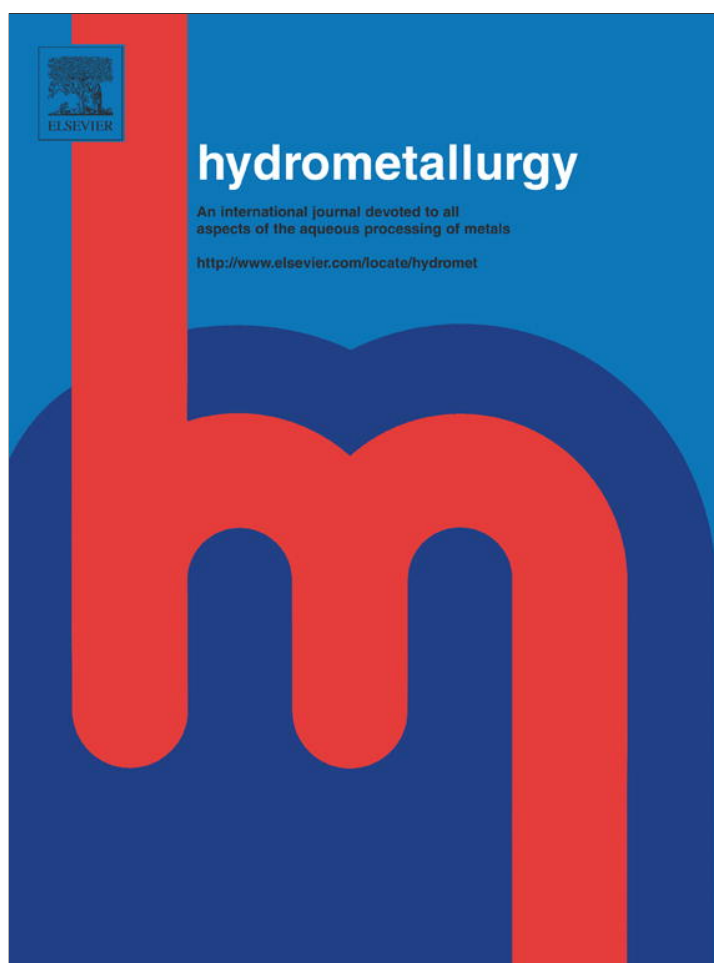


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Alkaline metal fluoride synthesis as a subproduct of β -spodumene leaching

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ABSTRACT

This paper investigated the development of new techniques to recover fluorine as three valuable fluorides: cryolithionite ($\text{Li}_3\text{Na}_3\text{Al}_2\text{F}_{12}$), sodium hexafluorosilicate (Na_2SiF_6) and cryolite (Na_3AlF_6). The synthesis of these compounds was carried out through three routes: I) by precipitation “in situ” during the leaching process of β -spodumene at different temperatures and different HF concentrations, to produce $\text{Li}_3\text{Na}_3\text{Al}_2\text{F}_{12}$; II) by precipitation adding NaOH to the leach liquor of β -spodumene, to produce Na_2SiF_6 and Na_3AlF_6 ; and III) by coprecipitation from pure reagents, to separately produce $\text{Li}_3\text{Na}_3\text{Al}_2\text{F}_{12}$, Na_2SiF_6 and Na_3AlF_6 . Reagents and products were characterized by X-ray diffraction (XRD), X-ray fluorescence (XRF), atomic absorption spectroscopy (AAS), scanning electronic microscopy (SEM) and electron probe microanalysis (EPMA). The experimental results indicate that the production of the fluorinated compounds was possible. Following route I), an enhancement of the crystal size was observed after increasing the concentrations of HF. It was also observed that a decrease in temperature favors precipitation of the solid. Furthermore, the presence of Na^+ from albite (gangue) was essential for the formation of $\text{Li}_3\text{Na}_3\text{Al}_2\text{F}_{12}$. The compounds Na_2SiF_6 and Na_3AlF_6 were synthesized together using route II), with a recovery of 92%. Through route III) the three compounds were synthesized separately and these compounds were used as standards for XRD analysis.

