to the $E$ distortion of the lattice at the ferroelectric transition. However at the orthorhombic-rhombohedral transformation, where the cubic oxygen arrangement is restored, both ions behave quite differently. Whereas the $A_{2g}$ singlet of $Mn^{4+}$ is still insensitive to the phase change, the $Cr^{4+}$ $T_{1g}$ state, whose orbital degeneracy is lifted in the distorted phases, resists the restoration of the quasicubic environment (leading again to degeneracy) most probably for energy reason (the temperatue at this transition is about 200 K lower than at $T_c$).

In the $O_2-N_2$-treated samples the Mn is incorporated partially as $Mn^{3+}$ which, when compared with $Ga^{3+}$, should stabilize the cubic structure due to the charge defect; however, the opposite is the case. This may be the consequence of the $E_g$-type $Mn^{3+}$ $3d^4$ ground state which, even when it is split due to the charge defect, strongly interacts with the $E$-type lattice distortion because of its electron distribution coming close to neighboring lattice sites. This coupling extends the existence range of the distorted structures. Further reduction of Mn to $Mn^{2+}$ with the $S$-type $3d^5$ state in connection with doubly ionized oxygen vacancies again favors the cubic structure as in the case of the singlet-type $Ni^{2+}$ state ($A_{2g}$).

Furthermore the reduction of $Cr^{4+}$ to $Cr^{3+}$, which would be singlet $A_{2g}$ within complete oxygen octahedra, and the corresponding creation of oxygen vacancies, leads to a stabilization of the cubic phases. This stabilization is stronger than that provided by $Ga^{3+}$ and comparable to that of the $Fe^{3+}$ compounds ($Fe^{3+}$, $3d^5$, $S$ type). This strengthens the conclusion that the difference compared with the $Ga^{3+}$ results is caused by the singlet state of the unfilled $3d$ shell, which extends the stability of the undistorted phase.

Comparing $Co^{3+}$ with $Ga^{3+}$ we see that there is an additional influence of the $3d$ electrons, but it is smaller than for $Fe^{3+}$. We assume that this reflects the original $T$-type symmetry of the $3d^6$ state which is split due to the charge defect but still does not couple so strongly to the $E$-type lattice deformation. The reduction of the $Co^{3+}$ to $Co^{2+}$ results in a behavior at the cubic-tetragonal transition which is similar to that of $Mn^{2+}$ and $Ni^{2+}$, both possessing a singlet electron ground state; the similarity probably indicates that the $Co^{2+}$ state, which is $T_{1g}$ in $O_h$ symmetry, is split such that the resulting ground state is a singlet ($A_2$ in $C_{4v}$ symmetry). The comparability with the results of $Ni^{2+}$ and $Mn^{2+}$ is not, however, so obvious at the orthorhombic-rhombohedral transition; nevertheless, the range of existence of the distorted structure is clearly diminished with respect to the $Co^{3+}$ compounds, and it is also slightly smaller than for $Zn^{2+}$.

To sum up, the results of this investigation suggest that the phase transition of $3d$-doped $BaTiO_3$ depends on the symmetry properties of the electrons in the dopants unfilled $3d$ shell in combination with the oxygen defects produced by the incorporation of $3d$ ions having an electrical charge smaller than 4. The charge defects of ions having a closed $3d$ shell ($Ga^{3+}$, $Zn^{2+}$) increase the existence range of the cubic and of the quasicubic rhombohedral phase. This range is further extended when the electronic ground state of the ion is derived from a singlet state in the original $O_h$ symmetry of the substituted Ti site (the $O_h$ symmetry is broken if neighboring oxygen vacancies are present). This is the case for $Cr^{3+}$ ($A_{2g}$), $Fe^{3+}$($S$), $Mn^{2+}$($A_{2g}$), and $Ni^{2+}$ ($A_{2g}$); probably the situation of $Co^{2+}$ ($A_2$ in $C_{4v}$) can be explained accordingly. $Co^{3+}$, which has $T$ symmetry, makes only a small contribution to the stability of the undistorted phases. On the other hand, in the case of $Mn^{3+}$, where the electronic ground state is of $E_g$ type and for which a strong coupling to the $E$-type lattice transformation is expected, one even observes a distinct lowering of the stability of the cubic phases despite the presence of the charge defects. In the case of $Mn^{4+}$ ($A_{2g}$) and $Cr^{4+}$ ($T_{1g}$) incomplete oxygen octahedra do not occur in the $3d$-doped compound and hence the phase stability is influenced only little by the symmetry of the electron configuration.

## IV. SUMMARY

$BaTiO_3$ ceramics doped with different $3d$ elements were sintered in air and annealed afterwards at 700 °C in pure oxygen at 150 bar and in $H_2-H_2O$ atmosphere (oxygen partial pressure $10^{-22}$ bar). The valence states of the doped $3d$ ions were determined by magnetic-susceptibility measurements. It was found that some of the ions (Cr, Mn, and Co) pos-

sess different valence states when the compounds are treated in three different atmospheres; others (Fe and Ni), however, do not. Concomitantly with the lowering of the valence of a particular ion we observed weight losses of the compounds which correspond to the creation of doubly ionized oxygen vacancies (positively charged with respect to the occupied oxygen lattice sites).

