On the Dielectric Constant of Zirconia and Lime-zirconia *

MANLIO SANESI and GIORGIO CREMANTE
Institute of Physical Chemistry, University, Pavia, Italy
and SERGIO PIZZINI ** and VITTORIANO WAGNER ***
Nuclear Materials Laboratory, CCR Euratom, Petten, The Netherlands

(Z. Naturforsch. **26 a**, 159—164 [1971]; received 31 October 1970)

The dielectric constant of monoclinic zirconia and of lime-zirconia (up to a CaO content of 20% mole) has been measured at 25 °C by the powder method. For pure ZrO_2 the D.C. is 13.5, while for lime-zirconia a non linear dependence on the CaO content has been observed in the measured range, with a maximum at about 14% mole CaO. The results are discussed, in the light of the authors previous density data for the same systems, in terms of the width of the homogeneity range of the solid solutions.

Introduction

A large scattering exists within the literature values of the dielectric constant of pure ZrO_2 $(11 < \varepsilon < 28)$, measurements having been made mostly on thermal or anodic films and only in very few cases on bulk material. In particular, HARROP and WANKLYN[1] gave a value of 22 ± 3 obtained on little single crystals[2], while COX[3] reported a value of 11 ± 1 for thermal and anodic films. Such strong discrepancies might be accounted for, among other factors, by the influence of the morphology of the samples and of the experimental methods, as it was recognized by the same authors[1,3].

As for lime-zirconia, KRÖGER[4] quoted a value of 12.5, while emphasizing that the dielectric constant of such system had not been systematically investigated as a function of lime concentration. From data reported by HARROP and WANKLYN[1] on calcia- and magnesia-stabilized zirconia, it might be inferred that the dielectric constant in these cases is practically insensitive to quite large changes in composition. This would be somewhat surprising, if one considers, e. g., that VAN VESSEM[5] showed the dielectric constants of NaCl + NaBr and KJ + KBr solid solutions to be strongly in excess over the additive values.

Thus, the questions of the dielectric constant of pure zirconia and of lime-zirconia are still open to further investigation. The latter presents some interesting theoretical connections with the defect solid state of solid solutions or, at least, with the equilibrium phase diagram of the system $ZrO_2 - CaO$. Moreover, to our knowledge, no other research has been carried out after that of Van Vessem on the dielectric constant of solid solutions of ionic solids.

In this paper, the results of dielectric constant measurements, by the powder method, on pure ZrO_2 and some $ZrO_2 + CaO$ solid solutions in the composition range $8 \div 20$ mole % CaO are reported. Although the powder method suffers from a largely approximate theoretical treatment, it turns out convenient since it allows the use of finely ground powders instead of large and flat slabs of single crystals or large size pressed pellets, being at the same time free from the errors involved in the film method.

The Powder Method

By this method one determines the apparent dielectric constant of the heterogeneous system formed with the investigated solid, in powdered form, and a gaseous phase (or the vacuum). The pre-

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Reprints request to Prof. MANLIO SANESI, Istituto di Chimica Fisica dell'Università, Viale Taramelli, *I-27100 Pavia*, Italy.

* Work supported by the European Atomic Energy Commission (EURATOM), through Contract N. 56-2-68 PET-I.

** Present address: Istituto di Elettrochimica, Università di Milano, Via Venezian 21, Milano, Italy.

*** Present address: Società Nazionale Cogne, Aosta, Italy.

[1] P. J. HARROP and J. N. WANKLYN, Brit. J. Appl. Phys. **18**, 739 [1967]. This paper should be consulted for further references.

[2] These authors also report that measurements at the NPL (U. K., TEDDINGTON), made by both the immersion and the condenser method on single crystals of monoclinic ZrO_2 gave a common value of 24 ± 1 for ε.

[3] B. COX, Brit. J. Appl. Phys. [2] **1**, 671 [1968].

[4] F. A. KRÖGER, J. Amer. Ceram. Soc. **49**, 215 [1966].

[5] J. C. VAN VESSEM, Thesis, Utrecht 1947. — J. C. VAN VESSEM and J. M. BJVOET, Rec. Trav. Chim. **67**, 191 [1948].

eminent importance of the relationship existing between the measured value and the true D. C. of the solid is clear. After BRUGGEMAN's theoretical work [6], the subject was critically reviewed by VAN VESSEM [5], BÖTTCHER [7], BROWN [8] and MORABIN [9].

