

## IONIC MECHANISM OF CHARGE TRANSPORT IN STABILIZED ZIRCONIA AND THORIA

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In the present paper a theoretical model of ionic charge transport in stabilized cubic zirconia and thoria is suggested. It is shown that by doping with bivalent (trivalent) impurity some association of cationic defect with anion vacancy may appear in the form of complex  $(\text{e}_s) [\text{M}_{\text{ThZr}}^{2+} \square_{\text{O}}^{2-}]$  and  $[2\text{M}_{\text{ThZr}}^{3+} \square_{\text{O}}^{2-}]$ . This model is supported by experimental results obtained by measuring electric conductivity, and dielectric and mechanical losses.

### ИОННЫЙ МЕХАНИЗМ ПЕРЕНОСА ЗАРЯДА В СТАБИЛИЗИРОВАННОМ ЦИРКОНИИ И ТОРИИ

В работе приводится теоретическая модель переноса ионного заряда в стабилизированных кубических кристаллах циркония и тория. Показано, что при соизмерении двувалентной или трехвалентной примеси может образоваться ассоциация катионного дефекта и анионной вакансии в виде комплекса  $[\text{M}_{\text{ThZr}}^{2+} \square_{\text{O}}^{2-}]$  или комплексов  $[\text{M}_{\text{ThZr}}^{2+} \square_{\text{O}}^{2-}]^+$  и  $[2\text{M}_{\text{ThZr}}^{3+} \square_{\text{O}}^{2-}]$ . Модель подтверждается экспериментальными результатами, полученными при измерении электропроводности, а также диэлектрических и механических потерь.

#### 1. INTRODUCTION

The concentration of point defects in metallic oxides is a function of temperature and partial pressure of oxygen provided that the oxide is in a thermodynamic equilibrium with its surroundings. In principle, it is possible to identify the dominating defects, and the mechanism of transport can be studied by measuring a suitable combination of physical and transport properties as functions of the above mentioned variables. Such a combination usually consists of the measurements of density, lattice parameters, EMS, transport numbers, and electrical conductivity.

It is well known from literature (just from measurements of the given combination of properties) that solid solutions on the basis of zirconia and thoria exhibit a combined electric conductivity: both ionic and electronic [1—7]. The presence of

both conductivity types (their domination) depends basically on temperature and partial oxygen pressure. Generally speaking, both types of solid solutions are at low temperatures and low pressures primarily ionic conductors.

When stabilizing the cubic fluorite structure of  $\text{ZrO}_2$  (Fig. 1) by substitution of some divalent oxides (such as e.g.,  $\text{CaO}$ ,  $\text{MgO}$ ,  $\text{Y}_2\text{O}_3$  and some oxides of rare earths), oxygen anionic vacancies are formed, thus highly increasing electric conductivity [1—7].

$\text{ThO}_2$  has a  $\text{CaF}_2$ -like cubic structure up to the melting point (3300 °C). Solid solutions of thoria with some cubic oxides ( $\text{CaO}$ ,  $\text{Y}_2\text{O}_3$ ) are characterized by a filled cation sublattice and anion vacancies as in the case of stabilized zirconia.

The ionic contribution to the character of solid solutions based on zirconia and thoria forms the contents of this work. A theoretical model for the ionic mechanism of charge transport is given, and it is compared with experimental results of electric conductivity, dielectric and mechanical losses.

#### II. THEORETICAL MODEL FOR CHARGE TRANSPORT MECHANISM IN STABILIZED ZIRCONIA AND THORIA

The extraordinary attention devoted to solid solutions of thoria has provided a general agreement with the assumption that the oxygen vacancy is the dominant defect whilst ionic conductivity exists at lower pressures of oxygen (at pressures  $> 0.1$  Pa a significant hole conductivity appears) [6].

In stabilized zirconia no proof of the electron contribution to conductivity at an oxygen partial pressure above 5 Pa was observed [4]; it was demonstrated by polarization [8] and transport number [9] measurements. Furthermore, diffusion measurements in calcium stabilized zirconia indicate that selfdiffusion of cations is at least  $10^6$  times smaller than that of oxygen anions [10]. Thus it is reasonable to assume that under suitable conditions the conductivity of stabilized zirconia is caused by the mobility of oxygen ion vacancies only.

