

Densification and Electrical Conductivity of Mn-doped CeO₂

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Abstract. The influence of Mn addition (from 1 up to 10 mol%) on densification and electrical conductivity of CeO₂ was studied in detail. Bulk specimens were prepared by the conventional technique of mixing suitable amounts of cerium dioxide and manganese carbonate, followed by pressing and sintering. The apparent density of sintered specimens was determined by the immersion method and electrical characterization was carried out by impedance spectroscopy measurements in the 300 to 550 °C range. High densification (> 95% of the theoretical density) was obtained for small addition of Mn (1 mol%) to CeO₂ sintered at 1300 °C for only 0.1 h. Electrical conductivity changes in sintered pellets depend on the sintering procedure, but not on the manganese content.

Introduction

Cerium dioxide, CeO₂, has been extensively studied because of its technological applications as polishing medium, catalyst, and high-temperature ceramic material [1-3].

Ceria crystallizes in the cubic fluorite structure, with cations in eightfold and anions in fourfold coordination, which is known to tolerate a considerable reduction without phase change. It is also known that ceria-based materials are difficult to sinter below 1500 °C [4,5]. The main approaches to overcome this problem are the use of very fine powders or the addition of a sintering aid. Transition metal oxides have been investigated as activators to promote densification in cerium dioxide [6-10].

In general, the addition of transition metal oxides enhances the densification rate of ceria. However, almost all of these activators exert an undesirable effect in the electrical property by increasing the electronic component of the conductivity.

In this work, the addition of Mn to CeO₂ was investigated aiming an optimization of the sintering process, in order to obtain high densification without significant changes in the electrical conductivity.

Experimental details

Cerium dioxide (CeO₂, 99.9%, Aldrich) and manganese carbonate (MnCO₃, 99.9%, Alfa Aesar) were used as precursor materials. Powder mixtures of CeO₂-x mol% Mn with x = 0, 1, 2, 3, 4, 5, 7, and 10 were prepared by wet mixing (Turbula, model T2C) the precursor materials for 2 h with zirconia balls. The mixtures were calcined at 600 °C for 2 h and deagglomerated. Cylindrical pellets were prepared by uniaxial pressing and sintering at dwell temperatures in the 1000-1350°C range for 0.1 h. Sintering experiments were also carried out at 1350 °C for 1, 2, 5, and 10 h.

The morphology of powder materials was observed by scanning electron microscopy (Philips, model XL30) using secondary electrons. The sintered density was determined by the immersion method. The electrical conductivity was determined by impedance spectroscopy measurements

using a low-frequency analyzer (Hewlett Packard, model 4192A) in the 5 Hz to 13 MHz frequency range. Silver paste was applied by painting onto large surfaces of sintered pellets to act as electrode material.

Results and discussion

The particle morphology of the as-received materials does not differ. Cerium dioxide as well as manganese carbonate consist of fine and agglomerated particles. The mixing step produced spherical agglomerates of varying sizes, as shown in Fig. 1 for CeO₂-4 mol% Mn sample.

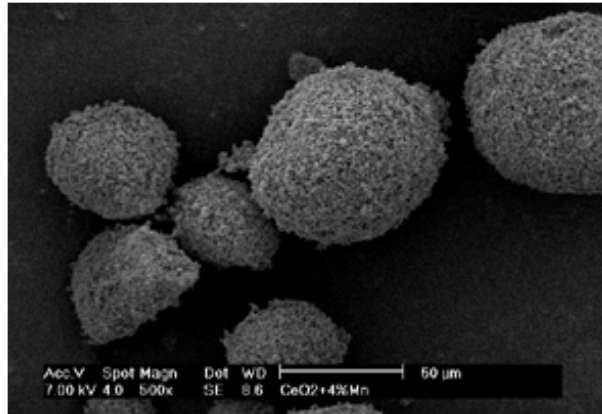


Fig. 1: SEM micrograph of mixed CeO₂-4 mol% Mn.

All other Mn-containing mixtures exhibit a similar morphology, which is suitable to obtain a good particle packing structure of the green compacts.

Fig. 2 shows the behavior of the sintered density for several dwell temperatures for CeO₂ pellets containing 0, 1 and 4 mol% Mn. The soaking time was 0.1 h.

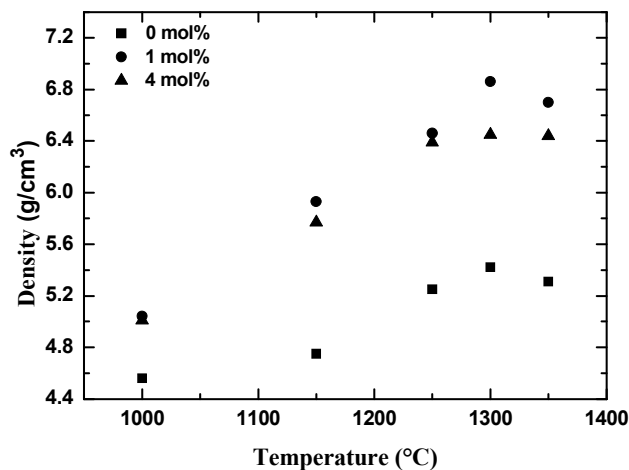


Fig. 2: Evolution of sintered density with dwell temperature. Soaking time = 0.1 h.

