Es ist geplant, die Messungen zunächst auf vieratomige lineare Molekeln auszudehnen, wobei mit verbesserter Apparatur die Möglichkeit der Untersuchung kombiniert angeregter Knickschwingungsmoden besteht. Es sollte dann möglich sein, den Gültigkeitsbereich des einfachen Ansatzes in Gl. (11) experimentell zu überprüfen.

Wir danken Herrn Prof. Dr. W. ZEIL, der die ihm von der Deutschen Forschungsgemeinschaft überlassenen Geräte für die Messungen zur Verfügung stellte.

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On the Thermoelectric Power of Stabilized Zirconia

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Thermoelectric power of stabilized zirconia, at different CaO and MgO concentrations within the cubic phase, has been measured.

The results show a concentration dependence of the thermoelectric power which is preliminarly discussed.

The homogeneous part of the thermoelectric power, moreover, is discussed with the classical approach of irreversible thermodynamics.

Introduction

FISCHER[1] and RUKA et al.[2] have recently discussed results obtained by operating a thermo-cell consisting of a doped zirconia electrolyte with two reversible oxygen electrodes.

While RUKA deals with a single ZrO_2-CaO solid solution, FISCHER studies yttria stabilized zirconia and calcia stabilized zirconia (CSZ). Both authors operate their cells at different partial pressures of oxygen.

In this paper the dependence of the thermoelectric power on the concentration of the oxygen vacancy within the single phase field of the system $ZrO_2-CaO-MgO$ is studied. The knowledge of the concentration dependence of the thermal emf is in fact important for a deeper understanding of the non-isothermal transport processes, as stabilized zirconia can be considered, to some extent, as a model system for ionic solids.

The reversibility of oxygen electrodes allows[3-4] to describe unambiguously the heterogeneous part of the thermoelectric power[5], and the defect model for CSZ as well as the isothermal transport properties are sufficiently well known to discuss the homogeneous part of the thermoelectric power.

Recent experiments[6] demonstrated that at 1600 °C the classical model of "pure anion vacancies" is

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effectively followed, which can be described by the equations

$$\mathrm{MeO} \rightarrow \mathrm{Me}_{\mathrm{Zr}}^{\prime\prime} + \mathrm{O}_{\mathrm{O}} + \mathrm{V}_{\mathrm{O}}^{\cdot\cdot} \qquad (1\,\mathrm{a})$$

$$\mathrm{Me}_2\mathrm{O}_3 \rightarrow 2\,\mathrm{Me}_{\mathrm{Zr}}^{\prime} + 3\,\mathrm{O}_{\mathrm{O}} + \mathrm{V}_{\mathrm{O}}^{\cdot\cdot} \qquad (1\,\mathrm{b})$$

where the KROGER and VINK symbols have been used, $\mathrm{Me}_{\mathrm{Zr}}^{\prime\prime}$ being a bi-valent impurity on a cationic lattice position, O_{O} and oxygen ion on a regular lattice site and $\mathrm{V}_{\mathrm{O}}^{\cdot\cdot}$ an oxygen vacancy.

The transport number of the anion in stabilized zirconia is known to be very close to one [3, 7–10]. Table 1 shows some relevant data for isothermal transport processes in cubic zirconia. From these data the ratio of the calcium and oxygen ion diffusion coefficients at 1000 °K results to be

$$D_{\mathrm{Ca}^{++}}/D_{\mathrm{O}^{--}} = 2.27 \cdot 10^{-9}\,.$$

The transport number for the electrons t_e has been experimentally determined with oxygen permeation experiments by supposing that oxygen diffuses across a stabilized zirconia lattice only if an electronic transport takes place.

