**1. Introduction**

An indispensable structural and functional material with excellent physical and chemical properties, zirconia is recognized as an inorganic non-metallic material featuring high-temperature resistance, wear resistance and corrosion resistance [1]. Numerous methods that can be used to prepare zirconia powders, among which the electrochemical gas phase deposition and hydrothermal methods require raw materials of high purity as well as expensive equipment, while the wet chemical method may result in serious environmental pollution and strong-base synthesis can be harmful to human health. Color zirconia ceramics characterized by a brilliant metallic luster, favorable mechanical properties and environmentally friendly properties offer extensive application prospects. Today, in addition to white ceramics, color ceramics in various hues such as black, blue, green and red have been developed and widely applied in industries such as medicine, decoration and jewelry, especially as ceramic mobile phone backplanes. In order to avoid signal shielding by mobile phones, color ceramics are used to replace metal phone backplanes. At the same time, the mechanical properties are excellent, the colors are diverse, and the needs of daily applications are met. However, problems such as unitary hues, poor stability at high temperatures, uneven color rendering and high energy consumption still exist under the circumstance of a handful of development efforts conducted on shades of purple zirconia ceramics.

Rare earth oxide (REO) exhibits fascinating physical and chemical properties due to its f or d electrons [2–5]. According to research findings, doping with colorful REO based on yttrium aluminium garnet (YAG) can lead to the creation of color ceramics presenting different hues. Purple Nd: YAG ceramics with high transparency can be obtained. For example, by doping YAG with neodymium oxide. Due to this high synthesis temperatures and poor mechanical properties, however, corresponding applications in structural ceramics may result in failure because of high energy consumption and processing requirements [6–8]. There is an urgent need to develop a new kind of purple ceramics with simple processes, saturated colors and excellent mechanical properties. The solid-state method was adopted in this study to synthesize purple zirconia ceramics with doping of neodymium oxide as a colorant, which greatly lowers the sintering temperature. As no requirements are made concerning the sintering atmosphere and pressure, moreover, simple production processes featuring environmental protection and energy savings can be developed for ceramic materials. Based these findings, continuously adjustable purple zirconia ceramics can be prepared with excellent mechanical properties guaranteed [1,9].

**2. Experimental**

**2.1. Materials preparation**

Ceramic materials in this paper are prepared by the solid-state method, with stable nanoscale tetragonal polycrystalline zirconia powders including (3Y-TZP), (2Y-TZP) and (2.5Y-TZP) used as basic materials. Al₂O₃ is used as a raw material for grain refinement with a doping amount of 1.5 wt%. Since Nd₂O₃ is a kind of...
purple oxide, the mechanism of solid solution diffusion of Nd$_2$O$_3$ in the zirconia lattice can be used in preparing purple zirconia ceramics [10]. Specifically, ZrO$_2$ is mixed with Y$_2$O$_3$ and Al$_2$O$_3$ at a certain ratio before ball-milling for 12 hours, after which 3 hours of high-energy ball-milling is conducted at a rotation speed of 2500 r·min$^{-1}$. Nd$_2$O$_3$ is then added to the dried powder as a colorant to prepare the power (consisting of 3 YSZ−1.5 wt% Al$_2$O$_3$, 2 YSZ−1.5 wt% Al$_2$O$_3$ and 2.5 YSZ−1.5 wt% Al$_2$O$_3$). Using this process, purple zirconia ceramics are prepared with pressureless sintering. The effects of the dopants on the structure and properties of zirconia ceramics can be explored according to the regulated doping amount of Nd$_2$O$_3$.

(a) Masses of the initial raw materials required for each component are weighed in accordance with the stoichiometric ratio. The instrument used is a YP-2001N electronic precision balance. Absolute ethanol is added at a ratio of 1.5:1 corresponding to the raw materials, and all the raw materials are ball-milled for 12 hours, the purpose is to thoroughly mix the powders.

(b) High-energy ball-milling is adopted for 3 hours at the rotational speed of 2500 r·min$^{-1}$. Afterwards, the mixed powder is dried in an electrothermal constant-temperature dry oven at 75°C.

(c) The dried mixed mass of powder is milled with an agate mortar before sieved with an 80-mesh standard sieve.

(d) The powder prepared in step c is placed in a mold for forming on an electric tablet machine at 8 MPa. Finally, the sample matrix can be obtained through cold isostatic pressing at 200 MPa.

