Short communication

A new method for alkaline-earth monouranates preparation by solid state and chlorination reactions

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GRAPHICAL ABSTRACT
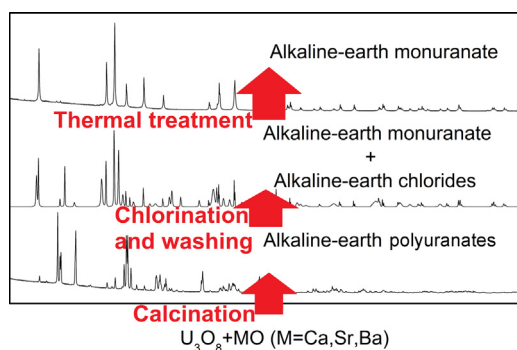
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ABSTRACT

Alkaline-earth monouranates with the formula MUO_4 (M = Ca, Sr, Ba) were synthesized using a novel method which consists of a combination of solid state reaction between U_3O_8 and alkaline-earth oxide or carbonate in air, and chlorination reaction of the product of the solid state reaction using $Cl_2(g)$ as chlorinating agent. The chlorination temperature was optimized to obtain the desired uranate. The products obtained after the chlorination reactions were washed with deionized water and thermally treated to crystallize the uranates. $MgUO_4$ could not be synthesized and presents a different behavior due to the similarity in the starting temperatures of the magnesium and uranium oxide chlorination reactions. The monouranates were characterized by PXRD, SEM and chemical analysis to determinate their structures.

1. Introduction

Metal monouranates, MUO_4, are of considerable interest due to their importance in actinide chemistry and nuclear technology, with barium and strontium being important fission products [1]. Uranates are essentially insoluble in aqueous, non-aqueous and molten salt systems [2,3].

Preparation methods for alkaline-earth uranates have been reported in the literature and include two different methodologies:

- Solid state methods: alkaline-earth monouranates are prepared by mixing powdered MCO_3 or $M(NO_3)_2$ with U_3O_8 or UO_3, in appropriate stoichiometric quantities. The powdered mixtures are compacted into pellets and calcined in air at high temperatures (generally around 900 °C) for a long time with intermittent cooling, crushing, mixing and pressing to ensure homogeneity during the reaction until the completion of the reactions and sample purity and to prevent the formation of secondary phases. This method requires more than one heating of mixtures due to the formation of secondary phases such as polyuranates, polyalkaline uranates or unreacted reactants [2–8].
- Precipitation methods: stoichiometric ratios of uranyl acetate or uranyl nitrate and alkaline-earth cation are mixed in water until pH reaches 9 to form precipitate, and heated for complete drying. Generally, the precipitates are calcined under O_2 or air at high temperature to grow the crystals. These reactions are sometimes carried out in CO_2-free atmospheres to prevent precipitation of MCO_3 [9–12].

In a previous study we observed the formation of single phase $CaUO_4$ as a result of the reaction between a mixture of calcium uranates and $Cl_2(g)$ at 400 °C. This study proposes a new method of alkaline-earth monouranates synthesis using a combination of one solid state reaction and a chlorination reaction to eliminate secondary phases. U_3O_8 and excess MCO_3 are used as solid reactants and $Cl_2(g)$ as chlorinating agent [12].

The present study focuses on the preparation of alkaline-earth monouranates using a novel method which enables the synthesis of MUO_4 (M = Ca, Sr or Ba). The advantage of this method is that it does not need several steps of intermittent cooling, crushing, mixing and pressing, such as is required in the solid state method to avoid formation of other species. The first step of the proposed method consists of thermal treatment of U_3O_8 with excess MCO_3 (or the respective oxide) for 8 to 10 h, the second step involves chlorination of the product formed in the previous treatment and finally, the chlorination products are washed and heat treated in order to obtain the monouranates.

2. Experimental

Initially, alkaline-earth uranates (initial uranates) were prepared by heating the respective analytical grade carbonates with U_3O_8 in 3:1 molar ratios of alkaline-earth and uranium in air at 900 °C, except for the mixture of magnesium oxide and U_3O_8, which was treated at 1000 °C in a muffle furnace for about 6 h in an alumina boat. The reactants were previously mixed in an agate mortar. Samples were characterized by room temperature powder X-ray diffraction (PXRD), Scanning Electron Microscopy (FEI Nova Nano SEM 230). PXRD data were collected using a D8 Advance diffractometer (Bruker AXS, Germany) with Bragg-Brentano θ/θ geometry and Cu Kα radiation (40 kV, 30 mA). The diffraction angles were measured from 10 to 100° of 2θ in 0.02° steps with a counting time of 3 s per step. The X-ray diagrams of the initial uranates and of the alkaline-earth monouranates were refined and the phases present were quantified by the Rietveld method using DIFFRACplus TOPAS 4.2 software [13]. The following parameters were refined: scale factor, background coefficients (Chebyshev polynomial of 7 order), crystallite size, zero-shift and sample displacement, peak shape parameters (using Fundamental Parameters FP), atomic positional and unit-cell parameters. The structures were refined using reference patterns from the ICDD PDF database [14] as initial structural model for each compound.