Composition in molar ratio of CaO	Diffusion coefficient $\mathrm{cm}^2\,\mathrm{sec}^{-1}$	Activation energy of electric conductance $\mathrm{cal\ mole}^{-1}$	Ref.
$x = 0.15$	$D_0 = 0.018 \cdot \exp\{-31200/RT\}$		12
	$D_0 = 6.9 \times 10^{-3} \cdot \exp\{-30500/RT\}$		13
$0.10 < x < 0.20$		$6640 \cdot (1 + 22{,}9\,x)$	14
$x = 0.16$	$D_{\mathrm{Ca}} = 0.44 \cdot \exp\{-100200/RT\}$		15
$x = 0.12$	$D_{\mathrm{Zr}} = 0.035 \cdot \exp\{-92500/RT\}$		
$x = 0.15$		28.000	16
$0.13 < x < 0.20$		$25000 < E_{\mathrm{act}} < 30500$	9

Table 1. Relevant data for the isothermal transport processes in $\mathrm{ZrO}_2-\mathrm{CaO}$ solid solutions.

The resulting transport numbers for the electrons were 0.002 and 0.006 when the partial pressure of oxygen equalled $2 \cdot 10^{-1}$ and 10^{-17} atm respectively [11].

The validity of the Nernst-Einstein equation for the experimental conductivity and diffusion coefficient yields an indirect proof of the single carrier model for the electrical conductivity [12].

The influence of order-disorder reactions which are relevant for the long-range order in the cationic and anionic sublattices represents a hard point to be overcome when interpreting thermal emf or electrical conductivity data in the temperature range where the ordering process is relatively fast. This subject was discussed by several authors [13–16] with respect to electrical conductivity experiments, but nothing is known neither on the order of the reaction, nor on the value of the critical temperature, which however should be lower than 1400 °C.

As for the influence of structural transformations at temperatures lower than 1200 °C there is the contradictory evidence of the stability of cubic zirconia solid solutions at temperatures as low as r. t. [17, 18] and the phase transformation toward equilibrium conditions in powdered materials [19, 20]. The surface energy seems to play a role on this phase transformation process.

To investigate the effects of ordering on the thermal emf, samples were annealed at 1000 °C for 240 hours and others were heated to temperatures higher than 1400 °C.

As no appreciable difference was noted between the thermal emf of treated and untreated samples, the presents results refers to samples which have been sintered at 1600 °C and then furnace cooled to room temperature.

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On the Thermal Transport in CSZ

As emphasized above, for stabilized zirconia a transport model with one single charge carrier (i. e. the oxygen ion) can be employed.

Therefore, because of the electroneutrality an oxygen ion concentration gradient never builds up and one has the phenomenological relationships [21]

$$J_{O^=} = L_{O^=,O^=} X_{O^=} + L_{O^=,q} X_q , \qquad (4\,a)$$

$$J_q = J_{q,O^=} X_{O^=} + L_{q,q} X_q . \qquad (4\,b)$$

Here $J_{O^=}$ and J_q are the oxygen ion [25] and heat fluxes referred to the cation lattice; $L_{O^=,O^=}$, $L_{O^=,q}$, $L_{q,O^=}$ and $L_{q,q}$ are the phenomenological coefficients. The forces $X_{O^=}$ and X_q are defined as:

$$X_{O^=} = 2\,F \operatorname{grad} \varphi , \qquad (5\,a)$$

$$X_q = -(\operatorname{grad} T)/T . \qquad (5\,b)$$

Dividing (4 b) by (4 a), for $X_q = 0$ ($T = \text{const}$), one obtains

$$(J_q/J_{O^=})_{T=\text{const}} = L_{q,O^=}/L_{O^=,O} \equiv Q^*_{O^=} \qquad (6)$$

The parameter $Q^*_{O^=}$ is the heat of transport of the oxygen ion. From Eq. (4 a) by an Onsager relationship ($L_{i,j} = L_{j,i}$) one obtains

$$J_{O^=} = L_{O^=,O^=} (X_{O^=} + Q^*_{O^=} X_q) \qquad (7)$$

an therefore, for $J_{O^=} = 0$

$$2\,F \operatorname{grad} \varphi - Q^*_{O^=} \cdot \frac{\operatorname{grad} T}{T} = 0 . \qquad (8)$$

It results that the homogeneous part ε_{hom} of the thermoelectric power is

$$\varepsilon_{\text{hom}} \equiv \frac{\operatorname{grad} \varphi}{\operatorname{grad} T} = \frac{Q^*_{O^=}}{2\,F\,T} . \qquad (9)$$

In the literature [2] one may find also equations which in our case should be written as:

$$\varepsilon_{\text{hom}} = \frac{1}{2\,F} \left(\frac{Q'_{O^=}}{T} - \frac{\overline{H}_{O^=}}{T} \right) . \qquad (10)$$

In this equation $Q'_{O^=}$ is a heat of transport different from $Q^*_{O^=}$, ($Q^*_{O^=} = Q'_{O^=} - \overline{H}_{O^=}$) and $\overline{H}_{O^=}$ is the partial molar enthalpy of the oxygen ion [28].

