



Donor-Acceptor Charge Complex Formation in Barium Titanate Ceramics: Role of Firing Atmosphere

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Submitted February 26, 1998; Revised July 22, 1998; Accepted July 24, 1998

Abstract. BaTiO₃ ceramics containing Mn acceptors and various Mo, W and Nb donor dopants have been fired in reducing atmosphere and re-oxidized in N₂/O₂. In single Mn-doped ceramics, Mn²⁺ is completely oxidized to Mn³⁺; in N₂ containing 50 ppm O₂ at $T > 800^\circ\text{C}$. Changes of the Curie point and sample length under reduction and re-oxidation have been detected using dielectric and thermomechanical measurements. Charge compensation and complex formation between acceptors and donors have been observed. In donor-acceptor charge complexes, Mn²⁺ cannot be oxidized.

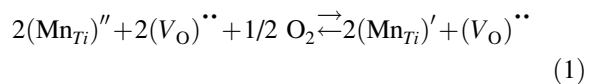
Keywords: base metal electrodes, multilayer capacitors, re-oxidation BaTiO₃, donor-acceptor complex

1. Introduction

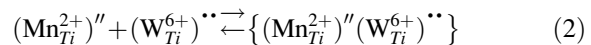
Barium titanate based dielectrics are commonly used in the production of ceramic multilayer capacitors (MLCC). Manufacturers of MLCCs usually employ precious metals such as palladium or silver palladium alloys for the inner electrodes [1]. For cost reduction, the expensive noble metals are now beginning to be replaced by cheaper nickel [1]. These so-called “BME” (Base metal electrode) capacitors have to be fired in protective atmospheres of N₂/H₂ or CO/CO₂. In reducing atmospheres BaTiO₃ ceramics form large numbers of ionized oxygen vacancies [3], (V_O)^{••}, and conduction electrons which give rise to very poor insulation resistances (IR). The conduction electrons can be effectively trapped by incorporation of acceptor ions in the perovskite lattice. BME capacitors containing acceptor doped BaTiO₃ dielectrics show satisfactory values of IR [4,5]. However, due to electromigration of the ionized oxygen vacancies [6–8] a residual ionic conductivity maintains in BME materials. Strong electric fields and temperature stresses thus give rise to electrical degradation [9,10] and rapid termination of the life of BME MLCCs [11].

The life stability of BME-MLCCs [11] could be

largely improved by use of dopant mixes of acceptors and donors, e.g. Mn[•]-Nb[•], Mn[•]-W^{••}, in combination with a re-oxidation treatment at 800–1100°C. Re-oxidation of Mn-acceptor doped BaTiO₃ ceramics leads to a valence change of Mn²⁺ to Mn³⁺ or even Mn⁴⁺ [6]. The number of oxygen vacancies necessary to compensate the acceptors is considerably diminished by re-oxidation.



Donors like (W_{Ti}⁶⁺)^{••} are capable of compensating the acceptors in place of oxygen vacancies. Donors and acceptors are assumed to form complexes.



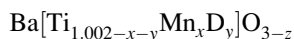
The mobility of donor-acceptor complexes in the electric field is reported as extremely low [3].

The aim of this investigation is to study the formation and stability of donor-acceptor complexes in BaTiO₃ at various partial pressures of oxygen. The occurrence of such complexes has been already suspected in dielectric materials of composition (Ba,Ca)(TiZr)O₃ [13]. The valence changes of Mn give rise to small changes of the ionic radius which

are detectable in a sensitive dilatometer. Valence changes modify the number of oxygen vacancies as well, which should have a measurable effect on the length of a ceramic body. In addition, valence changes of Mn-ions dissolved in ferroelectric BaTiO₃ ceramics [14] are detected by Curie point changes.

2. Experimental

BaTiO₃ ceramics have been prepared to study the effect of Mn and various donor co-dopants on the Curie point (T_C) and length change in oxidizing and reducing atmospheres. The ceramic materials prepared had the following general composition:



D = Nb or W or Mo; $0 \leq x \leq 0.01$; $0 \leq y \leq 0.01$

z varies slightly around zero, depending on the oxygen partial pressure of the sintering atmosphere.