(e) All samples were sintered without pressure at 1450°C for 3 h.

2.2. Characterization techniques

An X’Pert Pro X-Ray diffractometer is utilized for phase determination of purple ceramic chips. The diffraction target is made of metallic copper at the scanning speed of 2°/min, of which, the scanning range is between 20° and 80° with the rated operational voltage of 40 kV and the rated current of 35 mA. An S-3400N scanning electron microscope is adopted to observe the morphology feature of the purple ceramic.

CIE 1976L*a*b* colorimetric method is used to determine the color. To identify color changes of the ceramic samples more precisely, $L^*$, $a^*$ and $b^*$ values of different components in the ceramic samples are measured with a CM-3600 colorimeter, where, $L^*$ represents the brightness; $a > 0$ is the red, $a < 0$ the yellow, and $b < 0$ the blue [11]. Color differences between the samples are compared automatically with the instrument. Furthermore, three sets of $L$, $a$, and $b$ data as well as four sets of $E$, $a\Delta$, $\Delta a$ and $\Delta b$ color difference data are outputted after the color comparison. The diffuse reflectance of the ceramic samples is measured using a UV-Vis spectrophotometer (UV-Vis Spectra, Hitachi, UV-3900) within a range at 200 nm to 550 nm, for which the briquetting of alumina is used as a white standard sample. The wavelength of UV-Vis is within the reflectance (R) range of from 200 nm to 550 nm, and the corresponding values of the Kubelka-Munk absorbing function for analyzing absorption edges are shown as follows:

$$F(R) = \frac{(1 - R)^2}{2R} \quad (1)$$

Numerous methods are available for characterizing the material hardness, using which variance hardness values can be obtained. In this study, the material hardness was measured using Vickers hardness. The surfaces of the polished ceramic chips are dotted with an HV-50 Vickers hardness tester at a pressure of 1 kg and the holding time of 15 seconds, the process of which is observed using a ZEISS metallographic microscope at 200x magnification. In the meantime, the diagonal length of the tetragonal holes is measured to further calculate the hardness of each ceramic chip, as shown by Formula 2 [12,13]:

$$HV = \frac{1.8544P}{d^2} \quad (2)$$

The test force expressed by $P$ in the experiment is taken as 1000 gf (9.8N) with a holding time of 15 seconds; and $d$ indicates the diagonal length.

In this experiment, toughness is tested by the indentation method. The surface of the polished ceramic chips is dotted with an HV-50 Vickers hardness tester at a pressure of 10 kg and a holding time of 15 seconds; and a ZEISS metallographic microscope is used to observe the dotting process at 200x magnification. In the meantime, the crack length of the holes and the diagonal length of the tetragonal holes are measured to calculate the toughness of each ceramic chip further, as shown in Formula (3):

$$\frac{c}{a} > 2.5 \quad K_{IC} = 0.035 \left(\frac{l}{a}\right)^{-0.5} \frac{H}{3E} \quad (3)$$

$$\frac{c}{a} < 2.5 \quad K_{IC} = 0.129 \left(\frac{c}{a}\right)^{-0.2} \frac{H}{3E} \quad (3)$$

where $a$ is half the diagonal length of the indentation; $l$ is the extended length of the crack; and $c$ is the half length of the crack. $H$ represents the Vickers hardness of the green ceramic chip; the value 210 GPa is taken as the elastic modulus $E$; $K_{IC}$ is the fracture toughness.
(MPa·m$^{1/2}$); and $c/a$ is the proportion of the crack length to the diagonal length of the indentation.

Density is determined by the pycnometer method in this experiment, with a Tianmei FA2204B electronic scale as the instrument, and the calculation formula presented as follows:

$$\rho = \frac{m_2 - m_1}{(m_2 - m_1 + m_3)} m_3$$  \hspace{1cm} (4)

where $\rho$ is the liquid used for test purposes. In this experiment, distilled water is taken with the value of $1$ g/cm$^3$. $m_1$ is the mass of the pycnometer, $m_2$ is the mass sum of the pycnometer and the test sample, $m_3$ is the mass of the pycnometer when the sample is added with filled liquid, and $m_4$ is the mass (sample excluded) of the pycnometer with filled liquid.