Equation (10) is obtained when using instead of the force defined in Eq. (5 a) the following one

$$X_{O^=} = 2\,F \operatorname{grad} \varphi - T \operatorname{grad} (\mu_{O^=}/T) \qquad (5\,c)$$

which however implies a system of fluxes and forces not independent.

When considering, as before, that the oxygen ion is a constitutive part of the system and ignoring any microscopic description, the heterogeneous part ε_{het} of the total thermoelectric power, for an electrode reaction

$$O^= \rightleftarrows 0.5\,O_2 + 2\,e \qquad (11)$$

results to be [22]

$$\varepsilon_{\text{het}} = -\frac{1}{2\,F} (0.5\,S_{O_2} - \overline{S}_{O^=}) \qquad (12)$$

where S_{O_2} and $\overline{S}_{O^=}$ are the molar entropy of the pure oxygen gas and the partial molar entropy of the oxygen ion in the electrolyte respectively.

From Eqs. (9) and (12) one has, for the total thermoelectric power

$$\varepsilon = \frac{1}{2\,F} \left(\overline{S}_{O^=} - 0.5\,S_{O_2} + \frac{Q^*_{O^=}}{T} \right) . \qquad (13)$$

Experimental

Thermal emf measurements have been carried out on cylinders 13 mm in diameter and 4 – 15 mm in height. The preparation of the solid solution has been accomplished with standard ceramic methods (the sin-

Table 2. Analytical data for the different ZrO_2 Batches.

	Batch I ppm	Batch II ppm
Al	50	20
B	n.d.	0.2
Co	< 1	< 1
Cr	100	200
Cu	1	0.3
Fe	300	100
Mg	3.4%	80
Mn	30	10
Ni	10	10
Si	100	200
Ti	40	20
Hf	1%	1%

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[21] When using irreversible thermodynamics as was already done by different authors for the thermoelectric power of ionic solids [5, 22–24].

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[25] Where the oxygen ion here coincides with a "constitutive part" of the system according to Refs. [26] and [27].

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[27] H. J. SCHOENERT and C. SINISTRI, Z. Elektrochem. **66,** 413 [1962]. — C. SINISTRI, Ric. Sci. **32(II-A),** 492 [1962].

[28] With the symbols used, for instance, by S. R. DE GROOT the fluxes-forces of Eq. (4) are indicated with double primes, the heat of transport of Eq. (6) (defined as a "reduced heat af transport") is indicated with double stars and the heat of transport of Eq. (10) is indicated with a single star (see also Ref. [5]).

