

Colored Zirconia with high absorbance and solar selectivity

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ABSTRACT

White Zirconium oxide is featured by low absorptance, but addition of specific secondary coloring agents enables to increase its solar selectivity comparable to that of conventional materials used in solar power plants. Colored zirconia, generally used for decorative purposes, has thus the possibility to widen its application fields and to be a cheaper competitor of other non-oxide materials that require expensive processing routes. Optical characterization put forth this novel aspect for constituting bulk solar absorbers operating at high temperatures.

Keywords: ZrO₂; scanning electron microscopy; solar absorbance; optical properties.

Nowadays, the use of clean and renewable energy sources is one of the main factors to limit climate-changing pollution, mostly caused by fossil-fuel burning power plants. Increasing energy efficiency and the amount of energy that we get from renewable sources are essential steps to reduce the usage of fossil fuels. For example, solar energy can generate electricity and/or heat, and holds enormous potential, especially as the technology will be advancing and prices considerably fallen. However, one of the actual stumbling block in the development of Concentrating Solar Power (CSP) plant is the efficiency of the radiation collection and heat transfer that improve with increasing working temperature. Stability of the receiver above 650°C is still a critical issue [1,2]. The exploration of novel ceramic materials for use as bulk absorbers in thermal solar energy plants operating at temperatures higher than current systems is a key for enhancing the overall system efficiency and is attracting always more interest [3]. The perfect sunlight absorber for CPS technology must possess good mechanical and chemical stability at high temperatures, high ratio between sunlight absorbance and thermal emittance, good thermo-mechanical properties. One typical ceramic material currently under consideration for tower solar receivers is silicon carbide (SiC), a non-oxide dark semiconductor with good sunlight absorption and high oxidation resistance, but also featured by expensive and delicate production techniques that include the use of reducing sintering environment [4,5].

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Refractory oxides, like yttria, alumina, hafnia, zirconia are by now materials with large technological interest, well-assessed production techniques and, most of all, their consolidation is achievable in air furnace, thus enabling to get near net complex shapes at low costs. Conventional white or yellow zirconia ceramics are not suitable for being used as sunlight receiver due to low absorption towards sunlight radiation, but addition of secondary phases may change the overall scenario. This is the case of black zirconia and black alumina which displayed optical properties and thermal emissivity appropriate for solar absorber applications [6–8].

In the case of Zirconium oxide (ZrO_2), various colorations can be attributed by oxygen vacancies [9], carbon permeation in reducing environment [10] or by change of the amount and type of dopant or secondary phase. These start from white, yellow, orange and span to pink, purple, green, blue, brown and black. Details on coloring agent type, phase composition and processing method are very scanty and mostly regard white-yellow nuances for dental applications [11,12], a minor market slice also includes ceramic back plate for cellphone, parts for colored watch and ceramic jewelry [13]. The advantageous use of modified ZrO_2 for sunlight harvesting would further increase and ennoble the market of such a relatively cheap ceramic. Therefore, in the search for always better performing materials, we have addressed our interest towards colored zirconia, i.e. containing different types and amount of coloring agents.

Yttria-stabilized zirconia (YSZ) cermet-based spectrally-selective surfaces have been explored for high-temperature solar absorber applications in the form of multilayered surfaces comprising two sunlight-absorbing W–Ni–YSZ cermet layers with different W–Ni volume fractions inside the YSZ matrix giving promising results even upon long term exposition at 600°C under vacuum [14].

The present study deals with the characterization of secondary phases in colored zirconia and correlation with their optical properties in view of their possible use as bulk solar absorbers for high temperatures.

Commercial Tosoh powders (white: TZ-3YB, orange: TZ-PX-283, green: TZ-PX-560, cyan: TZ-PX-498A, black: TZ-Black-B) were linearly pressed under 100 MPa and sintered at 1500°C for 1 hour in air furnace (Nannetti 1800) to obtain discs with about 15 mm diameter and 3 mm height. After sintering, the bulk densities were measured by Archimedes' method. Crystalline phases of the sintered ceramic were identified by X-ray diffraction (XRD, mod. D8 Advance - Bruker, Germany). The microstructures were polished with diamond paste to 0.25 μm and were analyzed with scanning electron microscopy (FE-SEM, Carl Zeiss Sigma NTS GmbH, Oberkochen, Germany) and energy dispersive spectroscopy (EDS, X-Act, INCA Energy 300, Oxford Instruments, Abingdon, UK). Mean matrix grain size, amount of porosity and secondary phases were determined on micrographs of polished sections using image analysis (Image-Pro Analyzer 7.0, Media Cybernetics, Silver Spring, MD, Rockville, USA).

