

Synthesis of MgO-ZrO₂ by Co-Precipitation Method and Study Its Structure and Characteristics

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Abstract:

The ceystalline phase of magnisum zirconate (MgZrO₃) white colored was obtained by co-precepitation method in an alkali solution. The zirconium chloride (ZrCl₄), magnesium chloride (MgCl₂.6H₂O) and the alkaline solution of sodium hydroxide (NaOH) were used as starting materials. The solution of starting materials were prepared in different concentration. The precipitation of two solution was accomplished at the same time. Then the products were filtred, dried and burned at different temperatures to obtain required crystals. After that, the samples studied by x-ray powder diffraction method and thermal differential analysis (DTA). This study appears that adding enough amount of magnesium oxide keep the crystal type of zirconium oxide with tetragonal type and the magnesium zirconate with cubic crystal type can synthesized in temperature (800- 1000)°C.

Key words: co-precepitation, magnisum zirconate, MgZrO₃.

1. Introduction:

Perovskites of the type ABO₃ display a wide range of chemical composition and attributes, and for this reason have been called "inorganic chameleons" [1]. Magnisum zirconate (MgZrO₃) forms the perovskite structure and possesses excellent mechanical, optical and electrical properties [2]. The properties of MgZrO₃ depend on the synthesis method employed. The most common method for powder synthesis is the solid mixing technique [3, 4]. Although the method is simple and inexpensive, wet chemical methods like sol-gel [5, 6], hydrothermal routes and co-precipitation can improve cation homogeneity and reduce the temperatures required for phase formation [7, 8]. These methods also help produce more surface active powders that sinter better and thus produce higher density ceramics [9].

General Zirconium Oxide Information

Pure zirconia exists in three crystal phases at different temperatures. At very high temperatures (>2370°C) the material has a cubic structure. At intermediate temperatures (1170°C to 2370°C) it has a tetragonal structure. At low temperatures (below 1170°C) the material transforms to the monoclinic structure. The transformation from tetragonal to monoclinic is rapid and is accompanied by a 3 to 5 percent volume increase that causes extensive cracking in the material. This behavior destroys the mechanical properties of fabricated components during cooling and makes pure zirconia useless for any structural or mechanical application [10]. Several oxides which dissolve in the zirconia crystal structure can slow down or eliminate these crystal structure changes. Commonly used effective additives are MgO, CaO, and Y₂O₃. With sufficient amounts added, the high temperature cubic structure can be maintained to room temperature. Cubic stabilized zirconia is a useful refractory and technical ceramic material because it does not go through destructive phase transitions during heating and cooling [11]. The controlled, stress induced volume expansion of the tetragonal to monoclinic inversion is used to produce very high strength, hard, tough varieties of zirconia available from Accuratus for mechanical and structural applications. There are several different mechanisms that lead to strengthening and toughness in zirconias that contain tetragonal grains [12].

2. Materials and Instruments:

ZrCl₄ (MERK, 98%), MgCl₂.6H₂O(MERK, 98.0-101.0%), NaOH(MERK, 99%) AgNO₃(SURECHEM PRODUCTS LTD). Dehydrator (memmert), furnace (Carbolite), X-Ray Powder Diffractometer XRD (Philips-PW-1840), Differential Thermal Analysis DTA (Chimadzu).

3. Experimental:

The perovskite MgZrO₃ was synthesized using co-precepitation method, calculated amounts of ZrCl₄, MgCl₂.6H₂O were added dropwise into an alkaline solution of NaOH which prepared in different amounts. The resultant solution was stirred for 15 min and then aged for 3 h. The aged solution was filtered and the precipitate was washed three times using water to remove Cl⁻ ions. An AgNO₃ was used to check for any residual Cl⁻

contaminants, as a curdy white precipitate of AgCl would form immediately if Cl⁻ was present. The precursor powder was dried for 3 h at 100°C and then calcined in different temperatures (800-1000)°C. All powders were characterized using X-ray diffraction (XRD), Differential Thermal Analysis (DTA).

