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Structural and chemical properties of cerium-magnetoplumbite in cerium based IT-SOFC compounds

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Yttria doped ceria reinforced with yttria doped alumina compound for IT-SOFC applications has been prepared by sol-gel method and sintered at 1300 °C, 1400 °C, 1500 °C. XRD, and SEM show the presence of a needle-like cerium-magnetoplumbite ($CeAl_{11}O_{17}$) phase in the compound; the oxygen deficient phase grows from the alumina phase by using ceria from the surrounding matrix and releasing oxygen ions As the sintering temperature is increased, the alumina phase is gradually transformed into $CeAl_{11}O_{17}$. Compared to the yttria doped ceria without reinforcement, the obtained compounds with ceria-magnetoplumbite show only a slight decrease of the Young elasticity modulus. However, the samples become brittle after backing in oxygen atmosphere (1000 °C, and 1500 °C).

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1. Introduction

Doping of ceria with various cations has been previously used to increase the ionic conductivity with one order of magnitude and to stabilize its crystalline structure into cubic-tetragonal phase [1-3], however the mechanical properties begin to degrade around 10% mol doping. Reinforcement of the doped ceria matrix with alumina, or yttria doped (150 ppm) alumina, has been proposed to further improve mechanical properties while slightly decreasing the ionic conductivity. In this case the appearance of the residual phase of hexagonal cerium-magnetoplumbite ($CeAl_{11}O_{17}$) has been previously reported [4] for this compound.

In order to investigate the influence of cerium-magnetoplumbite on IT-SOFC properties we have systematically prepared the sintered Ce-Y-Al complex of (10%)Y_2O_3:CeO_2 reinforced with (150 ppm)Y_2O_3:Al_2O_3, with the mass concentration ratio of the reinforcement (*0, 5, 10, 15)%* and analyzed the structural and chemical properties of sintered compound samples.

2. Experiment

The sintered bodies have been prepared from sol-gel nanopowders followed by mechanical homogenization and compaction in cylindrical shape, isostatic pressing at 10 M Pa, and sintering for two hours at 1300 °C, 1400 °C, si 1500 °C. The crystalline structure of the sintered bodies has been investigated by X-ray diffraction and Rietveld analysys using a Bruker-AXS D8 ADVANCE diffractometer equipped with a high-resolution array detector, and the morphology has been investigated by scanning electron microscopy using a Hitachi 2600N with LaB_6 cathode, clearly showing the presence of the acicular shape cerium-magnetoplumbite $CeAl_{11}O_{17}$. The chemical state of the samples has been further investigated by X-ray photo-electron spectroscopy using a VG ESCA MK-II system with VG 850 (R=100 mm, 150°) analyzer, VG310 spectrometer (0.96 eV resolution with Mg Kα), and p ~ 10^{-9} mbar pressure in the analysis chamber.

3. Results and discussion

X-ray diffraction (XRD) of the Ce-Y-Al sintered samples show the presence of three main crystalline phases: face-centered-cubic structure of CeO_2 (Fm-3m space-group) [5], rombohedral hexagonal structure of α-Al_2O_3 (R-3c:H space-group) [6], and the hexagonal structure of cerium-magnetoplumbite $CeAl_{11}O_{18}$ (P63/mmc space-group) [7]. No Y_2O_3 or other yttrium compounds crystalline phases were identified from the X-ray diffraction spectra of the sintered samples.

For the samples with 15% initial preparation content of α-alumina (see Fig. 1), during the sintering process a part of α-alumina phase is transformed into cerium-magnetoplumbite while using cerianite from the surrounding matrix. The process is enhanced at higher temperatures. when and a slight decrease of the α-alumina content can be observed. All XRD spectra have been analysed by Rietveld method in order to refine the phase structure and their relative weight content. The Popa anisotropic size-strain model [8] implemented in the MAUD [9] Rietveld analysis program was used in order to take into account the anisotropy of the crystallite growth rate along c-axis for cerium-magnetoplumbite. Previous studies show that during the transformation of ceria and α-alumina into cerium-magnetoplumbite, first, CeO_2 is converted to Ce_2O_3 in reductive atmosphere, and then is reacted with Al_2O_3 [10]. In the process oxygen is exhausted from the system which can not be evaluated in the refinement of XRD spectra. As the total mass of the system is not conserved in the transformation, the Rietveld results of quantitative analysis are not relevant for this compound system.