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1. Introduction

Spodumene occurs naturally in α phase, with a monoclinic structure of the pyroxene type. This structure is resistant to the attack of chemical agents, either gaseous or liquid. Spodumene transforms into its β phase through calcination at 1100 °C; this phase is much more reactive and less resistant to ordinary chemical agents. Spodumene responds to the formula $\text{LiAlSi}_2\text{O}_6$ with a maximum theoretical content of Li_2O of 8.03%. For this reason it is considered, together with salar brines, one of the best resources for the extraction of lithium (Habashi, 1980).

The most common industrial processes for the extraction of lithium from spodumene are acid and alkaline digestion, and the ionic exchange method. The obtained products can be lithium carbonate, lithium hydroxide and lithium chloride, respectively. Acid digestion is carried out with concentrated sulphuric acid at temperatures higher than 250 °C, whereas alkaline digestion is carried out with concentrated $\text{Ca}(\text{OH})_2$ at 1040 °C. In the process of ionic exchange, β -spodumene is heated with organic salts of sodium and potassium at temperatures between 825 and 875 °C, depending on the type of salt used (Garret, 2004; Habashi, 1980).

Kumar et al. (2010) report that the dissolution in HF of aluminum silicates, or minerals that contain them as gangue, is accompanied by the

formation of hexafluoroaluminate acid (H_3AlF_6) and hexafluorosilicate acid (H_2SiF_6). The formation of these acids is fundamental to explain the behavior of the system HF–mineral, and therefore to achieve precipitation of the dissolved metals. Moreover, these authors propose the addition of Na_2CO_3 in order to increase the pH of the solution, and hence, precipitate the compounds cryolite (Na_3AlF_6) and sodium hexafluorosilicate (Na_2SiF_6). Both compounds are some of the most common alkali-metal fluorides, and are widely used in the industry (Kumar et al., 2006, 2010). The main application of cryolite is as fluxing agent in the process of obtention of aluminum using the Byrns method (Byrns, 1961; Kemnitz et al., 2002; Moekrin, 1954). It is also used, to some extent, in the manufacture of insecticides (Carter, 1930). However, most of the cryolite used is synthetic since it is not a naturally abundant mineral. Its industrial preparation is carried out through the following reaction: $6\text{NH}_4\text{F} + \text{Al}(\text{OH})_3 + 3\text{NaOH} \rightarrow \text{Na}_3\text{AlF}_6 + 6\text{NH}_3 + 6\text{H}_2\text{O}$ (Kemnitz et al., 2002; Moekrin, 1954).

All fluoroaluminates of alkaline metals tend to form solid solutions. This can be observed in their phase diagrams, where, varying the concentrations of each metal, substitutions in the original structure are produced. In one end of the series of the Na and Li phase diagram Na_3AlF_6 is found. Then Na^+ can be partially replaced by Li^+ until it reaches the opposite end where a totally substituted species exists, called lithium cryolite (Li_3AlF_6). At intermediate concentrations, a compound called cryolithionite ($\text{Li}_3\text{Na}_3\text{Al}_2\text{F}_{12}$) may be obtained (Garton and Wanklyn, 1967). This mineral only occurs in hydrothermal deposits (Takeda et al., 1977a).

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Na_2SiF_6 is a white synthetic compound, very hygroscopic, which in alkaline solutions is decomposed and produces sodium fluoride and silicon dioxide. Na_2SiF_6 has numerous industrial applications (Jeong and Huh, 2010).

Most of the common processes used to synthesize $\text{Li}_3\text{Na}_3\text{Al}_2\text{F}_{12}$, Na_2SiF_6 and Na_3AlF_6 can be divided into three groups: sol-gel, hydrothermal, and co-precipitation (Ahrens et al., 2006; Garton and Wanklyn, 1967; Takeda et al., 1977a,b).

Preliminary studies showed that in the leaching process of β -spodumene with HF, high dissolutions of the mineral were obtained, and sometimes, this process is accompanied by precipitation of metal fluorides, such as $\text{Li}_3\text{Na}_3\text{Al}_2\text{F}_{12}$ (Rodriguez et al., 2010).

The fluoride ions in the leach liquor from the dissolution of β -spodumene with HF impair the use of this process at industrial scale.