The Böttcher equation [10], when the second phase is air or vacuum, takes the form

$$(\varepsilon-1)/3\,\varepsilon=\delta[(\varepsilon_0-1)/(\varepsilon_0+2)] \qquad (1)$$

where ε is the apparent D. C. of the heterogeneous system, ε_0 is the true D. C. of the solid and δ is the volume fraction of the same solid in the condenser-cell. Equation (1) was shown by VAN VESSEM [5] to be more reliable than that proposed by BRUGGEMAN [6] and especially good when $\delta>0.5$.

BROWN [8] gave a more refined treatment, which however holds when the true D. C. of the solid is not too far from that of the medium, liquid or gas, in which the solid is immersed. Brown also suggested the use of the LANDAUER [11] formula

$$\delta\,\frac{\varepsilon_0-\varepsilon}{\varepsilon_0+2\,\varepsilon}+(1-\delta)\,\frac{1-\varepsilon}{1+2\,\varepsilon}=0\,. \qquad (2)$$

It is noteworthy that Eqs. (1) and (2) coincide in their explicit form for ε_0, though obtained via different physical models.

Finally, we remember that recently LOOYENGA [12], making no assumption on the shape of the solid particles, developed the equation

$$\varepsilon=[(\varepsilon_0^{1/3}-1)\,\delta+1]^3\,. \qquad (3)$$

Since for the Böttcher equation the spherical shape was specifically assumed, while in our samples a statistical distribution of shapes is most likely to occur, in this paper use has been made both of Eq. (1) and of Eq. (3) for a better comparison of experimental results. Only Eq. (1) has been employed for determining the condenser-cell capacitance.

Another important point to be considered is the influence of grain size on the measured D. C. values. Indeed VAN VESSEM [5] showed a strong effect of this kind, mainly when small condensers and relatively big grain-size powders, of high true D. C., were used (e. g., TlCl, $\varepsilon_0=31.9$; $TlNO_3$, $\varepsilon_0=16.5$). The effect, however, was much smaller with crystals of low D. C.: with KCl ($\varepsilon_0=4.68$) the difference in the measured values for powders ranging in grain size from about 3 to 0.1 mm was of 1.5% only.

Experimental

Materials

Pure ZrO_2 samples from commercial sources (Koch-Light; C. Erba) were used without further purification both for density and D. C. measurements, as well as for the preparation of the solid solutions with CaO. The latter was also a commercial product of good analytical grade.

Solid solutions were prepared by mixing the oxide components, sintering at 1600 °C in air, cooling down slowly to room temperature and ball milling the obtained pellets. Every sample was analyzed for structure by X-rays, and for Ca concentration by X-ray fluorescence or wet chemical methods. The mean composition values are reported in Table 3.

For D. C. measurements, the powdered samples both of ZrO_2 and of lime-zirconia were classified for grain size by means of standard ASTM sieves. Also pure ZrO_2 (originally in the form of very fine powder) was previously submitted to the process of sintering at 1600 °C, furnace cooling and grinding.

Density Measurements

Since remarkable discrepancies exist among literature density data both for ZrO_2 and ZrO_2+CaO solid solutions, the values to be used for the evaluation of δ in Eqs. (1) and (3) were experimentally determined on each of the samples employed. Details of the experimental procedure have been reported in a previous note [13].

Dielectric Constant Measurements

An instrumental set-up was designed for the determination of the apparent D. C. of oxide powders under a controlled atmosphere, i. e. under a reasonably high vacuum or known pressures of gaseous components. A gravimetric section, which could be operated as a side facility or as a completely independent part, was provided in order to follow the outgassing of samples or to detect adsorption isotherms.

The block diagram is shown in Fig. 1. The vacuum-line and the vessels were of pyrex glass; the connections of containers 8 and 9 with the respective covers were made by stainless steel flanges (sealed to glass by high vacuum epoxide-resin cement) and O-rings. The gravimetric balance consisted of a helicoidal steel

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[6] D. A. G. BRUGGEMAN, Ann. Phys. [5] **24,** 636, 644 [1935].

[7] C. F. J. BÖTTCHER, Theory of Electric Polarization, Elsevier Publ. Co., Amsterdam 1952, pp. 415–420.

[8] W. F. BROWN, JR., J. Chem. Phys. **23,** 1514 [1955].

[9] A. MORABIN, A. TETE, and R. SANTINI, Rev. Gen. Elect. **76,** 1504 [1967].

[10] C. F. J. BÖTTCHER, Rec. Trav. Chim. **64,** 47 [1945].

[11] R. LANDAUER, J. Appl. Phys. **23,** 779 [1952].