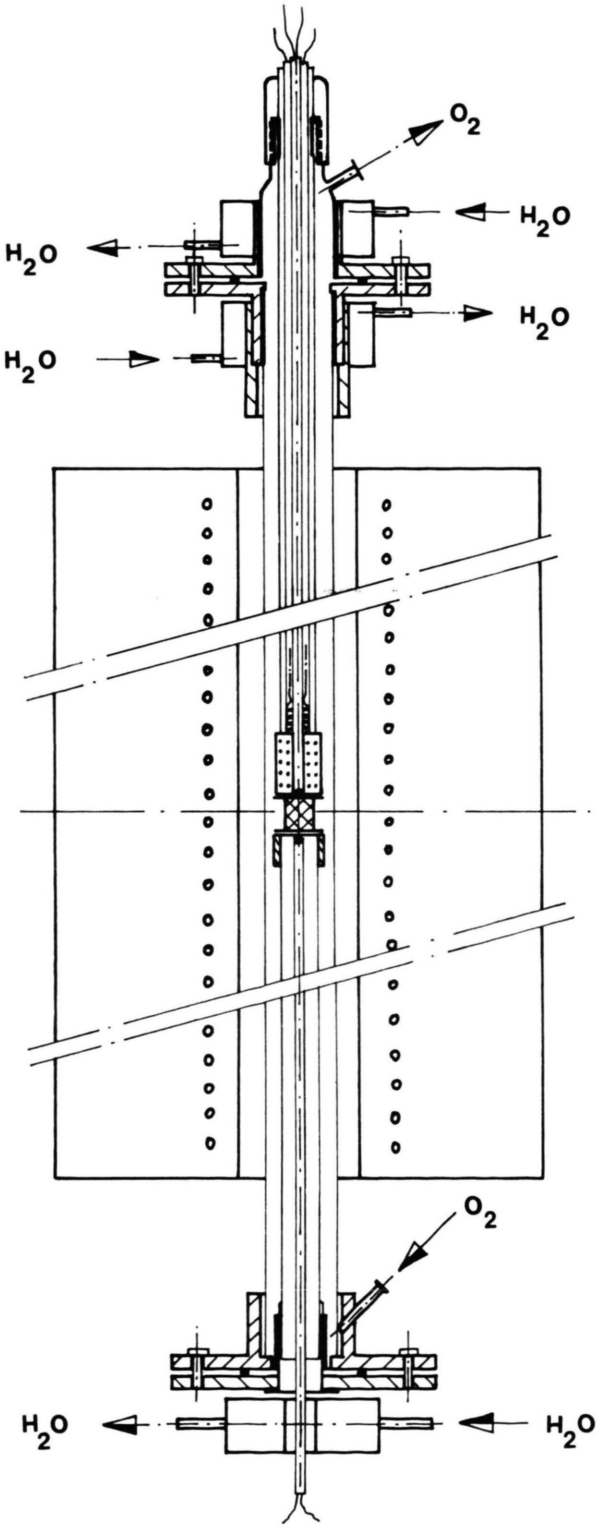

Fig. 1. View of the cell for thermal emf measurements and oven.

tering temperature is 1600 °C) with two different batches of ZrO_2 (see Table 2 for analytical data). In both batches Hf is present, which behaves nevertheless as zirconium. The entire set of samples was checked for Ca-content with X-ray fluorescence analysis and for structure. X-ray patterns indicated the presence of a single cubic phase for the entire set of compositions investigated.

Sintered samples were platinized on both sides to ensure good triphasic contacts. Vacuum sputtered platinum as well as fired Pt paste contacts were indifferently used without relevant differences.

The cell for thermal emf measurements is shown in Fig. 1, where it appears that a small auxiliary oven ($\sim$ 20 VA) is used for obtaining a temperature gradient[29]. A thick Pt tube at the cold electrode works as a heat sink and allows sensibly constant temperature gradients to be maintained within the zirconia electrolyte; the maximum temperature gradient used is 30 °C. Thermal emf and electrode temperatures are automatically measured and recorded by means of a digital voltmeter and digital recorder (Dymec system, Hewlett-Packard).

Emf's are measured with an accuracy better than $\pm 2.5\ \mu V$ and the experimental reproducibility was shown to better than $\pm 5\ \mu V$ when the system is brought for about two hours at $T > 1000$ °C as a preliminary conditioning step.

Results and Discussion

Fig. 2 shows as an example some ΔE vs. ΔT plots obtained at Pt/O_2 electrodes. A pressure of oxygen of one atmosphere was used in the entire set of measurements which are discussed here.

Thermoelectric power results are reported in Table 3 where the result of a single experiment carried out on a yttria stabilized zirconia is reported as well[30].

It is a common trend of the electrical transport parameters (as the electrical conductivity and its activation energy) of the ZrO_2-base systems to depend on the concentration of the substitutional impurity[13–20, 22–27, 30–32]. However, whereas the electrical conductivity isotherms show a maximum near the lower limit of stability of the homogeneous cu-

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[29] The design of the oven was suggested to us by Dr. A. STINGELE who utilized this type of oven for hot stage microscopic investigations. The oven consists of two or three coaxial alumina tubes on which 0.1 mm diameter Pt wire is wound.

