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Effect of Crystalline Size on the Structure of Copper Doped Zirconia Nanopaticles Synthesized via Sol-Gel

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Abstract

The stabilized zirconia with different Cu contents synthesized via sol-gel method. The samples were prepared by hydrolysis and condensation of orgnomatelic sol. After that the result gels were dried at 80 °C and then calcined at various temperatures. The differential thermal analysis (DTA), X-ray diffraction (XRD), field emission scanning electronic microscopy (FESEM) and transmission electronic microscopy (TEM) were used to determine the characteristics of nanoparticles. Unlike the stable pure ZrO_2 that has monoclinic structure at room temperature, the synthesized pure ZrO_2 and ZrO_2-CuO powders have been cubic and tetragonal structure at room temperature after calcinations. Moreover, it is obtained those changes in the crystallite size affect the stabilization of tetragonal or cubic structure at room temperature, and increase in content of dopant favored decrease of the crystallite size and metastabilization of both tetragonal and cubic polymorphs.

1. Introduction

Zirconia (ZrO_2) shows significant resistance to high temperatures and corrosion; therefore it has become increasingly important in a number of high-tech applications and as raw material for new ceramics [1]. Also Zirconium dioxide is an important support material for catalysis because of its mechanical and thermal stability, high surface area, and acid-base properties [2]. Zirconia exists in three crystalline forms of monoclinic, tetragonal and cubic structures at atmospheric pressure [3]. Depending on the preparation and pretreatment, different zirconia crystalline isomorphs could be obtained [2]. Although monoclinic phase is thermodynamically stable for pure zirconia at temperatures up to 1170°C, the tetragonal phase of zirconia could be produced preferentially during crystallization of amorphous hydrous zirconia [3].

However, the tetragonal form exhibits better textural and acid-base properties and is mostly used in catalysis [2]. Several techniques are available for producing zirconia nanoparticles such as sol/gel method, pyrolysis, spray pyrolysis, hydrolysis, and microwave plasma. Depending on the method, different production rates and particle size ranges can be covered [1]. The stabilization of doped zirconia by metals in the tetragonal and cubic phases has been earlier reported [4-10]. Stabilizers such as Y_2O_3, MgO, CaO, Cr_2O_3, Fe_2O_3, NiO and CuO are commonly added to zirconia to promote the retention of the high temperature polymorphs. The main aim of using these metal oxides as dopants is to obtain zirconia in the cubic and tetragonal phases with a high BET surface. Also, increasing the content of stabilizers favors metastabilization of both tetragonal and cubic polymorphs [4-10]. Another way of stabilizing the high temperature cubic and tetragonal phases is to reduce the particle size [5, 7]. Zirconia powders were predominantly in a metastable cubic and tetragonal structure with a small amount of monoclinic phase in a pure zirconia prepared by sol-gel method and calcined below 700°C. It could be resulted that appearance of metastable cubic or tetragonal structure was due to crystalline size [4, 5, 11]. However some reports show that the dopants inhibit the increase of crystalline size and let the lattice parameter to decrease [12]. In the previous research we worked on the Cu30%-ZrO_2 that synthesized by sol-gel method and their parameters of synthesis [13]. In this study we are working on the effect of crystalline size on the structure by sol-gel method.

2. Experimental procedure

In this work pure zirconia and 5-mol%, 10-mol% and 30-mol% Cu doped ZrO_2 ($ZrO_{2-x}CuO$) nano powders were synthesized via sol-gel method. Zirconium alkoxide ($Zr(OCH_2CH_2CH_3)_4$) was used as precursor for synthesis process. To synthesize pure ZrO_2, 34cc zirconium alkoxide was added to 150cc ethanol then stirred well. Ethanol was used as a media to complete the polymerization uniformly. After adding 5cc nitric acid (HNO_3) to adjust the pH at 2-4, a mixture of 11.88cc water and 50cc ethanol was added slowly to the prior mixture of zirconium alkoxide and ethanol, and then was allowed to stir for extra two hours to complete the polymerization and aging processing. To synthesize the Cu doped ZrO_2 with 5%, 15% and 30% molar rate, other three sols were prepared. Table 1 shows the compositions of these sols. After mixing the precursors according to table 1, to adjust of pH at 2-4, 5cc nitric acid was added. The process was continued as the same as pure zirconia until three uniform gels were prepared. The result gels were dried at 80ºC for 18 hours; then amorphous powders were calcined at 400, 500, 600, 700 and 900ºC for 5 h to remove of structural water and burn of the organic compounds. Amorphous powder transitions to crystalline structure occurred during the calcinations.

