THE INFLUENCE OF FOREIGN IONS ON THE CRYSTAL LATTICE OF BARIUM TITANATE

G. H. Jonker
Department of Electrical Engineering
Technical University Twente, Enschede

and

E. E. Havinga
Philips Research Laboratories
Eindhoven, The Netherlands

(Received December 22, 1981; Communicated by A. Rabenau)

ABSTRACT

From investigations of phase diagrams of ternary oxides the lattice sites of foreign ions and compensating vacancies are established. Large trivalent ions occupy barium sites and are completely compensated by titanium vacancies. Small pentavalent ions occupy titanium sites and are mainly compensated by titanium vacancies. During these investigations a new compound was found, $\text{BaLa}_4\text{Ti}_4\text{O}_{15}$ isomorphous with $\text{Ba}_5\text{Nb}_4\text{O}_{15}$.

Introduction

In the literature on P.T.C. thermistors based on semiconducting $\text{BaTiO}_3$ it is generally assumed that the various dopants (Nb, Sb, La) are for one part compensated by electrons and for the rest by vacancies on the barium sites of the perovskite lattice\(^1\)\(^2\). The choice of these vacancies is analogous to the case of $\text{SrTiO}_3$ and $\text{CaTiO}_3$, where it is known that both Sr and Ca can be replaced to large extent by La or Ti by Nb accompanied by the creation of Sr or Ca vacancies\(^3\)\(^4\). In an older paper, however, it was shown that $\text{Ta}^{5+}$ and $\text{Nb}^{5+}$ as substitutes for $\text{Ti}^{4+}$ are most probably compensated by a mixture of Ba and Ti vacancies\(^5\).

Furthermore it is known that in $\text{PbTiO}_3$, doped with La, both Pb and Ti vacancies can exist with a ratio depending on the PbO partial pressure during the preparation\(^6\)\(^7\). This means that for every compound the vacancy model needs a separate and careful examination.

During our investigations of the phase diagrams $\text{BaO}\text{-TiO}_2\text{-Nb}_2\text{O}_5$ and $\text{BaO}\text{-TiO}_2\text{-La}_2\text{O}_3$, we found indications pointing to the formation of Ti vacancies rather than Ba vacancies. Therefore we made a detailed study of the parts of these diagrams around the perovskite phase. Although different methods have been used, the relations found in these systems are more or less consistent.
Especially interesting is the fact that in both diagrams isomorphous phases are found on extrapolating the line of perovskite solid solutions, namely \( \text{Ba}_5\text{Nb}_4\text{O}_{15} \) and a new compound \( \text{BaLa}_4\text{Ti}_4\text{O}_{15} \).

**Experimental methods**

After several orientational experiments we prepared series of samples with constant dope concentrations (\( \text{Nb}, \text{Sb}, \text{La} \)) and varying \( \text{BaO-TiO}_2 \) ratio around the value expected for the pure perovskite phase. A usual ceramic technique was applied for the preparation, starting from mixtures of oxides or carbonates of the composing metals, milling, prefiring in air at 900°C during 20 hours, second milling, compressing to pellets, and then, as a last step, firing these pellets in air at high temperature (1250 or 1350°C) and slowly cooling together with the furnace.

All samples prepared in this way were white or slightly coloured (yellow or green shade), so that we assumed that all metal ions had obtained their highest valency states (\( \text{Ba}^{2+}, \text{Ti}^{4+}, \text{Nb}^{5+}, \text{Sb}^{5+}, \text{La}^{3+} \)) and no free electrons were present.

A first indication of the position of the pure phase was the sharp transition in sintering behaviour. Excess \( \text{BaO} \) caused a high porosity, excess \( \text{TiO}_2 \) a high density. The latter samples consisted of rather large crystallites, >10 \( \mu \)m.

The samples were further investigated by X-ray powder diagrams and by microscopic examination of polished sections. The latter method proved to be the accurate one, as samples prepared with excess \( \text{TiO}_2 \) at 1350°C showed a non-crystallized glassy phase and rounded crystal boundaries, as is also known in the pure \( \text{BaO-TiO}_2 \) systems.

By these methods we could determine the position of the perovskite phase with an accuracy in the \( \text{BaO-TiO}_2 \) ratio of about 1%.

The system \( \text{BaO-TiO}_2-\text{Nb}_2\text{O}_5 \)

The investigations in this system at 1200°C formed part of a general study of the phase equilibria between the many compounds. The results of this study are less accurate in the exact position of the series of solid solutions. They are shown in figure 1. The most striking point is that the compounds \( \text{BaTiO}_3 \) and \( \text{Ba}_5\text{Nb}_4\text{O}_{15} \) form series of solid solutions from both sides, but with a broad miscibility gap. The width of the solid solution area indicates the inaccuracy of these experiments. Equilibria with the surrounding phases will not be discussed in this paper.