A quartz fixed-bed reactor was used in chlorination reactions with the aim of obtaining alkaline-earth monouranates. The reactor consisted of a horizontally mounted tube 30 mm in diameter located inside an electric furnace where the sample was introduced using a silica glass crucible (area = 1 cm², height = 0.5 cm). The reactant gas was introduced when the system reached the working temperature. The

experimental conditions were: $pCl_2(g) = 1$ atm; $Cl_2(g)$ flow = $3\,L\,h^{-1}$; $m_0 = 20$ mg. To end each run, the reactant gas was cut off and a nitrogen stream was introduced to purge the reactor. The products were washed three times with deionized water; the precipitated solids were separated and dried at 100 °C in air. Subsequently, samples were thermally treated to crystallize the uranates due to their hydration during the washing step [10]. The thermal treatment for crystallization step depends on the monouranate. To synthesize $CaUO_4$ and $BaUO_4$ it was performed in a muffle in air at 900 °C. For $SrUO_4$ synthesis (chlorination reaction at 425 °C) an O_2 atmosphere (1 atm) and 700 °C was used. The products obtained after these treatments were analyzed by PXRD (*Final PXRD*).

Chlorination reactions were performed at different temperature ranges for each system: between 350 and 400 °C for Ca, between 400 and 500 °C for Sr, between 500 and 600 °C for Ba and 800 °C for Mg. The temperatures were chosen in order to achieve the lowest temperature at which the reaction takes place and the reaction times are no longer than 6 h. After the chlorination reactions (and before the washing step) the hygroscopic products were opened inside a glove box to be characterized by PXRD (*reaction product PXRD*).

Calcium was analyzed by atomic absorption spectroscopy and uranium was analyzed by UV spectroscopy according to the Arsenazo-III method (pH: 1.5–2 and λ: 650 nm) with standard addition to correct matrix effects [15] in the calcium uranate which was digested with HNO_3 until its dissolution to perform these analyzes. Energy Dispersive Spectroscopy (EDAX Genesis 2000) was used to analyze Sr, Ba and U in strontium and barium uranate.

3. Results and discussion

3.1. Initial uranates

A first thermal treatment is performed with the aim of producing uranates that can be transformed into monouranates by the chlorination method. Table 1 shows the Rietveld analyses of alkaline-earth uranates obtained after these thermal treatments in air at 900 °C. They were analyzed in order to verify that the formed uranates did not have phases of uranates with U/alkaline-earth molar ratios higher than 1 because these uranates could not be transformed into monouranates by the chlorination method proposed in this work.

3.2. Calcium uranate

The isothermal chlorination experiments were performed and the chlorination products (*reaction product PXRD*) were washed and crystallized (*Final PXRD*) as described in the Experimental section. The difference between *reaction product PXRD* and *Final PXRD* was the

Table 1
Rietveld refinement of initial Uranates obtained after thermal treatments in air at 900 °C.

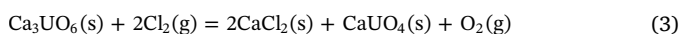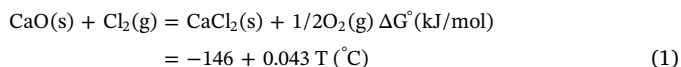| Sample	Compositions	wt%	Space group	Lattice parameter (Å)
Magnesium uranate	$MgUO_4$	68.8	Imam	6.519, 6.592, 6.922
	MgO	31.2	Fm-3 m	4.211
Calcium uranate	Ca_3UO_6	55.9	P1211	5.727, 5.954, 8.297, β = 90.55°
	Ca_2UO_5	4.8	P1211	7.914, 5.437, 11.448, β = 108.88°
	$CaUO_4$	24.5	R-3 mR	6.265, α = 36.04
	CaO	14.7	Fm-3 m	4.810
Strontium uranate	Sr_3UO_6	100	P121/n1	6.011, 6.213, 8.613, β = 90.21°
Barium uranate	Ba_3UO_6	–	I4/mmm	12.624, 17.534
	$BaUO_4$	–	Not reported	5.755, 8.141, 8.233
	$BaUO_3$	–	Pbcm	12.600,17.96, α = 90.1° β = 90.2°
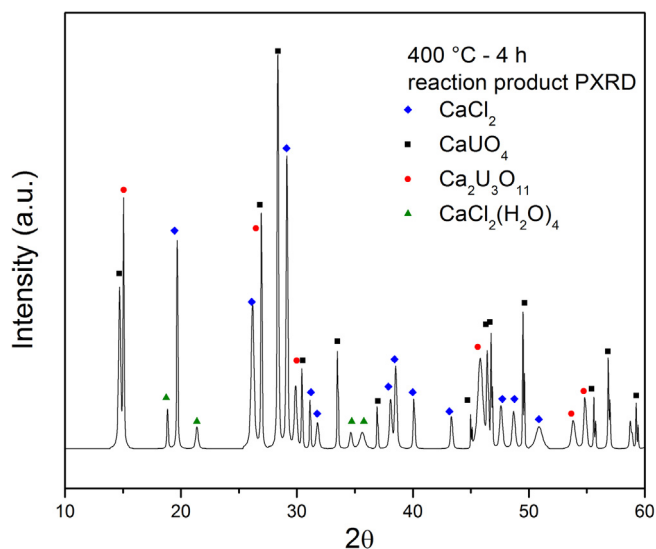
Fig. 1. *Reaction product PXRD of the reaction at 400 °C for 4 h in the Ca/U system.*

presence of $CaCl_2$ in all reactions as is observed in Fig. 1 for the reaction at 400 °C for 4 h.