[12] H. LOOYENGA, Physica **31,** 401 [1965].

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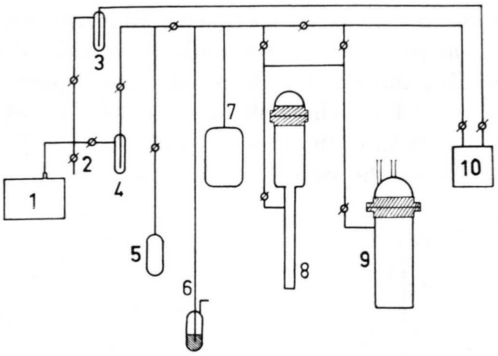

Fig. 1. Block diagram of the experimental set-up: 1: pumping section with vacuum monitoring (Pirani and Penning gauges to 10^{-5} Torr); 2: vent valve; 3 and 4: liquid air traps; 5: reservoir of liquid water (or other liquids) for adsorption experiments; 6: Hg manometer; 7: pressure compensation chamber for adsorption experiments; 8: container for adsorption spring balance; 9: container for dielectric cell; 10: digital reading quartz Bourdon manometer.

spring (suspended in tube 8) monitored by a cathetometer. Its sensitivity (0.002 cm per 0.0001 g) was deemed adequate to the purposes of the present work. It was possible to thermostate the lower part of containers 8 and 9, by means of removable water-jackets, or to heat at higher temperatures by winding tape-resistors around them. Temperature control was effected by chromel-alumel thermocouples. The pressure measuring instrument was a "Precision pressure Gage" of the silica Bourdon type (Texas Instruments Co.), and allowed an accuracy of $\pm 3 \cdot 10^{-3}$ Torr in the range $0 \div 300$ Torr.

Details of the dielectric cell, of the concentric cylinders type, are shown in Fig. 2. The stainless steel electrodes 1 and 2 were rigidly mounted on the teflon base 3, and held in position by the threaded rod 5 and the auxiliary steel cylinder 4. The cell could be easily disassembled for cleaning and reassembled with very good reproducibility of its geometric capacitance. From the electrode dimensions the geometric (or vacuum) capacitance should be of about 60 pF, while the useful volume of the condenser was about 27 cm^3, which required for filling some 100 – 120 g of the oxide powders. The electrical connections with the external circuit were made at the threaded holes 6 and 7 by means of the brass rods 5 as shown in Fig. 3; these were soldered to the brass sockets 7, which in turn were sealed to the syringe-formed and vacuum-tight pyrex connections 1. For temperature control, a thermocouple reached point 10, through tube 9.

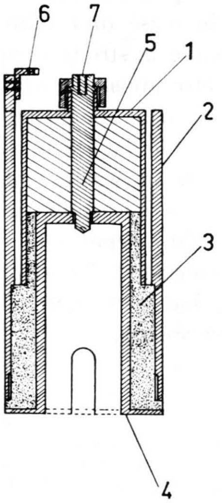

Fig. 2. Simplified vertical section of the dielectric cell.

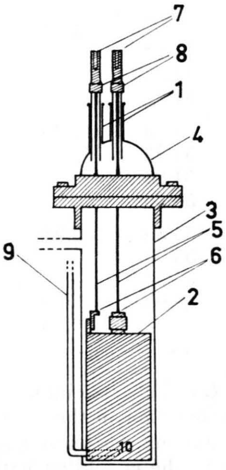

Fig. 3. Dielectric cell container with cell and electrical connections.

The electric capacitance measurements were made by means of a General Radio Co. assembly, including a Schering type bridge (No. 716-C), oscillator (No. 1302-A) and frequency filter (No. 1231-P5). The connection to the dielectric cell was accomplished via an adaptor to a standard G. R. coaxial connector and coaxial cable.

As a routine procedure, the cell and the bucket of the gravimetric section, filled with an accurately weighed amount of the powder, were introduced in the containers 8 and 9 of Fig. 1. Then the samples were outgassed at 110 °C at about 10^{-5} Torr for several hours, while the outgassing process was followed by means of the balance. After cooling to room temperature and thermostating at 25 ± 0.1 °C, the dielectric measurements were made at 10, 20, 50 and 100 kc/s, in the vacuum and at different equilibrium pressures of water vapour.