Table 1. Characteristics of the sols to synthesize Cu doped ZrO_2 powders.

CuO/ZrO_2 %mol	Zirconium alkoxide	Ethanol	$Cu(NO_3)_2 \cdot 3H_2O$
5	29.638 cc	150 cc	1.208 gr
15	26.518 cc	150 cc	3.624 gr
30	21.838 cc	150 cc	7.248 gr

The differential thermal analysis (DTA) of the ZrO_2 powders were examined in flowing air by a thermal analyzer (Mettler Toledoe A851) with Al_2O_3 as the reference material at a heating speed of 10˚C/min. The crystal phases of the ZrO_2 powders were identified by X-ray diffraction (XRD) analysis using a diffractometer (Philips

X`Pert), equipped with a Ni-filtered Cu Kα radiation source. The voltage and current settings of the diffractometer were 40 kV and 30 mA, respectively. The scan angle ranges from 10-90° (2θ) at a scanning speed of 0.05°/s and a step size of 0.02°. A field emission scanning electron microscopy (FE-SEM) (Hitachi S416) was used to characterize the size and morphology of the powder particles. Scherrer's equation was also used to calculate the crystalline size of powders.

3. Results and discussion

Fig. 1 shows the DTA curves for the dried ZrO_2 and ZrO_2-30%CuO powders carried out in air. Both curves show one endothermic peak at about 130ºC that is due to removing of structural water. There are also two exothermic peaks occurring at 261 and 431ºC for pure ZrO_2. The first peak attributes to the burning (oxidation) of the organic compounds and the second shows the calcination of amorphous ZrO_2, resulting the crystalline structure. Both of these peaks also exist for ZrO_2-30%CuO sample which the first one is clear, but the other peak at 430ºC is distinguished hardly. Fig. 1-b shows another endothermic peak for ZrO_2-30%CuO at 1050ºC that is due to fusion of copper oxides. ZrO_2-5%CuO and ZrO_2-15%CuO had the same behavior as ZrO_2-30%CuO one.
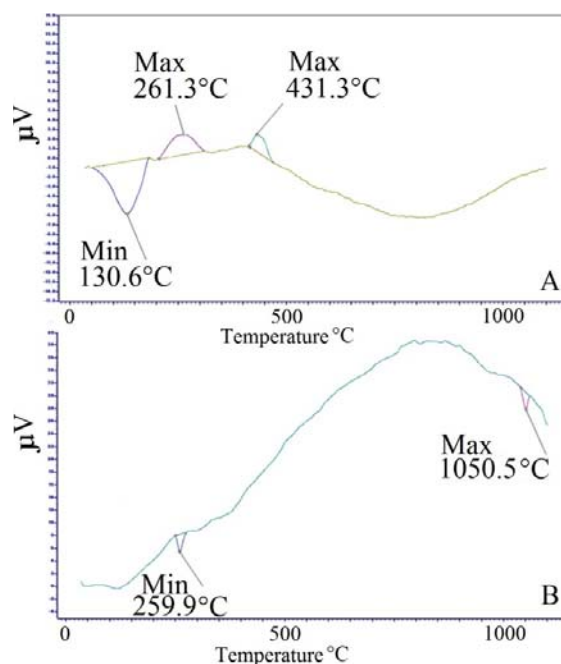

Fig. 1. The DTA results for dried bodies carried out in air up to 1100ºC, (a) pure ZrO_2 (b) ZrO_2-CuO.