Fig. 2 shows the *Final PXRD* of the reactions at 350, 375 and 400 °C for 4 h, 4 h and 1 h respectively and the reference patterns of $CaUO_4$, Ca_3UO_6, CaO, Ca_2UO_5 and $Ca_2U_3O_{11}$. Table 2 shows the *Final PXRD* analyses of chlorination reactions under different reaction conditions.

The following reactions are expected:

$$CaO(s) + Cl_2(g) = CaCl_2(s) + 1/2O_2(g) \ \Delta G°(kJ/mol)$$
$$= -146 + 0.043 \ T \ (°C) \quad (1)$$

$$Ca_2UO_5(s) + Cl_2(g) = CaCl_2(s) + CaUO_4(s) + 1/2O_2(g) \quad (2)$$

$$Ca_3UO_6(s) + 2Cl_2(g) = 2CaCl_2(s) + CaUO_4(s) + O_2(g) \quad (3)$$

The $\Delta G°$ could only be calculated for reaction (1) because thermodynamical data for Ca_3UO_6 and Ca_2UO_5 are not available.

At 350 °C, $CaUO_4$ was formed, but the presence of Ca_3UO_6 and Ca_2UO_5 indicate that the formation of $CaUO_4$ was not complete. A
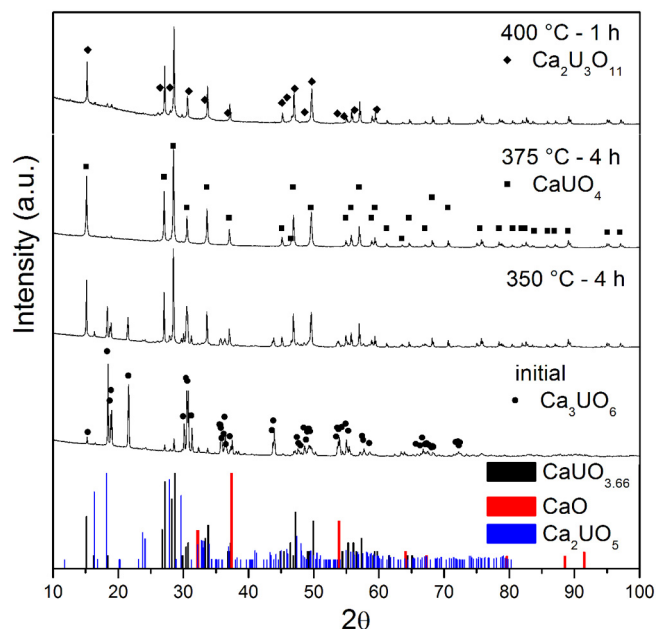
Table 2
PXRD analyses of the washed and crystallized products (*Final PXRD*) in the Ca/U system.

Temperature (°C)	Time (h)	Final PXRD
350	4	$CaUO_4$
		Ca_2UO_5
		Ca_3UO_6
		CaO
		(The same as initial sample)
375	4	$CaUO_4$
375	6	$CaUO_4$
		$Ca_2U_3O_{11}$
400	1	$CaUO_4$
		Ca_2UO_5
		$Ca_2U_3O_{11}$
400	2	$CaUO_4$
		$Ca_2U_3O_{11}$
400	4	$CaUO_4$
		$Ca_2U_3O_{11}$

single calcium monouranate phase ($CaUO_4$) was formed at 375 °C during 4 h, indicating that CaO, Ca_2UO_5 and Ca_3UO_6 reacted with $Cl_2(g)$ according to reactions (1) to (3) to form $CaUO_4$ and $CaCl_2$; the chemical analysis indicated that the calcium monouranate had a Ca/U molar ratio of 1.

In the reactions at 375 °C for 6 h and 400 °C for 1, 2 and 4 h, $Ca_2U_3O_{11}$ phase was formed. Fig. 3 shows the *Final PXRD* of the reaction at 375 °C for 4 h with the reference patterns of $CaUO_4$ and $Ca_2U_3O_{11}$, it can be seen that the *Final product* in the reaction at 375 °C for 4 h is composed by $CaUO_4$ and $Ca_2U_3O_{11}$. The formation of $Ca_2U_3O_{11}$ is due to the reaction between $CaUO_4$ and $Cl_2(g)$ according to the following reaction:

$$CaUO_4(s) + 1/3Cl_2(g) = 1/3Ca_2U_3O_{11}(s) + 1/3CaCl_2(s) + 1/6O_2(g) \quad (4)$$
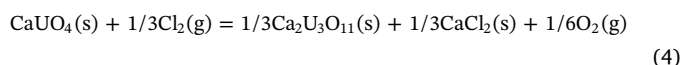
The ratio of the peak intensities for the two uranate phases: $Ca_2U_3O_{11}$:$CaUO_4$ increases with the reaction time (i.e. 1 h, 2 h and 4 h), indicating that more $Ca_2U_3O_{11}$ is being formed through reaction (4). The $Ca_2U_3O_{11}$ phase is not desired, it is a contamination in the synthesis of the desired phase, since it has a U/Ca molar ratio higher than 1 and cannot be transformed to $CaUO_4$ by further chlorination.
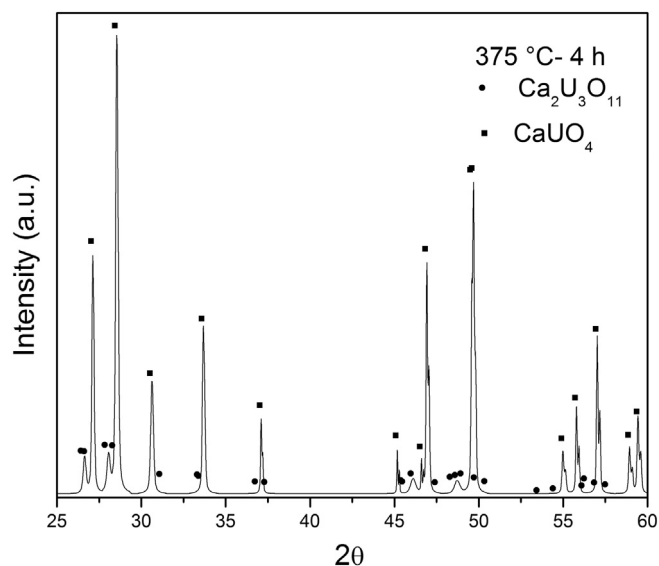

Fig. 2. *Final PXRD of the reactions at 350, 375 and 400 °C in the Ca/U system.*

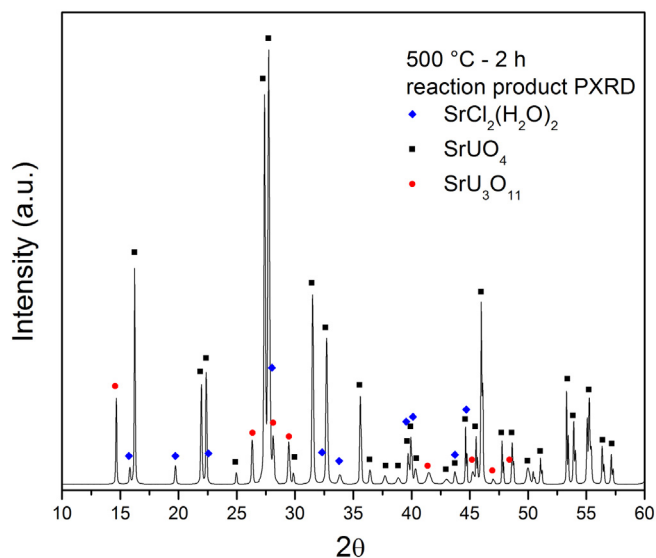**Fig. 3.** *Final PXRD of the reaction at 375 °C for 6 h in the Ca/U system.*

Fig. 4. *Reaction product PXRD of the reactions at 500 °C for 2 h in the Sr/U system.*

3.3. Strontium uranate

Isothermal chlorination experiments were performed and the chlorination products were analyzed by PXRD (*reaction product PXRD* shown in Fig. 4 for the reaction at 500 °C), washed and crystallized (*Final PXRD*). The difference between *reaction product PXRD* and *Final PXRD* was the presence of $SrCl_2$ in all the reactions. Fig. 5 shows the *Final PXRD* of the reactions at 425, 450 and 500 °C for 4 h, 4 h and 2 h respectively and the reference patterns of $SrUO_4$, Sr_3UO_6, $SrUO_{3.597}$ and SrU_3O_{11}. Table 3 shows the *Final PXRD* analyses of the chlorination reactions. At 400 °C for 6 h, $SrUO_4$ was formed, but the presence of Sr_3UO_6 indicates that the formation of $SrUO_4$ was not complete. The formation of $SrUO_4$ is due to the reaction between Sr_3UO_6 and $Cl_2(g)$ according to the following reaction:

$$Sr_3UO_6(s) + 2Cl_2(g) = SrUO_4(s) + 2SrCl_2(s) + O_2(g) \qquad (5)$$
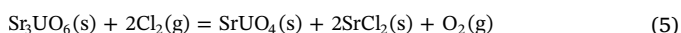
Strontium monouranate is triphasic: α and γ $SrUO_4$ are rhombohedral ($CaUO_4$-type), and β-$SrUO_4$ is orthorhombic ($BaUO_4$-type) [5]. On
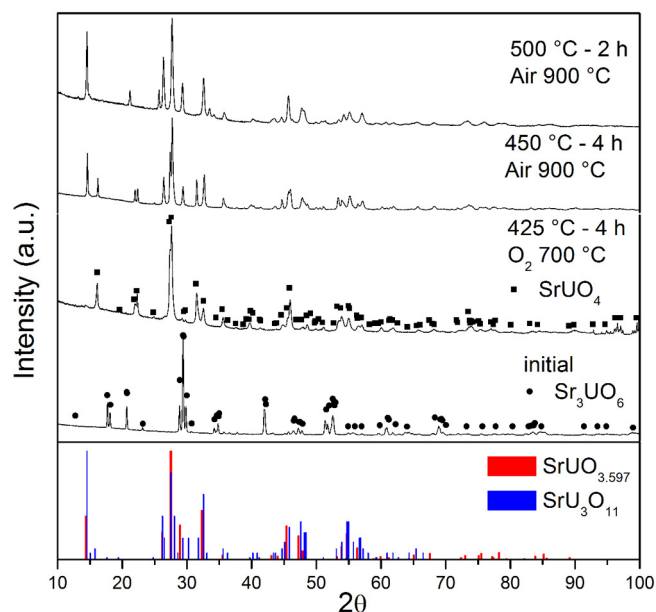

Fig. 5. *Final PXRD of the reactions at 425, 450 and 500 °C in the Sr/U system.*

Table 3
PXRD analyses of the washed and crystallized products (*Final PXRD*) in the Sr/U system.