The dielectric cell was calibrated by means of powdered pure KCl and NaCl (grain size $0.063 \div 0.125$ mm) assuming for the density the values: KCl, $d_4^{25} = 1.99$; NaCl, $d_4^{25} = 2.16$ [14]. From the knowledge of the cell volume and of the powder weight and density, the

[14] From International Critical Tables.

solid volume fraction δ in the cell was evaluated, in order to calculate by the Böttcher formula (1) the apparent D. C. (ε) of the heterogeneous system with vacuum. For ε_0 the following literature values at 25 °C were chosen: KCl, $\varepsilon_0 = 4.68$; NaCl, $\varepsilon_0 = 5.62$ [15].

Table 1. Dielectric cell calibration with KCl and NaCl.

Run	Frequency (kc/s)	KCl C_0 (pF)	KCl $\overline{C}_0$ (pF)	NaCl C_0 (pF)	NaCl $\overline{C}_0$ (pF)
1	100	55.98	56.01	55.04	55.10
	50	55.99		55.05	
	20	56.04		55.15	
	10	56.04		55.15	
2	100	54.14	54.21	54.88	54.91
	50	54.18		54.88	
	20	54.23		54.95	
	10	54.26		54.95	
3	100	54.19	54.25	54.79	54.83
	50	54.25		54.81	
	20	54.26		54.87	
	10	54.30		54.87	
4	100	55.89	55.94	54.77	55.07
	50	55.90		54.87	
	20	55.96		55.24	
	10	56.00		55.41	
Mean			55.10		54.98

Indicating by C_A the capacitance reading with the empty cell (corresponding to the sum of the geometric capacitance, C_0, and of the leads capacitane) and by C_X the reading with the cell filled with the heterogeneous system "powder + vacuum", having an apparent D. C. equal to ε, it follows immediately that

$$C_0 = (C_X - C_A)/(\varepsilon - 1). \quad (4)$$

The whole procedure was repeated several times on each compound, giving the results reported in Table 1. It is apparent that the effect of frequency (in the experimental range) was negligible, as confirmed by the fact that the dissipation factor also proved to be negligible; an average value, $\overline{C}_0$, was therefore accepted for each run. A very good agreement between the mean values for KCl and NaCl is shown in Table 1 [16]. An average mean value of 55.04 pF was consequently adopted for the cell constant C_0.

Results and Discussion

On each sample of zirconia and lime-zirconia two or more independent runs were always performed.

Some preliminary experiments were carried out on a sample of pure ZrO_2 and on a solid solution with 15% mole CaO: the results are reported in Figs. 4 and 5, where the increments, $\Delta\varepsilon$, of the apparent D. C. of the systems "solid + vapour" over the value for the system "solid + vacuum", are plotted vs. the relative pressure of water vapour, p_R [17]. A considerable increase of ε with water pressure can be noted, while a strong dependance on frequency becomes also apparent, which is not observed when measuring with completely outgassed samples. This effect could be essentially attributed to physical adsorption of water molecules onto the solid substrate [18]; the adsorption was reversible, as shown in Fig. 6, which reports the results of a measuring process consisting in stepwise increasing, thereafter decreasind and finally increasing again the water vapour pressure.

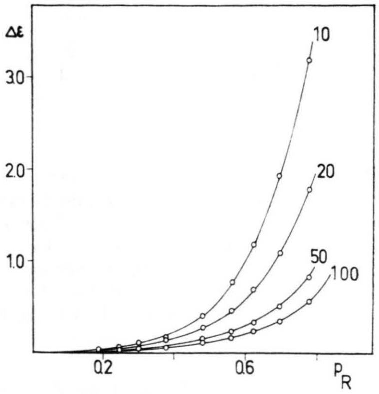

Fig. 4. Change of the apparent D.C. of ZrO_2 as a function of water vapour p_R, at the indicated frequencies in kc/s.

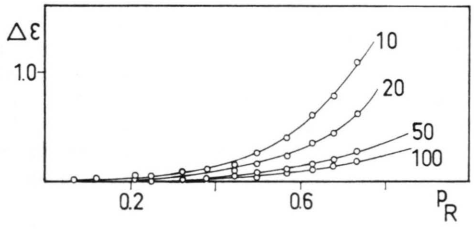

Fig. 5. Change of the apparent D.C. of a lime-zirconia (15% mole CaO) as a function of water vapour p_R, at the indicated frequencies in kc/s.

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[15] K. Højendahl, Kgl. Danske Vidensk. Selskab. **16**, 2 [1938].

[16] The agreement is not so good when using the Looyenga formula (3). This is the reason why only the Böttcher formula was employed for the cell calibration.

