ISSN 0036-0236, Russian Journal of Inorganic Chemistry, 2019, Vol. 64, No. 14, pp. 1829–1835. © Pleiades Publishing, Ltd., 2019.

PHYSICOCHEMICAL ANALYSIS OF INORGANIC SYSTEMS

Synthesis and Characterization of Thorite Nanoparticles by Hydrothermal Method

A. Ghadiri[a], M. Abdollahy[a, *], A. Khanchi[b], M. R. Khalesi[a], and M. Akbari[c]

[a] *Mineral Processing Department, Tarbiat Modares University, Tehran, 14115-143 Iran*

[b] *Nuclear Science and Technology Research Institute (NSTRI), Tehran, 14155-1339 Iran*

[c] *School of Mining, College of Engineering, University of Tehran, Tehran, 4563-11155 Iran*

**e-mail: minmabd@modares.ac.ir*

Received June 26, 2019; revised September 26, 2019; accepted September 27, 2019

Abstract—The synthesis of thorium silicate (thorite) was carried out to characterize the parameters affecting the process. A synthetic thorite with formula $ThSiO_4$ was prepared by hydrothermal method with a mixture of 0.14 M thorium chloride ($ThCl_4$) solution and sodium silicate containing 0.14 M SiO_2. The effect of several experimental parameters on synthesis of thorite was investigated. The most important of these parameters were the pH of solution in hydrothermal process and volumetric ratio of SiO_2 : $ThCl_4$. The optimum pH in the hydrothermal process was 8–9, which was obtained by buffering with sodium bicarbonate. The increasing of volumetric ratio of SiO_2 : $ThCl_4$ led to gelatinization of synthetic material. The operating conditions of synthesis of thorite were determined as follows: volumetric ratio of SiO_2 : $ThCl_4$ = 0.9; pH after adding of 8 M NaOH, 8–8.5; pH after adding 0.5 M sodium bicarbonate, 8–9; temperature of heating in furnace, 250°C; time of heating in furnace, 24 h; pH after hydrothermal process, 8–9; temperature of drying in oven, 60°C; time of drying in oven, 24 h. In each batch of synthesis process, about 2.2 g or 7 mmol of thorium silicate was produced. The purity of thorite was determined 97.80%.

Keywords: hydrothermal method, thorite, thorium, silicate

DOI: 10.1134/S0036023619140122

INTRODUCTION

Thorium is most abundant actinide in nature and a very high radioactive element and could be considered as a candidate for replacement with uranium in nuclear power reactors. Abundance of thorium in the earth's crust is estimated to be three times of uranium and more potential production of energy than both uranium and the fossil fuel reserves [1, 2]. Thorite ($ThSiO_4$) is an orthosilicate of thorium, isostructural with zircon ($ZrSiO_4$) and coffinite ($USiO_4$) [3–7], that is crystalizes in the tetragonal system. It is dimorph with huttonite and has paramagnetic and radioactive properties. The occurrence of this mineral is in felsic igneous rocks and their associated pegmatites [8]. Today several routes are developed to synthesize $ThSiO_4$: via hydrothermal method [9–11], thermal gradient flux technique [7, 12, 13], sol-gel approach [14], solid-state synthesis [15, 16] and vapor-phase reaction [17].

In hydrothermal method for the production of synthetic thorite, Frondel and Collette synthesized by mixing of silica (SiO_2) and thoria (ThO_2) gels in water at range of 150° and 4.8 bars to 700°C and 1000 bars as temperature and pressure of synthesis, in different duration times [9]. Thorite was synthesized by Prasad in sealed pyrex glass tubes by heating thorium chloride solution at 180°C. For synthesis, a 0.02 M solution of thorium chloride was heated in a stout sealed pyrex tubes to 180°C for 48 h. The synthesized solid was separated, washed and dried at room temperature [10]. Mumpton and Roy synthesized thorite successfully with $Th(NO_3)_4 \cdot 4H_20$ and $SiCl_4$. These components were dissolved in ethanol separately and then mixed with together by the addition of distilled water. By rapid mixing, the resulting solution was added as slowly to concentrated ammonium hydroxide solution (NH_4OH) in a beaker. After that, thorium hydroxide and $Si(OH)_4$ were formed as gel precipitate. The precipitate was filtered and dried overnight, and then was ignited at 350°C for 24 h. At temperature of 1175°C and below, the equal ratio of SiO_2 and ThO_2 was resulted to formation of thorite in all water pressure [11].

