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Fabrication of black-colored CuO–Al_2O_3–ZrO_2 ceramics via heterogeneous nucleation method

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Abstract

We have reported the fabrication of black-colored CuO–Al_2O_3–ZrO_2 ceramics via a heterogeneous nucleation method. The as-prepared ZrO_2 ceramics exhibit a deep and genuine black color with a uniform color distribution. PEG2000 has been used as the dispersants for the preparation of ZrO_2 nanopowder solutions. Then Cu and Al hydrates have been introduced into the solutions with tailored pH values for the fabricated coated ZrO_2 powders, to induce the heterogeneous nucleation of the colorants within ZrO_2 matrixes. CuO and Al_2O_3 transformed from Cu and Al hydrates act as the black colorant and colorant stabilizer, respectively, which make the fabrication of black ZrO_2 at a relatively low sintering temperature of 1200 °C. The fabricated black-colored ZrO_2 ceramics are characterized by scanning electron microscopy, X-ray diffraction and optical reflectance spectrum. It can be believed that current work could present a facile and cost-saving method for fabrication of black-colored ZrO_2 ceramics without using any toxic chromophore elements.

Keywords: A. Grain growth; B. Composites; C. Optical properties; E. Functional applications

1. Introduction

Recently, colored ZrO_2 ceramics have attracted great interest due to their beautiful colors, metallic lusters, none hypersusceptibility, excellent mechanical properties and high wear resistance [1]. It is believed that colored ZrO_2 ceramics could be an excellent candidate to replace metallic decorative materials, which are widely used as ornament components, optical components, and structural parts [2–5]. Among the colored ceramic family, black-colored ceramics are required to completely absorb all the visible lights. However, it is a great challenge to fabricate the ZrO_2 ceramics with a deep and genuine black color, especially at high sintering temperatures [6].

Many efforts have been put into the fabrication of black-colored ZrO_2 ceramics. Up to date, there have been two common strategies to fabricate black-colored ceramics. One is to permeate the carbons into the ceramic matrix in reducing atmosphere or carbon atmosphere [7]. However, it is inevitable to generate the color difference between the inside and the surface within one sample. The other is to introduce coloring components into the ceramic matrix to absorb all of the visible lights, in which a number of oxide group such as Cr, Co, Er, Ho, Fe, Mn, Nb, Ni, Pr, Tm, Ti, and V, are often utilized as the colorants. For example, colorants containing Cr have been used to black ZrO_2 ceramics [8]. Meanwhile, Cr is a severe pollution source due to its high toxicity nature. Progress has been made to limit the quantity used in the host matrix [9], or restrict from using the toxic elements (e.g. $CoFe_2O_4$ spinels were used as the black colorant [9]) However, the coloring elements (e.g. Co and Fe) would evaporate easily at elevated temperatures. In order to lower the sintering temperature, transition metal oxides such as Fe_2O_3 [10] and CuO [11] are often used as the sintering additives.

Even much progress has been made for the fabrication of black-colored ceramics as motioned above, new techniques are still highly desired to meet the challenges, e.g. to get a deep and genuine black color with a uniform color distribution via a green method. In this paper, we report the fabrication of uniform and deep black-colored CuO–Al_2O_3–ZrO_2 ceramics

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via a heterogeneous nucleation method [12]. CuO and Al_2O_3 have been used as the black colorants and colorant stabilizations, respectively. It is can be expected that current work could present an alternative green route for coloring ZrO_2 ceramics by reducing the sintering temperature.

2. Experimental procedure

A commercially available nanosized 3Y-TZP powder (ZrO_2–3 mol%Y_2O_3, YSZ-DM-3.0, Farmeiya advanced materials Co. Ltd., China) with a purity of 99.4% was used as the raw materials. The average size and the specific surface area of the powders are ∼124 nm and 17.9 m^2/g, respectively. In present work, the black-colored ZrO_2 ceramics are fabricated by the heterogeneous nucleation method. In a typical process, 3Y-TZP particles, mixed with 1 wt% dispersants of polyethylene glycol (PEG2000), were firstly dispersed in water up to 5% (w/v) under ultrasound for 60 min to limit the particle agglomeration. The precursor solution was prepared by dissolution of metal nitrates in aqueous solution. 0.1 mol/L $Cu(NO_3)_2$ (Sinopharm Chemicals, analytically pure) and 0.1 mol/L $Al(NO_3)_3$ (Sinopharm Chemicals, analytically pure) were slowly added into the powder suspension as 10 vol% under magnetic stirring at room temperature. At this stage, the pH value of the precursor solution was measured to be ∼4.5. Then 0.01 mol/L aqueous ammonia was dropped into the suspension under strong magnetic stirring to tailor the pH value of the suspension ranged in 7.1–7.5. Then stop the addition of aqueous ammonia. The resultant suspension was continuously stirred for 2 h and then filtered. The obtained powders were washed by the de-ionized water for more than three times and dried in a conventional oven at 60 °C for 24 h in air. The prepared powders were then pressed into pellets and sintered at 1200, 1300 and 1450 °C with an annealing time of 2 h in a Nabertherm electric furnace at a heating rate of 5 °C/min.