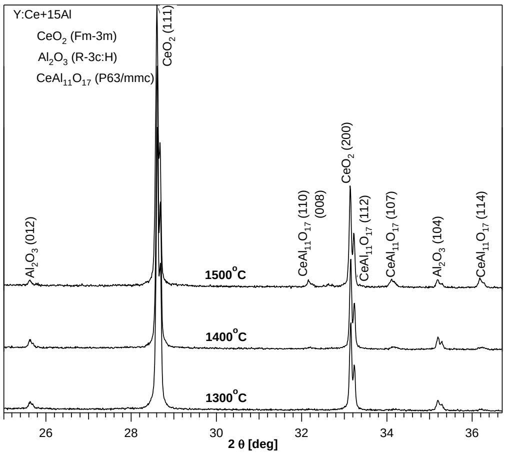

Fig. 1. X-ray diffraction patterns of (10%) yttria doped ceria with (15%) ((150 ppm) yttria doped alumina compound samples sintered at 1300 °C, 1400 °C, and 1500 °C samples and crystalline phases indexing of CeO_2 (Fm-3m), α-Al_2O_3 (R-3c:H), and Ce $Al_{11}O_{18}$ (P63/mmc).

Three codoped samples with initial content of 5%, 10%, and 15% doped alumina reinforcement and sintered at 1500 °C have been measured by *X-ray photoelectron spectroscopy* (XPS). For comparison a nanometric powder of ceria has been used as reference sample. For these samples the corresponding regions for cerium Ce 3d5/2 and Ce 3d3/2, aluminum Al 2p3/2, ytrium Y 3d5/2, oxygen O 1s, and carbon C 1s have been measured. Electrostatic chargeup has been compensated by electron shower and the energy calibration has been performed at the peak-top of the carbon C-C binding energy of 285 eV.

The Ce 3d spectra show the 3d5/2 and 3d5/2 doublets corresponding to the $4f^0$, $4f^1$, and $4f^2$ valence band electrons of Ce 4^+. Compared to CeO_2, the Y-Ce-Al compound samples sintered at 1500 °C show a energy shift toward higher binding energy which is increasing with the initial content of alumina in the compound, however the chemical state remains Ce 4+. This could be caused by local polarization of the crystallites during the reduction process of CeO_2 to Ce_2O_3. Similar effects caused by crystallites gradient composition, of surface reduction by Ar+ bombardment of ceria micro- and nanopowders [11] have been previously reported.

The Y 3d spectra for the Y-Ce-Al compound samples sintered at 1500 °C show a single photoelectron peak at 158.5 eV binding energy, similar to binding energy of YOx/Y of passivation layers on yttrium [12]. No states corresponding to Y_2O_3 can be observed. This shows that yttrium is fully doping ceria in the compound, and no residual phase of yttria remains in the preparation process.

The Al 2p3 spectra show both chemical states corresponding to Al_2O_3 (74.2 eV), and chemical states similar to that of suboxides AlO_x [13] (75.5 eV), the contribution of the later being about two times higher than the previous.

The O 1s spectra of CeO_2 nanopowder (see Fig. 2) show a maximum for the -OH anion at 532 eV, and a second maximum for the surface adsorbed molecular oxygen and/or H_2O at 534.5 eV. The Y-Ce-Al 1500 °C sintered compounds show photoelectron peaks, corresponding to CeO_2 (529.2 eV), Al_2O_3 (531.4 eV), and –OH (532 eV). As the initial content of Al_2O_3 increases, and therefore the content of the oxygen-deficient cerium-magnetoplumbite increases, one can observe that the content of the –OH photoelectron peak (532 eV) becomes larger than that of the CeO_2 photo-electron peak (529.2 eV), probably due to expelled oxygen ions remaining on the surface of the crystallites

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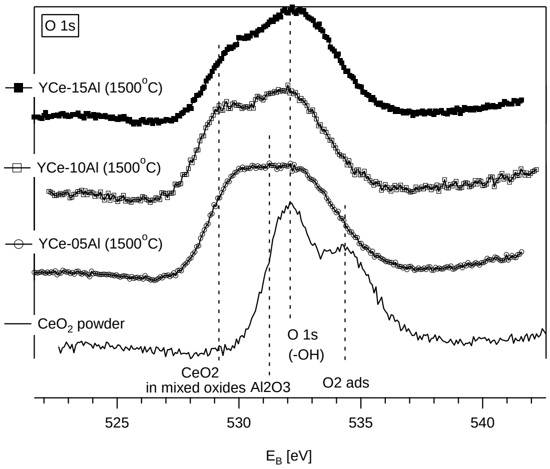

Fig. 2. O 1s XPS spectra for CeO_2 nanopowder and Y-Ce-Al compound samples with initial alumina content of 5%, 10%, and 15% sintered at 1500 °C.