2.1. Sample Preparation

Reagent grade (Merck, Darmstadt) BaCO₃, TiO₂, MnCO₃ and dopant oxides Nb₂O₅, WO₃ or MoO₃ were weighed and milled together for 16 h in isopropanol, using 2 mm \varnothing Y-stabilized ZrO₂ balls. The mixtures were dried and calcined for 6 h at 1100°C. X-ray diffraction of calcined powders revealed monophase perovskite materials. The calcined powders were de-agglomerated for 2 h in cyclohexene, using 10 mm \varnothing agate balls and thereafter milled down to a mean particle size of 0.8 μm , using again 2 mm \varnothing ZrO balls in isopropanol.

A slight wear of the milling balls resulted in an uptake of 0.003 mol ZrO₂ per mol BaTiO₃ powder. The final ratio of B- to A-site ions is thus expected to be B/A \approx 1.005 for all compositions prepared.

The powders were granulated with poly-vinyl alcohol and mechanically predensified under a pressure of 400 MPa to green discs of 6 mm \varnothing and 0.6 mm thickness. Ceramic bars of 17 mm length and 5 \times 5 mm width were formed in stainless steel dies and thereafter cold isostatically predensified at 320 MPa. The ceramic materials were fired for 2 h at 1300°C in a reducing atmosphere of moist (saturated with H₂O at 20°C) N₂, containing 1 vol% H₂. The oxygen partial pressure of the sintering atmosphere

corresponded to $p = 2.1 \cdot 10^{-5}$ Pa at 1300°C. The relative densities of sintered samples were found to be between 96 and 99% of the theoretical value. Re-oxidation of ceramic discs was carried out at 1000°C (2 h) in an atmosphere of N₂, containing 50 ppm O₂ ($p = 5$ Pa).

2.2. Electrical and Dilatometric Measurements

Ceramic disc capacitors (CDC) were prepared by evaporating 50 nm Cr-Ni/Au onto the sintered discs. Curie points were determined from dielectric temperature characteristics which were measured at 1 KHz and 1V_{rms}, using a Hewlett Packard LCR meter 4284A. The heating rate was 0.25°C/min in the range -60° to $+145^\circ\text{C}$.

Dilatometric measurements were carried out in a differential quartz dilatometer. For these measurements sintered ceramics were cut into 10 mm bars with parallel surfaces at the long ends. A 10 mm bar of pure quartz served as reference. The length calibration was performed by measuring the thermal expansion of a 10 mm sapphire crystal. The effect of the oxidation/reduction treatment on the expansion/shrinkage behavior of the samples was measured in thermal equilibrium at 888°C by switching the gas atmosphere several times between reducing conditions of moist N₂ – 1% H₂ ($p = 10^{-10}$ Pa) and oxidizing conditions of N₂ – 50 ppm O₂. The resulting length change was recorded when equilibrium was obtained, as indicated by negligible swing of the dilatometer.

3. Results

3.1. Curie Point Shift

3.1.1. Single Mn-doped BaTiO₃. Donor and acceptor dopants tend to restore the cubic symmetry of the perovskite unit cell of BaTiO₃, thus shifting the Curie point (T_C) to lower temperatures. The Curie point shift depends on the amount and kind of dopant as well as their valence and ground state [14]. In the case of acceptor ions, the oxygen vacancies have also a strong influence on T_C [13]. Figure 1 shows the T_C shift of Mn-doped BaTiO₃ for the reduced as well as the re-oxidized state. In both states, an almost linear dependence on the Mn concentration was found. The slope for reduced Mn is much steeper. The slight