Such vacancies can be considered as ionic defects with an effective charge of  $2e$ . Conductivity results from the hopping of oxygen ions to neighbouring equivalent positions. The activation energy for this process,  $U$ , is related to the height of the barrier which the ions have to overcome while hopping. The mobility of the vacancy can be deduced from the statistical theory [11] as

$$\mu = 6 \frac{a^2(2e)}{KT} v \exp\left(-\frac{U}{KT}\right), \quad (1)$$

where  $a$  the anion-anion distance equal to one half of the lattice parameter  $a_0$  for the cubic fluorite-like structure, and  $v$  denotes the vibrational frequency of an oxygen vacancy in its potential well given as  $v_0 \exp(-\Delta S/k)$ .  $\Delta S$  is the activation

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entropy for the migration of the anion vacancy and  $\nu_0$  is usually considered to be the Debye frequency. The numerical factor is due to the fact that a vacancy can jump into any of the six positions in front of it. The conductivity due to the concentration of anion vacancies  $n$  is defined as

$$\sigma = n(2e)\mu. \quad (2)$$

If constant barrier heights are assumed (independent of the vacancy concentration) one may expect that the experimental data could be interpreted with the help of the effective concentration  $n$  of the vacant carriers. In doped oxides (e.g. yttrium stabilized zirconia — YSZ) the volume concentration of anion vacancies is fixed (without any temperature dependence) by substituting aliovalent oxide, and it greatly exceeds the concentrations due to thermal disorder. According to this one may expect a mechanism containing some centres that catch vacancies, and it yielding their association with cation defects and form nonconducting complexes. Such mechanisms are well known in doped alkali halogenides [11, 12]. The following procedure represents their extension.

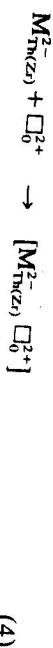
### II.1. Stabilization by a bivalent oxide

The only cation defects present in thorium (zirconia) are stabilized by a bivalent oxide,  $\text{MO} - (\text{Th}, \text{Zr})\text{O}_2$ , are  $M_{\text{Th}}^{2-}$  ( $M_{\text{Zr}}^{2-}$ ) ions. They cause the formation of an anion oxygen vacancy,  $\square_0^{2+}$ , at each bivalent ion. The conductivity  $\sigma$  in the impurity conduction range (i.e. the contribution of intrinsic defects can be neglected) can be written as

$$\sigma T = 2eNYB \exp\left(-\frac{U}{KT}\right) \quad (3)$$

( $e$  — charge of an electron,  $N$  — number of  $\text{Th}^{4+}$  ( $\text{Zr}^{4+}$ ) ions in  $1 \text{ cm}^3$ ,  $Y$  — total concentration of impurities,  $B$  — a constant,  $U$  — activation energy for the mobility of oxygen vacancies. Further, it is assumed that the temperature is so high that oxygen vacancies do not associate with cation defects  $M_{\text{Th}}^{2-}$  ( $M_{\text{Zr}}^{2-}$ ). In these cation defects one may expect that they will act as pinning centres for anion vacancies.

When taking into account association, i.e. the fact that at sufficiently low temperatures vacancies preferably stay in the vicinity of cation defects, by applying the mass action law to the association process



the following formula for conductivity is obtained:

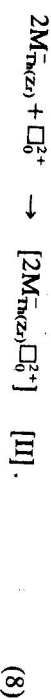
$$\sigma T = \frac{1}{2} (2e) NKB \exp\left(-\frac{U+W}{KT}\right) \left\{ \left[ 1 - \frac{4Y}{K} \exp\left(\frac{W}{KT}\right) \right]^{1/2} - 1 \right\} \quad (5)$$