In thermal gradient flux technique, thorite was synthesized according to different procedures. Taylor and Ewing grew thorite crystals in 5 mm Pt tubes from a Na_2WO_4 melt which was 10% by weight $ThO_2 \cdot SiO_2$. The mixture was maintained at 1250°C for 2 days in an air-atmosphere muffle furnace [7]. Mazeina et al. synthesized thorite with the mixture of SiO_2 and ThO_2 in

a 1 : 1 molar ratio. Then the crystals of thorite were grown in solvent of $Li_2O \cdot 2WO_3$ in air at 1200°C [12]. Finch et al. performed thorite synthesis experiments with the mixture of SiO_2 and ThO_2 in a 1 : 1 molar ratio. Then the crystals of thorite were grown in di-tungstate or di-molybdate solutions in air atmosphere in covered platinum container at temperature below 1225 ± 10°C [13]. Li et al. synthesized $K_2ThSi_2O_7$ with thorium nitrate, silicon oxide, potassium fluoride and chloride at initial components ratios of 1/8/80/40 and mixed with acetone and then ground in an agate mortar. The mixture was poured into a Pt crucible and inserted into a furnace at 900°C in air for 24 h [14].

Vance synthesized thorite with sol-gel approach. For this propose, the mixture of $Th(NO_3)_4 \cdot 4H_2O$ and colloidal SiO_2 (30 wt %) with solid concentration of 0.1 moles were prepared, to obtain a relatively clear solution having a pH ~ 1. Then pH was adjusted in 6 or 11 with addition of 2 M NH_4OH. For drying, the gelatinous precipitate was heated overnight and calcined at temperature about 500°C for several times to eliminate the organic and nitrate materials. The calcines were ground in alumina grinder by wet process in 2-propanol for ~2 days, and then evaporated to dryness [15].

In some studies, thorite was synthesized by solid-state method. Vilmin et al. grew thorite crystals with solid-state method. A stoichiometric ratio of $Th(NO_3)_4 \cdot 4H_2O$ solution and tetra ethyl orthosilicate (TEOS) in ethanol in a Parr bomb was resulted to formation of thorite. The temperature and time of synthesis were adjusted at 200°C and 2 days, respectively. The thorite nano-particles are absolutely crystalline and approximately 30 nm in diameter [16]. Fuchs grew crystals of thorite up to 1 mm in diameter in described manner. A mixture of 55 mol % ThF_4 and 45 mol % $KThF_5$ were melted at 875°C. After that, 0.2 g of this mixture, 0.11 g of powdered ThO_2 and 0.04 g of powdered vitreous silica were poured in Monel cup. Argon atmosphere was added and the cup was sealed. Then sample was heated in a muffle furnace for 13 days at 920°C and slowly cooled to room temperature over a period of 2 days [17]. Knyazev et al. synthesized $Ca_2Th(Si_8O_{20})$ in a platinum crucible. In the first step, the thorium and calcium nitrates were annealed at 920 K to remove nitrate from component, after which the temperature was elevated stepwise (250 K step) in presence of silicon oxide, with intermediate grindings in an agate mortar [18].

In vapor-phase reaction method, Kamegashira synthesized thorite as a single crystal by the reaction of thorium chloride with pyrex glass. In this process, ThO_2 as a main material was poured in a quartz tube with HCl or $C1_2$ gas and was heated in 1050°C (hot zone) for the formation of $ThCl_4$. Then some parts of $ThCl_4$ (in vapor state) would react with the quartz tube in 950°C (cold zone) and was resulted in the formation of $ThSiO_4$ as a single crystal [19].

In this study, thorite was synthesized by hydrothermal method. The propose of this study, is to investigate the effective parameters on synthesis process and to develop a reproducible synthesis procedure for thorite from which would produce enough synthetic thorite to study the dissolution mechanism of thorite in different media.

EXPERIMENTAL

Materials and Synthesis Procedure

All the reagents used here were supplied from Merck and were analytical grade, except thorium nitrate from Chinese Company.