The multiple XRD patterns of ZrO_2 powders are given in Fig. 2 It shows that the tetragonal and even cubic phase of zirconia have formed preferentially to the monoclinic phase during crystallization of amorphous hydrous pure zirconia at 400ºC. It is too hard to distinguish tetragonal from cubic because both have almost the same XRD patterns. Although appearance of double peaks around 35° and 60° at upper temperatures can prove these patterns belong to tetragonal phase. As the calcinations temperature increases from 400 to 700 ºC, monoclinic phase was also detected and begins to increase. Finally, at 900ºC monoclinic becomes the predominant phase. After calcinations of amorphous powders at upper temperatures, it is supposed only monoclinic zirconia be observed.
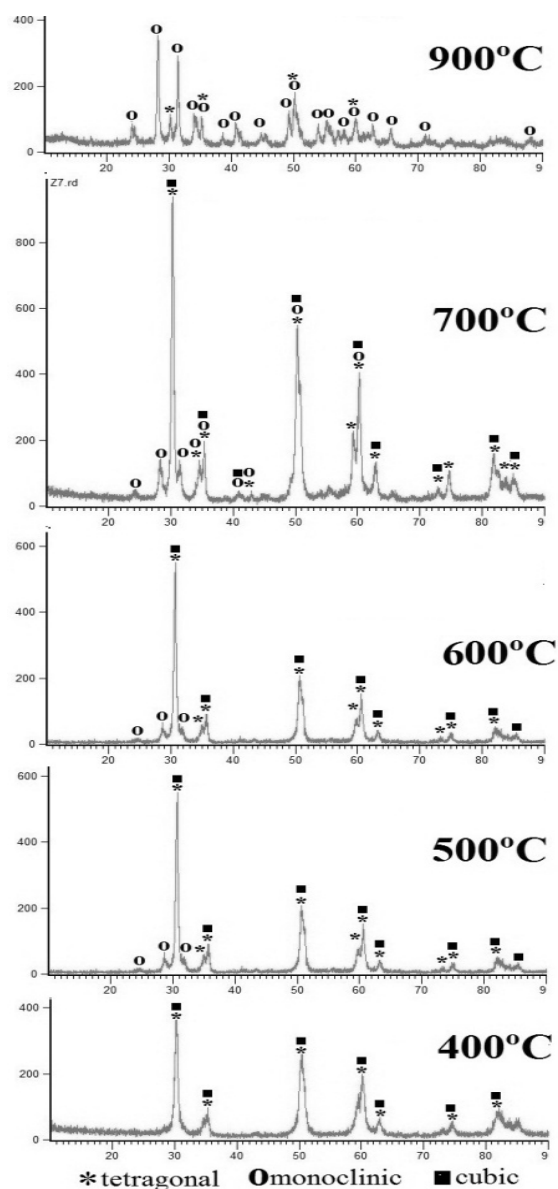
Fig. 2. (a) XRD patterns of ZrO_2 powders calcined at 400, 500, 600, 700 and 900 °C.

Fig. 3 shows the multiple XRD patterns of ZrO_2-5%CuO powders. Like pure zirconia, during crystallization of amorphous powders at 400°C tetragonal and cubic phase of zirconia have formed and it is still hard to distinguish the tetragonal phase from cubic ones. There are not any double peaks (around 35° and 60°) for calcinations at 400 or 500°C, so it results cubic is the predominant phase. Appearance of double peaks for calcinations

at 700°C indicates that the predominant phase is tetragonal. As the calcinations temperature increases from 400 to 600°C, according to Fig.3, monoclinic phase is not detected yet. During the calcinations above 600°C monoclinic phase forms and complete transformation occurs at about 900°C, then only monoclinic phase is observed.
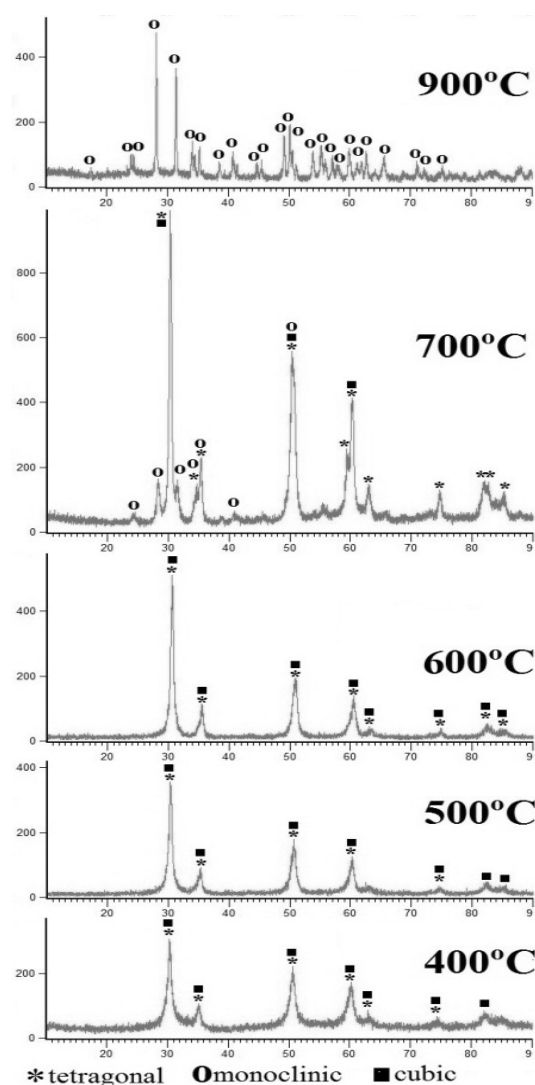