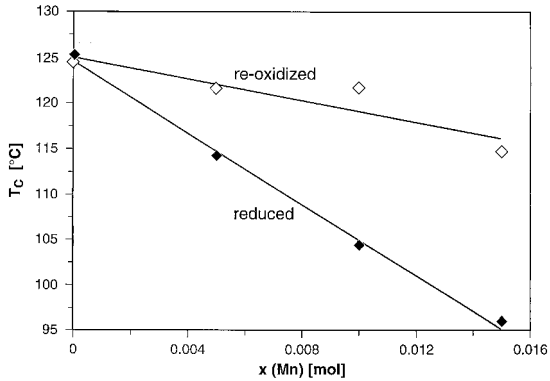


Fig. 1. Curie points of $\text{Ba}[\text{Ti}_{1.002-x}\text{Mn}_x]\text{O}_3$, sintered $P_{\text{O}_2} = 2.1 \cdot 10^{-5}$ Pa at 1300°C and re-oxidized at $P_{\text{O}_2} = 5$ Pa at 1000°C .

decrease of the Curie point observed in reduced “pure” BaTiO_3 is most probably caused by small levels of impurities, e.g. Fe. Earlier investigations revealed [6] that under the present reducing conditions all Mn ions are in the divalent state, Mn^{2+} , $(\text{Mn}_{\text{Ti}})''$. The large number of charged oxygen vacancies in combination with divalent Mn acceptors, $[\text{V}_\text{O}]^{\bullet\bullet} = [\text{Mn}_{\text{Ti}}]''$ shift the Curie point by

$$\Delta T_{\text{C}}(\text{Mn}^{2+}) \approx 19.5^\circ\text{C}/ \text{at.}\% \text{ Mn}$$

In the re-oxidized state 1/2 of the oxygen vacancies are annihilated due to the valence change of Mn^{2+} to Mn^{3+} . Due to the smaller number of $(\text{V}_\text{O})^{\bullet\bullet}$ and reduced stress induced by the smaller Mn^{3+} and Mn^{4+} ions, the T_{C} shift in the re-oxidized state is much lower:

$$\Delta T_{\text{C}}(\text{Mn}^{3+}) \approx 5.7^\circ\text{C}/ \text{at.}\% \text{ Mn}$$

3.1.2. Mn/donor co-doped BaTiO_3 . In the case of mixed donor-acceptor doped BaTiO_3 a combined effect of donors and Mn-acceptors on T_{C} is expected. Figure 2 shows the Curie point shift of BaTiO_3 containing a fixed amount of 1 at% Mn-dopant and increasing amounts of $D = \text{W}$ or Mo co-dopant, $\text{Ba}[\text{Ti}_{0.992-y}\text{Mn}_{0.01}\text{D}_y]\text{O}_{3-z}$. In the reduced as well as the re-oxidized state, T_{C} decreases almost linearly with increasing W or Mo concentration, y . However, with increasing concentration of W and Mo the difference of T_{C} between the reduced and the re-oxidized state becomes smaller and smaller. For equivalent concentrations of Mn and W, $[\text{Mn}^{2+}] \approx [\text{W}^{6+}]$ the Curie points of reduced and re-

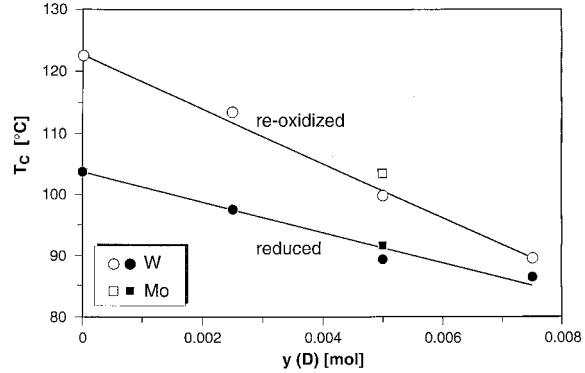


Fig. 2. Curie points of $\text{Ba}[\text{Ti}_{0.992}\text{Mn}_{0.01}\text{D}_y]\text{O}_{3-z}$, sintered at $P_{\text{O}_2} = 2.1 \cdot 10^{-5}$ Pa at 1300°C and re-oxidized at $P_{\text{O}_2} = 5$ Pa at 1000°C . $D = \text{W}$ and Mo .

oxidized material coincide. From this one can deduce that a stable donor-acceptor complex $[\text{Mn}_{\text{Ti}}'' - \text{W}_{\text{Ti}}^{\bullet\bullet}]$ has been formed in which the Mn^{2+} can no longer be oxidized to Mn^{3+} . Figure 2 demonstrates that Mo^{6+} forms a similar complex as W^{6+} , i.e. $[\text{Mn}_{\text{Ti}}'' - \text{Mo}_{\text{Ti}}^{\bullet\bullet}]$.