Differential Scanning Calorimetry (DSC) and thermogravimetric (TG) analyses were performed in a NETZSCH model STA 409 PC/PG. The experiments were carried out in an Al_2O_3 crucible from 30 to 1234 °C at a heating rate of 10 °C/min under air atmosphere. The average particle size of 3Y-TZP powders were measured by dynamic light scattering (3000HS Zetasizer, Malvern, England). The XRD patterns were recorded on a RINT-2500 spectrometer (Rigaku, Japan) with a Cu Kα radiation. Archimedes' principle was used to measure the bulk densities. The theoretical density values used for this calculation have been determined by Rietveld analysis of the diffraction data obtained from the samples of 3Y-ZrO_2 (5.80 g/cm^3 for *m*-ZrO_2 and 6.09 g/cm^3 for *t*-ZrO_2). The microstructure observation was carried out by field emission scanning electron microscope (FESEM, LEO1530, Germany), equipped with an energy dispersive X-ray analyzer (EDX). The UV–vis spectra were measured by a spectrophotometer (U-3310, Hitachi, Japan) at the room temperature.

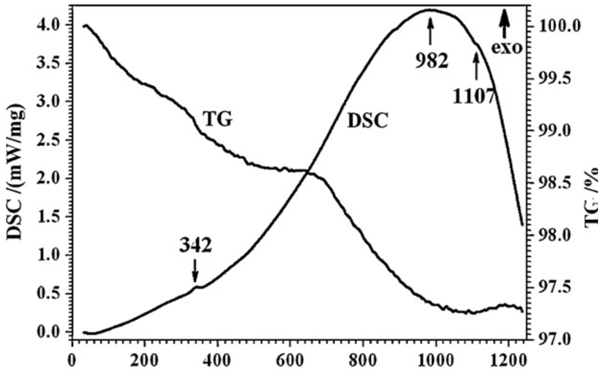

Fig. 1. DSC/TG curves of the 3Y-TZP powders coated by PEG2000 consisting $Al(NO_3)_3$ and $Cu(NO_3)_2$.

3. Results and discussion

Metal hydroxides precipitated from the solutions are usually through two routes, namely heterogeneous nucleation and homogeneous nucleation. Normally, the preparation of powders with controlled characteristics by chemical methods relies on the homogeneous nucleation [13]. However, for 3Y-TZP powders coated by PEG2000 with tailored pH values, the nucleation of the ceramic colorants from the coated materials could be predominantly heterogeneous rather than homogeneous [12]. The large surface of 3Y-TZP nanopowders could be the preferred heterogeneous nucleation sites, thus diminishing the free energy barrier and facilitating nucleation [14]. This could promote the formation of coloring phases, significantly decrease the volatilization and improve the uniformity of coloring elements within the ceramic matrix. To determine the sintering process of the black ZrO_2 ceramics, we have performed DSC/TG analyses of the powders coated by PEG2000 consisting $Al(NO_3)_3$ and $Cu(NO_3)_2$, shown as Fig. 1. The TG curve suggests that the total weight loss of the sample after sintering is ∼2.7 wt%. The weight loss of ∼1.2 wt% below 400 °C can be mainly attributed to the vaporization of H_2O and removal of PEG2000 within the samples. It therefore discloses the weight loss with respect to the volatilization of the colorants is ∼1.5 wt%, suggesting current work is environment-friendly method for the fabrication of colored ceramics through reducing the volatilization of toxic metal. Considering the DSC scans, the exotherm reaction at ∼342 °C can be assigned to the decomposition of ammonium nitrates within the coated layer of 3Y-TZP powders including ammonium hydroxide, Cu nitrate and Al nitrate. A second weight loss occurred between ∼700 and 1000 °C might be attributed to some complex interactions between the oxides and 3Y-TZP (e.g. the dissolution of CuO in 3Y-TZP). Moreover, a slight endothermic reaction occurs at ∼1107 °C, which cannot be derived from the reactions among CuO, Al_2O_3 and ZrO_2, due to the limited solubility of CuO in ZrO_2 and the lack of existence of Cu–Zr–Al–O compounds [16]. Thus, we attribute it to the reaction between CuO and Y_2O_3 [17–19]. This could lead to the formation of a low-melting point interfacial compound at the grain boundaries and particle surfaces [20], to make the uniform distribution of the colorant phases within the ceramic matrix. According to the analysis mentioned above, we carry out the fabrication of the colored ZrO_2 ceramics by