( $K$  — concentration of acting matter,  $W$  — association energy of oxygen anion vacancies with  $M_{\text{Th}(\text{Zr})}^{2-}$  cation defects). Within the range of validity of Eq. (3) conductivity will be proportional to the concentration of impurities, i.e. the concentration of free vacancies. At sufficiently low temperatures, where the value of free vacancies concentration can be practically considered as zero, one may approximately write

$$\sigma T = 2eNB(KY)^{1/2} \exp\left(-\frac{U+1/2W}{KT}\right). \quad (6)$$

### II.2. Stabilization by a trivalent oxide

In thorium (zirconia) stabilized by a trivalent oxide,  $\text{M}_2\text{O}_3 - (\text{Th}, \text{Zr})\text{O}_2$ ,  $M_{\text{Th}}^{3-}$  ( $M_{\text{Zr}}^{3-}$ ) cation defects are present. They cause the formation of one ionic vacancy,  $\square_0^{2+}$ , per two doping trivalent cations. The vacancies can associate with cation defects into complexes. In such a case there is a theoretical possibility of the occurrence of processes described by the following statistical equilibria:



When applying the mass action law to the processes (7) and (8) the following equations are obtained

$$\frac{x_M x_V}{x_I} = K_1 \exp\left(-\frac{W_1}{KT}\right) \quad (9)$$

$$\frac{x_M x_M}{x_{II}} = K_{II} \exp\left(-\frac{W_{II}}{KT}\right) \quad (10)$$

where the symbols have the following meaning:  $x_M$  — concentration of free cationic defects  $M_{\text{Th}(\text{Zr})}^{3-}$ ,  $x_V$  — concentration of free anionic vacancies,  $x_I$  — concentration of  $[M_{\text{Th}(\text{Zr})}^{3-} \square_0^{2+}]$  complexes,  $x_{II}$  — concentration of  $[2M_{\text{Th}(\text{Zr})}^{3-} \square_0^{2+}]$  complexes,  $K_1$  and  $K_{II}$  are constants for association energies of the complexes.

Furthermore the following equations are to be fulfilled:

$$y = x_M + x_I + x_{II} \quad (11)$$

$$x_V = \frac{1}{2} x_M + x_I. \quad (12)$$

The concentration of free anion vacancies which determines the behaviour of the impurity conductivity range can be now calculated from equations (9)–(12) as obtained. It can be solved numerically.

However, if we restrict ourselves to a qualitative discussion of solutions only, in certain temperature range the following approximations can be done:

Range I: Temperature is so high that no association exists ( $x_I = x_{II} = 0$ ), thus yielding

$$y = x_M \quad (13)$$

$$x_V = \frac{1}{2} x_M.$$

Range II: The process of neutral  $[2M_{\overline{M}(Z_2)}\square_0^{2+}]$  complex formation is negligible compared to the process of charged  $[M_{\overline{M}(Z_2)}\square_0^{2+}]^+$  complex formation ( $x_{II} \approx 0$ ). This yields:

$$y = x_M + x_I, \quad x_V = \frac{1}{2} x_M + x_I,$$

$$\frac{x_M x_V}{x_I} = \Phi_1, \quad x_V^2 - x_V(y - \Phi_1)^2 - \frac{\Phi_1}{2} y = 0$$

where  $\Phi_1$  is the left-hand side of Eq. (9). This gives

$$x_V = \frac{1}{2} (y - \Phi_1) + \frac{1}{2} [(y - \Phi_1)^2 + 2\Phi_1 y]^{1/2}. \quad (14)$$

Range III: Both complexes are formed with the same probability so that no reasonable approximation is possible.

Range IV: No free anion vacancies exist any more ( $x_V = 0$ ), i.e. only the process II of complex formation is allowable. The qualitative course of concentration of defects obtained in this manner can be schematically shown (see Fig. 2).

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The above mentioned theoretical models for the ionic mechanism of charge transport in stabilized  $ZrO_2$  and  $ThO_2$  are supported by experimental data of electric conductivity and dielectric and mechanical losses.

### III. A COMPARISON OF THEORETICAL MODELS WITH EXPERIMENTAL DATA

The role of impurities is very important but it is difficult to define it precisely. For instance, the ionic conductivity dominates at lower temperatures (i.e. below 650 °C), the electron conductivity is substantial at higher temperatures, both types of conductivity always occur and they are to be treated separately. The separation of conductivity types is usually performed by means of transport numbers [13]. From now on, we shall consider the ionic part of the charge transport only.