Hemispherical reflectance and total transmittance of samples were measured using two instruments: a double-beam spectrophotometer (Perkin Elmer Lambda900) with a 150-mm diameter

Spectralon®-coated integrating sphere for the spectral range 0.25-2.5 μm , and a Fourier Transform spectrophotometer (FT-IR Bio-Rad "Excalibur") with a gold-coated integrating sphere and a liquid N_2 -cooled detector for the wavelength region from 2.5 to 15.7 μm . All the data have been taken for quasi-normal light incidence angle. High temperature emittance and spectral selectivity were then extrapolated using Kirchhoff's law.

Vickers microhardness (HV) was measured on the polished surface, with a load of 9.81 N, using a Innovatest Falcon 505 (Rupac, The Netherlands) indenter. The value provided is the average of 10 indentations.

Representative images of the microstructure of the various Zirconia samples are reported in Figure 1, with microstructural details summarized in Table I. The main crystalline phase was for all samples yttria-stabilized ZrO_2 , with traces of baddeleyite in the orange and black samples. Secondary phases detected (Table 1) were NiO in the green sample, NiAl_2O_4 in the cyan sample and to and Zn/Co-oxide in the black one. By coupled SEM-EDS analysis only in the case of white zirconia no secondary phase was found. According to EDS identification, scattered alumina particles, below 0.5 vol%, were found in the orange sample. The coloring agent of the green sample was 3.5-4 vol% NiO; cyan disc contained both Al_2O_3 and a Ni-based spinel, NiAl_2O_4 , in amount around 1 and 18 vol%, respectively, while the black sample contained about 2.5 vol% of a mixed Co-Zn ferrite, $(\text{Co,Zn})\text{Fe}_2\text{O}_4$.

Zirconia mean grain size (see Table I) was rather homogeneous and similar amongst the samples, displaying average mean grain size between 0.25 and 0.45 μm ; for each sample the grain size distribution was monomodal with limited coarsening compared to the initial grain size. Only the black disk displayed some grains coarsened up to about 2 μm . Porosity was null for colored samples, whereas around 0.1-0.3 vol% for the white and orange, respectively.

Al_2O_3 is a common additive for ZrO_2 -based materials for promoting densification, when doping amounts are introduced [15], or improving the mechanical properties, when higher contents originate a wide series of composites [16]. When the Al^{3+} ion substitutes Zr^{4+} ion in yttria-stabilized tetragonal zirconia polycrystals within the solubility limit, oxygen vacancies might be generated to compensate effective charges. Over the solubility limit, around 0.2 wt%, secondary phases are formed [17], in agreement with our experimental findings (white and orange samples).

As for the other secondary phases present in more abundant content, NiO has been already considered in a commercial product consisting of Ni–NiO graded-index solar selective absorber on aluminium substrate for mid-temperature selective surfaces [18,19]. This commercial absorber coating has a solar absorptance in the range 0.94–0.96 and thermal emittance of 0.13–0.15 and has passed stability tests according to the procedures recommended by International Energy Agency (IEA) Task X Working Group on accelerated life testing of solar energy materials. Moreover, NiO has been used as pigment for aluminum oxide with enhanced high-angle solar absorptance [20,21]. To date, no data are available for NiO dispersed as second

phase in a zirconium oxide matrix, but in view of NiO high melting point, 1955°C, and promising results in form of coating, its stability at operation temperatures of 1000°C should be guaranteed.

As for the cyan sample, NiAl_2O_4 is a partially reverse spinel with nickel ions in octahedral sites and aluminum ions in tetrahedral sites. Due to its high activity and resistance to corrosion, nickel aluminate has been used in various catalytic applications and high temperature fuel cells, but is currently unknown for solar absorbers [22]. However, given its solubility in water, it should be protected from direct exposure to atmospheric agents and designed in protected environment, like for other non-oxide materials which are sensitive to oxygen at high temperatures.

Lastly, Cobalt-ferrite has been widely studied as thin-film light absorber for solar cells and has been successfully deposited on glass demonstrating an increased absorbance in the visible-UV region [23]. In addition, annealing tests up to 1000°C demonstrated a notable stability of this phase, this suggesting suitability for employ as bulk receiver [24].