In Fig. 3 the results obtained on Mn-Nb co-doped BaTiO_3 are shown. With increasing Nb concentration a linear shift of T_{C} was observed again. The difference in T_{C} between the reduced and re-oxidized state decreases with increasing concentration of Nb. Again complex formation between Mn^{2+} and Nb^{5+} seems to occur. Corresponding to the single charge of the Nb donor, 2 $(\text{Nb}_{\text{Ti}})'$ donors are required for compensation of one $(\text{Mn}_{\text{Ti}})''$ acceptor. The T_{C} curves of reduced and re-oxidized $\text{Ba}[\text{Ti}_{0.992-y}\text{Mn}_{0.01}\text{Nb}_y]\text{O}_{3-z}$ thus

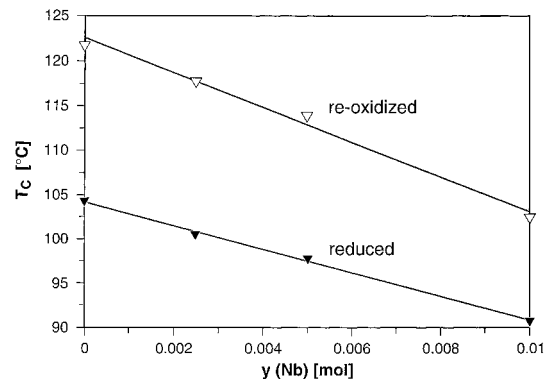


Fig. 3. Curie points of $\text{Ba}[\text{Ti}_{0.992}\text{Mn}_{0.01}\text{Nb}_y]\text{O}_{3-z}$, sintered at $P_{\text{O}_2} = 2.1 \cdot 10^{-5}$ Pa at 1300°C and re-oxidized at $P_{\text{O}_2} = 5$ Pa at 1000°C .

coincide at the Nb concentration $y \approx 0.02$. Similar to Mn-W and Mn-Mo, the Mn^{2+} -ions in the complex $[\text{Mn}_{\text{Ti}}'' - 2\text{Nb}_{\text{Ti}}']$ seem also to be resistant against oxidation to Mn^{3+} and Mn^{4+} .

3.2. Dilatometric Results

3.2.1. Single Mn-doped BaTiO_3 . Figure 4 shows the length change of a 10 mm ceramic bar of $\text{Ba}[\text{Ti}_{0.992}\text{Mn}_{0.01}]\text{O}_{3-z}$ at the change from reducing to oxidizing atmosphere at 888°C . The atmosphere was switched between a buffered mixture of 1% H_2 in moist N_2 ($T_{\text{H}_2\text{O}} = 20^\circ\text{C}$, $P_{\text{O}_2} = 10^{-10}$ Pa) and N_2 containing 50 ppm O_2 ($P_{\text{O}_2} = 5$ Pa) at 888°C . After a short time necessary to exchange the gas, a rapid change of the sample length, ΔL , occurred until equilibrium was obtained, recognizable by a constant sample length. The original length of the sample could be regained by switching back the atmosphere. Corresponding to the slow increase of P_{O_2} at the replacement of moist N_2/H_2 by $\text{N}_2 - 50$ ppm O_2 , ΔL also changed rather slowly.