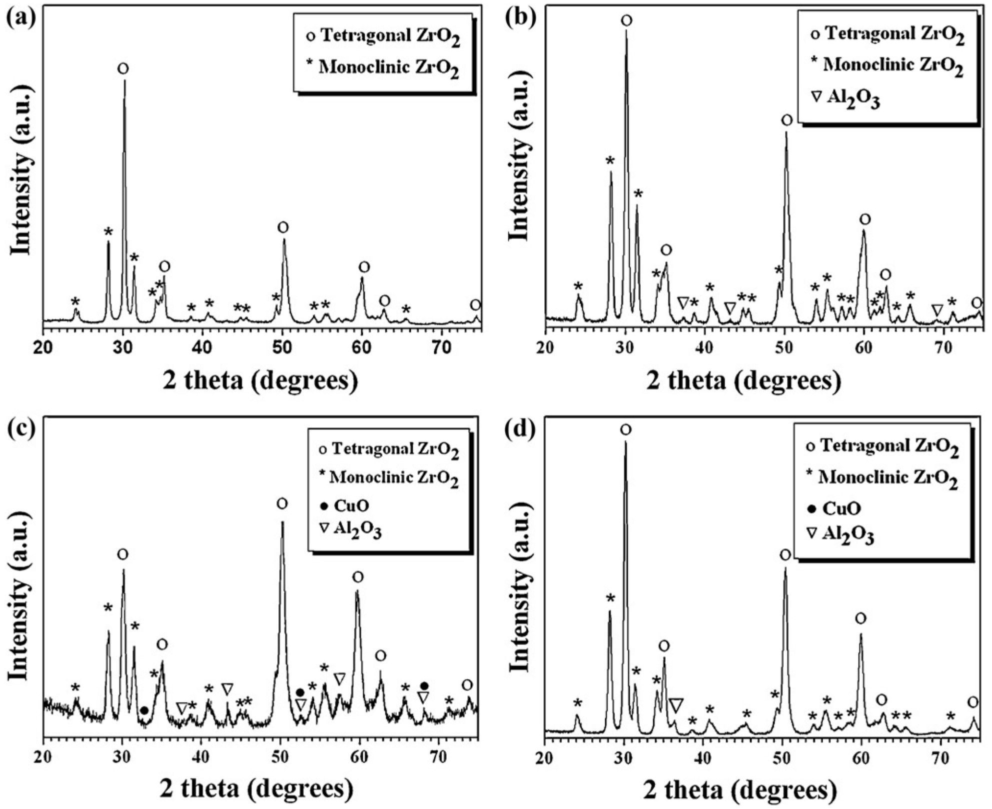

Fig. 2. (a) XRD pattern of the as-prepared coated powders. (b–d) XRD patterns of black-colored $CuO–Al_2O_3–ZrO_2$ ceramics sintered at 1200, 1300 and 1450 °C, respectively.

sintering at 1200–1450 °C, to ensure the complete reactions of the inorganic pigment within the ceramic matrix and get the optimal sintering temperature.

Fig. 2 shows the phase evaluation of the as-prepared composite powders with the sintering temperatures. Fig. 2a is the XRD pattern of the 3Y-TZP powders dispersed by PEG2000 and coated by Al and Cu hydrates. No other phases can be observed besides tetragonal and monoclinic ZrO_2, which are the same as that of the raw materials. It implies that the hydrates of Al and Cu are amorphous at this stage. When sintered at 1200 °C for 2 h (Fig. 2b), the peaks of Al_2O_3 exhibit rather clear, indicating that Al_2O_3 crystals have developed well. The co-existence of tetragonal and monoclinic ZrO_2 can be attributed to the introduction of Cu hydrates in the raw materials of 3Y-TZP powders [18,21,22]. Cu hydrates will be transformed into CuO [15], followed by the solid–liquid reaction between CuO and Y_2O_3, leading to the depletion of Y_2O_3. With further reaction between molten CuO and Y_2O_3 as segregated to the grain boundaries, more tetragonal ZrO_2 is destabilized and transformed to monoclinic phase. No any phase containing Cu has been detected, suggesting the coloring phase of CuO is still amorphous. CuO is crystallized once the sintering temperature is up to 1300 °C (Fig. 2c) and will be evaporated at a higher temperature of 1450 °C, which results in too a little CuO phase to be detected by XRD (Fig. 2d).

