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SYNTHESIS OF TIO_2-ZRO_2 BY HYDROTHERMAL METHOD AND STUDY ITS STRUCTURE AND CHARACTERESTICS

Abstract: *The ceystalline phase of zirconium titanate ($ZrTiO_4$) white colored was obtained by hydrothermal method. The zirconium chloride ($ZrCl_4$), titanium chloride ($TiCl_4$) and the alkaline solution of ammonium hydroxide (NH_4OH) were used as starting materials. The precipitation solution was accomplished together, then the resulting precursor suspension was transferred to Teflon lined stainless steel autoclave at 180C° for 2h. the product was filtred, dried and burned at 500C° to obtain required crystals. After that, the sample studied by x-ray powder diffraction method and thermal differential analysis (DTA). This study appears that the zirconium titanate with orthorhombic crystal type can synthesized arounnd 500C°.*

Key words: *hydrothermal, zirconium titanate, $ZrTiO_4$.*

СИНТЕЗ TIO_2-ZRO_2 ГИДРОТЕРМАЛЬНЫМ МЕТОДОМ И ИССЛЕДОВАНИЕ ЕГО СТРУКТУРЫ И ХАРАКТЕРИСТИК

Аннотация: *Цейсталическая фаза титаната циркония ($ZrTiO_4$) белого цвета была получена гидротермальным методом. В качестве исходных материалов использовали хлорид циркония ($ZrCl_4$), хлорид титана ($TiCl_4$) и щелочной раствор гидроксида аммония (NH_4OH). Осаждение раствора осуществляли вместе, затем полученную суспензию предшественника переносили в автоклав с тефлоновой футеровкой из нержавеющей стали при 180C ° в течение 2 часов. продукты отфильтровывали, высушивали и сжигали при 500C° до получения требуемых кристаллов. После этого образцы исследуют методом рентгеновской порошковой дифракции и термодифференциального анализа (ДТА). Это исследование показывает, что титанат циркония с орторомбическим типом кристаллов может синтезироваться около 500C°.*

Ключевые слова: *гидротерм, титанат циркония, $ZrTiO_4$.*

1. Introduction:

Ceramic materials based on zirconium titanate ($ZrTiO_4$) are extensively used in humidity sensors [1-2], resonators for microwave telecommunications [3], catalysis [4], and optical devices [5]. Other materials, based on zirconium titanate, have found applications as high temperature pigments and ceramic composites [6]. Classical $ZrTiO_4$ synthesis involves a solid state reaction of a stoichiometric mixture of zirconium and titanium oxides at temperatures above 1400C° [7]. More recently, the preparation of agglomerated 0.5-3.0 μm single phase $ZrTiO_4$ particles at 1300C° from the precursor oxides was reported [8]. Solid state reactions involve grinding and thorough mixing of precursor powders followed by high temperature prolonged sintering; the results are usually low specific surface area powders. The sol-gel technology may overcome these problems because highly sinteractive (high specific surface area) powders may be prepared, requiring much lower sintering temperature [9]. A number of ZrO_2-TiO_2 binary oxides prepared by the sol-gel technique have been

reported [10]. Fully crystalline and stoichiometric $ZrTiO_4$ have been obtained with a crystallization temperature of 400C° by preparing TiO_2 and ZrO_2 gels and mixing them on a 1:1 ratio [10]. The low temperature synthesis of $ZrTiO_4$ from different precursors with a Zr:Ti concentration ratio of 1:1 has been reported [11], with $ZrTiO_4$ phase formation around 700C°.

2. Experimental:

Materials:

$ZrCl_4$ (MERK, 98%), $TiCl_4$ (SIGMA-ALDRICH, 99%), NH_4OH (SURECHEM PROUDUCTS LTD, 25%) $AgNO_3$(Medex,99%).