Moreover, the change of the valence state was found to cause a change of the phase-transition temperatures, and in those compounds where the valence of the doped ions is independent of the annealing in different atmospheres the phase transitions also remain unaffected. From the correlation between the phase stability, the valence of the dopes and their $3d$ configuration we conclude that the phase transitions of $3d$-doped BaTiO$_3$ depend both on the symmetry properties of the electrons in the unfilled $3d$ shell and on the presence of oxygen vacancies required for the compensation of the charge defect.

The critical dependence of the valence states of the dopes, of the correlated presence of oxygen vacancies and of the phase stability on the experimental and preparative circumstances shows that a careful control of the thermodynamic boundary conditions during preparation is required whenever BaTiO$_3$ is doped with $3d$ ions, either in fundamental research on, e.g., phase transitions or in materials engineering for industrial purposes.

## ACKNOWLEDGMENT

The authors are very grateful to M. Klerk (Philips Research Laboratory, Eindhoven, The Netherlands) for the microprobe analysis and to L. J. F. M. Monten (Philips Research Laboratory, Eindhoven) for the high-pressure annealing.

---

[1] K. Carl and K. H. Härdtl, Ferroelectrics 17, 473 (1978).

[2] H.-J. Hagemann, J. Phys. C 11, 3333 (1978).

[3] B. Lewis, Proc. Phys. Soc. London 73, 17 (1960).

[4] H. Ueoka, Ferroelectrics 7, 351 (1974).

[5] T. Matsuoka, Y. Matsuo, H. Susaki, and S. Hayakawa, J. Am. Ceram. Soc. 55, 108 (1972).

[6] I. Burn and G. H. Maher, J. Mater. Sci. 10, 633 (1975).

[7] S. A. Long and R. N. Blumenthal, J. Am. Ceram. Soc. 54, 515, 577 (1971).

[8] J. Daniels, K. H. Härdtl, D. Hennings, and R. Wernicke, Philips Res. Rep. 31, 487 (1976).

[9] N. H. Chan and D. M. Smyth, J. Electrochem. Soc. 123, 1584 (1976).

[10] B. W. Faughnan, Phys. Rev. B 4, 3623 (1971).

[11] M. Nakahara and T. Murakami, J. Appl. Phys. 45, 3795 (1974).

[12] E. M. Rockar and R. A. Forman, Phys. Status Solidi A 33, 91 (1976); K. W. Blazey, *ibid.* 38, 97 (1976).

[13] R. L. Wild, E. M. Rockar, and J. C. Smith, Phys. Rev. B 8, 3828 (1973).

[14] K. A. Müller, Helv. Phys. Acta 31, 173 (1958).

[15] S. E. Stokowski and A. L. Schawlow, Phys. Rev. 178, 457 (1969).

[16] P. Koidl, K. W. Blazey, W. Berlinger, and K. A. Müller, Phys. Rev. B 14, 2703 (1976).

[17] E. S. Kirkpatrick, K. A. Müller, and R. S. Rubins, Phys. Rev. 135, A86 (1964).

[18] R. A. Serway, W. Berlinger, K. A. Müller, and R. W. Collins, Phys. Rev. B 16, 4761 (1977).

[19] H. Ihrig, J. Phys. C 11, 819 (1978).

[20] B. Jaffe, W. R. Cook, Jr., and H. Jaffe, *Piezoelectric Ceramics* (Academic, London, 1971).

[21] R. Wernicke, thesis (Rheinisch-Westfälische Technische Hochschule Aachen, 1975) (unpublished).

[22] Crystal-field effects could in principle serve to distinguish between local and nonlocal charge compensation by oxygen vacancies. Level splittings which are sensitive to the crystal field are expected to be observable below 4 K but this is out of the scope of our investigations which were directed towards the determination of the valence states.

[23] S. M. Ariya, T. N. Verbitskaya, N. M. Enden, and W. Wintruff, J. Phys. Soc. Jpn. Suppl. 28, 131 (1970).

[24] H. L. Schläfer and G. Gliemann, *Einführung in die Ligandenfeldtheorie* (Akademische Verlagsgesellschaft, Frankfurt am Main, 1967).

[25] A. M. J. H. Seuter, Philips Res. Rep. Suppl. 3, 1 (1974).

[26] O. F. Schirmer, W. Berlinger, and K. A. Müller, Solid State Commun. 16, 1289 (1975).

[27] For the $dT_c/dc$ of the O$_2$–N$_2$-treated Co-doped compounds the whole doping range is considered because of unexplained irregularities of the $T_c$ dependence on the doping concentration.

[28] By "phase stability" we denote the existence range of the undistorted cubic and the quasicubic rhombohedral phase. Strong phase stabilization is then reflected by large values of $-dT_c/dc$ and $+\,dT_{0-R}/dc$.

[29] Curie-temperature depression $-dT_c/dc$ for the Ga$^{3+}$ ion [ionic radius 0.62 Å; $-dT/dc \simeq 8$ K/mole%, see Fig. 6(a)] is smaller than for the bigger Zn$^{2+}$ ion [0.74 Å; 14 K/mole%, see Fig. 6(a)]. Thus, one may conjecture that the phase stability is mainly connected with the ion sizes but not with the valencies. However, the opposite behavior found for the isoelectronic ions Sn$^{4+}$ (0.71 Å, 8 K/mole%) (Ref. 20) and Zr$^{4+}$ (0.80 Å, 5.3 K/mole) (Ref. 20) does not strengthen such a supposition.