Fig. 3 presents the microstructures of different specimens fabricated at various sintering temperatures. They densities of the samples sintered at 1200, 1300, and 1450 °C are measured to be ∼96.2%, 97.4% and 98.7%, respectively (the presence of *m*-ZrO_2 phase in the sintered sample has been taken into account for the calculation of the theoretical density). Fig. 3a and b are the SEM images of the samples sintering at 1200 °C under different magnifications. It implies that they possess equiaxial grains with an average size of ∼400 nm. The size distribution of the gains is relatively uniform. Notably, liquid-like phases can be commonly observed within the matrix grain boundaries, which is distinctively different from the samples sintered at 1300 (Fig. 3e and f) and 1450 °C (Fig. 3g and h). The similar structures were also observed in the reported work that Cu-enriched grain-boundary layer of several nanometers had been formed in CuO doped 3Y-TZP matrix [23]. Fig. 3c and d display the typical EDX spectra recorded from the boundaries and grains, respectively, shown as the marked areas of A and B in Fig. 3b. They clearly suggest the grains are ZrO_2 and the boundaries contain Al, Cu, O and Zr elements, suggesting the Cu-enriched colorant phase might exist mainly within the boundary regions. According to the XRD results, it suggests that the liquid-like phase should be amorphous. It can be interpreted as the fact that CuO derived from the decomposition of the Cu hydrates melt at 1134 °C in air [15]. The molten CuO then reacts with Y_2O_3 at the powder surfaces to form CuO-high-content liquid phase within the grain boundaries [21]. The liquid-like phase within the grain boundaries has two effective efforts for the fabrication of the colored ceramics. One is to enhance the ion mobility during the sintering process. The high ion mobility can be related to a fast grain-boundary diffusion,