3. Results and discussion

3.1. X-ray diffraction analysis

Figure 1 shows the results for the XRD patterns of the samples, the main phase of all systems is t-ZrO$_2$. The diffraction peak of the $x$ mol% Nd$_2$O$_3$ ($x = 0.5, 1.0, 1.5, 2.0$) doped 3YSZ ceramic system is compared with that of standard tetragonal zirconia (PDF17-0923). Of particular note, no characteristic peaks of the monoclinic phases m(−111) and m(111) are found at 28.5° and 31°. Meanwhile, characteristic peaks of the partial cubic phases c(400) and c(200) are found between the standard diffraction peaks of two tetragonal phases, i.e. t(004) and t(400) as well as t(200) and t(002). At the same time, the content of the cubic phases increases with the increasing doped amount of Nd$_2$O$_3$. The reason for that is Nd$_2$O$_3$ is partially dissolved in the zirconia lattice, while the undissolved portion is present in the ceramics in the form of cubic phases.

In the $x$ mol% Nd$_2$O$_3$−2YSZ ($x = 1.5, 2, 3, 4$) system, two characteristic peaks of the monoclinic phases m(−111) and m(111) appear at 2θ = 28.5° and 31°. The reason for that is that zirconia fails to become completely stabilized in a single tetragonal phase due to a small amount of stabilizer segregation occurring in the ceramic material of the system. As regards the $x$ mol% Nd$_2$O$_3$−2.5 YSZ ($x = 3, 4$) system, its diffraction peak is consistent with the characteristic peak of standard tetragonal zirconia according to the XRD results. In this way, a single tetragonal structure can be formed with the deepest color and optimal mechanical properties of purple ceramics in the system.

3.2. Chromatic property analysis

Figure 2 shows typical photos of $x$ mol% Nd$_2$O$_3$−YSZ purple ceramics. As shown in Table 1, the same rule is followed in all systems with increases in Nd$_2$O$_3$: $L^*$ decreases gradually; $a^*$ increases gradually; and $b^*$ increases gradually in the negative direction. This indicates that the color of purple ceramics depends on the amount of Nd$_2$O$_3$. $L^*$ is higher than 70, which indicates that purple ceramics have a higher brightness, and any reduction in brightness is attributable to enhanced light absorption intensity. At same time, the ratio of Nd/Y has little effect on the color of the ceramics.

As shown in Figure 3, with increases in N$_2$O$_3$, the absorption is shifted to low energy and low wave numbers (e.g. in the longer wavelength direction). In this case, the color is shifted towards shorter wavelengths and becomes increasingly purple [14–16]. Within the 500 – 550nm visible wavelength range, the reflectance is below 40%, and great yellow-green light absorption occurs, as a result of which the complementary light we observe is purple. At wavelengths of 420 – 430 nm, 440 – 460 nm and 460 – 480 nm, the reflectance is significantly lower. The absorption peaks agree well with the characteristic absorption peaks of Nd$^{3+}$ ions, which are ascribed...
to the electron transitions of Nd$^{3+}$ ion manifolds from $4I_{11/2} \rightarrow 4F_{5/2}$, $4I_{13/2} \rightarrow 4F_{9/2}$, and $4I_{15/2} \rightarrow 4H_{11/2}$, $4G_{5/2}$, respectively [6]. The saturation of the samples decreases with narrow absorption peaks, as a result, leading to poor color properties.

3.3. Structural and mechanical performance analysis

Figure 4 shows micrographs of Nd$_2$O$_3$-doped YSZ ceramics. It can be observed that the grains of the ceramic series are uneven in size. Three average grain sizes of three systems are distributed at 170 – 320 nm with increasing amounts of Nd$_2$O$_3$.

Figure 5 shows the indentation of purple ceramics, with the cracks can be clearly visible. Table 2 shows the density, Vickers hardness and toughness with different concentrations of Nd$_2$O$_3$ in a YSZ system. The density of ceramic materials is closely related to the mechanical properties, thermal stability, thermal conductivity and chemical resistance of the products. A general rule is that the lower the density, the lower the intensity. The density of different systems is similar, and its value is distributed at around 6.04–6.07 g·cm$^{-3}$, which is close to the theoretical density of 6.10 g·cm$^{-3}$. Clearly, the density of the three sets of components, 3YSZ–1.5wt%Al$_2$O$_3$, 2YSZ–1.5wt%Al$_2$O$_3$ and 2.5YSZ–1.5wt%Al$_2$O$_3$, decreases slightly with increases in Nd$_2$O$_3$. In general, the density values of the three sets of components are similar to each other with satisfactory particle uniformity.