The range of temperatures above which impurities influence the structure of defects can sometimes be determined using the plots  $\log \sigma T$  vs  $1/T$ , where two or three intersecting lines are present (according to the complexity of the association process). The complexity of the association process follows also from the measurements of dielectric losses, where it is demonstrated by a greater number of relaxation peaks. An analysis of the peaks (their location, height, relation to the applied frequency) helps to get some ideas of the charge transport mechanism and the important factors characterizing the mechanism.

The following experimental results correspond to calcium stabilized zirconia (CSZ) and solid solutions of thorium with calcium and yttrium oxides. A qualitative analysis of the presented data is performed.

#### III.1. $ZrO_2 + CaO$ , $ThO_2 + CaO$

In the study of the ionic mechanism of charge transport it is important to know, besides other things, how impurities are built-in. When  $Zr^{4+}$  ( $Th^{4+}$ ) ions are replaced by  $Ca^{2+}$  ones, the charge neutrality can be obtained by one of the following structural schemes: i) the cationic sublattice is filled completely by  $Zr^{4+}$  ( $Th^{4+}$ ) and  $Ca^{2+}$  ions so that the corresponding amount of anionic vacancies is created; ii) the anionic sublattice is completed and excessive cations set in interstitial positions.

In order to distinguish between these two models, densities are calculated using the known lattice parameters. These densities are compared with experimental values. On the basis of these data it was concluded that in the case of calcium (acting as stabilizer of zirconia) the incorporation at high concentrations ( $\geq 20$  mole %) is substitutional (model i) at all temperatures [2]. However, at lower concentrations ( $\sim 10$  Mole %) the substitutional incorporation is combined with the interstitial one (model ii), with the substitutional mechanism dominating at

lower temperatures ( $T < 10000^\circ\text{C}$ ) but at high temperatures only interstitial incorporation of calcium in  $\text{ZrO}_2$  remaining [14].

The solid solutions of  $\text{ThO}_2 + \text{CaO}$  have filled the cationic sublattice and anion vacancies occur in the whole temperature and concentration ranges (model 1) [15].

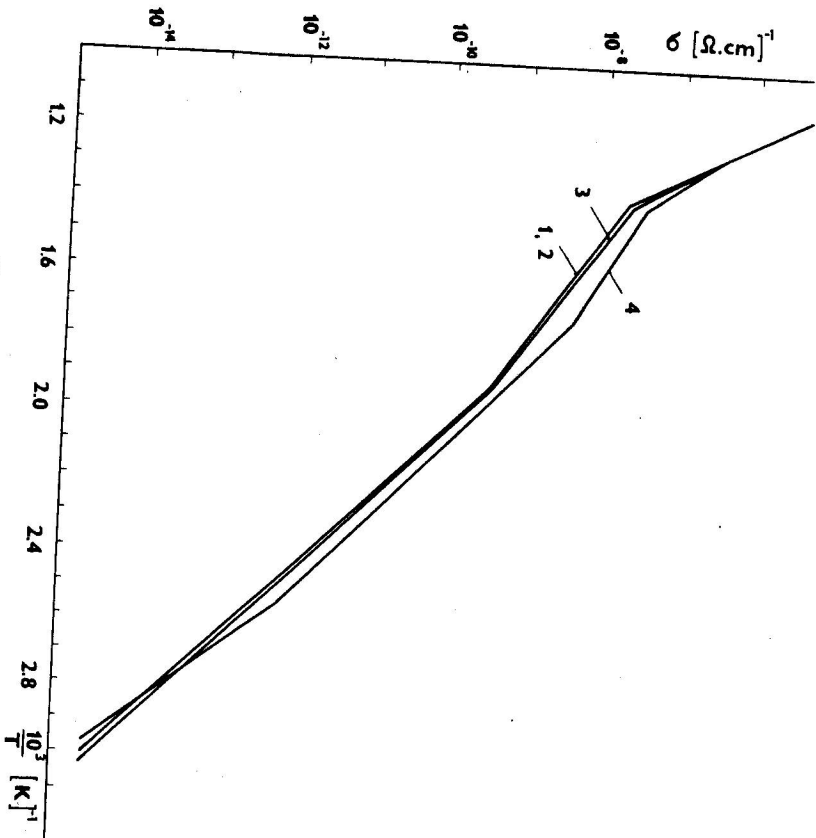


Fig. 1. Fluorite-like  $\text{CaF}_2$  structure.