[30] P. BIANCHESSI, S. PIZZINI, and V. WAGNER, work in progress.

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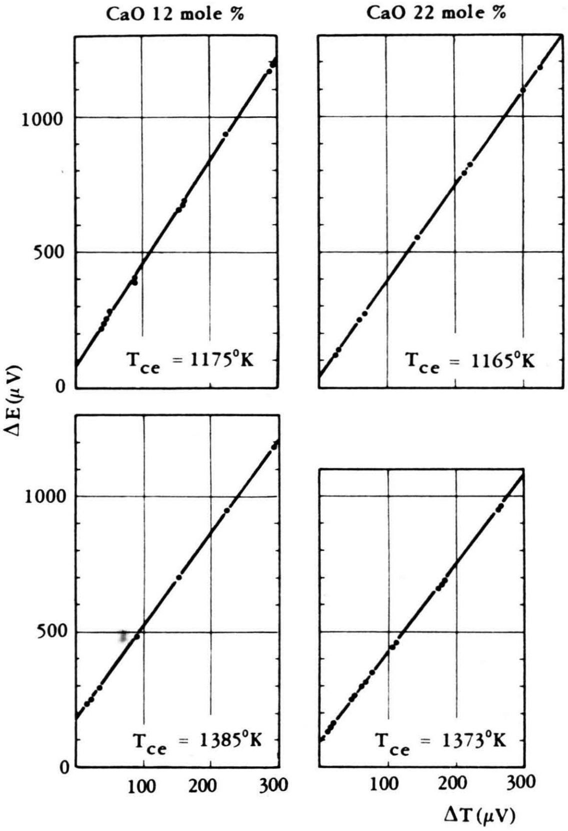

Fig. 2. Thermal emf vs. temperature plots (temperature is measured with a Pt/Pt 10% Rh couple) for different lime zirconias. T_{ce} is the temperature of the cold electrode.

bic phase[33], the activation energy for the electrical conductivity depends linearly on the composition.

This behaviour has been discussed as resulting from the size differences between the substitutional cation and the cations of the host lattice[9].

Within the experimental accuracy, it appears from Fig. 3 that a concentration dependence is also observed when plotting the total thermoelectric power vs. the vacancies concentration. In the same figure the results of RUKA, FISCHER and the single result coming from our experiments on the yttria-zirconia system are reported.

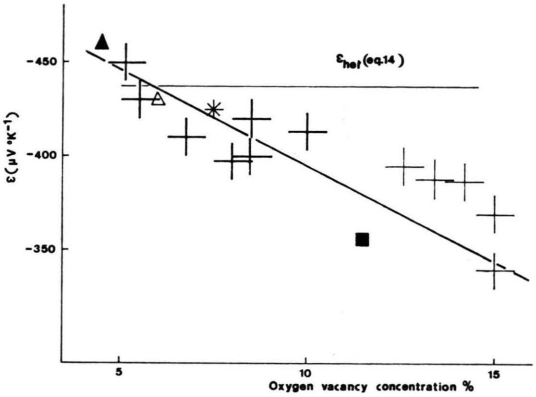

Fig. 3. Plot of the thermoelectric power vs. oxygen vacancies concentration. ▲ FISCHER[1] system $ZrO_2-Y_2O_3$; △ FISCHER system ZrO_2-CaO; ∗ RUKA[2] system ZrO_2-CaO; ■ This work, system $ZrO_2-Y_2O_3$; + This work, system ZrO_2-CaO and $ZrO_2-CaO-MgO$.

Neither RUKA nor FISCHER could discover this dependence, due to the lacking of sufficient and systematic data as a function of the solute concentration.

According to Eq. (12) one could calculate the heterogeneous part of the thermoelectric power if it were possible to do an "a priori" estimation of the partial ionic entropy value of the oxygen ion (see also the Appendix) according to the Fischer formula

$$\overline{S}_{O^=} = \frac{1}{3-x}\{S_{(ZrO_2)_{1-x}(CaO)_x} - \tfrac{3}{2}R \cdot [\ln(m_{Zr^{4+}}/m_{O^=}) - x\ln(m_{Zr^{4+}}/m_{Ca^{2+}}]\} \qquad (14)$$

in which it is assumed that the entropy of the mixture is evaluated additively from the pure components values.