In this investigation, the synthesis of thorite ($ThSiO_4$) was carried out using a hydrothermal method, roughly in accordance with the protocols for the synthesis of coffinite and uranothorite ($Th_{1-x}U_xSiO_4$) [20–24]. In first stage, thorium tetra chloride ($ThCl_4$) was prepared by multi successive batches of dissolution of hydrated thorium nitrate ($Th(NO_3)_4 \cdot 5H_2O$) in 8 M HCl and evaporation that was resulted in the elimination of nitrate and substitution of chloride (Eq. (1)):

$$Th(NO_3)_4 \cdot 5H_2O + 8HCl \rightarrow ThCl_4 + 4NO_2\uparrow + 9H_2O\uparrow + 2Cl_2\uparrow. \quad (1)$$

With individually dissolving of thorium chloride ($ThCl_4$) and sodium silicate solution (Na_2O = 7.5–8.5, SiO_2 = 25.5–28.5%) in deionized water, solutions of $ThCl_4$ and SiO_2 with concentrations of 0.14 M were prepared. 0.14 M $ThCl_4$ solution was added drop wise to a 0.14 M SiO_2 solution at a certain volumetric ratio of SiO_2 : $ThCl_4$. After that, 8 M NaOH solution was added drop wise to reach pH to 8–8.5 (Eq. (2)). In this point, white gelatinous phase was formed. Finally, the pH of gelatinous phase was buffered around 8–9 by adding 0.5 M $NaHCO_3$.

$$ThCl_4 + SiO_2 + Na_2O + 8NaOH \xrightarrow{\text{pH 8–8.5}} Th(OH)_4\downarrow + Si(OH)_4\downarrow + 4NaCl + 3Na_2O. \quad (2)$$

The gel, containing $Th(OH)_4$ and $Si(OH)_4$ was poured in to PTFE (polytetrafluoroethylene) autoclave (volume = 200 mL), then was heated to 250°C for 24–48 h (Eq. (3)):

$$Th(OH)_4 + Si(OH)_4 \rightarrow ThSiO_4 + 4H_2O. \quad (3)$$

After heating, the resulting precipitate was filtered from supernatant solution. For the removal of soluble compounds and probably organic compounds, precipitate was washed with deionized water and ethanol. Finally, precipitate was dried in 60°C for 24 h.

Based on the described conditions, the production of significant amount of synthetic thorite (50 g) is the

main objective for the investigation of the mechanism and kinetic of thorium silicate dissolution in acidic media. The increase in the amount of produced material in any synthesis batch, in comparison with previous work, is a distinguishing feature of this research. In each batch of synthesis process of uranothorite and coffinite [20–22], 1 mmol thorium chloride was used, but in this research, 7 mmol thorium chloride was prepared under similar volume of autoclave. In the synthesis process of thorite, the effect of volumetric ratio of SiO_2 : $ThCl_4$, precipitation pH after adding of 8 M NaOH, amount of 0.5 M $NaHCO_3$, pH of solution after hydrothermal process and time of heating in furnace were investigated.

Characterization Techniques

Scanning electron microscopy (SEM). Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray Spectroscopy (EDXS) analysis were conducted on a ZEISS EVO 18 Scanning Electron Microscope; operating at 25 kV with 200 nm resolution at a working distance of 8.5 mm and EDAX SSD detector. The powdery sample was pressed on an adhesive carbon tab then was coated with gold.

X-ray diffraction (XRD). X-ray Diffraction (XRD) patterns were recorded on a STOE STADI, MP, GERMANY, equipped with the IP detector using CuK_α radiation (λ = 1.5405 Å). XRD analysis was performed at room temperature in the $5° < 2\theta < 100°$.

X-ray fluorescence (XRF). X-Ray fluorescence was done with an Oxford Instruments spectrometer ED 2000, equipped with an Ag-anode tube, operating at 40 kV, 6 μA and a Si–Li detector with liquid nitrogen cooling, with an energy resolution 140 eV for the 5.9 keV MnK_α line.

Brunauer–Emmett–Teller (BET). Surface area analysis was performed on a Quantachrome Nova Win2 instrument. The synthesized sample was degassed for 4 h at temperature of 290°C. Nitrogen was used as the analysis gas.