Fig. 3. XRD patterns of ZrO_2-5%CuO powders calcined at 400, 500, 600, 700 and 900 °C.

According to Fig. 4 which shows XRD patterns of calcined ZrO_2-15%CuO powders at various calcinations temperatures, cubic appeared as the

main phase for calcinations at 400, 500 and 600 ℃. Furthermore monoclinic phase was first detected at 700 ℃ and complete transformation occurred at about 900 ℃. Also some new peaks were observed which were signed by +. These peaks are linked to CuO and they show that the synthesized powders formed composite powders.
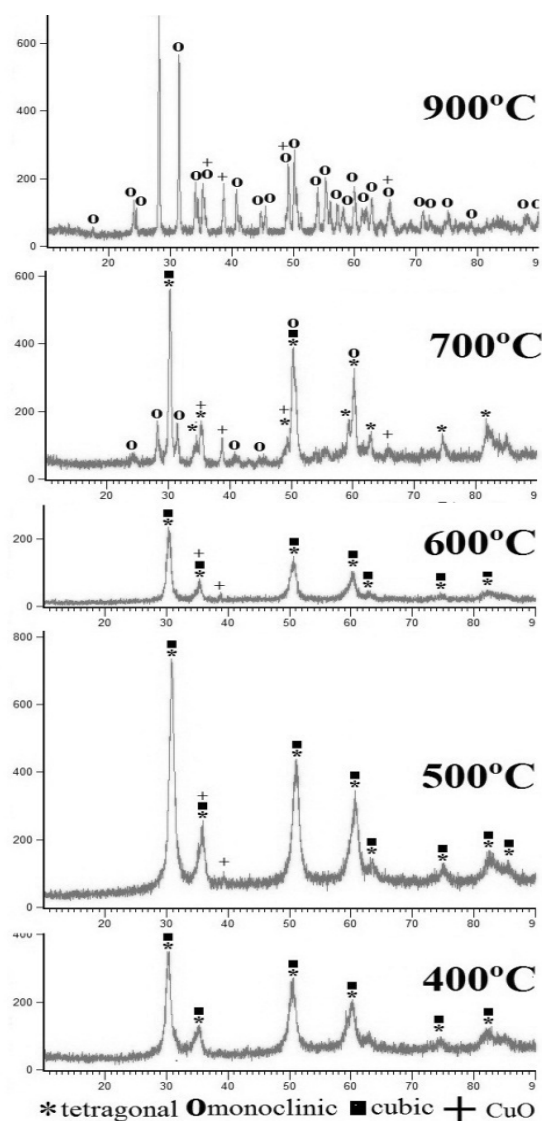

Fig. 4. XRD patterns of ZrO$_2$-15%CuO powders calcined at 400, 500, 600, 700 and 900 ℃.

XRD patterns of ZrO$_2$-30%CuO powders are given in Fig. 5 which shows the same results as