The results plotted in Fig. 3 for ε_{het} have been obtained from the literature values for the binary mixture ZrO_2-CaO. It is apparent that the calculated heterogeneous power accounts for the total thermoelectric power at the lower limit of stability of the cubic phase (about 6% of oxygen vacancies) whereas it does not account for the higher concentration values. The function itself is very little sensitive on the concentration. As we got evidence, with separate experiments on the isothermal concentration cell[35]

$$Pt(O_2)\,|\,CaO\,\|\,CaF_2\,\|\,CaO(x)\,ZrO_2(1-x)\,|\,Pt(O_2)$$

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[33] A very recent work of FORRESTIER[34] on the system $ZrO_2-CeO_2-Y_2O_3$ shows that the position of the maximum of the electrical conductivity seems to be only dependent on the nature of the specific system considered and does not correspond at all, as it was previously supposed, with the lower limit of stability of the solid solution.

[34] M. FORRESTIER, Thesis, Univ. Grenoble, July 7th, 1969.

[35] R. MORLOTTI and S. PIZZINI, work in progress.

1. *Solid Solution*
ZrO_2 74,8% CaO 11,8% MgO 13,4%

$T_{c.e.}$ °K	$-\Delta E/\Delta T$ (μV °K^{-1})
1.359	358
1.291	373
1.228	374
1.159	381
1.087	380
1.009	396
1.369	358

$-\varepsilon = 488 - 0{,}093\ T$

2. *Solid Solution*
ZrO_2 73,2% CaO 13,7% MgO 13,1%

$T_{c.e.}$ °K	$-\Delta E/\Delta T$ (μV °K^{-1})
1.389	347
1.321	358
1.247	362
1.159	368
1.095	387
1.097	377
1.197	360

$-\varepsilon = 498 - 0{,}109\ T$

3. *Solid Solution*
ZrO_2 71,6% CaO 15,5% MgO 12.9%

$T_{c.e.}$ °K	$-\Delta E/\Delta T$ (μV °K^{-1})
1.273	361
1.230	365
1.185	373
1.141	371
1.097	377
1.053	381
1.003	390
1.319	357

$-\varepsilon = 485 - 0.097\ T$

4. *Solid Solution*
ZrO_2 70,1% CaO 17,4% MgO 12.5%

$T_{c.e.}$ °K	$-\Delta E/\Delta T$ (μV °K^{-1})
1.104	353
1.151	349
1.195	360
1.239	353
961	374
1.038	373
1.152	367

$-\varepsilon = 446 - 0.076\ T$

5. *Solid Solution*
ZrO_2 89,3% CaO 10,7%

$T_{c.e.}$ °K	$-\Delta E/\Delta T$ (μV °K^{-1})
1.349	408
1.250	412
1.198	423
1.271	418
1.228	428
1.175	432
1.385	408

$-\varepsilon = 557 - 0.109\ T$

6. *Solid Solition*
ZrO_2 88,9% CaO 11,1%

$T_{c.e.}$ °K	$-\Delta E/\Delta T$ (μV °K^{-1})
1.381	397
1.313	411
1.263	412
1.229	422
1.169	418
1.112	418
1.155	411
1.288	414

$-\varepsilon = 507 - 0{,}077\ T$

7. *Solid Solution*
ZrO_2 70.1% CaO 17,4% MgO 12,5%

$T_{c.e.}$ °K	$-\Delta E/\Delta T$ (μV °K^{-1})
1.409	339
1.323	341
1.268	347
1.135	338
1.082	343
1.367	344

$-\varepsilon = 341 + 0{,}001\ T$

8. *Solid Solution*
ZrO_2 83% CaO 17%

$T_{c.e.}$ °K	$-\Delta E/\Delta T$ (μV °K^{-1})
1.412	379
1.339	385
1.271	387
1.215	396
1.093	395
1.165	387
1.289	393
1.373	383

