Structural Transformations and Deviations from the Pure Anion Vacancy Model in Lime Zirconia *

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Small but not negligible deviations from the pure anion vacancy model have been observed in samples of lime zirconia with a lime content ranging from 10 to 14 mole percent lime. Such deviations have been discussed in terms of the subsolidus equilibria occurring within this composition range.

In order to discuss the results of dielectric constant measurements, which have been carried out [1] on samples of pure zirconia and of lime zirconia as a function of the lime content, the pycnometric density of samples coming from the same batches used for the dielectric measurements was determined.

As a standard procedure a 25 ml pycnometer filled with pure benzene (sodium dried and distilled) or carbon tetrachloride and 2 g samples was used. Measurements were carried out, after a preliminary careful outgassing of the samples and of the pycnometer, at 25 °C ± 0.05.

Density measurements on 30 – 40 g samples were carried out, as well, by the gas pycnometric method, in order to verify the possible influence of the smallest open porosities and of some closed porosities on the measurements made by the liquid pycnometric method.

A Beckmann mod. 930 air compensation pycnometer (which gives a nominal accuracy of 0.05 cm^3 over the 50 cm^3 volume of the sample holder) and helium as pycnometric gas were used, measurements being made after the purging of the samples under vacuum.

Finely powdered samples were prepared by ball milling zirconia and lime zirconia, sintered at 1600 °C and furnace cooled to room temperature.

X-ray diffraction spectra of the powdered samples were also recorded, showing the pattern of the cubic solid solution when the CaO concentration ranges between 10 and 20 mole-% [2]. On the same samples X-ray fluorescence and chemical anlyses were used for Ca determination.

Results are given in Fig. 1, where some literature data [3–9] are also reported together with the theoretical plots corresponding to the "pure anion vacancy" model calculated from their own X-ray diffraction data by Diness and Roy [3] for the 1600 °C isotherm and by Hund [4] for the 1460 °C isotherm.

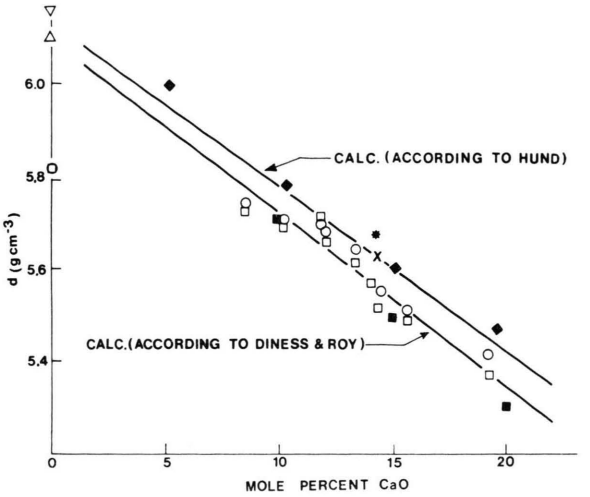

Fig. 1. Plot of the pycnometric densities of stabilized zirconia as a function of the lime content. Solid lines are calculated according to the X-ray data of Diness and Roy [3] and Hund [4].
○ present work, liquid pycnometry,
□ present work, helium pycnometry,
◆ Hund (Ref. [4]),
■ Dinesss and Roy (Ref. [3], samples quenched from 1600 °C),
▲ Kingery and Pappis (Ref. [6]),
∗ Carter and Roth (Ref. [5], samples cooled from 1600 °C),
× Hoffmann and Fischer (Ref. [9]),
▽ Ruff and Ebert (Ref. [7], tetragonal ZrO_2),
△ Pascal (Ref. [8], tetragonal ZrO_2).
The value by McCullough and Trueblood (Ref. [10], monoclinic ZrO_2), not shown in diagram, is coinciding with those found in the present work.

For pure zirconia the average density value (for samples coming from different sources, after annealing at 1600 °C) is 5.825 g cm^{-3} which well agrees with the value 5.82 for baddeleyte (monoclinic zirconia) [10]. For tetragonal zirconia the reported values are 6.10 [7] and 6.16 [8].

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[11] From Fig. 1 it can be seen that a satisfactory agreement was generally found within the values determined by the liquid- and by the gas-pycnometric methods.