Dynamic Light Scattering (DLS). For determination of size distribution of synthesized thorium silicate was used from Malvern Zetasizer Nano ZS (red badge) (ZEN 3600, Malvern, United Kingdom). For measurement of size distribution, a diluted suspension of synthesized material was prepared. Then, 2 mL of this mixture was poured in a polymer cuvette and then was inserted in DLS instrument for measuring of size distribution. Temperature of measurement was set to 25°C.

RESULTS AND DISCUSSION

The Effect of Volumetric Ratio of SiO_2 : $ThCl_4$

Due to the stoichiometric condition (Eq. (2)), the volumetric ratio of SiO_2 : $ThCl_4$ is equal to one; however, different volumetric ratios were investigated. Table 1 shows the effect of different parameters on thorite synthesis.

According to Table 1, an increase in amount of SiO_2 result in the formation of gelatinous precipitate, this is probably due to the presence of excess SiO_2. In volumetric ratios of 1 and less, the precipitates were completely powdery. The results show that the volumetric ratio did not have a direct effect on the synthesis of thorium silicate. The high volumetric ratio of SiO_2 : $ThCl_4$, can leads to gelatinization and an increase in the amount of amorphous phase in the synthesized material. The volumetric ratios of 1, 0.96 and 0.9 (Experiments nos. 7–10) resulted in the successful synthesis of the thorite. The volumetric ratios of 0.9–1 were selected for synthesis experiments. In the synthesis of uranothorite, 1.03 mmol of silicate was added to 1 mmol $ThCl_4$ (volumetric ratio of SiO_2 : $ThCl_4$ was equal to 1.03) [20, 21].

The Effect of Adding NaOH and $NaHCO_3$

Table 1 presents the effect of adding NaOH and $NaHCO_3$ on the synthesis of thorite. Comparison of experiments 7 and 8 indicated that by adjusting the pH at 8 and 8.5 by adding 8 M NaOH, it was not observed any change in the synthesis process in this range.

The results on the effect of sodium bicarbonate in Table 1 show that this compound has a significant effect in the synthesis process of thorite. When the pH of solution was fixed around 8–9 with adding certain amounts of sodium bicarbonate after precipitation stage, the synthesis process was well completed. In experiments nos. 1–6, by adding 10 or 25 drops from 0.5 M $NaHCO_3$, the pH of solution reached 8.6, but after the hydrothermal process, the pH of solution was not buffered and decreased. As can be seen in Table 1, several of compounds were produced in the synthesis process; therefore, the process was not performed successfully. For this reason, $NaHCO_3$ was added to solution equivalent to 0.5 M. Accordingly to this, pH after the hydrothermal process fixed in the range of 8–9. In this situation, thorite was obtained as the only synthesis product (experiments nos. 7–10). Therefore, it can be concluded that maintaining pH in the range of 8–9 has a major role in the hydrothermal synthesis of thorite.

The Effect of Time of Hydrothermal Process

The results of experiments nos. 1 and 6 in Table 1 show that the increasing of heating time in the furnace from 24 to 48 h did not have any significant effect on the elimination of unwanted compounds and the improvement of synthesis process of thorite.

A total of 10 synthesis experiments were carried out in different conditions. The synthesized samples were characterized using XRD. The set of XRD diffracto-