The decrease of the sample length at re-oxidation is partly due to the valence change of the large Mn^{2+} -ions ($r = 0.083$ nm) [15] to the smaller Mn^{3+} - ($r = 0.0645$ nm) or Mn^{4+} -ions ($r = 0.053$ nm) respectively. ΔL also partly depends on the change of the number of oxygen vacancies. The correlation between ΔL and the Mn concentration x is illustrated for $\text{Ba}[\text{Ti}_{0.992-x}\text{Mn}_x]\text{O}_{3-z}$ in Fig. 5. For increasing Mn concentrations x , a linear increase of ΔL between the reduced and oxidized state was observed. In the case of Mn-free ‘‘pure’’ BaTiO_3 a slight ΔL of

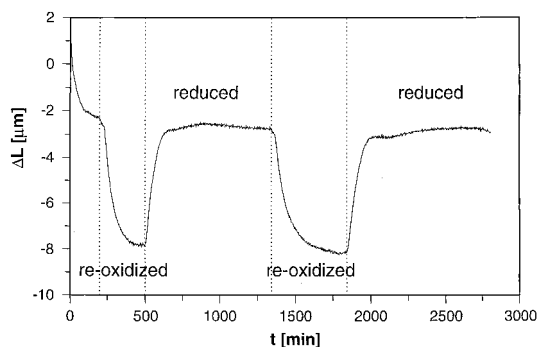


Fig. 4. Reversible length change of a 10 mm ceramic bar of $\text{Ba}[\text{Ti}_{0.992}\text{Mn}_{0.01}]\text{O}_{3-z}$ at reduction ($P_{\text{O}_2} = 10^{-10}$ Pa) and oxidation ($P_{\text{O}_2} = 5$ Pa) at 888°C .

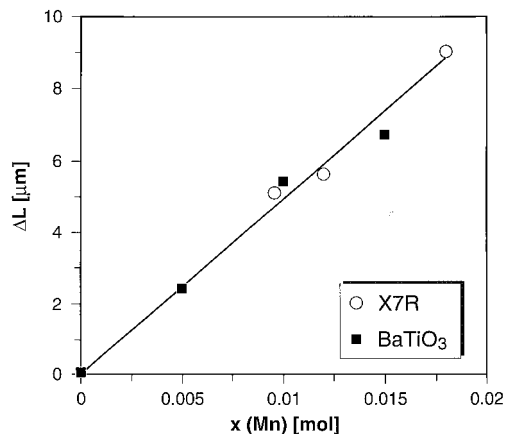


Fig. 5. Reversible length changes of a 10 mm ceramic bar of composition $\text{Ba}[\text{Ti}_{1.002-x}\text{Mn}_x]\text{O}_{3-z}$ and of Mn containing dielectric X7R material at reduction ($P_{\text{O}_2} = 10^{-10}$ Pa) and oxidation ($P_{\text{O}_2} = 5$ Pa) at 888°C .

$\approx 0.1 \mu\text{m}$ between oxidized and reduced samples could be observed. This effect might be due to the formation of small amounts of (V_{O}) and Ti^{3+} in the reduced state as well as to certain impurities in the BaTiO_3 . For comparison, ΔL of three commercial BME-X7R dielectric materials, containing different amounts of Mn were also included in Fig. 5. These materials show an equivalent ΔL with respect to their Mn content.

3.2.2. Donor-acceptor co-doped BaTiO_3 . Figure 6 shows the length change ΔL between the reduced and oxidized state for 1 at.% Mn-doped ceramics, containing various amounts of Nb, W and Mo. As

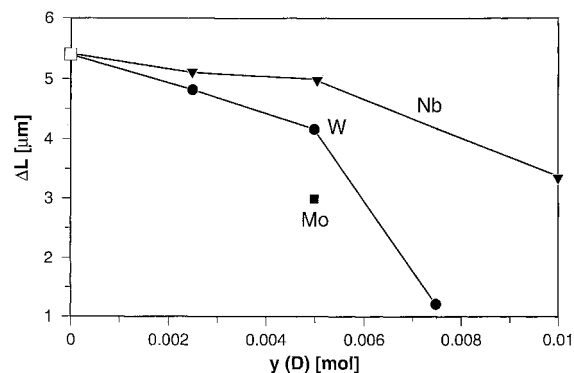


Fig. 6. Reversible length changes of 10 mm ceramic bars of composition $\text{Ba}[\text{Ti}_{0.992}\text{Mn}_{0.01}\text{D}_y]\text{O}_{3-z}$ at reduction ($P_{\text{O}_2} = 10^{-10}$ Pa) and oxidation ($P_{\text{O}_2} = 5$ Pa) at 888°C . D = Nb, W, Mo.