Entering into the optical properties, conventional (white) ZrO_2 is known to show some regions of optical transparency. Therefore, to assess the samples spectral absorptance, both the spectral hemispherical reflectance $\rho'(\lambda)$ and the total transmittance $\tau(\lambda)$ needed to be measured. Figure 2a shows the experimental transmittance curves, while Figure 2b depicts the spectral absorptance $\alpha(\lambda)$ (which, from the Kirchhoff's law is equal to the spectral emittance $\varepsilon(\lambda)$), obtained from the measured quantities according to the following relationship:

$$\alpha(\lambda) = 1 - \rho'(\lambda) - \tau(\lambda) = \varepsilon(\lambda) \quad (1)$$

From Figure 2a it is possible to see that the different doping species added to white ZrO_2 powders progressively decrease the sample transmittance, introducing additional absorption bands in the samples. This is particularly evident comparing the white and orange transmittance curves: the orange spectrum can be easily seen as an envelope of the white sample spectrum with additional absorption bands given by the orange dyes. The green and black samples show increasingly lower residual transmittance, while the cyan pellet results completely opaque. As for the absorptance, Figure 2b, the most absorptive sample is the black one. Cyan and green ceramics are also highly absorptive, with some spectral differences each other due to their different doping. All samples are characterized by a high absorption (or emittance) range located between 6 and 13 μm wavelength.

The described optical properties allowed to estimate the optical parameters useful for solar thermal applications, i.e. the integrated solar absorptance α and integrated thermal emittance $\varepsilon(t)$ at the temperature T:

$$\alpha = \frac{\int_{0.3\mu\text{m}}^{3\mu\text{m}} \alpha(\lambda) \cdot S(\lambda) d\lambda}{\int_{0.3\mu\text{m}}^{3\mu\text{m}} S(\lambda) d\lambda} \quad (2)$$

$$\varepsilon = \frac{\int_{0.3 \mu m}^{15.7 \mu m} \varepsilon(\lambda) \cdot B(\lambda, T) d\lambda}{\int_{0.3 \mu m}^{15.7 \mu m} B(\lambda, T) d\lambda} \quad (3)$$

Where $S(\lambda)$ is the sunlight spectrum [25] and $B(\lambda, T)$ the blackbody spectrum at the considered temperatures, which have been varied between 400 and 1500 K.

The plots of calculated temperature-dependent thermal emittance and the spectral selectivity $\alpha/\varepsilon(T)$ are shown in Figure 3, together with α values. The data of a SiC reference pellet is also included for comparison [26].

The study of Figure 3 allows to make some comments: the black sample shows both the highest solar absorptance and thermal emittance of ZrO_2 ceramics at all temperatures, as expected. Its spectral selectivity is around unity, in agreement with a previous report [6]. It is worth to notice, however, that these characteristics make the black sample fully comparable to silicon carbide, which is the most advanced material used to date in high temperature solar applications, e.g. in solar tower plants. In fact, the solar absorptance of black ZrO_2 and SiC is similar, and even slightly higher in the oxide, and the spectral selectivity is practically the same for temperatures equal or higher than 700K. On the contrary, the white sample is not suitable for the proposed application, due to both poor sunlight absorptance and lacking of spectral selectivity at all temperatures. The orange ceramic behaves better than the white one (higher sunlight absorption and higher values of α/ε ratio), but the improvement is still not satisfactory. Cyan, and especially green samples are more promising. The cyan pellet shows $\alpha=0.6$ and the highest emittance among colorful samples. At lower temperatures the high emittance penalizes the spectral selectivity, but for temperatures from 1200K on, the α/ε value approaches unity, making the sample worth of evaluation for systems operating at these temperatures. Particularly promising among the investigated samples is the green ZrO_2 . In fact, it is characterized by a solar absorptance only slightly lower than the black sample (0.8 vs 0.9), but by an appreciably lower thermal emittance, especially at increasing temperatures, pushing above unity its spectral selectivity for temperatures higher than 600K and making it the only spectrally selective ZrO_2 sample among those examined. Therefore, the green sample favorably compares even to SiC, due to its spectral selectivity. The slightly lower solar absorptance does not seem a critical problem, as it has been shown that the absorptance can be increased, for instance with surface texturing induced by physical or chemical techniques [26,27]. Finally, as a general consideration about colored ZrO_2 ceramics, it is interesting to notice that typically the thermal emittance decreases with temperature. This is due to the peculiar band structure of their spectral absorptance, differentiating the behavior of these oxides from that of SiC, as well as from that, for instance, of some non-oxide refractory materials like UHTCs, which, instead show step-like absorptance spectra and consequently an emittance increasing with temperature [26,28,29].