Table 1. Effect of different parameters on thorite synthesis

Experiment no.		1	2	3	4	5	6	7	8	9	10
Volume of 0.14 M $ThCl_4$, mL		50	50	50	50	50	50	50	50	50	50
Volume of 0.14 M SiO_2, mL		50	75	80	100	120	50	50	50	48	45
Volumetric ratio of SiO_2 : $ThCl_4$		1	1.5	1.6	2	2.4	1	1	1	0.96	0.9
pH after adding of NaOH = 8 M		8.5	8.5	8.5	8.5	8.5	8.5	8	8.5	8.5	8.5
Amount of $NaHCO_3$ = 0.5 M		25 drop	10 drop	10 drop	10 drop	10 drop	25 drop	4.2 g solid $NaHCO_3$ was added to 100 mL of a mixture of $ThCl_4$ and SiO_2 (equivalent to 0.5 M sodium bicarbonate)	4.2 g solid $NaHCO_3$ was added to 100 mL of a mixture of $ThCl_4$ and SiO_2 (equivalent to 0.5 M sodium bicarbonate)	4.12 g solid $NaHCO_3$ was added to 98 mL of a mixture of $ThCl_4$ and SiO_2 (equivalent to 0.5 M sodium bicarbonate)	3.99 g solid $NaHCO_3$ was added to 95 mL of a mixture of $ThCl_4$ and SiO_2 (equivalent to 0.5 M sodium bicarbonate)
pH after adding of $NaHCO_3$ = 0.5 M		8.6	8.64	8.6	8.6	8.6	8.6	8.67	8.77	8.13	8.07
Heating in furnace	*T*, °C	250	250	250	250	250	250	250	250	250	250
	τ, h	24	24	24	24	24	48	24	24	24	24
pH after hydrothermal process		3.03	5.75	5.89	6.49	6.57	3.23	8.85	8.77	8.34	8.22
Drying in oven	*T*, °C	60	60	60	60	60	60	60	60	60	60
	τ, h	24	24	24	24	24	24	24	24	24	24
Compounds detected by XRD		Thorite, Thorium oxide	Thorium oxide, Th	Thorium oxide	Thorite, SiO_2	Thorite, Th	Thorite, Thorium oxide	Thorite	Thorite	Thorite	Thorite
Type of precipitate		Powder	Gelatinous	Gelatinous	Gelatinous	Gelatinous	Powder	Powder	Powder	Powder	Powder

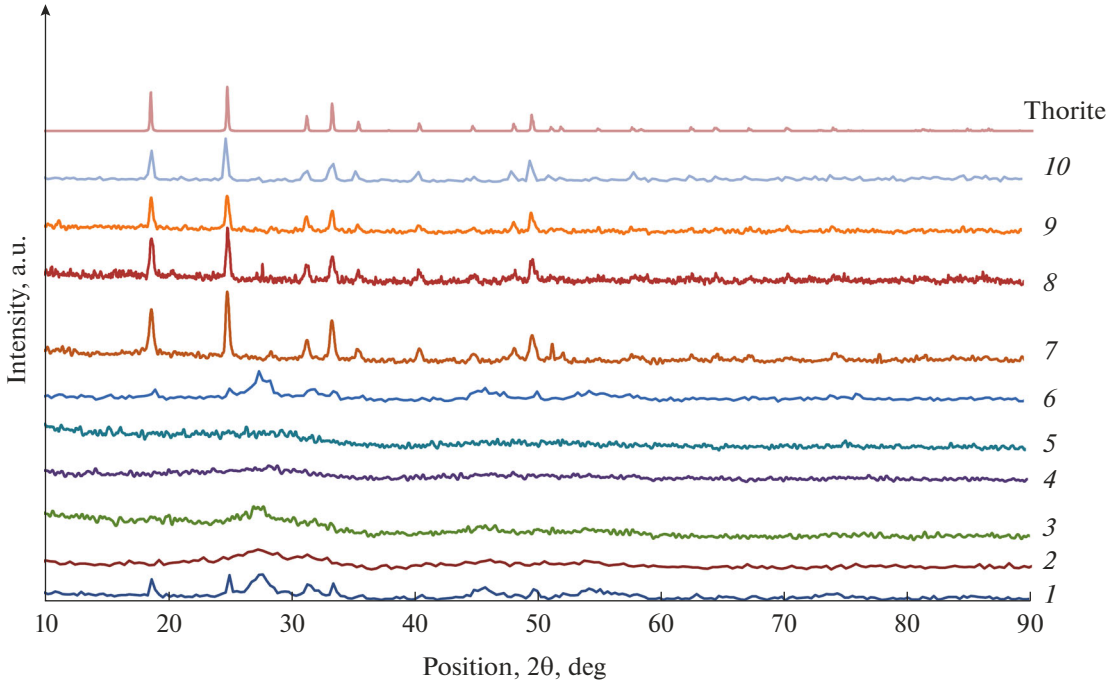

Fig. 1. XRD diagrams of 10 synthesized products compared with thorite ($ThSiO_4$).