An analysis of Figure 6 and Table 2, for hardness shows that, compared with the 2.5/3YSZ system, decreasing Y$_2$O$_3$ in the 2YSZ system, increases the Nd/Y ratio and leads to a decrease in hardness due to the appearance

Table 1. Chromatic properties of x mol% Nd$_2$O$_3$-doped YSZ

| System | x (mol%) | $L^*$ | $a^*$ | $b^*$ | $dE^{ab}$ |
|--------|----------|-------|-------|-------|-----------|
| 3YSZ   | 0.5      | 77.28 | 0.73  | -2.77 | 0.43      |
|        | 1.0      | 76.36 | 2.21  | -3.01 | 2.14      |
|        | 1.5      | 74.20 | 2.26  | -3.89 | 3.21      |
|        | 2.0      | 73.93 | 3.26  | -4.31 | 3.39      |
| 2YSZ   | 1.5      | 77.86 | 2.80  | -2.52 | 2.02      |
|        | 2.0      | 75.16 | 3.76  | -4.28 | 4.10      |
|        | 3.0      | 77.65 | 3.78  | -5.16 | 2.52      |
|        | 4.0      | 71.96 | 5.26  | -9.78 | 9.36      |
| 2.5YSZ | 3.0      | 77.86 | 2.80  | -2.52 | 2.02      |
|        | 4.0      | 71.70 | 5.57  | -7.58 | 4.10      |

Figure 2. Ceramic sample and chromaticity diagram.

Figure 3. UV-vis diffuse reflectance spectra of purple ceramics.
of m-ZrO$_2$. For the 2/3YSZ system, increasing Nd$_2$O$_3$ to increase the Nd/Y ratio leads to a decrease in hardness, because excessive Nd$_2$O$_3$ leads to a decrease in density. The hardness of the ceramics obtained in this study exceeds 12.0 GPa, which meets the application requirements. In summary, it was found that the hardness of zirconia ceramics is greatly affected by increasing the ratio of Nd/Y.

As shown in Figure 7 and Table 2, the toughness values of the sampled chromium oxide ceramics with different Nd$_2$O$_3$ doping amounts can be obtained by the toughness calculation formula. Also, the changes in the fracture toughness of the samples with the doping amount can be described with a curve. For the 3YSZ system, when Nd$_2$O$_3$ is doped from 0.5 mol% to 1.0 mol%, the toughness declines gradually and reaches the minimum at 1.0 mol%, then gradually rebounds with increases in neodymium oxide afterwards. The reason for the lower fracture toughness is the increase in the cubic phase content of the matrix, which is related to the increases in Nd$_2$O$_3$ and in the corresponding ratio of Nd/Y. For the 2/2.5YSZ system, fracture toughness has been raised by increasing Nd$_2$O$_3$. Since the martensite phase transformation is induced by the stress introduced to shift the phase from tetragonal metastable to monoclinic, the matrix of zirconia ceramics can be toughened and strengthened [1].

In short, the mechanical properties of purple zirconia ceramics are closely related to the Nd$_2$O$_3$ content.
In all the systems, an appropriate increase in Nd$_2$O$_3$ can cause a benign phase transition and an increase in hardness and toughness.

4. Conclusions

In this paper, Nd-doped 2/2.5/3 YSZ purple ceramics were synthesized and mechanical & optical properties studies were conducted. XRD results show that the optimum contents of stabilizer and colorant in zirconia ceramics are 2.5 mol% Y$_2$O$_3$ and 4.0 mol% Nd$_2$O$_3$, respectively, and that a single structure of the tetragonal phase is formed. As a colorant, a sufficient amount of Nd$_2$O$_3$ improves the color saturation and exerts a negative impact on its mechanical properties due to the appearance of miscellaneous phases. The hardness and toughness of the purple ceramics in 2.5 YSZ−1.5 wt% Al$_2$O$_3$ doping with 4.0 mol% Nd$_2$O$_3$ are 12.37 GPa and 5.77 MPa·m$^{1/2}$, respectively, meeting the market requirements with promising application prospects.

Disclosure statement

No potential conflict of interest was reported by the authors.

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