

netically fully saturated material. Unmagnetized specimens could not be measured because the attenuation was too high.

We therefore determined the longitudinal wave velocity of a 99.6% dense polycrystalline specimen of $Mn_{0.49}Zn_{0.45}Fe_{2.06}O_4$. The measured value of $7.190 \text{ km sec}^{-1}$ agrees very well with the one calculated from the single crystal elastic constants ($7.157 \text{ km sec}^{-1}$) according to the Voigt–Reuss–Hill or Hashin–Shtrikman averaging scheme. In our case too, excessive damping prevented the measurement of the shear-wave velocity in polycrystalline ferrite.

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Phase equilibrium diagram of the system ceria–yttria for temperatures between 900 and 1700° C

Interest in the search for compounds of high melting point oxides suitable for non-traditional applications prompted an investigation of ceria-based materials. Previously reported results [1, 2] have indicated that these materials could be successfully employed at high temperatures as semiconductors. Mixtures of ceria with alkaline-earth oxides have been examined in earlier papers [3–12]. Investigations have also been made of the system CeO_2 – ZrO_2 [13, 14], and of those ternary systems containing the two oxides mentioned and other high melting point oxides such as CaO [15], MgO [16], Al_2O_3 [17, 18] and BeO [19].

The present paper reports on an investigation of solid-state phase relationships in the system ceria–yttria in the temperature range between 900 and 1700° C. No information about this system could be found in the literature.

The materials used were CeO_2 (99.9% pure) and Y_2O_3 (99.99% pure). To prepare the stoichiometric mixtures, the compounds were weighed, homogenized by hand-mixing in agate mortars for 4 h, pressed, at a pressure of 3000 kg cm^{-2} , into discs and pre-heated in an oxidizing atmosphere (air) for 500 h at 1400° C. After this treatment, the specimens were re-fired at the following tem-

peratures and time periods: 1700° C, 8 h; 1600° C, 16 h; 1500° C, 500 h; 1400° C, 1000 h; 1300° C, 1200 h; 1200° C, 1500 h; 1100° C, 1800 h; 1000° C, 2000 h; 900° C, 2500 h. All firings were conducted in an oxidizing atmosphere (air); the firing times were all long in order to ensure the attainment of true equilibrium conditions. In all cases the completion of the reaction was checked experimentally by microscopic and X-ray analyses carried out on the specimens at regular intervals in the course of firing. Equilibrium was considered attained and the reactions completed when successive microscopic observations revealed no more variations in the number and proportions of the phases present and the intensities of their diffraction lines remained unchanged in successive X-ray diffraction pattern measurements. To freeze the equilibrium phase relations at the various firing temperatures, the specimens were always quenched in air. The phase relations at the different firing temperatures were determined for the quenched specimens by reflected-light optical microscopy and X-ray diffractometry. The techniques used and the precautions taken, in the preparation of the specimens for the microscopic and X-ray examinations, are described elsewhere [15, 17].

The results obtained are presented in the phase equilibrium diagram between 900 and 1700° C (see Fig. 1). There existed two relatively extensive areas of binary solid solution and no

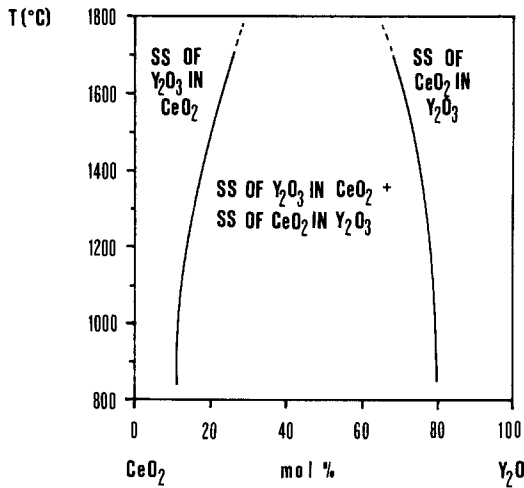


Figure 1 Phase equilibrium diagram of the ceria-yttria system for temperatures between 900 and 1700°C. (SS = solid solution).

ternary compound was formed under the operating conditions. The saturation limits for the solid solution of Y_2O_3 in CeO_2 and for the solid solution of CeO_2 in Y_2O_3 at the various temperatures were determined on the quenched specimens by accurate measurements of the lattice parameters of the solid solutions with varying composition of the mixtures (see Figs 2 and 3). All the data obtained at the various temperatures in the

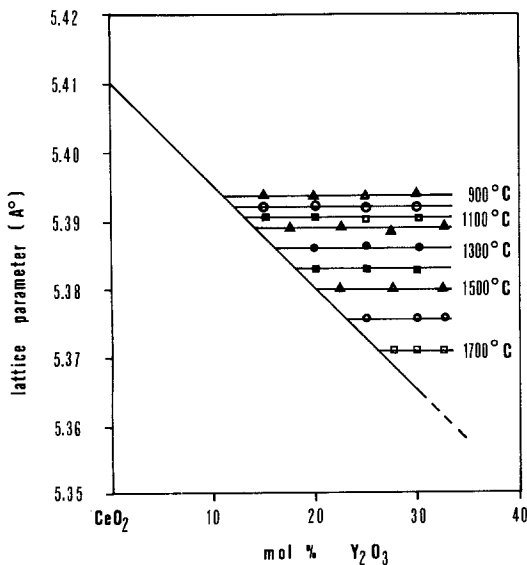


Figure 2 Lattice parameters of solid solution of Y_2O_3 in CeO_2 against mol% Y_2O_3 for various temperatures.