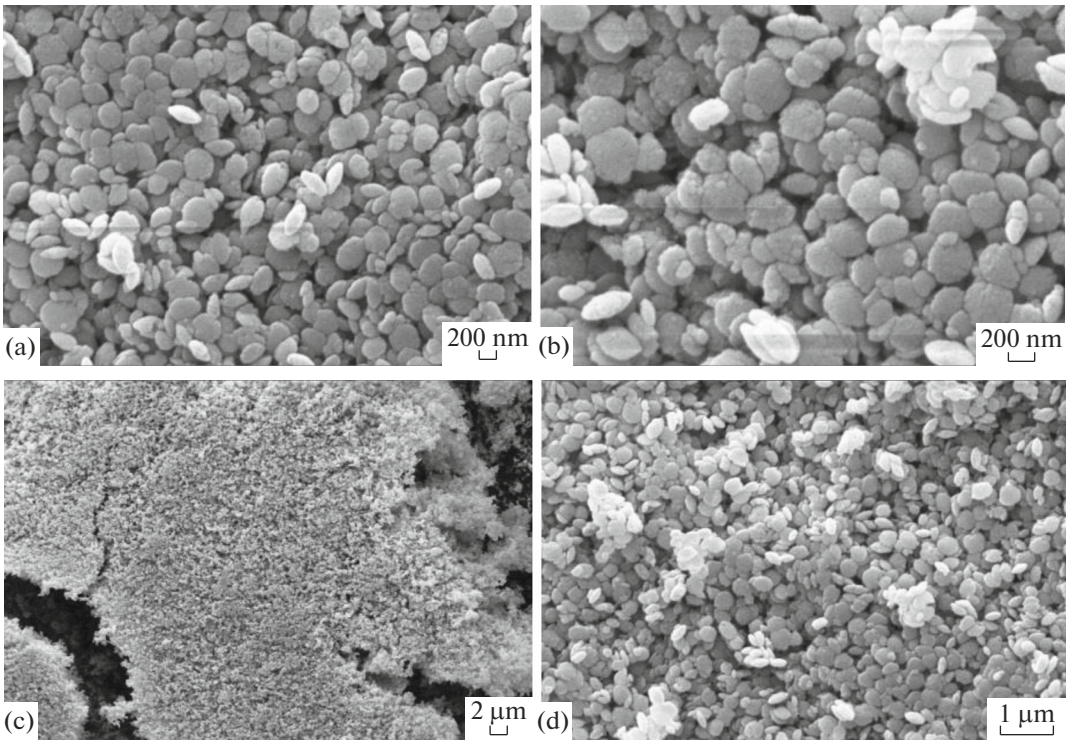

Fig. 2. SEM observations of synthetic thorite.

grams of 10 samples and comparison of these with pure thorite are shown in Fig. 1.

As can be seen, the peak of synthesis materials in experiments nos. 7–9, and especially sample 10, shows a good consistency with the peak of pure thorite. Accordingly, the operating conditions of sample 10 were selected for synthesis of thorite. Table 2 shows these conditions for the synthesis of thorium silicate (thorite).

Table 2. Operating conditions for the synthesis of thorite

Volumetric ratio of SiO_2 : $ThCl_4$	pH after adding of NaOH = 8M	Amount of $NaHCO_3$	pH after adding of $NaHCO_3$ = 0.5 M	Heating in furnace		pH after hydrothermal process	Drying in oven	
				T, °C	*t*, h		*T*, °C	*t*, h
0.9	8–8.5	Equivalent to 0.5 M sodium bicarbonate	8–9	250	24	8–9	60	24

Table 3. Result of EDXS analysis of synthetic thorite

Th, at %	Si, at %	Th/Si
17.01	17.56	0.97
15.69	14.81	1.06
14.57	17.52	0.83
17.59	15.28	1.15
18.22	16.91	1.08
20.76	14.19	1.46
18.08	19.12	0.95
15.44	15.25	1.01
13.76	16.45	0.84
16.86	16.88	1.00
Experimental		
16.80 ± 2.04	16.40 ± 1.51	1.03 ± 0.18
Components in pure thorite		
16.67	16.67	1.00

Characteristic of Synthesized Thorite

Figure 2 shows the SEM micrograph of synthesized thorium silicate at different magnification from 5 to 75 KX. The morphology of the sample is similar to synthesized uranothorite ($Th_{0.5}U_{0.5}SiO_4$) were reported by Costin et al. as bi-pyramidal morphology [21]. Grain size distribution of synthesized thorite was determined with dynamic light scattering analysis (DLS) (Fig. 3). The synthesized sample consisted in crystals ranging from 220.2 to 1990 nm in length. The average length of synthesized thorite was 731.30 nm.