$-\varepsilon = 442 - 0{,}043\ T$

9. *Solid solution*
ZrO_2 83,1% CaO 16,9%

$T_{c.e.}$ °K	$-\Delta E/\Delta T$ (μV °K^{-1})
1025	411
1067	404
1157	399
1239	394
1320	386

$-\varepsilon = 489 - 0{,}0776\ T$

10. *Solid solution*
ZrO_2 86,5% CaO 13,5%

$T_{c.e.}$ °K	$-\Delta E/\Delta T$ (μV °K^{-1})
978	426
1018	417
1068	415
1153	404
1238	407
1318	391

$-\varepsilon = 508 - 0{,}0869\ T$

11. *Solid Solution*
ZrO_2 70% Y_2O_3 30%

$T_{c.e.}$ °K	$-\Delta E/\Delta T$ (μV °K^{-1})
1083	372
1125	334
1171	355
1216	338
1259	360
1301	339
1343	355

$-\varepsilon = 386 - 0{,}0293\ T$

* $T_{c.e.}$ is the temperature of the cold electrode.

Table 3. Thermoelectric power of stabilized zirconia.

where calcium fluoride works as the solid electrolyte, that the entropy of mixing of the solid solutions of CaO in ZrO_2 deviates only little from the ideal value, the procedure used for calculating the ionic entropy terms could be accepted without too severe criticism.

The nearly linear dependence on concentration of the total thermoelectric power therefore expresses that of the heat of transport of the oxygen ion.

It could be deduced from these results that both the activation energy for the conductivity and the heat of transport seem to be similarly influenced by the difference between the ionic radii of the substitutional cations and the cations of the host lattice. We will however account for these and other experimental results (on solid solutions of yttria and ytterbia in zirconia) with a less qualitative treatment in a later paper. It is nevertheless whorth to remark that Ruka and Fischer carried out thermal emf measurements in a large interval of partial pressures of oxygen, demonstrating that the differences in the thermoelectric powers are

$$\varepsilon_1(p'_{O_2}) - \varepsilon_2(p''_{O_2}) = -\frac{R}{4F}\ln\frac{p'_{O_2}}{p''_{O_2}} \qquad (15)$$

where $p'(O_2)$ and $p''(O_2)$ are the partial pressures of oxygen utilized in two different thermoelectric power measurements.

This rather obvious conclusion indicates that the heat of transport as well as the ionic entropy terms do not depend on the partial pressure of oxygen, in good agreement with the well known insensitiveness of the vacancy concentration on the partial pressure of oxygen, for these systems and for the experimental range of oxygen pressures chosen [11].

Appendix

While it is not experimentally possible to measure the entropies of the individual ions, a theoretical calculation is however possible, based on a corollary of Maxwell's equipartition of energy principle.

WAGNER [36] proposed for a solid salt of the type MX and for the case the masses of the ions M^+ and X^- are very close in value, the use of the molar entropy value of MX for calculating the partial ionic entropies, according to the equation

$$\overline{S}_{X^-} = \overline{S}_{M^+} = 0.5\, S_{MX}\,.$$

In the case of a solid solution the use of the weighed sum of the partial molar entropies of the components allows, almost in the same way, to calculate the entropies of the single ions from the entropy of the mixture. The accomplishment of additivity conditions implicit in such an approximation, means that the solution is ideal and that the partial molar quantities equal the corresponding quantities for the pure components.

Some excess terms could be calculated in a more refined treatment, such as the excess configurational and vibrational entropies. Whereas the configurational terms have little influence on the entropy of the mixture, excess vibrational terms are significant and could be calculated according to FISCHER [1] and PITZER [37] by using the partition functions for the translational entropy.

Acknowledgments

We are sincerely indebted to Dr. G. STERNHEIM for having encouraged this work and to Prof. A. KLEMM for many sugestions and for having greatly improved the text. — We acknowledge also the help of the colleagues G. VOS and C. J. TOUSSAINT who carried out the determination of the impurity concentration as well as of the calcium content.

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[36] C. WAGNER, Ann. Phys. Leipzig **3**, 629 [1929].

[37] K. S. PITZER, J. Phys. Chem. **65**, 147 [1961].