ZrO$_2$-15%CuO powders except that the peaks of CuO are more intense for ZrO$_2$-30%CuO. All of the synthesized powders according to the XRD results are in metastable phases for calcinations at low temperatures.
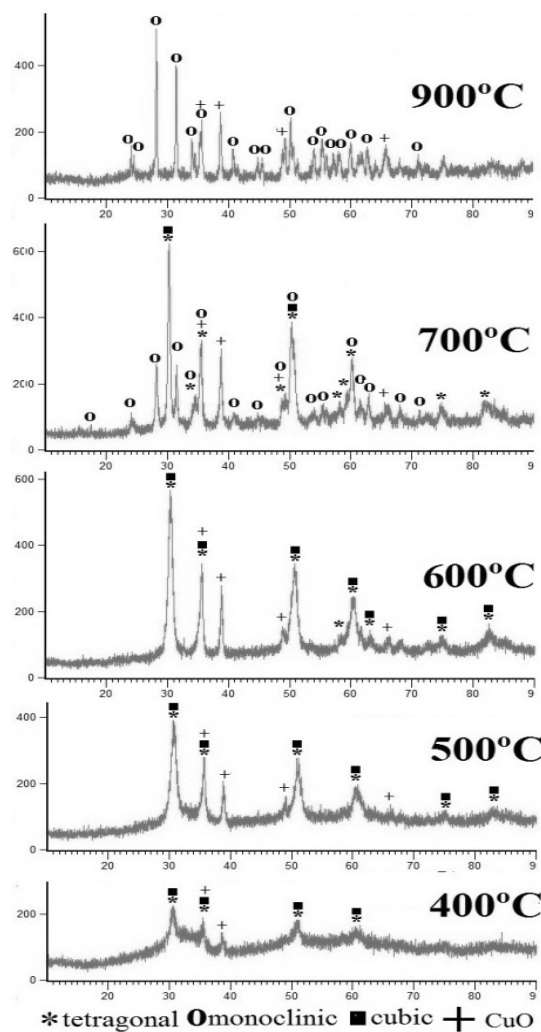

Fig. 5. XRD patterns of ZrO$_2$-30%CuO powders calcined at 400, 500, 600, 700 and 900 ℃.

To calculate the crystalline size of powders, Scherrer's equation was used and table 2 shows the results. Table 2 shows that an increase in calcinations temperature causes growth in crystalline size. Also it indicates that adding of Cu as dopant decreases the crystalline size at low

calcinations temperatures, but for calcinations at high temperature (above 700ºC) CuO doped ZrO$_2$ powders have bigger crystalline size than pure ZrO$_2$ which is due to low melting point of CuO. Scherrer's calculation also shows that as the CuO content increases, the crystalline size of CuO doped ZrO$_2$ decreases, so it results that the dopant inhibits the increase of crystalline size.

Table 1. Characteristics of the sols to synthesize Cu doped ZrO$_2$ powders

Calcinations temperature	ZrO$_2$	ZrO$_2$-5%CuO	ZrO$_2$-15%CuO	ZrO$_2$-30%CuO
400ºC	21nm	14nm	9nm	-
500ºC	32nm	19nm	10nm	8nm
600ºC	30nm	21nm	12nm	12nm
700ºC	30nm	26nm	26nm	25nm
900ºC	47nm	112nm	95nm	71nm

As the calcinations temperature increases, the growth in crystalline size happens and over a certain crystalline size about 40nm, monoclinic phase becomes the predominant phase. XRD patterns for ZrO$_{2-x}$CuO powders have broader peaks compare to pure ZrO$_2$ powders, so it can prove that adding of the CuO as dopant decreases the crystalline size of ZrO$_2$. According to XRD results and calculation of crystalline size, it is clear that decrease in crystalline size is the most effective parameter to form tetragonal phase at low temperatures and adding CuO causes much more decrease in crystalline size, so cubic phase can also be observed at room temperature. Calcination of amorphous powders at high temperatures such as 900ºC results much coarser crystalline; then monoclinic becomes the predominant phase. Complete transformation occurs as the calcinations temperature is risen above 900 ºC; then only monoclinic zirconia is observed.

Some reasons were reported for the existence of the metastable tetragonal [14]. Basically, in a single crystal, monoclinic structure has significantly less bulk energy compare to tetragonal structure. Therefore, the thermodynamically stable phase at equilibrium conditions is monoclinic phase. On the other hand, the specific surface energy of tetragonal phase is considerably lower than monoclinic phase. If the particle size is reduced, the contribution of the surface energy to the total energy increases. Thus, below a characteristic critical crystalline size, tetragonal phase is more stable than monoclinic phase and this critical particle size depends on the temperature [14].