Temperature (°C)	Time (h)	*Final PXRD*
400[a]	6	$SrUO_4$
		Sr_3UO_6
425[b]	4	$SrUO_4$
450[a]	4	$SrUO_4$
		$SrUO_{3.597}$
500[a]	2	$SrUO_4$
		$SrUO_{3.597}$
		SrU_3O_{11}

[a] Treated in air at 900 °C.
[b] Treated in oxygen at 700 °C.

heating in oxygen at various partial pressures, α-$SrUO_4$ is reduced to $SrUO_{<3.9}$ [5]. This behavior was observed in our experiments. When the chlorination was carried out at 425 °C for 4 h and the products were separated by washing and treated at 700 °C in an O_2 atmosphere ($pO_2(g) = 1$ atm), a single strontium uranate phase (β-$SrUO_4$) was obtained which was checked by EDS analysis what indicated it has a Sr/U molar ratio of 1. But if the washed products of the chlorination reaction at 450 and 500 °C are crystallized at 900 °C in air, β-$SrUO_4$, α-$SrUO_4$ and $SrUO_{3.597}$ phases are observed.

The SrU_3O_{11} phase is formed at 500 °C as a result of the reaction between chlorine and $SrUO_4$ according to the following reaction:

$$3SrUO_4 + Cl_2(g) = Sr_2U_3O_{11} + SrCl_2 + 1/2O_2(g) \qquad (6)$$
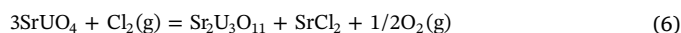
Thermodynamical data for Sr_3UO_6 and $Sr_2U_3O_{11}$ are not available in the literature to calculate the ΔG° values of reactions (5) and (6).

The formation of SrU_3O_{11} is not desired for the synthesis of the pure $SrUO_4$. This behavior, formation of a secondary undesired phase, is analogous to that observed in the Ca/U system for 6 h of reaction at 375 °C and at 400 °C and different reaction times.

3.4. Barium uranate

Isothermal chlorination experiments were performed between 500 and 600 °C. Fig. 6 shows the *reaction product PXRD* of the chlorination at 500 °C for 4 h and the reference patterns of $BaCl_2$, $BaUO_4$ and Ba_3UO_6. Fig. 7 shows the *Final PXRD* (washed and crystallized products) of the chlorination at 500, 550 and 600 °C for 4 h, 6 h and 4 h respectively.
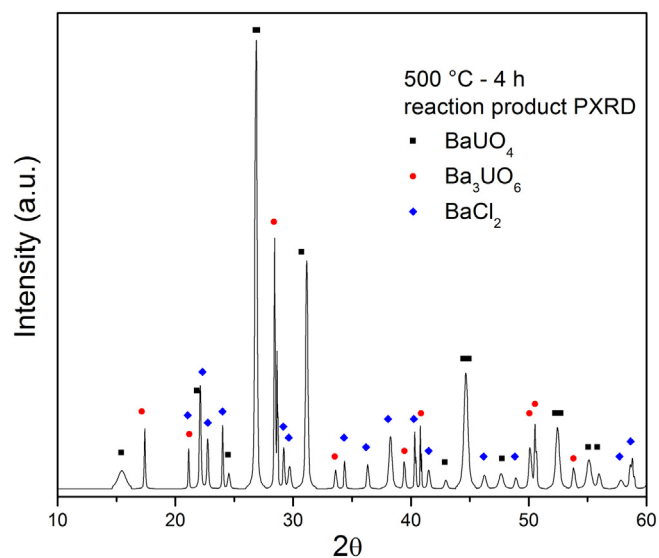

Fig. 6. *Reaction product PXRD of the reaction at 500 °C for 4 h in the Ba/U system.*
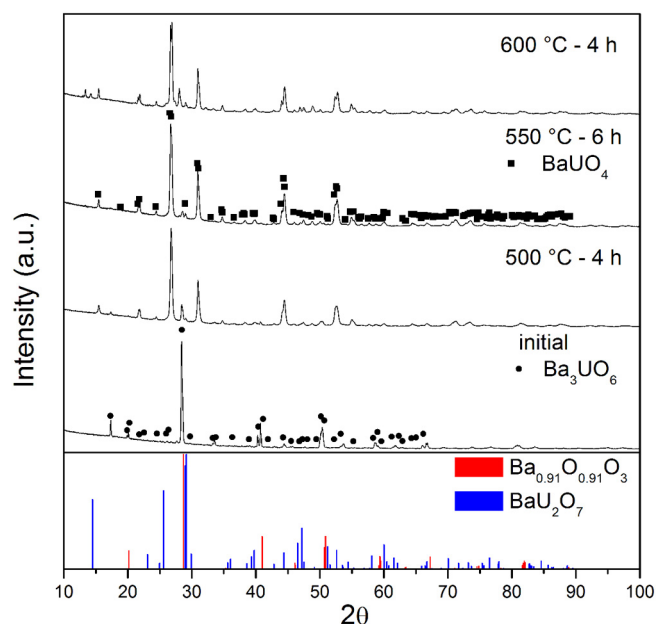
Fig. 7. *Final PXRD* of the reactions at 500, 550 and 600 °C in the Ba/U system.