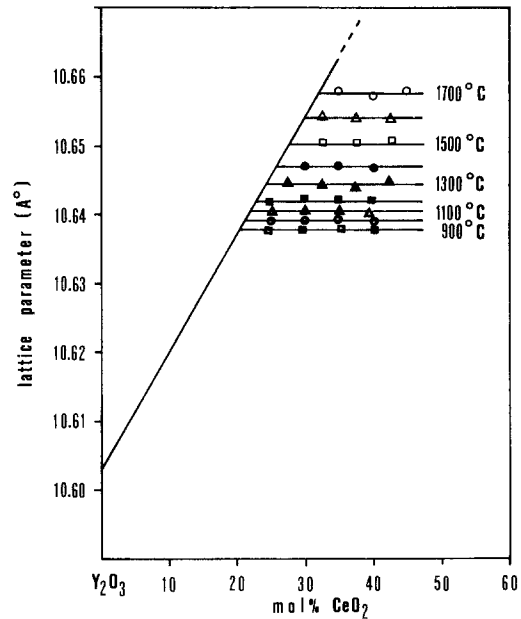


Figure 3 Lattice parameters of solid solution of CeO_2 in Y_2O_3 against mol% CeO_2 for various temperatures.

single-phase regions were fitted to the same line by linear regression analysis. This method was considered to be valid since the variations of the lattice parameter of the two solid solutions as a function of composition were always in good agreement with Vegard's Law, and the slopes of the lines at the various temperatures practically coincided (confidence limit 95%). The equations showing the linear composition dependence of the lattice parameters of the two solid solutions of Y_2O_3 in CeO_2 and of CeO_2 in Y_2O_3 are

$$y_{CeO_2} = 5.410 - 0.0015x_{Y_2O_3} \quad (1)$$

and

$$y_{Y_2O_3} = 10.603 + 0.0017x_{CeO_2}, \quad (2)$$

respectively, where y_{CeO_2} is the unit cell parameter (Å) of the solid solution of Y_2O_3 in CeO_2 and $x_{Y_2O_3}$ is the mole per cent of Y_2O_3 in this solid solution, $y_{Y_2O_3}$ is the unit cell parameter (Å) of the solid solution of CeO_2 in Y_2O_3 and x_{CeO_2} is the mole per cent of CeO_2 in this solid solution. The indices of linear correlation for the two equations are very close to unity: 0.9996 for Equation 1 and 0.9987 for Equation 2.

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The influence of CaO-doping on the fracture toughness of hot-pressed Al₂O₃

Only very few investigations on the fracture toughness of hot-pressed alumina have been reported [1, 2]. The influence of impurities was not investigated in these experiments. CaO is a typical impurity frequently found in Al₂O₃. In order to obtain more information on this system Al₂O₃ powders with different CaO-doped levels were hot-pressed. No MgO was added since this dope is not necessary for hot-pressing. The resulting specimens were annealed for various times in order to vary the grain size. The results are discussed and compared with literature data [1-4].

For the experiments a commercial alumina powder, containing no more than 300 ppm impurities was used. The powder was mixed with calcium acetate in ethanol and the mixture was intensively stirred at a temperature of about 80° C. Stirring continued until a reasonably dry powder resulted. The product was dried for 24 h at 120° C. In order to obtain a CaO-dope from the acetate addition, the powder was pre-fired at 600° C for

4 h in oxygen and afterwards sieved. Continuous hot-pressing [5-7] was carried out at 1400° C, 120 MPa with a feeding rate of 1.25 cm h⁻¹. These being the optimum hot-pressing conditions as described by Peelen [8]. This procedure was carried out for dope levels of 0 to 250 ppm CaO in steps of 50 ppm. The resulting relative densities were all greater than 98.5%.

From the resulting bars, fracture toughness specimens of 1 mm x 3 mm x 15 mm were sawn, in such a way that the fracture planes were perpendicular to the pressing direction. Due to diameter limitations no specimens could be prepared with the fracture planes parallel to the pressing direction. Specimens were annealed at 1550° C, the optimum annealing temperature in the work by Simpson and Merreth [1], for 3, 5 and 8 h in 10⁻⁵ torr vacuum.* The microstructure of each type of material (characterized by the combination dope level-annealing time) was revealed after polishing by thermal etching at 1450° C at a pressure of 10⁻⁵ torr for 4 h [9]. Some typical microstructures are given in Figs 1 and 2.

Area distributions of the grains in the scanning

*Astro 1100 V.