The next table show the mass of starting materials

Mass of materials (gr)	C (M)	
	X= 0.9	X = 1
ZrCl ₄	20.97	23.3
MgCl ₂ .6H ₂ O	8.577	9.53
C _{NaOH} (M)	5.5	6
M _{NaOH} (gr)	22	24

4. Results and discussion:

4.1. Result of XRD:

4.1.1. In 800°C: fig. 1 confirm the formation of the cubic phase in powders prepared from the co-precipitation route, and the table 1 was shown the results of analysis:

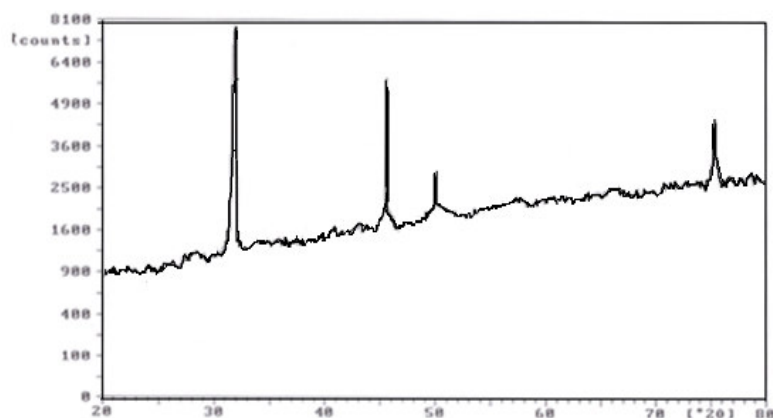


Fig. 1 XRD of MgZrO₃ prepared by co-precipitation for (Mg:Zr=0.9:0.9) and NaOH (5.5 M) in 800°C.

Table 1 result of analysis by XRD:

MgZrO ₃ (Mg:Zr=0.9:0.9) , (T = 800°C)					
Peak	2θ	θ	I / I ₀	d , Å	hkl
1	31.6125	15.80625	100	2.8279	100
2	45.335	22.6675	86.48	1.9987	110
3	50.110	25.055	18.92	1.8189	101
4	75.19	37.595	32.43	1.2626	210

Table 1 was shown 4 peaks three of them indicate of shaped magnisium zirconate (2θ=31.6125, 45.335, 75.19), a=2.8279Å, while the peak (2θ=50.110) can be attributed to the tetragonal of ZrO₂ based on JCPDS.

4.1.2. In 1000°C: fig. 2 confirm the formation of the cubic phase in powders prepared from the co-precipitation route, and the table 2 was shown the results of analysis:

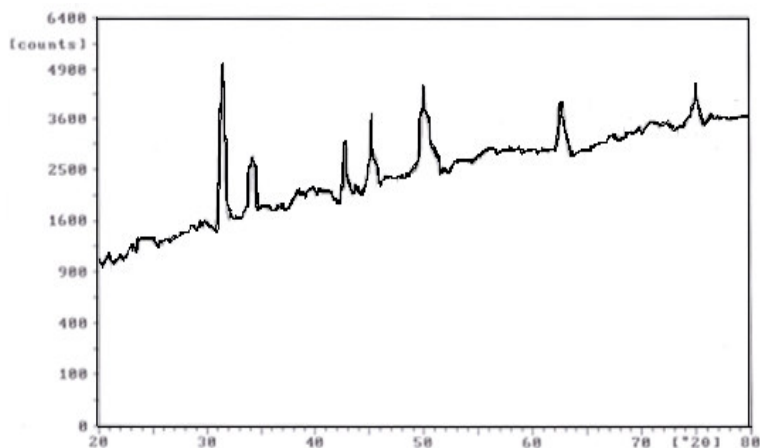


Fig. 2 XRD of $MgZrO_3$ prepared by co-precipitation for (Mg:Zr=0.9:0.9) and NaOH (5.5 M) in $1000^\circ C$.

Table 2 result of analysis by XRD:

MgZrO ₃ (Mg:Zr=0.9:0.9) , (T = 1000°C)					
Peak	2θ	θ	I / I ₀	d , Å	hkl
1	31.6125	15.80625	100	2.8279	100
2	34.023	17.0115	38.36	2.6329	010
3	42.917	21.4585	26.92	2.1056	011
4	45.335	22.6675	50	1.9987	110
5	50.121	25.0605	53.84	1.8185	101
6	62.304	31.152	26.92	1.4890	200
7	75.19	37.595	19.23	1.2626	210

Table 2 was shown 4 peaks in addition to three peaks return to magnesium zirconate ($a=2.8279\text{Å}$), two peaks in ($2\theta=34.023, 50.121$) can be attributed to the tetragonal of ZrO_2 , while two peaks in ($2\theta=42.917, 62.304$) return to cubic of MgO based on JCPDS, this appear that adding enough ammount of magnesium oxide keep to structure of ZrO_2 .