Table 3 shows EDXS analysis for synthetic thorite. From 10 points of analyzed, the Th/Si atomic percent ratios were calculated and the average of these points were 1.03 ± 0.18 that confirm the success of the synthesis of thorium silicate. According to this, the chemical formula of the synthesized sample was determined as $Th_{1.03 \pm 0.18}SiO_4$ which correspond to the synthesis experimental results.

The results of the quantitative analysis of synthesized thorite by EDXS (10 points analyzed) and XRF analysis are presented in Table 4. The results have good consistency with pure thorite. According to Table 4, the lowest estimated purity of the thorite is determined 97.80%.

CONCLUSIONS

Among the different parameters, pH of suspension after hydrothermal process and volumetric ratio of SiO_2 : $ThCl_4$ were considered as affecting parameters on synthesis of thorite. Buffering the pH of the suspension solution at 8–9 in hydrothermal process with the addition of 0.5 M sodium bicarbonate resulted in the high purity of synthesized thorite. At pH < 8, impurities such as SiO_2, Th and ThO_2 were observed

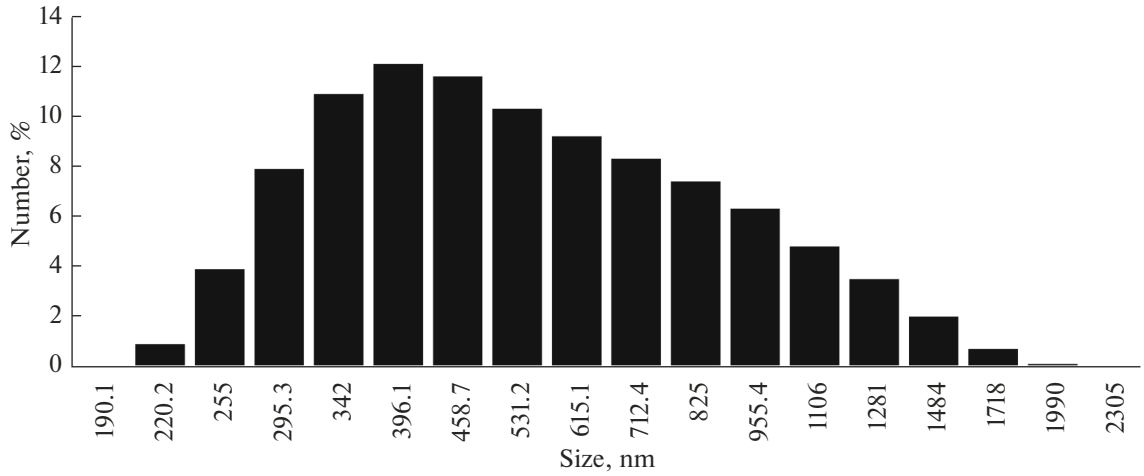

Fig. 3. Grain size distribution of synthesized thorite with DLS.

Table 4. Quantitative analysis of synthesized thorite by EDXS and XRF

Components	Components in synthesized thorite, w/w %		Components in pure thorite, w/w %	Synthesized thorite purity based on components, %	
	EDXS	XRF		EDXS	XRF
Th	71.61	71.41	71.6	100	99.73
Si	8.54	8.45	8.64	98.84	97.80

in the synthesized product. The volumetric ratio of SiO_2 : $ThCl_4$ greater than 1, resulted in gelatinization of the precipitate. The volumetric ratio of SiO_2 : $ThCl_4$ equal to 0.9 was found to be appropriate for synthesis process. Change the pH from 8 to 8.5 by adding 8 M NaOH and also increasing the heating time in the hydrothermal process from 24 to 48 h did not affect the synthesis of thorite.

Operating conditions of synthesis of thorite were determined as follows:volumetric ratio of SiO_2 : $ThCl_4$: 0.9; pH after adding of 8 M NaOH, 8–8.5; pH after adding 0.5 M sodium bicarbonate, 8–9; temperature of heating in furnace, 250°C; time of heating in furnace, 24 h; pH after hydrothermal process, 8–9; temperature of drying in oven, 60°C; time of drying in oven, 24 h. In each batch of synthesis process, about 2.2 g or 7 mmol of thorium silicate was produced. Szenknect et al. [20] and Costin et al. [21] synthesized 1 mM urano-thorite in similar operational conditions. The lowest estimated purity of the thorite was determined 97.80%.