Another relevant aspect for the use of these materials for absorbers in solar power plants is the resistance to abrasion that may be caused by dust wind in desert areas. In this respect, it seems that the addition of the present coloring agents does not compromise the hardness of the native white ZrO_2 , as summarized in Table I. Actually, hardening has been measured upon addition of the spinel phase in the cyan sample.

The present study is a first investigation of the emissivity of colored zirconia as a function of coloring phase and calculated over the 400 to 1500K temperature range.

This work poses a novel perspective over conventional ceramic oxides generally used for decorative purposes to an absolutely new application as solar absorber. We believe that some of the colored refractory oxides can have a promising potential for sunlight exploitation, once their optical properties will be thoroughly characterized and understood.

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Figures captions

Graphical abstract

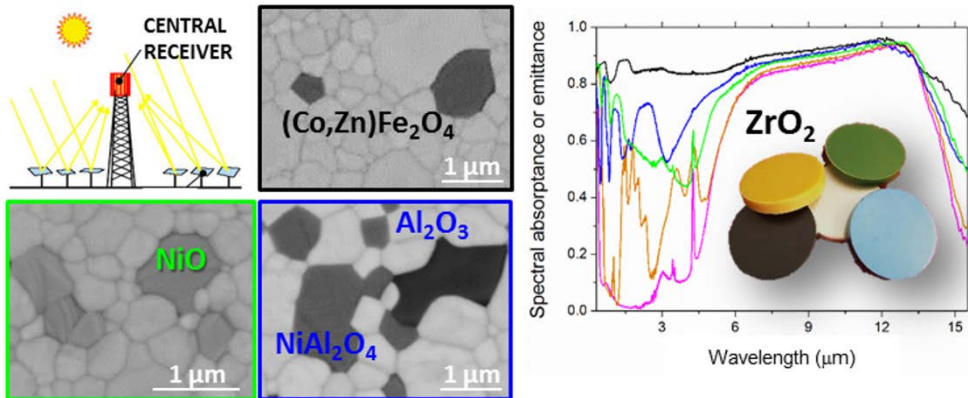


Figure 1: SEM-EDS analysis and phase identification of conventional a) white and b) orange ZrO_2 and of colored ones: c) green, d) cyan and e) black.