The sintered density increases up to 1300 °C reaching a steady value at that temperature. The sintered density of pure CeO₂ is lower than that of Mn-containing pellets. At 1300 °C, for example, the relative density of pure ceria is only 77%, whereas for 1 mol% Mn it attained 97%. This result shows that the additive increases the densification rate of ceria, as previously observed [6,7].

Increasing of the soaking time up to 10 h does not improve the sintered density for Mn-containing CeO₂ as shown in Fig. 3. For pure ceria a slight increase of the density occurs up to 5 h. These results suggest that the sintering mechanism may be different in ceria and in Mn-doped ceria.

The evolution of the sintered density with Mn content is shown in Fig. 4.

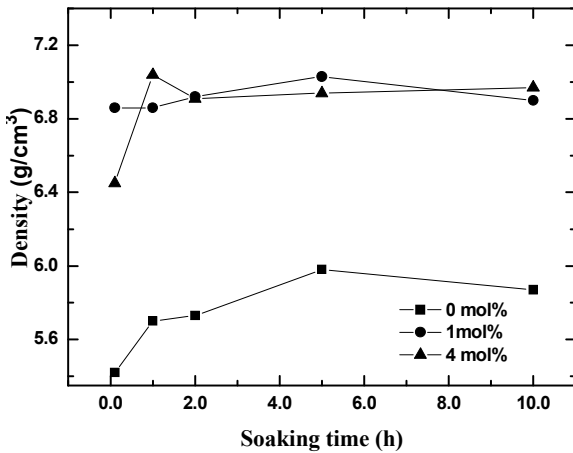


Fig. 3: Sintered density versus soaking time. Dwell temperature = 1300°C.

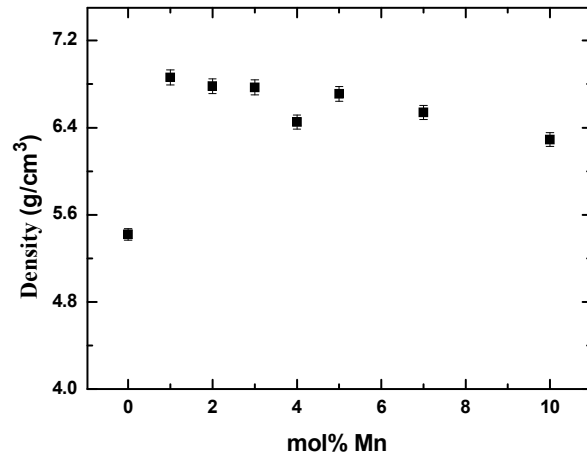


Fig. 4: Variation of the sintered density with Mn content.

The sintered density increases abruptly with small manganese additions. The optimized Mn content for densification occurs for $0 < x \leq 1$ mol%. For higher manganese contents a gradual decrease of the sintered density was verified, although that value for 10 mol% Mn is still higher than that of pure ceria. This effect was attributed to an increase in the temperature for maximum shrinkage with increasing of the Mn content [6].

These results show that Mn is an effective activator for cerium dioxide. In addition, small amounts of manganese (up to 1 mol%) and short soaking times (~ 0.1 h) are sufficient to produce high densification at only 1300 °C allowing for reducing the sintering temperature of ceria by more than 200 °C.

It was previously proposed that this effect was due to a liquid phase mechanism [8] by which a fast densification may be attained even in the first stage (rearrangement) of sintering. In a subsequent study [11], a different mechanism was proposed. Taking into consideration the increase in the grain size, it was suggested that Mn ions enhances the grain boundary mobility, due to large distortion of the surrounding lattice. It is important to note, however, that manganese may be present in different valence states, and its oxides are highly complex [12]. In addition, it was recently shown that the nature of manganese species in ceria may vary with the method of synthesis [13]. Moreover, after sintering Mn ions may be in solid solution with CeO_2 , or as a segregated phase along the grains boundaries, or even on the surface of grains. Then, the sintering mechanism of this system is a very complex phenomenon and requires further experiments.

The X-ray diffraction pattern of CeO₂-10 mol% Mn is shown in Fig. 5.