When replacing  $\text{Zr}^{4+}$  ( $\text{Th}^{4+}$ ) by calcium ions the number of oxygen ions reduces and some anionic vacancies are formed with (as usually described) high electric conductivity. These vacancies can be either free or associated in the form of complexes.

The presence of an anion oxygen vacancy as a free charge carrier or associated in the form of a complex is demonstrated in the  $\log \sigma T$  vs  $1/T$  curves by the occurrence of two straight lines: ranges of impurity conductivity. A characteristic course of such a dependence can be shown, e.g., in Fig. 4. Range I corresponds to

free vacancies with the concentration given (in this range) by the amount of impurities only — in our case by the calcium contents. In the region of low temperatures and low concentrations value ranges from 0.40 to 0.51 eV at  $\text{ZrO}_2 + \text{CaO}$  [15, 16] and 0.73 to 0.92 eV at  $\text{ThO}_2 + \text{CaO}$  [17, 18]. On the other

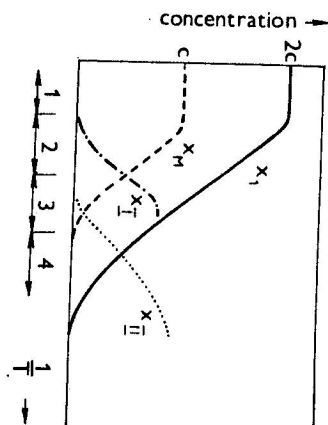


Fig. 2. A schematic illustration of the course of the concentration of defects as a function of temperature. Association of cationic vacancies with a substitutionally incorporated cation (concentration  $c$ ) is assumed.

hand, a lower absolute value of  $\sigma$  and a higher activation energy in range II are connected with the motion of vacancies and formation of complexes. The neutral complexes do not contribute to conductivity; however, their formation causes a drop in the concentration of free vacancies demonstrated by the decrease of the conductivity absolute value and the appearance of range II in the curve of  $\log \sigma T$  vs  $1/T$ .

The "ordering" of cations and vacancies in the  $\text{ZrO}_2 + \text{CaO}$  system below 1273 K was also observed by Carter and Roth [19] by the neutron diffraction.

The process of association, i.e. formation of complexes, will cause in the dielectric losses in the curve of the dissipation factor  $\tan \delta$  vs  $T$  (or  $\tan \delta$  vs  $f$ ) an appropriate relaxation maximum. Similarly as in the investigation of the mechanical relaxation in these systems (Fig. 3) Wachtman [20] assumed on the basis of a theoretical treatment of the relaxation modes characteristic electrical and mechanical relaxation times. Measurements confirmed that the maximum of internal friction in  $98.5 \text{ ThO}_2 + 1.5 \text{ CaO}$  appears at the double value of frequency of that corresponding to the maximum of the dissipation factor ( $\tan \delta$ ) and, at the same temperature (515 K). Wachtman also calculated the activation energy for the motion of a vacancy around the  $\text{Ca}^{2+}$  position, 0.93 eV, in a rough agreement with the values obtained from electric conductivity measurements [21—24]. In pure  $\text{ThO}_2$  no such relaxation maxima have been observed.