The results obtained with samples prepared at 1350°C are shown in figure 2. In the first place the compositions with the purest perovskite phase are indicated. These form a straight line pointing from \( \text{BaTiO}_3 \) in a direction to the composition \( 1\text{BaO}-1\text{NbO}_2 \) (not a compound). From a series of compositions along this line we found the endpoint of the solid solution formation at about 12.5% \( \text{Nb} \). This endpoint is not sharp, because a very fine segregation occurred, due to the decreasing solubility during the slow cooling process. The results obtained at this temperature are in agreement with those mentioned in 7).

These two investigations show that \( \text{Nb}^{5+} \) can be substituted for \( \text{Ti}^{4+} \) to a high percentage, ν20% at 1200°C and ν25% at 1350°C. However, there is an obvious difference in the compensation mechanism showing the formation of mainly Ti-vacancies at 1200°C and of equal concentrations of Ti and Ba vacancies at 1350°C. In figure 5 the variation of the cubic cell parameters is shown.
The system BaO-TiO$_2$-Sb$_2$O$_5$

In this system only one series of compositions was investigated, with 6% Sb, fired at 1350 °C. These compositions correspond to those with 6% Nb in the BaO-TiO$_2$-Nb$_2$O$_5$ diagram. The purest perovskite phase was found at the same ratio. This means that Sb is taken up in the lattice as Sb$^{5+}$ and with the same vacancy compensation as in the case of Nb. A remarkable point is that in this case the porous samples with excess BaO were yellow, but that the dense samples with excess TiO$_2$ were greenish.

![Diagram](image)

Figure 1: Part of the ternary phase diagram BaO-TiO$_2$-NbO$_5$ at 1200 °C showing the equilibria between Ba$_5$Nb$_4$O$_{15}$ ss and BaTiO$_3$ ss with the surrounding compounds. The binary BaO-NbO$_2$ system is taken from 13). In the binary system BaO-TiO$_2$ the phase BT$_3$ has possibly to be replaced by BT$_{3+}$ (see 8).

Figure 2: Enlarged part of the phase diagram BaO-TiO$_2$-NbO$_5$ at 1350 °C. xxx series of compositions investigated, with 000 for the purest perovskite phases. V$_{Ti}$ and V$_{Ba}$ denote the direction of the perovskite phase for either Ti vacancy or Ba vacancy compensation.

The system BaO-TiO$_2$-La$_2$O$_3$

This system was investigated at 1350 °C only, again by first preparing a series of samples with constant dope concentration (8% La) in order to find the position of the line of perovskite solid solutions. On extension this line points to the composition La$_4$Ti$_3$O$_{12}$. The endpoint of the solid solutions line is near 13% La, but not sharply defined, because of a precipitation of very fine particles, probably during the cooling process. These results are indicated on figures 3 and 4.

Here, the conclusions can be drawn, that the La$^{3+}$ ions replace Ba$^{2+}$ ions, and that the excess charge is completely compensated by Ti vacancies.

Another result is that on line from BaTiO$_3$ to La$_4$Ti$_3$O$_{12}$ a new compound was detected, BaLa$_4$Ti$_4$O$_{15}$, which showed a powder X-ray diagram very similar to that of the compound Ba$_2$Nb$_4$O$_{15}$.

Finally a series of samples containing 8% La was fired at 1350 °C in a gas mixture consisting of 95% CO$_2$ and 5% H$_2$. 

![Graph](image)
Figure 3: Part of the ternary phase diagram BaO-TiO$_2$-LaO$_{1.5}$ at 1350°C with BaTiO$_3$, BaLa$_2$Ti$_4$O$_{15}$, and La$_4$Ti$_3$O$_{12}$ on the V$_{Ti}$ line. The binary La$_{1.5}$-TiO$_2$ system after 4) and 12).

Figure 4: Enlarged part of figure 3 showing the series of compositions investigated, and the pure perovskite compositions.

The dark blue, electrically conducting samples showed their highest phase purity at composition C of figure 4, situated on the line from BaTiO$_3$ to the reduced compound LaTi$^{3+}$O$_3$. This means that under these highly reducing circumstances the excess charge of the La$^{3+}$ ions is completely compensated by Ti$^{3+}$ ions. This result at low oxygen pressure corresponds to those of Daniels and Härdtl and those of Hennings.

The variation of the cubic cell parameters is shown in figure 5. At present we have no explanation for the fact that linear extrapolation to pure BaTiO$_3$ in this case differs from the linear extrapolation of the Nb, Ta and Sb lines.