Table 4
PXRD analyses the washed and crystallized products (*Final PXRD*) in the Ba/U system.

Temperature (°C)	Time (h)	*Final PXRD*
500	4	$BaUO_4$
		Ba_3UO_6
550	4	$BaUO_4$
		Ba_3UO_6
		$Ba_{0.91}U_{0.91}O_3$
550	6	$BaUO_4$
		$Ba_{0.91}U_{0.91}O_3$
600	4	$BaUO_4$
		BaU_2O_7
		$Ba_2U_2O_7$
		Ba_3UO_6

Table 4 shows the *Final PXRD* analyses of the products of these reactions.

To analyze these results some thermodynamical calculations were performed with HSC software [16]. An equilibrium composition calculation considering an initial system containing three solid phases: $BaUO_3$, $BaUO_4$ and Ba_3UO_6, and $Cl_2(g)$ reveals that when equilibrium is reached for temperatures between 500 and 600 °C, formation of $BaCl_2$ and UO_3 is expected. This is in accordance with the reactions shown in the Ellingham diagram (Fig. 8), it can be seen that under standard conditions the most negative ΔG° value corresponds to reaction (14) leading to formation of $BaCl_2$ and UO_3. However, kinetics and none-equilibrium conditions also can influence the course of the reaction. The experimental setup used allows continuous removal of the gaseous reaction products (i.e., O_2). Consequently, O_2 partial pressures will tend to zero, whereas the partial pressure of Cl_2, which is fixed by the incoming chlorine stream, will remain constant. For this reason, the values of ΔG of the reactions leading to O_2 formation will be lower than the values of ΔG°.

In our experimental results formation of UO_3 was not detected at any temperature, indicating that reactions (8), (10) and (14), are not occurring.

In the 4 h reactions at every temperature Ba_3UO_6 was always
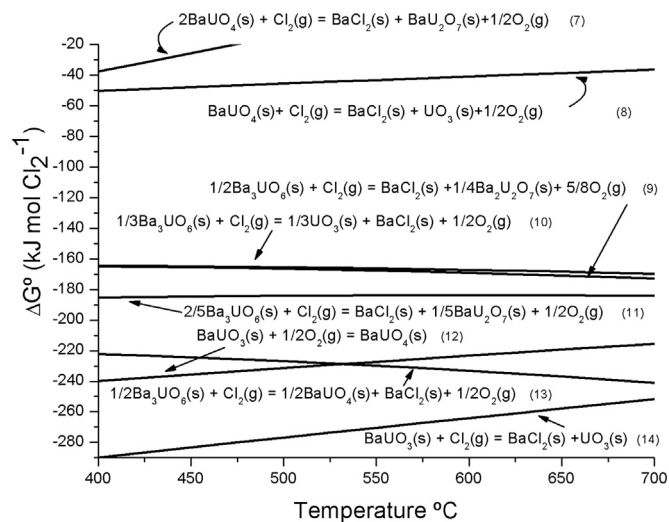

Fig. 8. Ellingham diagram showing ΔG° values for the formation of different compounds as function of temperature in the Ba/U/Cl system.

present, indicating that reaction (13) was not complete. At 600 °C the presence of BaU_2O_7 and $Ba_2U_2O_7$ is evidencing that reactions (11), (9) and may be even (7) are also occurring. The formation of barium diuranate is not desired, since it has a U/Ba molar ratio higher than 1 and cannot be transformed into monouranate by further chlorination. This behavior is similar to what happens in the previous cases, leading to formation of SrU_3O_{11} and $Ca_2U_3O_{11}$. In the chlorination at 550 °C and 6 h all the Ba_3UO_6 was consumed.

The absence of $BaUO_3$ at 500 and 600 °C can be understood considering reaction (12). The oxygen needed for this reaction can be provided by reactions (13) at 500 °C and reactions (13), (11) and (9) at 600 °C.

At 550 °C for 6 h, the presence of $BaUO_4$ and $Ba_{0.91}U_{0.91}O_3$ showed the formation of uranates with equal Ba/U molar ratio, a condition necessary to obtain the desired phase. This result was checked by EDS analysis. The $Ba_{0.91}U_{0.91}O_3$ phase can be transformed into the $BaUO_4$ by treatment in pure oxygen atmosphere [2,17].

3.5. Magnesium uranate

Due to the low reactivity of MgO with chlorine compared to other alkaline-earth oxides, the MgO reaction may occur at temperatures similar to those of uranium oxide chlorination [18]. This condition was observed in the experiments carried out in the Mg/U system.