4.1.3. In $800^\circ C$: fig. 3 confirm the formation of the cubic phase in powders prepared from the co-precipitation route, and the table 3 was shown the results of analysis:

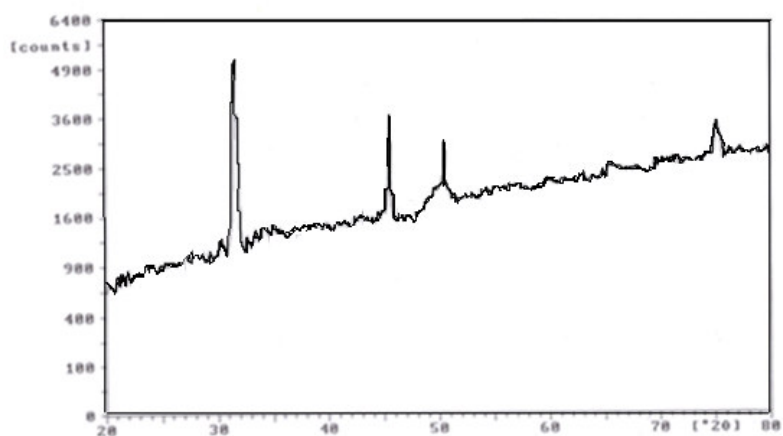


Fig. 3 XRD of $MgZrO_3$ prepared by co-precipitation for (Mg:Zr=1:1) and NaOH (6 M) in $800^\circ C$.

Table 3 result of analysis by XRD:

MgZrO ₃ (Mg:Zr=0.9:0.9) , (T = 1000°C)					
Peak	2θ	θ	I / I ₀	d , Å	hkl
1	31.6125	15.80625	100	2.8279	100
2	34.023	17.0115	38.36	2.6329	010
3	42.917	21.4585	26.92	2.1056	011
4	45.335	22.6675	50	1.9987	110
5	50.121	25.0605	53.84	1.8185	101
6	62.304	31.152	26.92	1.4890	200
7	75.19	37.595	19.23	1.2626	210

Table 3 was shown one peak in ($2\theta = 50.108$) return to tetragonal shape of zirconium oxide, in addition to three peaks appear $MgZrO_3$, ($a = 2.8279\text{Å}$).

4.1.4. In $1000^\circ C$: fig. 4 confirm the formation of the cubic phase in powders prepared from the co-precipitation route, and the table 4 was shown the results of analysis:

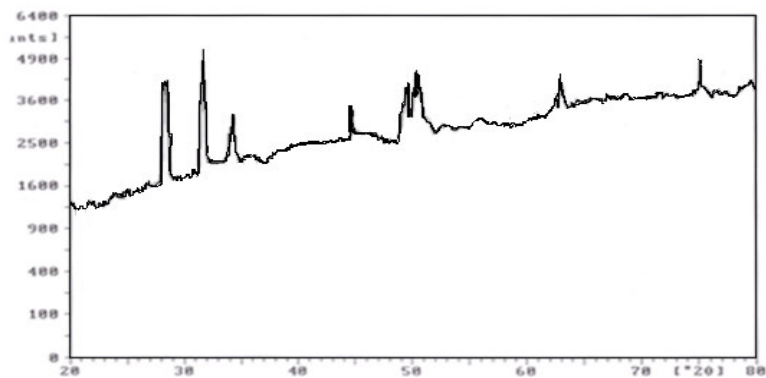


Fig. 4 XRD of MgZrO₃ prepared by co-precipitation for (Mg:Zr=1:1) and NaOH (6 M) in 1000°C.

Table 4 result of analysis by XRD:

MgZrO ₃ (Mg:Zr=1:1) , (T = 1000°C)					
Peak	2θ	θ	I / I ₀	d , Å	hkl
1	29.680	14.84	80.7692	3.0075	001
2	31.6125	15.80625	100	2.8279	100
3	34.101	17.0505	38.46	2.6270	010
4	45.335	22.6675	15.38	1.9987	110
5	49.498	24.749	26.92	1.8399	011
6	50.210	25.105	38.46	1.8155	101
7	62.295	31.1475	19.23	1.4892	200
8	75.19	37.595	23.08	1.2626	210

Table 4 was shown four peaks take numbers (1, 3, 5, 6) return to tetragonal shape of ZrO₂, while the peak that take number 7 return to cubic shape of MgO.