In this study, we have developed new techniques for the production of alkaline metal fluorides. $\text{Li}_3\text{Na}_3\text{Al}_2\text{F}_{12}$ was obtained as a subproduct of the leaching process of β -spodumene with HF. Na_2SiF_6 and Na_3AlF_6 were synthesized through the treatment of the liquor generated during the mineral leaching.

The purpose of this work is to synthesize valuable raw material with industrial application, and to diminish the polluting effect of effluents with high amounts of fluoride ions, generated from the extraction process of Li from β -spodumene with HF. In addition, solids of interest were synthesized from pure reagents and these compounds were used as standards for XRD analysis.

2. Experimental

2.1. Equipment and materials

The experimental tests were performed in a closed vessel of 450 ml built in Teflon, and equipped with magnetic stirring and temperature control systems.

The reagents used to synthesize the different compounds were LiCl, AlCl_3 , NaOH, SiO_2 and HF, all with analytical grade. The mineral used was α -spodumene, extracted from the "Las Cuevas" mine located in the Department of San Martín, San Luis, Argentina. The α -phase was calcined at 1100 °C to obtain the β -phase (Habashi, 1980). Characterization of the ore was performed by X-ray fluorescence (XRF) on a Philips PW 1400 equipment and by X-ray diffraction (XRD) in a Rigaku D-Max III C diffractometer, operated at 35 kV and 30 mA. The K_α radiation of Cu, and the filter of Ni, $\lambda = 0.15418$ nm were used. Determination of lithium and sodium content in the ore was performed by atomic absorption spectroscopy (AAS) using a Varian SpectraAA 55 spectrometer with a hollow-cathode lamp. Morphological analysis was done by SEM under a microscope LEO 1450 VP which was equipped with an X ray dispersive spectrometer EDAX, Genesis 2000, used to determine the semiquantitative composition of the synthesized compounds by EPMA.

The bulk composition of the ore is shown in Table 1, as determined by AAS (Li and Na) and XRF (Si, Al, Fe, Ca, Mg, K and Ti).

The results of the characterization by XRD are shown in Fig. 1.

In Fig. 1(a), XRD patterns show that the sample is composed of α -spodumene (JCPDS 33-786), with the presence of albite (ICDD 96-

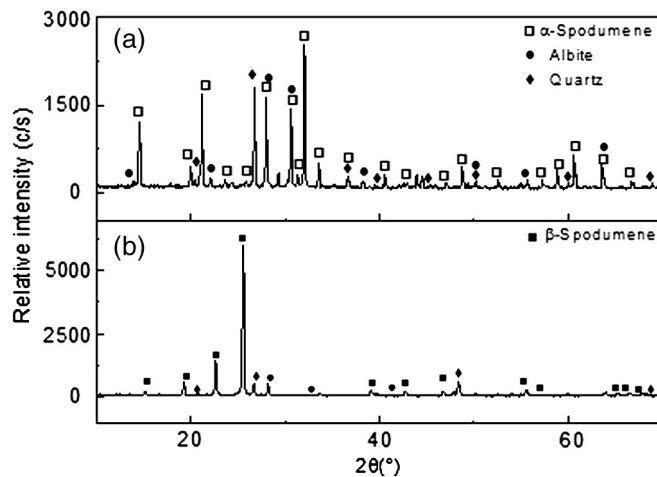


Fig. 1. Diffractograms of the mineral. (a) α -Spodumene and (b) β -spodumene.

900-1631) and quartz (JCPDS 33-1161) as gangue. Diffractogram in Fig. 1(b) shows the appearance of β -spodumene (JCPDS 35-797) after calcination. The α -phase is not detected, indicating that the transformation of α -phase to β -phase was completed. Besides, albite and quartz were detected. Quartz content in the sample (b) (8% (w/w)) was determined by XRD, using the standard addition method (diffraction line 26.7° of SiO_2 as standard). Albite percentage in the sample (b) (15% (w/w)) was calculated from sodium content determined by AAS.

The results of the studies carried out by SEM and EPMA on different particles of the sample, with and without thermal treatment, are compatible with those obtained by XRD.