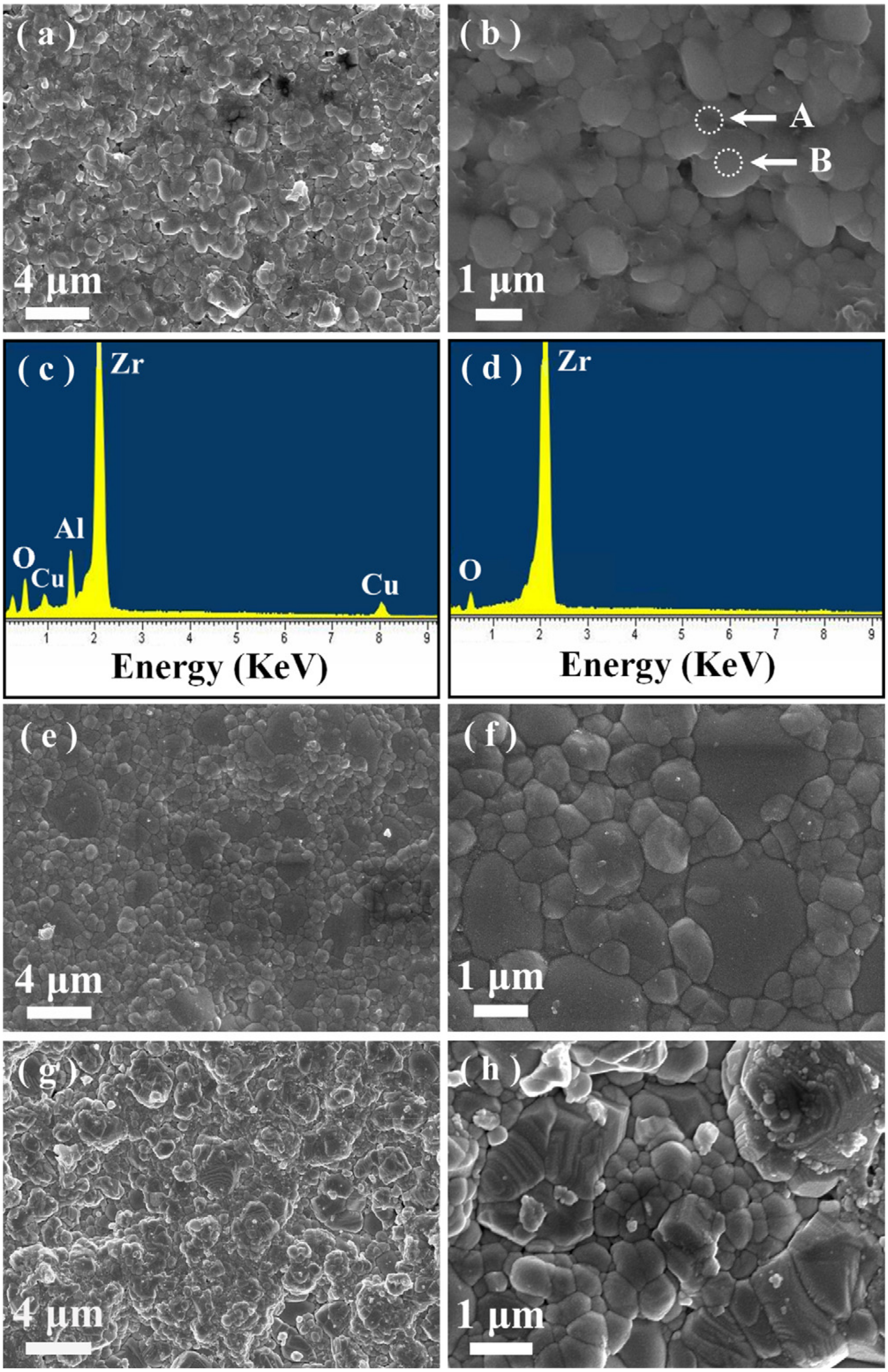

Fig. 3. (a and b) Typical SEM images of the black-colored CuO–Al_2O_3–ZrO_2 ceramics sintering at 1200 °C under different magnifications. (c and d) Typical EDX spectra recorded from the marked areas of A and B in (b). (e and f) Typical SEM images of the samples sintered at 1300 °C under different magnifications. (g and h) Typical SEM images of the sample sintered at 1450 °C.

which results in a higher densification rate, and consequently leads to remarkably accelerate the densification at lower temperatures and shorter sintering times. The other is that the CuO colorants can be prompted to be dissolved into the Y-TZP matrix by the Cu-enriched grain-boundary liquid layer, owing to the larger contact areas between 3Y-TZP particles and CuO-high-content liquid phase, which facilitates the uniform distribution of the colorants within the ceramic matrix. However, in higher sintering temperature of 1300 and 1400 °C (Fig. 3e–h), the liquid-like phase seems disappearing in the 3Y-TZP grain boundary areas, suggesting the coloring phase would evaporate caused by the high sintering tempera-