4.2. Results of DTA:

fig. 5, fig. 6 and table 5 were shown thermal behavior of magnisium zirconate without dried or calcined.

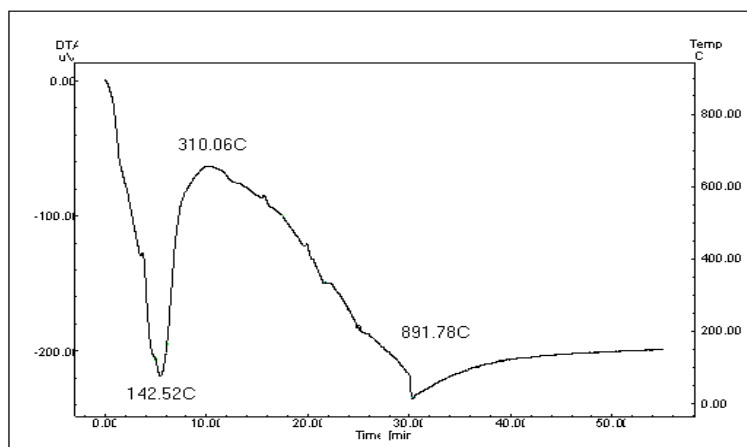


Fig. 5 DTA Of $MgZrO_3$ prepared by co-precipitation for (Mg:Zr=0.9:0.9) and NaOH (5.5 M).

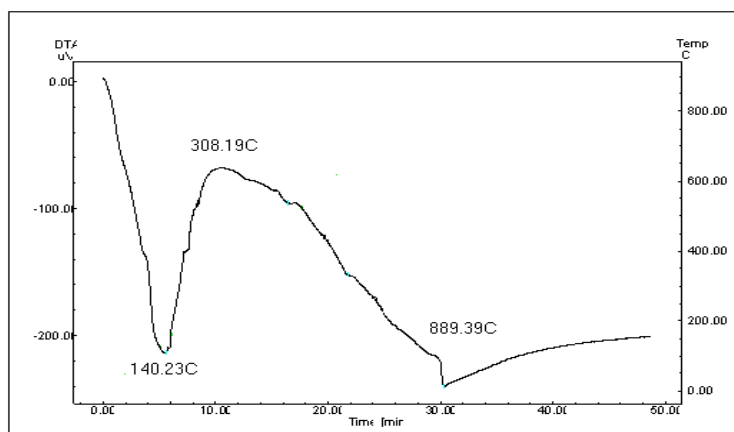


Fig. 6 DTA Of $MgZrO_3$ prepared by co-precipitation for (Mg:Zr=1:1) and NaOH (6 M).

Table 5 result of analysis by DTA:

Compound	Peak (DTA) (T°C)	Shape	Explanation
$MgZrO_3$ (Mg:Zr=0.9:0.9) [NaOH] = 5.5M	142.52	endo	-tearing out molecular of crystalline water
	310.06	exo	-starting crystallization of magnisium zirconate
	891.78	endo	-disassembly of magnisium zirconate
$MgZrO_3$ (Mg:Zr=1:1) [NaOH] = 6 M	140.23	endo	-tearing out molecular of crystalline water
	308.19	exo	-starting crystallization of magnisium zirconate
	889.39	endo	-disassembly of magnisium zirconate

5. Conclusions:

From the previous study of the (MgZrO₃) conclude the following:

1. The synthesis of magnisum zirconate deposition in a manner common, and different temperatures.
2. Been studying the spectra of X-ray diffraction of the crystals produced and demonstrate that thd addition of a sufficient quantity of magnesium oxide maintains the crystalline structure of the zirconium oxide, and through this technique has been values are calculated (d), which represents the distance between the crystalline levels, and identify evidence Miller, as well as calculate the dimensions of the crystal lattice.
3. The study of the thermal behavior of the crystals resulting davice (DTA) and the result was according to similarly the thermal behavior of the compounds produced all of which include three acts the first: endothermic refer to tearing out molecular of crystalline water, the second: exothermic refer to starting crystallization of magnisum zirconate, the third act type is endothermic indicates that the starting crystallization of magnisum zirconate.

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