### III.2. $\text{ZrO}_2 + \text{Y}_2\text{O}_3$ , $\text{ThO}_2 + \text{Y}_2\text{O}_3$

Yttrium is incorporated in both maternal materials ( $\text{ZrO}_2$  and  $\text{ThO}_2$ ) substitutionally in the whole range of temperature and concentration. The corresponding

solid solutions have filled the cationic sublattice and anionic vacancies acting in the function of charge carriers. This conclusion has been arrived at in a similar experimental way [5] as that in the case of calcium. According to the theoretical model, in the case of doping by a trivalent impurity,

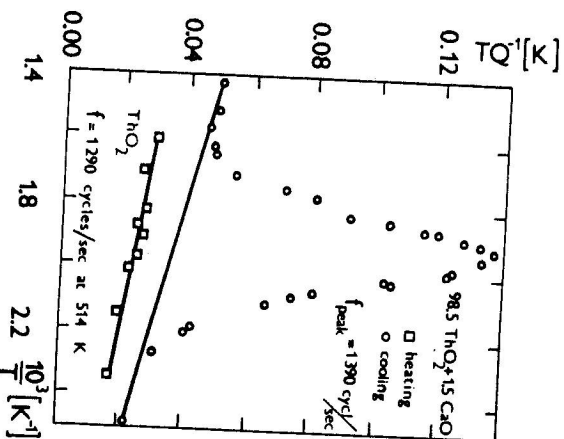


Fig. 3. The results of internal friction and absolute temperature (including background) in pure  $\text{ThO}_2$  and in 98.5  $\text{ThO}_2$ -1.5  $\text{CaO}$  as functions of inverse temperature [20].

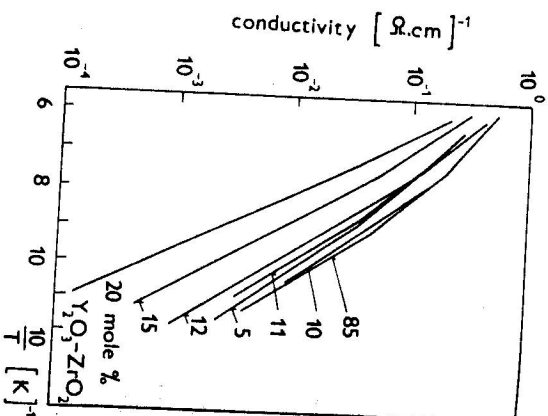


Fig. 4. Conductivity versus inverse temperature in polycrystalline yttrium-stabilized zirconia measured in air [26].

the association process consists of the formation of charged and neutral complexes. This fact should cause the appearance of two association ranges with the corresponding two different activation energies in the curves  $\log \sigma T$  vs  $1/T$ . This has actually been observed. As an example, Fig. 4 the temperature dependence of the conductivity for  $\text{Y}_2\text{O}_3$  in  $\text{ZrO}_2$  [4] is given; the association regions are denoted as 2 and 3. Region 1 corresponds to the motion of free anion vacancies and the activation energy is the enthalpy of motion. In the range of low temperatures and low concentrations its value ranges from 0.54 to 0.72 eV in  $\text{ZrO}_2 + \text{Y}_2\text{O}_3$  [4] and 0.98 to 1.04 eV in  $\text{ThO}_2 + \text{Y}_2\text{O}_3$  [25].

The presence of various kinds of complexes should according to the theoretical model be demonstrated in  $\tan \delta$  vs  $T$  (or  $\tan \delta$  vs  $f$ ) curves by the appropriate number of maxima. However, no measurements of this type have been known so far either in  $\text{ZrO}_2 + \text{Y}_2\text{O}_3$  or in  $\text{ThO}_2 + \text{Y}_2\text{O}_3$ .

#### IV. CONCLUSION

The presented theoretical and experimental data can be summarized as follows: 1. According to our theoretical model, in the case of doping zirconia and thorium by bivalent impurities, the cationic defects and anion vacancies can associate in the form of neutral complexes  $[\text{M}_{\text{Th/Zr}}^{2+}\square_{\text{O}}^{2-}]$ . This model is supported by a qualitative analysis of the electric conductivity and mechanical relaxation measurements. 3. When doping zirconia and thorium by trivalent impurities, the cationic defects and anion vacancies may associate in the form of charged  $[\text{M}_{\text{Th/Zr}}^{3+}\square_{\text{O}}^{2-}]^+$  and neutral  $[\text{2M}_{\text{Th/Zr}}^{3+}\square_{\text{O}}^{2-}]^0$  complexes. 4. This model is supported by electrical conductivity measurements.

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