Young elasticity modulus for 1500 °C sintered bodies with initial alumina reinforcement content of 5%, 10%, and 15% was measured to be 69.1 GPa, 61.6 GPa, and 66.2 GPa respectively, showing the decreasing tendency with the corresponding increase of the cerium-magnetoplumbite content.

Oxydative calcination of cerium-magnetoplumbite can transform this phase back into alumina. Two Y-Ce-Al samples have been calcinated: the first at 1000 °C using a closed furnace with low flowrate of oxygen, and the second at 1500 °C in an ventilated furnace. The calcinated samples have been analyzed by XRD and do not show the presence of cerium-magnetoplumbite phase, and at the same time the increase of the α-alumina content. As the sensitivity of XRD can not go below 1-2%, the samples surface have been further investigated by scanning electron microscopy (SEM).

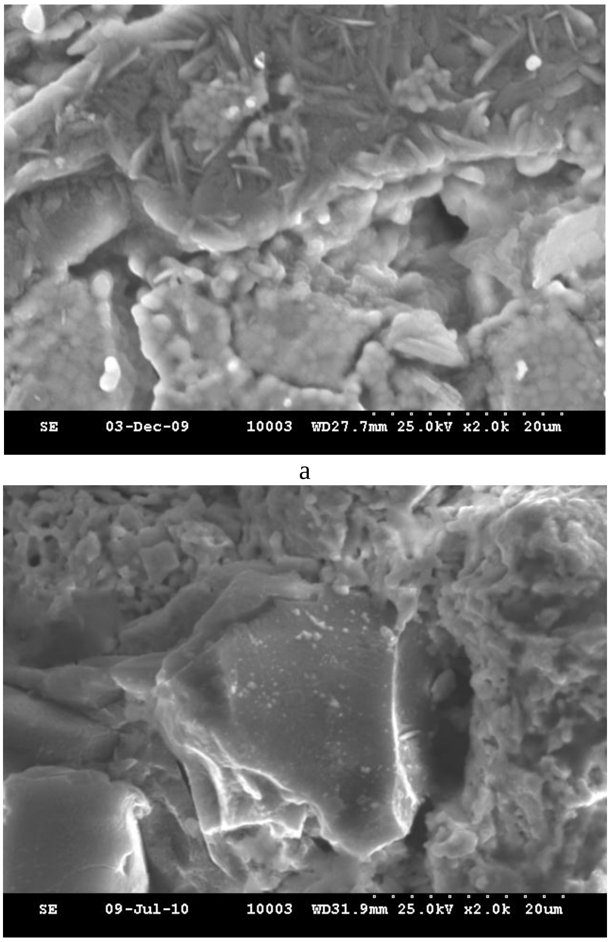

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Fig. 3. SEM image of 1500 °C sintered bodies of yttria doped ceria reinforced with yttria doped alumina showing: a) the acicular cerium-magnetoplumbite $CeAl_{11}O_{17}$, and b) the disappearance of $CeAl_{11}O_{17}$ after oxidative calcination

The cerium-magnetoplumbite in the sintrered samples (before oxidative calcination) can be distibguished by their acicular and lamellar shape (see Fig. 3a) and disappears almost completely on the calcinated samples (see Fig. 3b). However, the samples become brittle after calcinations.

4. Conclusions

Yttria doped ceria reinforced with yttria doped alumina codoped compounds prepared by sol-gel method and sintered at 1300 °C, 1400 °C, 1500 °C in closed ovens systematically show the presence of ceria, α-alumina, and cerium-magnetoplumbite. Phase composition refined from XRD spectra show that α-alumina is partly transformed into cerium-magnetoplumbite while consuming from ceria. No residual phase of yttria has been detected by XRD.

XPS analysis of yttrium show no Y_2O_3 chemical bondings and a photoelectron peak at the energy value similar to that of YOx/Y (158.5 eV), which could be attributed to the doping of ceria by yttria. Chemical bonding for aluminum show both chemical states corresponding to Al_2O_3 (74.2 eV), and a major contribution of suboxides AlO_x (75.5 eV) originating from the cerium-magnetoplumbite. XPS of cerium show 4+ chemical state and a slight energy shift of the Y-Ce-Al compounds due to possible polarization effects of the crystallites induced by concentration gradients. The oxygen XPS spectra show the presence of oxygen ions of the surface of crystallites which concentration increases with the percentage of cerium-magnetoplumbite in the Y-Ce-Al compound. Oxydative calcinations transform cerium-magnetoplumbite crystalline phase back into ceria and α-alumina.

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