Synthesis of zirconium titanate :

The orthorhombic $ZrTiO_4$ was synthesized using hydrothermal method, calculated amounts of $ZrCl_4$, $TiCl_4$ were added dropwise into an alkaline solution of NH_4OH. The resultant solution was transferred to Teflon lined stainless steel autoclave at 180C° for 2h. The product was filtred and washed three times using water to remove Cl^- ions. An $AgNO_3$ was used to check for any residual Cl^- contaminants, as a curdy white precipitate of AgCl would form immediately if Cl^- was present. Then the product was dried and burned at 500C° to obtain required crystals. The powder was characterized using X-ray diffraction (XRD), Differencial Thermal Analysis (DTA) and IR-Spectrometer.

The next table show the mass of starting materials

Table (1) mass of starting materials

Volume of materials	C (M) (Ti:Zr/0.1:0.1)
$ZrCl_4$ (gr)	2.3775
$TiCl_4$ (ml)	1.1
C_{NH4OH} (M)	0.8
NH_4OH (ml)	6

3. Results and discussion:

3.1. Result of XRD:

Fig. 1 confirm the formation of the orthorhombic phase in powders prepared from the hydrothermal route at 500°C, and the table 2 was shown the results of analysis:

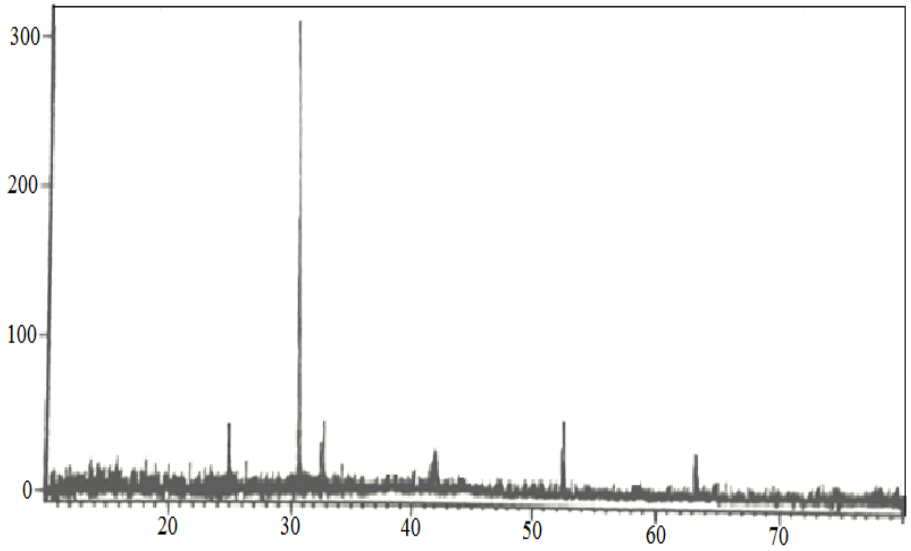

Fig. 1 XRD of $ZrTiO_4$ prepared by hydrothermal for (Ti:Zr=0.1:0.1)

Table (2) result of analysis by XRD:

Number	Peak	2 Ɵ	(I%)	d	(hkl)
1	$ZrTiO_4$	24.680	15.00	3.60438	(110)
2	$ZrTiO_4$	30.501	100.00	2.928456	(111)
3	$ZrTiO_4$	32.910	13.50	2.719389	(020)
4	$ZrTiO_4$	40.398	3.10	2.23093	(102)
5	$ZrTiO_4$	42.110	6.80	2.14410	(121)
6	$ZrTiO_4$	52.606	16.00	1.738363	(202)
7	$ZrTiO_4$	63.247	10.10	1.46910	(222)
8	$ZrTiO_4$	79.703	3.00	1.20209	(330)

Table 2 was shown 8 peaks all of them indicate of zirconium titanate. The values match with PDF No.; 01-074-1504.

Dimensions of the crystal lattice: a=4.81310 , b=5.43878 , c=5.02307

3.2. Results of DTA:

Fig. 2, was shown thermenal behavior of zirconium titanate without dried or calcined.