TEM image of CuO-ZrO$_2$ synthesized nanoparticles shows in fig. 6 that nanoparticles are round and good narrow size distribution. Fig. 7 shows SEM images for calcined powders at 600ºC which indicate the sol-gel method with alkoxide precursor has produced nanoparticles with particle size range from 10 to 40nm.
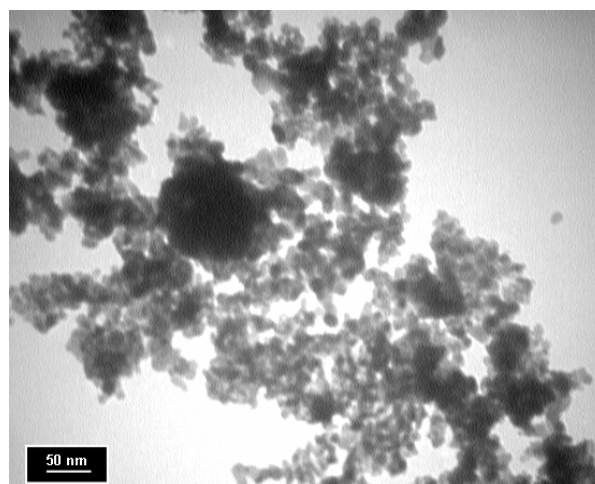

Fig. 6. **T**EM image of ZrO$_2$-30CuO synthesized and calcined at 600ºC.
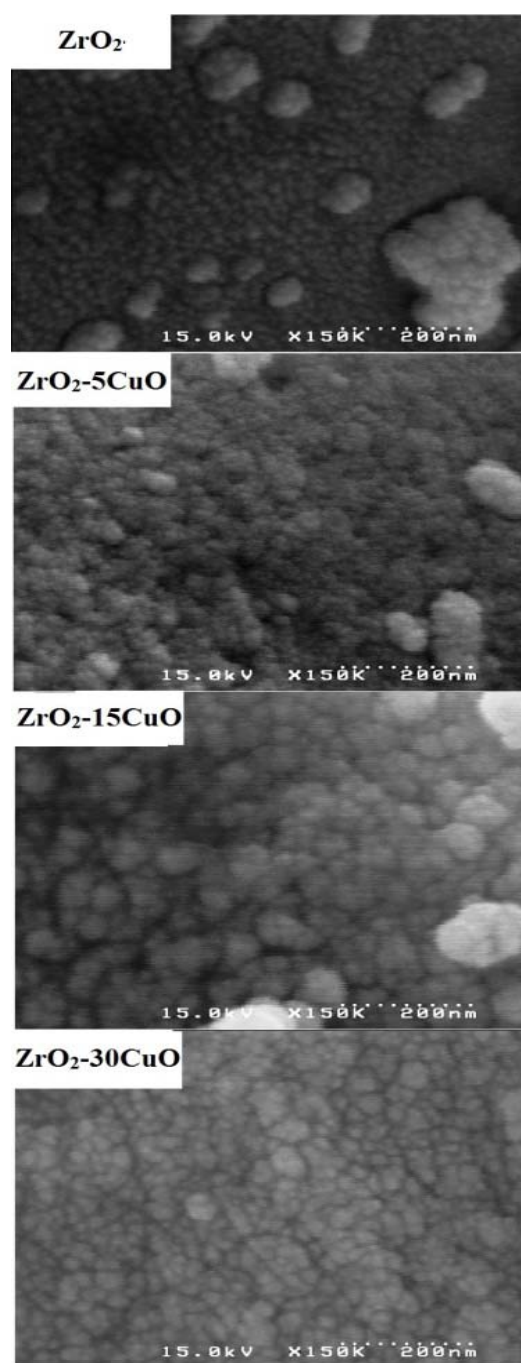
Fig. 7. SEM images of synthesized powders calcined at 600ºC.

4. Conclusion

Pure ZrO_2 nano powders which were calcined below 700ºC had tetragonal as the predominant phase that was due to fine crystalline size. Specific surface energy for the tetragonal structure of ZrO_2 is less than for the monoclinic one, thus the monoclinic structure becomes unstable when the size of the crystalline reaches below a certain critical level. Adding of CuO as dopant inhibits the increase in crystalline size, so cubic phase was observed as the main phase for calcinations at low temperatures. CuO content also affects the crystalline size thus high content causes fine crystalline size at low calcinations temperature. $ZrO_{2-x}CuO$ powders had not resistance to high temperatures quite as well as pure ZrO_2 that it was due to low melting point of CuO which causes the agglomeration at lower temperatures.

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