ACKNOWLEDGMENTS

The authors are grateful to AEOI (atomic energy organization of Iran) for the samples analysis by XRD, XRF, BET and SEM.

CONFLICT OF INTEREST

The authors declare that they have no conflict of interest.

REFERENCES

1. http://www.galleries.com/Thorite
2. L. B. Serezhkina, A. V. Savchenkov, and V. N. Serezhkin, Russ. J. Inorg. Chem. **62**, 633 (2017). https://doi.org/10.1134/S0036023617050217
3. C. Frondel, Am. Mineral. **38**, 1007 (1953). https://doi.org/10.3133/tei327
4. L. R. Stieff, T. W. Stern, and A. M. Sherwood, Am. Mineral. **41**, 675 (1956). https://doi.org/10.3133/tei538
5. L. H. Fuchs and E., Gebert, Am. Mineral. **43**, 243 (1958).
6. I. R. Shein, K. I. Shein, and A. L. Ivanovskii, Phys. Chem. Minerals. **33**, 545 (2006). https://doi.org/10.1007/s00269-006-0100-3
7. M. Taylor and R. C. Ewing, Acta Cryst., Sect. B **34**, 1074 (1978). https://doi.org/10.1107/S0567740878004951
8. J. W. Anthony, R. A. Bideaux, K. W. Bladh, and M. C. Nichols, *Handbook of Mineralogy* (Mineralogical Society of America, Chantilly, 2003).
9. C. Frondel and R. L. Collette, Am. Mineral. **42**, 759 (1957).
10. D. P. Sinha and R. Prasad, J. Inorg, Nucl. Chem. **35**, 2612 (1973). https://doi.org/10.1016/0022-1902(73)80343-4
11. F. A. Mumpton and R. Roy, Geochim. Cosmochim. Acta **21**, 217 (1961). https://doi.org/10.1016/S0016-7037(61)80056-2
12. L. Mazeina, S. V. Ushakov, A. Navrotsky, and L. A. Boatner, Geochim. Cosmochim. Acta **69**, 4675 (2005). https://doi.org/10.1016/j.gca.2005.03.053
13. C. B. Finch, L. A. Harris, and G. W. Clark, Am. Mineral. **49**, 782 (1964).
14. H. Li, P. Kegler, V. V. Klepov, et al., Inorg. Chem. **57**, 6734 (2018). https://doi.org/10.1021/acs.inorgchem.8b01072
15. E. R. Vance, Mat. Res. Bull. **21**, 321 (1986). https://doi.org/10.1016/0025-5408(86)90189-3
16. G. Vilmin, S. Komarneni, and R. Roy, J. Mater. Res. **2**, 489 (1987). https://doi.org/10.1557/JMR.1987.0489
17. L. H. Fuchs, Am. Mineral. **43**, 367 (1958)
18. A. V. Knyazev, N. G. Chernorukov, and M. E. Komshina, Radiochemistry **54**, 431 (2012). https://doi.org/10.1134/S1066362212050025
19. N. Kamegashira, J. Mater. Sci. **14**, 505 (1979). https://doi.org/10.1007/BF00589853
20. S. Szenknect, D. T. Costin, N. Clavier, et al., Inorg. Chem. **52**, 6957 (2013). https://doi.org/10.1021/ic400272s
21. D. T. Costin, A. Mesbah, N. Clavier, et al., Prog. Nucl. Energ. **57**, 155 (2012). https://doi.org/10.1016/j.pnucene.2011.10.004
22. V. Pointeau, A. P. Deditius, F. Miserque, et al., J. Nucl. Mater. **393**, 449 (2009). https://doi.org/10.1016/j.jnucmat.2009.06.030
23. H. Reynolds, J. Tardio, S. Bhargava, Proceedings of Chemeca, 1 (2011)
24. S. Labs, C. Hennig, S. Weiss, et al., Environ. Sci. Technol. **48**, 854 (2014). https://doi.org/10.1021/es403995b