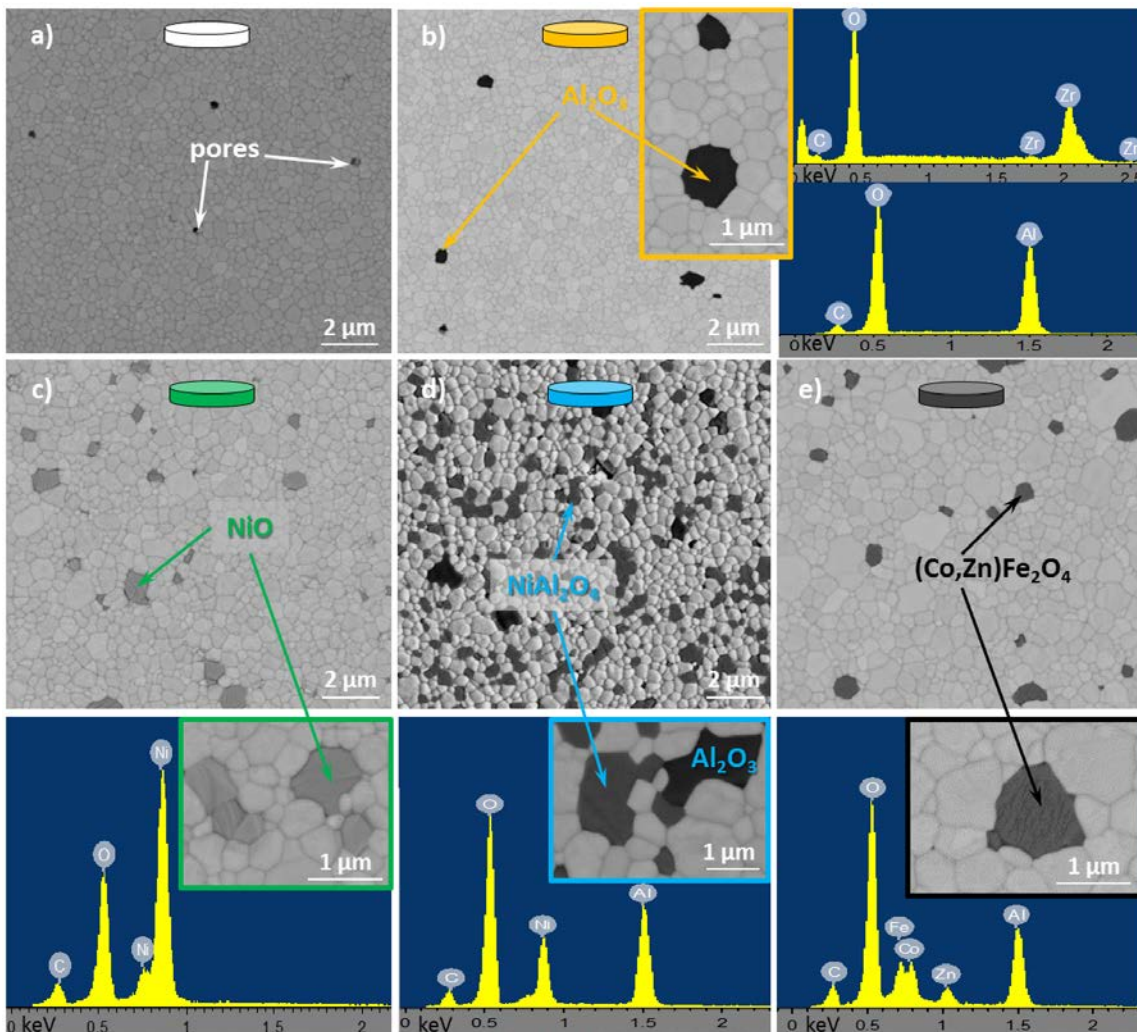


Figure 2: Experimental total transmittance (a) and spectral absorptance or emittance (b). The vertical axis in plot (a) is enlarged for a better readability of the curves.

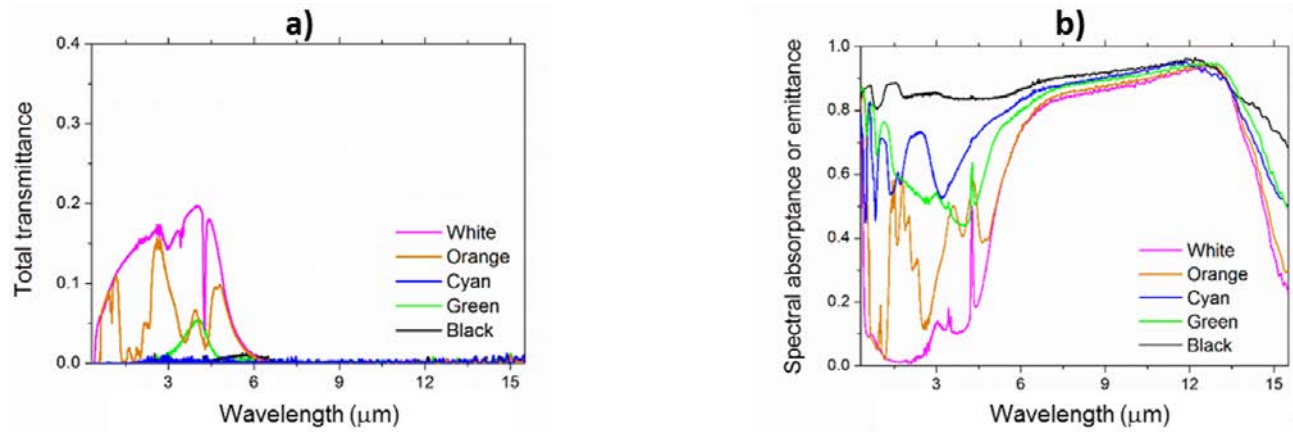


Figure 3: (a) Thermal emittance $\epsilon(T)$ and (b) spectral selectivity $\alpha/\epsilon(T)$ calculated for temperatures T from 400 to 1500K. Each plot also shows as histograms the values of the integrated solar absorptance α . SiC reference is reported for comparison [26]. The dashed red line in the histogram plots represents the solar absorptance value for SiC.