[17] p_R is defined as the ratio of the equilibrium pressure of water vapour over the solid and the vapour pressure of liquid water at the same temperature (25 °C).

[18] It had been verified that, with the empty dielectric cell, increasing the relative pressure of water vapour from 0 to about 0.8 caused no instrumentally detectable change in the electric capacitance. Moreover, with the systems "solid + water vapour" the dissipation factor was no longer negligible, and took values which rapidly increased with increasing pressure and with decreasing frequency.

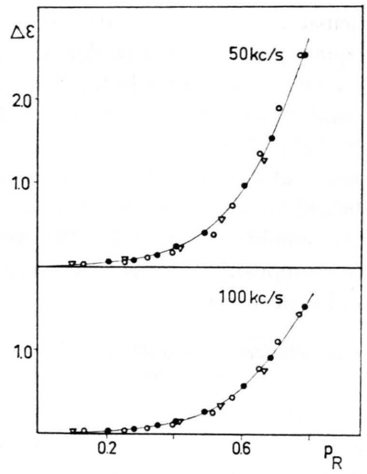

Fig. 6. Change of the apparent D.C. as a function of p_R in the reversible adsorption of water vapour on ZrO_2: ○ first adsorption run; ▽ desorption run; ● second adsorption run.

A similar behaviour was observed with every lime-zirconia composition investigated.

Measurements on pure ZrO_2 were carried out as a function of grain size, through two independent runs on each sample of a given grain size. From the ε values (averaged from the values measured at the specified frequencies), the corresponding ε_0 were calculated both with Eq. (1) and Eq. (3). The results are given in Table 2[19]. A good reproducibility among the results for different runs was achieved. The mean $\bar{\varepsilon}_0$ values appear to be reasonably independent of the grain size in the studied range. Consequently, the following average values of the dielectric constant of pure zirconia are obtained: 13.66 by Eq. (1) and 13.45 by Eq. (3).

Table 3. Dielectric constant measurements on lime-zirconia solid solutions.

CaO (% mole)	Run	d ($g.\cdot cm^{-3}$)	δ	ε	ε_0 Eq. (1)	ε_0 Eq. (3)
8.45	1	5.740	0.5006	6.15	17.77	18.88
	2		0.5120	6.30	17.46	18.68
	3		0.5156	6.37	17.46	18.37
	4		0.5094	6.20	17.30	18.47
11.91	1	5.687	0.5528	7.27	17.83	19.57
	2		0.5609	7.39	17.67	19.45
	3		0.5627	7.43	17.68	19.47
	4		0.5616	7.40	17.67	19.46
12.08	1	5.683	0.5506	7.13	17.58	19.25
	2		0.5443	6.96	17.46	19.05
	3		0.5370	6.89	17.71	19.27
13.31	1	5.654	0.5745	8.00	18.53	20.59
	2		0.5587	7.69	18.68	20.65
	3		0.5458	7.39	18.66	20.50
	4		0.5406	7.25	18.60	20.37
14.01	1	5.554	0.5344	6.53	16.76	18.13
	2		0.5550	6.90	16.61	18.15
	3		0.5524	6.83	16.56	18.06
	4		0.5517	6.89	16.79	18.33
15.30	1	5.510	0.5527	7.03	17.15	18.76
	2		0.5587	7.18	17.21	18.89
	3		0.5680	7.36	17.19	18.92
15.52	1	5.509	0.5520	6.95	16.94	18.51
	2		0.5495	6.83	16.73	18.24
	3		0.5322	6.46	16.66	17.96
	4		0.5454	6.65	16.43	17.86
19.18	1	5.416	0.5425	6.39	15.84	17.13
	2		0.5601	6.85	16.20	17.70
	3		0.5616	6.88	16.20	17.70
	4		0.5664	6.97	16.19	17.72

With the solid solutions of CaO in ZrO_2, the measurements were carried out on samples of the grain size 0.063 ÷ 0.125 mm, each sample being subjected to at least three independent runs. The results are given in Tables 3 and 4.