From Fig. 1 it appears that our present results [11] fit fairly well the plot of the calculated results by Diness and Roy and only deviate in the composition range 10 to 14% mole. The corresponding excess densities, plotted in Fig. 2, reach a maximum at about 14 mole percent lime. Single results by CARTER and ROTH [5] and by HOFFMANN and FISCHER [9] are also reported in Fig. 2 to support the conclusion that the observed trend is truly representative of a property of the system. Incidentally we remark that the sample used by Carter and Roth was a single crystal specimen.

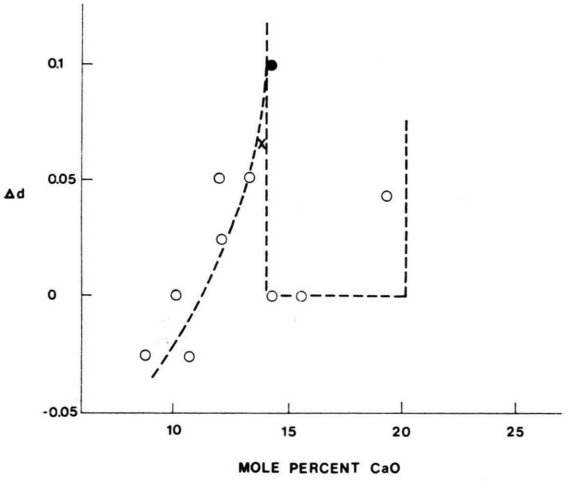

Fig. 2. Plot of the experimental excess density values of lime stabilized zirconia as a function of the lime content. ○ present work, ● Ref. [5], × Ref. [9].

It might be pointed out also that the main difference between our samples and those of Diness and Roy is in the quenching procedure. These authors claim for a quenching rate of 1000 °C sec^{-1}, whereas our samples are furnace cooled (and those of Carter and Roth were quenched at a rate of 200 °C sec^{-1}). The former only can be considered therefore as truly representative of the 1600 °C isotherm, while our samples (and presumably also those of Carter and Roth) reflect the metastabile equilibrium conditions within the broad range of temperatures where ordering processes [5] and subsolidus equilibria are sufficiently fast [12].

According to the phase diagrams reported by GARVIE [2] (who also critically reviewed the earlier results in literature), corresponding to the isotherm of 1600 °C the lower limit of stability of the cubic solid solution is about 10% lime. At lower temperatures a tetragonal solid solution is reported to be stable in equilibrium with the cubic phase, the lower limit of stability of the cubic phase at 1000 °C being about 14% lime. If this would be the case, then the precipitation of the tetragonal phase could account fairly well for the excess density values as well as for the maximum at about 14% lime.

There is, however, the contradictory evidence of the results by DINESS [12], COCCO [13] and BARBARIOL [14], who reported, on the basis of long term annealing experiments, a value for the lower limit of stability of the cubic phase ranging between 10 and 12% lime at temperatures as low as 1000 °C. The latter results, however, do not exclude that another mechanism might be operative, such as superlattice formation [2].

Acknowledgments

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Calculation of the Proton Chemical Shifts in Strongly Hydrogen Bonded Systems

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The all-electrons semiempirical SCF methods render the study of changes in the electron configuration with hydrogen bonding relatively easy. We wish to show that such methods can give valuable information about the magnetic properties of hydrogen bonded systems.

Proton shielding constants (σ) were calculated for HF, HF_2^- and $H_2F_3^-$ using the well known expression by POPLE [1]

$$\sigma = (e^2/3\,m\,c^2)\sum^{A} P_{\mu\mu}(r^{-1})_{\mu\mu} - 2\,N^{-1}\langle r^{-3}\rangle_A\,\chi_p{}^A - \tfrac{1}{3}\,N^{-1}\sum_{B\neq(A)}\chi_{\alpha\gamma}{}^B\,R_B{}^{-5}(R_B{}^2\,\delta_{\alpha\gamma} - 3\,R_{B\gamma}\,R_{B\alpha}).$$

All matrix elements were calculated with Slater orbitals and with Slater ζ values. The parametrization of the INDO method [2] was that proposed by SICHEL and WHITEHEAD [3] and the basic set consists only of 1s, 2s and 2p atomic orbitals.

Calculated values (Table 1) are separated into diamagnetic (σ_d) and paramagnetic (σ_p) parts. Though

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