Discussion

The investigations confirm in a simple way the known or expected sites of the substituted ions in BaTiO$_3$. The large trivalent La ions occupy Ba sites and the small pentavalent Nb and Sb ions occupy Ti sites.

The analogy between the Nb and the Sb system leads thus to a description of the Sb substitution that differs from that of Eberspächer.
In the case of La substitution the excess charge is completely compensated by Ti vacancies. In the case of Nb and probably also in the case of Sb substitution, however, a complete compensation by Ti vacancies occurs only at lower temperatures. At higher temperatures a mixed compensation by Ti and Ba vacancies is found.

This easy variation of the ratio of Ba and Ti vacancies points to a rather small value of the difference between the enthalpy of formation of a single Ti vacancy and that of two Ba vacancies.

At first sight one would expect the same vacancy compensation mechanism both for La and for Nb doped BaTiO$_3$ as the enthalpy difference mentioned above would be independent of the type of dope. However, in view of the high dope concentrations in our samples the formation of associated defects is very probable. For a La$^{3+}$ ion on a Ba site the shortest distance to a possible Ti vacancy ($\frac{a}{\sqrt{3}}$) is smaller than that to a possible Ba vacancy (a). For a Nb$^{5+}$ ion on a Ti site the opposite holds. For simple electrostatic reasons, therefore, one expects a stronger preference for Ti vacancies in the case of La dope than in the case of Nb dope. This is in accordance with the observed behaviour.

Daniels and Härdtl\textsuperscript{1)} assumed that in the system BaTiO$_3$-La compensation would take place by vacancies on the Ba sites, and calculated for that case from their experiments a value of 7.7 eV for the enthalpy of formation of a Ba vacancy. In view of the present results on this system the compensation takes place by Ti vacancies. A comparable calculation of the enthalpy of formation of one Ti vacancy with the help of their experimental data results in 12.4 eV.

Crystallography

The trigonal structure of Ba$_5$Nb$_4$O$_{15}$ is isomorphous with the structure of Ba$_5$Ta$_4$O$_{15}$ which has been described in detail in\textsuperscript{10) and 11). In principle this structure can be described as a sequence ABCAB of 5 BaO$_3$ layers perpendicular to the trigonal axis. This resembles the structure of BaTiO$_3$ viewed in the direction of the cube diagonal, which shows a repetition of an ABC sequence. Between the BaO$_3$ layers the Nb$^{5+}$ or Ti$^{4+}$ ions are situated in corner-sharing oxygen octahedra. In the Ba$_5$Nb$_4$O$_{15}$ structure the cubic sequence is interrupted after each five layers, as there, locally, a hexagonal sequence AB AB occurs, containing non-occupied double face-sharing oxygen octahedra. Therefore, this structure can be considered as a typical ordered structure with respect to the vacancies.

A comparable order will be present in the isomorphous structure of BaLa$_4$Ti$_0$O$_{15}$. From simple electrostatic considerations one expects that the Ba ions will be concentrated in the center of the cubic sequence and the La ions in the hexagonal sequence around the vacancy. However, the X-ray diagrams give no information about order of Ba and La ions as the scattering power of both is practically equal.

It is interesting that Ba$_5$Nb$_4$O$_{15}$ forms a long series of solid solutions with BaTiO$_3$, whereas BaLa$_4$Ti$_4$O$_{15}$ forms no solid solutions or only in a very restricted way. This again can be the result of a stronger stability of Ti vacancies between La neighbours than of Nb vacancies between Nb neighbours.

Table I gives the cell parameters of a number of the trigonal structures, compared with the cell dimensions of BaTiO$_3$.

Recently, a new compound La$_4$Ti$_3$O$_{12}$ is mentioned in literature\textsuperscript{12). The structure of this compound is described as a 12 layer hexagonal cell, also related to the perovskite structure, with 3/4 of the available oxygen octahedra occupied by Ti. In our study of the binary system La$_2$O$_3$-TiO$_2$ we have not yet identified this compound.
Table 1
Cell parameters of trigonal compounds

<table>
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<tr>
<th>Compound</th>
<th>a (Å)</th>
<th>c (Å)</th>
<th>c/a</th>
</tr>
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<tbody>
<tr>
<td>Ba$_5$Ta$<em>4$O$</em>{15}$</td>
<td>5.79</td>
<td>11.75</td>
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<td>5.80</td>
<td>11.80</td>
<td>2.03</td>
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<tr>
<td>Ba$<em>5$Nb$</em>{3.2}$Ti$<em>{1.0}$O$</em>{15}$</td>
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<td>2.002</td>
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<td>BaLa$_4$Ti$<em>4$O$</em>{15}$</td>
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<tr>
<td>Cubic BaTiO$_3$</td>
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<tr>
<td></td>
<td>5.66</td>
<td>11.59</td>
<td>2.04</td>
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References