From these results, it is seen that whereas the Böttcher and the Looyenga equations give practically the same value in the case of pure ZrO_2,

Table 2. Dielectric constant of monoclinic zirconia.

grain size (mm)	Run	d ($g\cdot cm^{-3}$)	δ	ε	Equation (1)		Equation (3)	
					ε_0	$\bar{\varepsilon}_0$	ε_0	$\bar{\varepsilon}_0$
0.210 — 0.250	1	5.825	0.4824	4.75	13.61	13.62	14.03	14.02
	2		0.4786	4.70	13.63		14.01	
0.125 — 0.177	1	5.825	0.3971	3.66	13.99	13.62	13.19	13.19
	2		0.4439	4.13	13.24		13.19	
0.044 — 0.063	1	5.825	0.3990	3.66	13.86	13.73	13.08	13.14
	2		0.4199	3.89	13.60		13.19	

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[19] Incidentally, it can be noted that our measured value of the density of ZrO_2 is in very good agreement with the datum (5.82 $g\cdot cm^{-3}$) for baddeleyite (monoclinic ZrO_2) by J. D. McCullough and K. N. Trueblood, Acta Cryst. **12**, 507 [1959]).

Table 4. Mean values, $\bar{\varepsilon}_0$, of lime-zirconia solid solutions.

CaO (% mole)	$\bar{\varepsilon}_0$ Eq. (1)	$\bar{\varepsilon}_0$ Eq. (3)
8.45	17.50	18.69
11.91	17.71	19.49
12.08	17.58	19.19
13.31	18.62	20.52
14.01	16.68	18.17
15.30	17.19	18.86
15.52	16.69	18.14
19.18	16.11	17.56 .

larger differences are shown with the lime-zirconia solid solutions, of higher D. C.

While such discrepancies cannot be immediately explained in a simple way, the general trend of D. C. as a function of composition is clearly indicated by both sets of values. This is shown in Fig. 7,

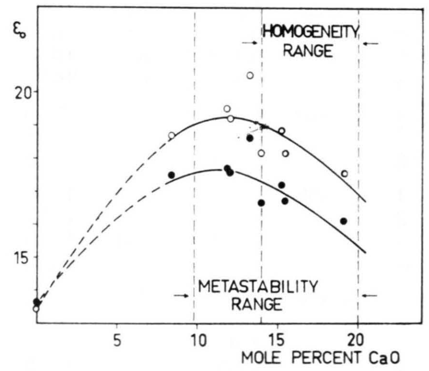

Fig. 7. Dielectric constants of pure zirconia and of lime-zirconia solid solutions: ● according to Eq. (1) ; ○ according to Eq. (3).

where large positive deviations from a purely additive behaviour can be observed[20]. This fact is similar to that observed by Van Vessem[5] with NaCl + NaBr and KJ + KCl solid solutions. A specific effect in the $ZrO_2 + CaO$ system is the sudden increase of the D. C. near the 14 mole % CaO composition.

This effect, however, disappears when calculating the molar polarization, which takes into account the effect of density. Although the use of the Mosotti-Clausius equation must be regarded as largely approximate, owing to the contributions from the crystal lattice and from dipole interactions, the values reported in Table 5 [the symbols $P(1)$ and $P(3)$ refer to polarizations calcultated employing the ε_0 values obtained by Eq. (1) and Eq. (3), respectively] are reasonably constant for the mixtures, in the studied composition range, and only slightly higher than for pure ZrO_2.

Table 5. Molar polarizations of ZrO_2 and of $ZrO_2 + CaO$ solid solutions.

CaO (% mole)	$P(1)$ (cm^3)	$P(3)$ (cm^3)
0.00	17.10	17.05
8.45	17.33	17.51
11.91	17.18	17.43
12.08	17.15	17.39
13.31	17.27	17.52
14.01	17.16	17.41
15.30	17.29	17.55
15.52	17.19	17.43
19.18	17.00	17.25

Thus the behaviour of the D. C. of these solid solutions might be explained by taking into account the results of our previous note[13] on the density changes with composition, and considering further that for samples sintered at 1600 °C and quenched to room temperature the homogeneity range might be expected to extend (according to Garvie[21] and to Diness[22]) from 10 to 20 mole % lime. The whole range of solid solutions is metastable at room temperature, but for samples slowly furnace cooled from 1600 °C to r. t. one might expect at lime concentrations lower than 14% (even when X-ray analysis does not reveal the existence of extraneous phases) the presence of small amounts (possibly up to 1 – 5%) of phases different from the cubic solid solution. The sudden change in density and D. C. of lime-zirconia observed at about 14% lime, apparently indicates the transition from a polyphasic to a truly monophasic region.

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[20] Some preliminary measurements on a sample of CaO (purity ~ 98%), by the same powder method, gave a value of 11.5 for the D. C.

[21] R. C. Garvie, J. Amer. Ceram. Soc. **51**, 554 [1968].

[22] A. M. Diness, Thesis, Penn. State Univ., Dept. Nat. Sci. 1967.