In the chlorination at 800 °C, the presence of a brown-yellow condensed phase was observed in the cold zone of the reactor, which can be attributed to the formation of $UO_2Cl_2(g)$ during the reaction [12,18]. This condition is not desired for obtaining the monouranate. Also, the phases $MgUO_4$, MgU_3O_{10} and MgO were identified in the *Final PXRD* analyses. The literature includes reports of U_3O_8 and MgO chlorination studies. In U_3O_8 chlorination with formation of UO_2Cl_2 a reaction starting temperature of about 750 °C was determined [18]. On the other hand, the starting temperature for MgO chlorination was about 700 °C [19]. The similarity in the starting temperatures could explain the behavior where the reaction of both oxides with chlorine can occur simultaneously. This behavior has been observed in a previous study [12]. For this reason, the proposed method in the current study was not applicable to the Mg/U system.
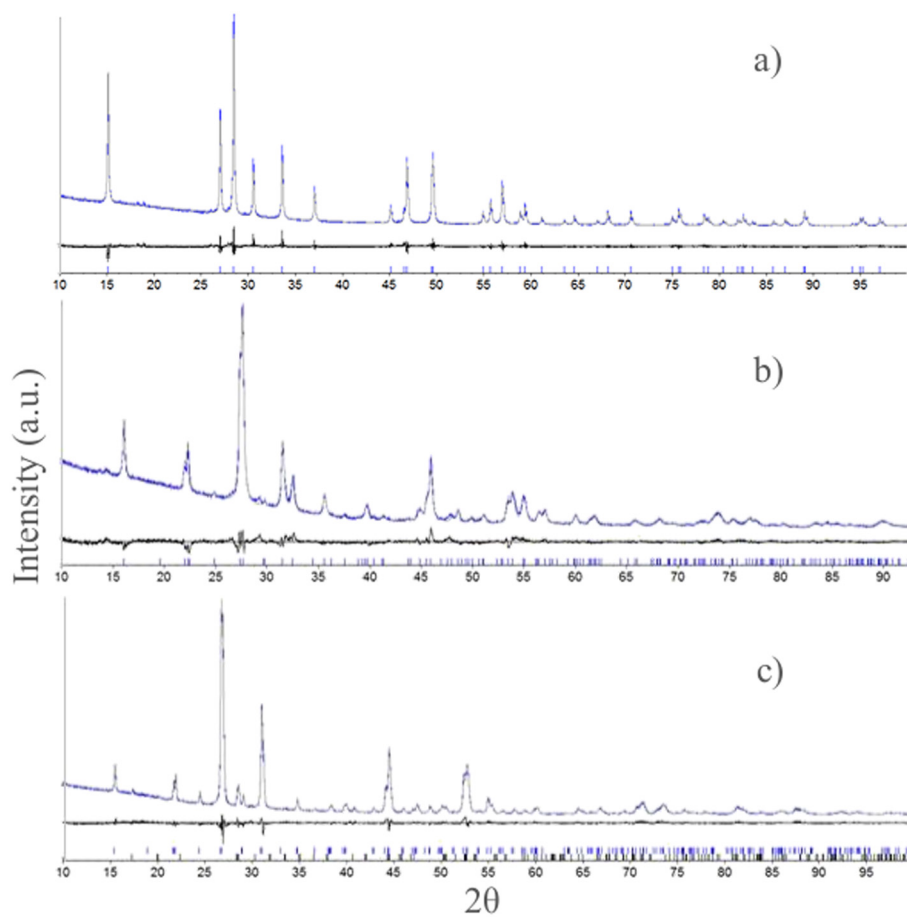
Fig. 9. Observed (dots), calculated (solid line) and difference (bottom line) for PXRD patterns after the refinement of the crystal structure of alkaline earth monouranates a) $CaUO_4$, b) $SrUO_4$, and c) $BaUO_4$.

Table 5
Reliability factors obtained in the Rietveld refinements of the monouranates.

Reliability factors	$CaUO_4$	$SrUO_4$	$BaUO_4$
GOF	2.41	2.21	2.31
R_p (%)	4.54	4.09	4.76
R_{wp} (%)	6.08	5.58	6.28
R_{exp} (%)	2.53	2.53	2.71
R_{Bragg} (%)	2.63	3.44	3.65

3.6. Ca, Sr and Ba monouranates characterization

Fig. 9 shows the Rietveld analyses of Ca, Sr and Ba monouranates. The $CaUO_4$ pattern can be fully indexed in a Rhombohedral unit cell with lattice parameters a ≈ 6.266 Å and α ≈ 36.14° and Space Group *R-3mR*. The $SrUO_4$ pattern was indexed in an Orthorhombic unit cell with lattice parameters a ≈ 5.508 Å, b ≈ 7.968 Å and c ≈ 8.081 Å and Space Group *Pbcm*. The $BaUO_4$ pattern was indexed in an Orthorhombic unit cell with lattice parameters a ≈ 5.753 Å, b ≈ 8.141 Å and c ≈ 8.222 Å and Space Group *Pbcm*. This refinement shows a content of ~7% of $Ba_{0.91}U_{0.91}O_3$ which crystallizes in an Orthorhombic unit cell with lattice parameters a ≈ 6.249 Å, b ≈ 8.876 Å and c ≈ 6.296 Å and Space Group *Pnma*. Table 5 shows the reliability factors of the refinements.

Finally, the morphology and microscopic structure of the monouranates were observed by SEM. Fig. 10 corresponds to calcium, strontium and barium monouranates. It can be observed that the uranates are formed by grains in the order of microns or even smaller for strontium, and the surface of these grains reveal a high degree of roughness and presence of pores of about 250 nm diameter.