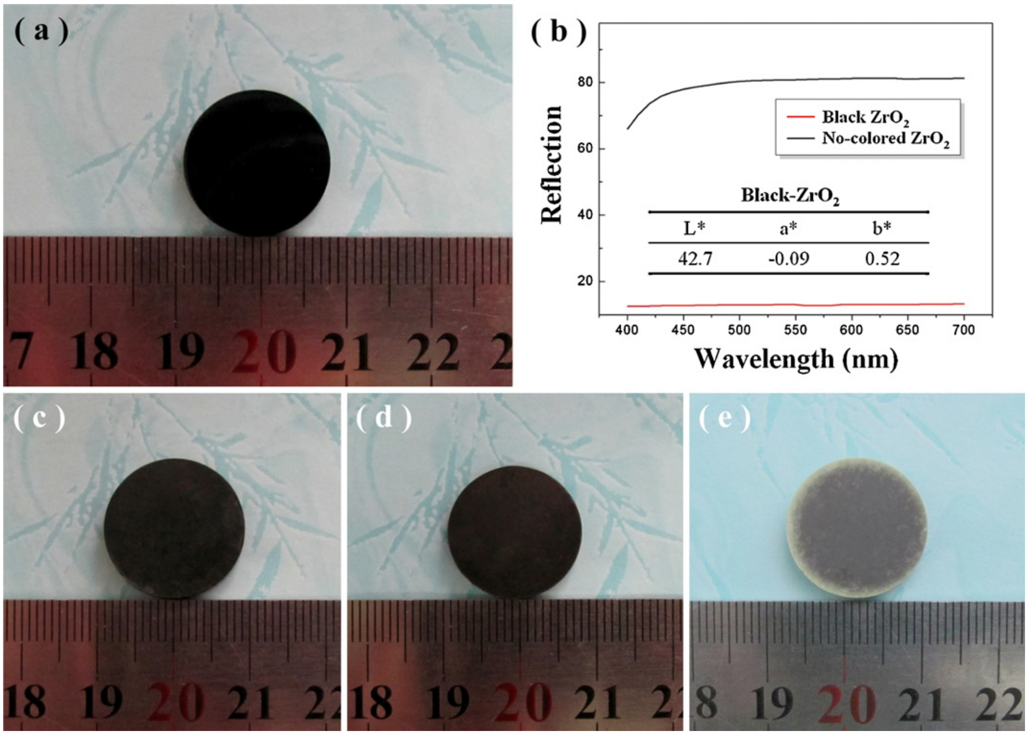

Fig. 4. (a) As-prepared black-colored CuO–Al_2O_3–ZrO_2 specimen sintered at 1200 °C with a deep and uniform black color. (b) Optical reflectance spectrum of black-colored CuO–Al_2O_3–ZrO_2 ceramics sintered at 1200 °C. (c and d) Black-colored CuO–Al_2O_3–ZrO_2 samples sintered at 1300 and 1450 °C, respectively. (e) A typical black-colored ZrO_2 sample fabricated without using the colorant stabilization of Al_2O_3 sintered at 1200 °C.

tures. These agree well to the XRD analysis (Fig. 3c and d). Moreover, abnormal grain growth usually occurs (Fig. 3f and h), which can be due to the increase of ion diffusivity induced by the low-melting point interfacial compound (e.g. 1100 °C melting point of $Y_2Cu_4O_5$ [21]) existing within the boundaries [19]. The abnormal grain growth would inevitably lead to the inhomogeneous distribution of colorants within the matrix, making the un-uniform coloring appearance of the fabricated ceramics.

Fig. 4a shows a typical round-shaped part sintering at 1200 °C with subsequently polishing treatments. It clearly suggests that fabrication black-colored ZrO_2 with a uniformly and vividly appearance has been achieved. The colorimetric properties of the as-prepared part are investigated under a spectrophotometer at room temperature. The black ZrO_2 ceramics exhibit an excellent reflectance (<10%). It absorbs across the whole visible light wavelength range, compared to the sample fabricated by using pure 3Y-TZP powders as the raw materials with the similar sintering process. Based on the reflectance spectra (Fig. 4b), CIE Lab chromatic coordinates of L^*, a^* and b^* are calculated to be ~42.7, ~−0.09 and ~0.52 (shown as the inset table in Fig. 4b), respectively, confirming the black-colored ZrO_2 ceramics have been successfully prepared. Fig. 4c and d displays the representative samples sintered at 1300 and 1450 °C, respectively, exhibiting a relatively light black color and un-uniformed coloring tone. It might be mainly attributed to the evaporation of the CuO colorants and the abnormal grain growth within the ceramic matrix at elevated sintering temperatures. Fig. 4e shows a typical sample fabricated by the similar processing of the one in Fig. 4a, in which only CuO is used as the colorants without $Al(NO_3)_3$ introduction during the preparation of coated 3Y-TZP powders. It implies that the color appearance of the sample is bad with a very light black color and un-uniform color distribution, especially within the regions from boundary to center of the sample. It suggests that Al_2O_3 plays a key role to stabilize the colorants of CuO within the matrix, since Cu ions can dissolve in Al_2O_3 to limit the vaporization of CuO at high sintering temperatures [24].

4. Conclusions

In summary, black-colored CuO–Al_2O_3–ZrO_2 ceramics with vivid appearance have been successfully fabricated. The as-prepared ZrO_2 ceramics exhibit a deep and genuine black color with a uniform color distribution. PEG2000 has been used as the dispersants for the preparation of ZrO_2 powder solutions. Then Cu and Al hydrates have been introduced into the solutions for the fabrication coated ZrO_2 powders with tailored pH values, to induce the heterogeneous nucleation of the CuO colorants on the surface of the ZrO_2 particles. The introduced Al_2O_3 transformed from Al hydrates play a key role on the stabilization of the CuO colorants, which make the fabrication of black-colored ZrO_2 ceramics at a relatively low sintering temperature of 1200 °C. It can be believed that current work could present a facile and cost-saving method for fabrication of black-colored ZrO_2 ceramics without using any toxic chromophore elements.

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