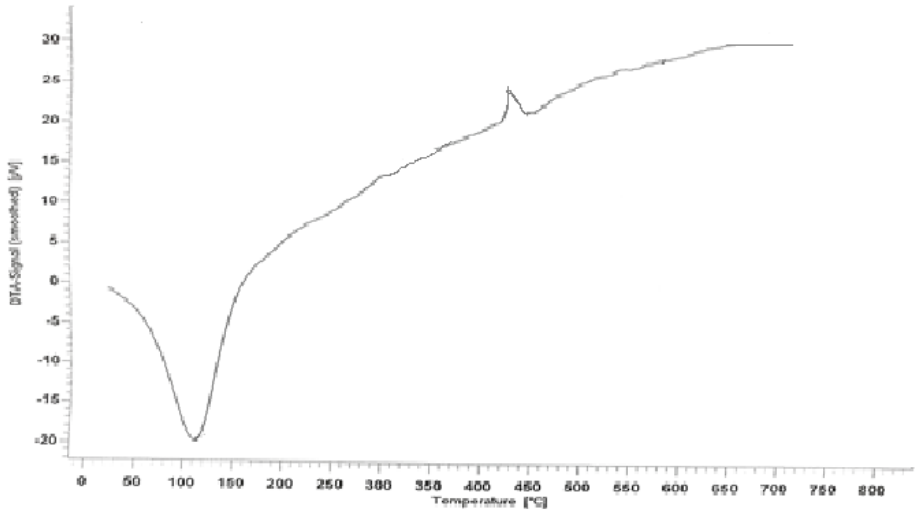

Fig. 2 DTA of $ZrTiO_4$ prepared by hydrothermal for (Ti:Zr=0.1:0.1)

Table (3) result of analysis by DTA

Compound	Peak (DTA) (T°C)	Shape	Explanation
$ZrTiO_4$ (Ti:Zr=0.1:0.1) [NH_4OH] = 6M	**111.2**	**endo**	**-tearing out molecular of crystalline water**
	425.3	**exo**	**-starting crystallization of zirconium titanate**

3.3. Results of FT-IR studies:

The infrared spectra (IR) of the zirconium titanate (fig.3) show the following peaks: 523.436 cm^{-1} (Zr-O-Ti str), 647.325cm^{-1} (Ti-O str),427.112cm^{-1} (Zr-O str),3426.89 – 1636.30cm^{-1} due to the vibration anddeformation frequency of OH group which absorb water during sample preparation, 1384.64,1321.00cm^{-1} (M-OH str;M=Ti,Zr).

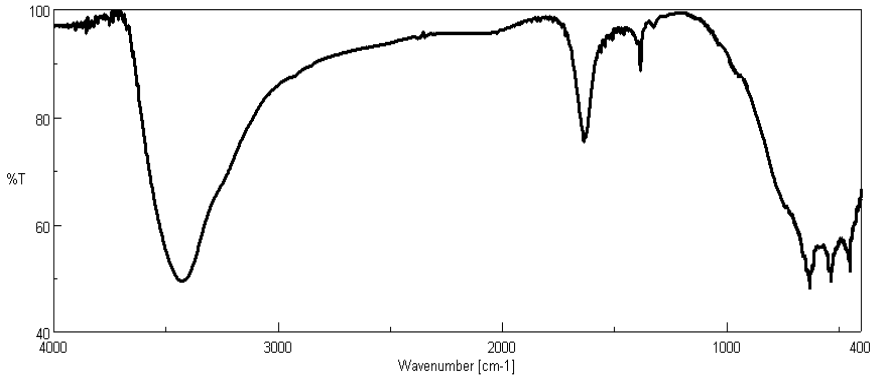

Fig.3 FT-IR of $ZrTiO_4$ prepared by hydrothermal for (Ti:Zr=0.1:0.1)

4. Conclusions:

In this work, the zirconium titanate was synthesized by the hydrothermal method, and the results of the study showed an X-ray that it crystallizes according to the specific pattern existing at the degree of 500C° and above, and this was confirmed by the results of the differential thermal analysis that showed the beginning of crystallization at the degree 425C° as well as the results of the study with the infrared spectrum, which showed an elongation of return for the association bond Zr-O-Ti.

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