expected, ΔL becomes smaller and smaller with increasing donor concentration. The diminution of ΔL is less pronounced for single charged Nb donors than for doubly charged W and Mo donors. Compared to W^{6+} and Mo^{6+} , double amounts of Nb^{5+} are necessary to compensate the Mn^{2+} -acceptors. Thus, ΔL of $BaTiO_3 - 1\%Mn - 0.5\%W$ is almost the same as for $BaTiO_3 - 1\%Mn - 1\%Nb$, see Fig. 6.

The length change ΔL corresponds to the amount of Mn^{2+} which can be oxidized to Mn^{3+} . With increasing donor concentration more and more of the stable donor-acceptor complexes are formed so that less amounts of free Mn^{2+} are available for oxidation. It is also apparent from Fig. 6 that the relation between ΔL and the donor concentration is not linear.

4. Conclusions

Curie point as well as dilatometric measurements strongly suggest that stable complexes form between Mn^{2+} -ions and W^{6+} -, Mo^{6+} - and Nb^{5+} -ions in $BaTiO_3$. With increasing concentration of donors the oxidizability of Mn^{2+} to Mn^{3+} ; thus decreases in BME materials. For equal charge concentrations of donors and acceptors, i.e., $[D]^{\cdot} \approx 2[Mn_{Ti}]''$, and $[D]^{..} \approx [Mn]''$, the Mn^{2+} ions cannot be oxidized to Mn^{3+} . For equal concentrations of donors and Mn^{2+} -acceptors the differences in Curie point and sample length between reduced and re-oxidized samples are both negligibly small: ΔT_C , $\Delta L \approx 0$.

Figure 7 shows ΔT_C between the reduced and re-oxidized state of $BaTiO_3 - 1\%Mn$, co-doped with Nb, W and Mo donors, as function of the donor charge concentration $c_D = [D]^{\cdot} + 2[D]^{..}$. In Fig. 8 the same is plotted for ΔL . In both curves it is apparent that all donors fit well onto a single parabolic curve. In Fig. 9 the relative changes of Curie point and sample length are plotted as function of the donor charge:

$$\left. \begin{aligned} \Delta T_C(\text{rel}) &= \Delta T_C / \Delta T_C(\text{max}), \\ \Delta L(\text{rel}) &= \Delta L / \Delta L(\text{max}). \end{aligned} \right\} = f(c)$$

The maximum change of the Curie point and sample length has been determined for 1 at% Mn (single) doped $BaTiO_3$ between the reduced and the re-oxidized state as:

$$\Delta T_C(\text{max}); 19.5^\circ\text{C};$$

$$\Delta L(\text{max}); 5.5 \mu\text{m}.$$

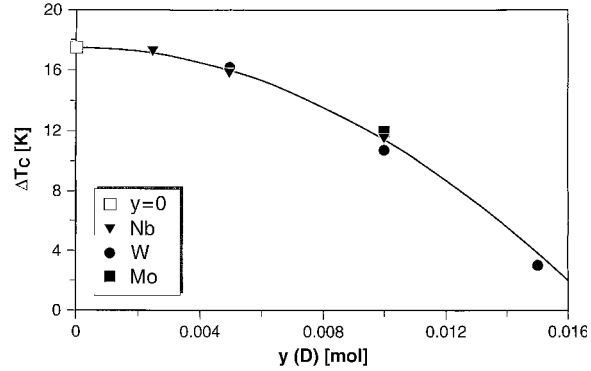


Fig. 7. Curie point difference ΔT_C between reduced ($P_{O_2} = 2.1 \cdot 10^{-5}$ Pa at 1300°C) and re-oxidized ($P_{O_2} = 5$ Pa at 1000°C) samples of composition $Ba[Ti_{0.992}Mn_{0.01}D_y]O_{3-z}$ as function of the donor concentration c_D ($D = Nb^{\cdot}, W^{..}, Mo^{..}$. ($c_D = [D]^{\cdot} + 2[D]^{..}$)).