4. Conclusions

Alkaline-earth monouranate synthesis procedures are proposed including thermal treatments in air of U_3O_8 with excess MCO_3 (or the respective oxide) and subsequent chlorination of the thermally treated product. The chlorination products of these reactions were washed with deionized water and thermally treated to crystallize the monouranates. It was possible to prepare monouranates of calcium, strontium and barium. The method proposed in this study constitutes a novel procedure which differs from those reported to the date. $MgUO_4$ could not be synthesized and showed different behavior because MgO has low reactivity with chlorine compared to other alkaline-earth oxides. The optimal conditions for the chlorination reaction to prepare the monouranates were: $CaUO_4$: 375 °C for 4 h; $SrUO_4$: 425 °C for 4 h and $BaUO_4$: 550 °C for 6 h.
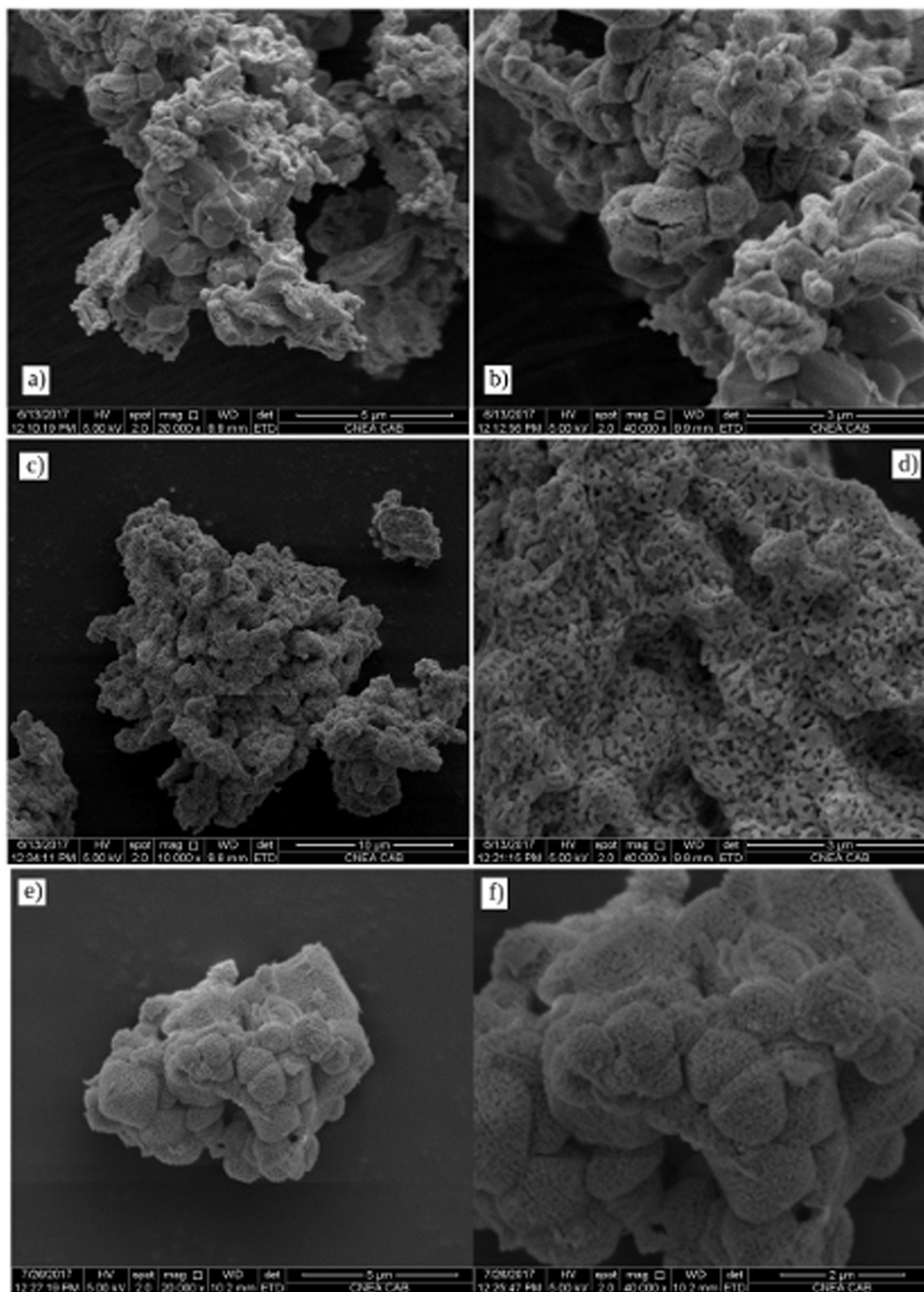
Fig. 10. a) and b) SEM images of CaUO$_4$ generated after chlorination reaction at 375 °C and crystallized at 900 °C in air c) and d) SEM images of SrUO$_4$ generated after chlorination reaction at 425 °C and crystallized at 750 °C in O$_2$,) and f) SEM images of BaUO$_4$ generated after chlorination reaction at 550 °C and crystallized at 900 °C in air.

Data availability statement

The data that support the findings of this study are available from "Comisión Nacional de Energía Atómica" from Argentina but restrictions apply to the availability of these data, and so are not publicly available. Data are however available from the authors upon reasonable request and with permission of "Comisión Nacional de Energía Atómica" from Argentina.

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