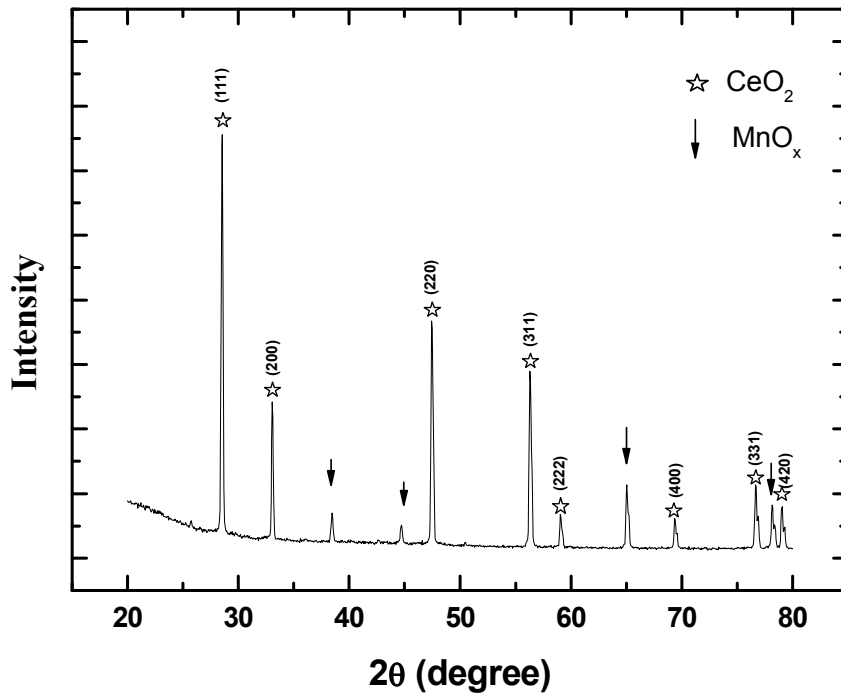


Fig. 5: X-ray diffraction pattern of CeO₂-10 mol% Mn sintered pellet.

In this pattern all diffraction peaks of pure CeO₂ (ICDD 34-394) were identified along with few low intensity peaks attributed to manganese oxide. It is known that the thermal decomposition process of manganese carbonate may give rise to several oxides. In addition, several other phenomena occur during the decomposition process such as phase change in the solid state, the release of CO₂, and reversible oxidation. For pure manganese carbonate [14] with increasing of the temperature, manganese dioxide (MnO₂) is first formed, followed by manganese sesquioxide (Mn₂O₃), and by hausmanite (Mn₃O₄) and, finally for temperatures in excess of 1027°C, manganese monoxide (MnO) is the most stable phase. However, the precise and unambiguous identification of MnO_x phases is not straightforward. Results in Fig. 5 indicates that Mn₃O₄ is the predominant phase formed at the sintering temperature.

Fig. 6 shows the Arrhenius plots of the total electrical conductivity of several sintered pellets. In the temperature range of measurements, the electrical conductivity of CeO₂ - x mol% Mn pellets does not exhibit any change of slope. Thus, independent on the content of the additive, the mechanism for conduction seems to be unchanged. The variation of the magnitude of the electrical conductivity for different samples is negligible, except for that containing 4 mol% Mn and sintered for 5 h at 1300 °C. This result indicates that manganese may be used as an activator to improve the densification of cerium dioxide without produce a considerable change in its electrical properties for the specific sintering conditions used in this work.

The increase in the electrical conductivity observed for 4 mol% Mn containing ceria sintered at 1300 °C for 5 h might be the result of increased electronic conductivity originating from the nature of the transition metal ion.

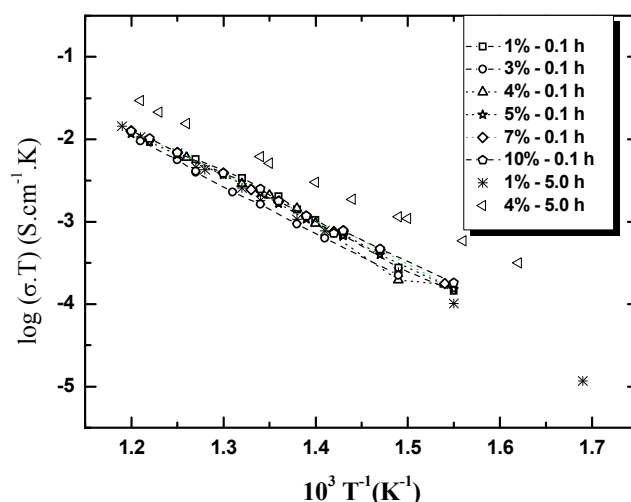


Fig. 6: Total electrical conductivity of CeO_{2-x} mol% Mn sintered pellets.

Conclusions

Cerium dioxide with high densification was obtained using Mn as sintering aid. The highest density values was attained for specimens containing 1 mol% Mn sintered at 1300 °C for only 0.1 h. The careful choice of the sintering profile allowed for obtaining specimens with similar electrical conductivity almost independent on the manganese content up to 10 mol%.

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