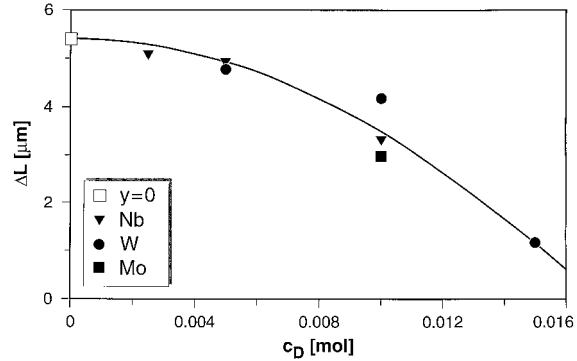


Fig. 8. Length difference ΔL between reduced ($P_{O_2} = 10^{-10}$ Pa at 888°C) and re-oxidized ($P_{O_2} = 5$ Pa at 888°C) 10mm ceramic bars of composition $Ba[Ti_{0.992}Mn_{0.01}D_y]O_{3-z}$; $D = Nb, W, Mo$, as function of the donor concentration c_D . ($c_D = [D]^{\cdot} + 2[D]^{..}$)).

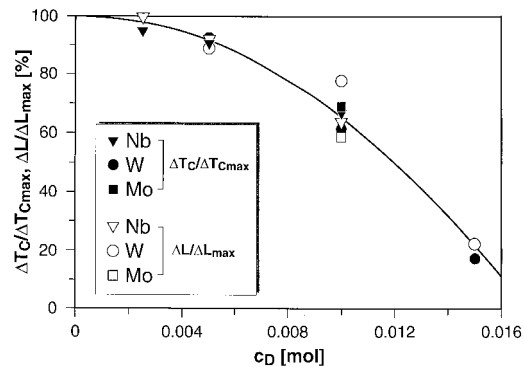
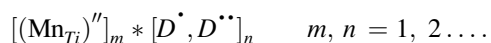


Fig. 9. Relative changes $\Delta L(\%)$ and $\Delta T_C(\%)$ between reduced and oxidized samples of composition $Ba[Ti_{0.992}Mn_{0.01}D_y]O_{3-z}$, $D = Nb, W, Mo$, as function of the donor concentration c_D .

From Fig. 9 it is apparent that all measured values of the Curie point as well as sample length fit well into one parabolic curve for all donor-acceptor combinations studied. From this one can deduce that charge compensation and complex formation are independent of the particular kind of donor ions. The stabilization of divalent Mn must therefore be discussed in terms of the donor charge concentration c_D . Since charge compensation of $(\text{Mn}_{\text{Ti}})''$ is not a linear function of the donor concentration c_D , we have to assume variable charge complexes between negative acceptors and positive donors in BaTiO_3 :



For a stable fixed ionic complex, e.g. $[\text{Mn}_{\text{Ti}}^{2+} - \text{W}_{\text{Ti}}^{6+}]$ or $[\text{Mn}_{\text{Ti}}^{2+} - 2\text{Nb}_{\text{Ti}}^{5+}]$ a simple linear relation should exist between the number of oxidizable Mn^{2+} and that of the donors, i.e. ΔT_C , and ΔL have to be linear functions of c_D . Moreover, the steric and thermodynamic differences between the ion complexes $[\text{Mn}^{2+} - \text{W}^{6+}]$ and $[\text{Mn}^{2+} - 2\text{Nb}^{5+}]$ are expected to be so large that the functions ΔL , $\Delta T_C = f(c_D)$ should be quite different from another.

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