2.2. Synthesis of fluorides $\text{Li}_3\text{Na}_3\text{Al}_2\text{F}_{12}$, Na_2SiF_6 and Na_3AlF_6

The compounds were synthesized following three different routes:

- I) $\text{Li}_3\text{Na}_3\text{Al}_2\text{F}_{12}$, by in situ precipitation during the leaching process of β -spodumene at different temperatures and different HF concentrations: for each test, a mass of the ore and a volume of distilled water were placed into the reactor. The mixture was subsequently heated in a water bath with stirring until final work temperature was reached (25 to 75 °C). Once the desired temperature was achieved, an appropriate amount of HF was added to the mixture, so as to obtain acid concentrations between 5 and 20% (v/v). From that moment onwards, reaction time was calculated. Once the experiment was finished, the reactor was cooled down for 25 min, without stirring, and the solid was filtered, dried for 2 h at 110 °C, and then weighed. In order to understand the influence of Na^+ on precipitation performance of $\text{Li}_3\text{Na}_3\text{Al}_2\text{F}_{12}$, different experiments have been carried out. Increasing amounts of Na^+ (as NaCl) were added to reach the stoichiometric values corresponding to reactions (1), (2) and (3), for a fixed amount of the ore (5 g). The course of the formation reaction of $\text{Li}_3\text{Na}_3\text{Al}_2\text{F}_{12}$ depending on Na^+ content was followed by XRD. The choice of NaCl as a source of Na^+ is founded on three reasons: i) it has high solubility; ii) it does not produce changes in pH; and iii) it does not generate chemical interference with the products formed.
- II) Na_2SiF_6 and Na_3AlF_6 , by precipitation adding different quantities of NaOH to the leach liquor from the β -spodumene leaching process with HF: each test was performed by stirring this solution in a Teflon vessel for 30 min. After that, a quantity of NaOH was added to the solution. Precipitated solids were separated by filtration, dried for 2 h at 110 °C, and then weighed.
- III) $\text{Li}_3\text{Na}_3\text{Al}_2\text{F}_{12}$, Na_2SiF_6 and Na_3AlF_6 , by co-precipitation from pure reagents: the stoichiometric amounts of the reagents (LiCl, AlCl_3

Table 1
The bulk composition of the ore.

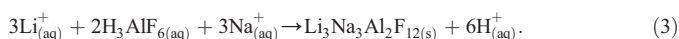
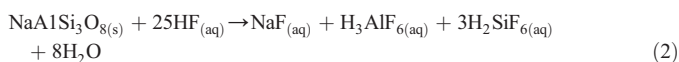
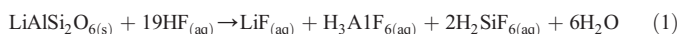
Component	% (w/w)
SiO_2	68.1
Al_2O_3	18.6
Fe_2O_3	3.1
CaO	0.52
MgO	0.3
K_2O	0.14
Na_2O	1.8
Li_2O	7.03
TiO_2	0.11

and SiO₂) needed to prepare each compound (Na₃AlF₆, Na₂SiF₆ and Li₃Na₃Al₂F₁₂) were dissolved in HF solutions with an adequate concentration. Then these solutions were placed in a Teflon vessel and mixed with a magnetic stirrer. Finally, the necessary amount of NaOH to complete the reaction of precipitation was added. Solids obtained were filtered, dried and weighed. The products synthesized by all three routes were characterized through XRD, SEM and EPMA.

3. Results and discussion

3.1. Synthesis through route I)

For the mineral dissolution and synthesis of Li₃Na₃Al₂F₁₂, the following reactions are proposed:



The formation of Li₃Na₃Al₂F₁₂ according to reactions (1) to (3) is due to the opening of the ore with the consequent release of metal ions, both from spodumene (LiAlSi₂O₆) and albite (NaAlSi₃O₈) initially present in the sample. This metal ions then react with fluoride ions of the leaching agent to form Li₃Na₃Al₂F₁₂.

Based on the Li content (determined by AAS) of a sample mass of 5 g of the ore, the maximum quantity of Li₃Na₃Al₂F₁₂ that can be formed is 2.88 g, corresponding to a stoichiometric amount of 0.53 g of Na. Moreover, Na content from albite (0.066 g of Na) is insufficient to react with all the Li present in the solution and to form 2.88 g of Li₃Na₃Al₂F₁₂. In accordance to the Na content from albite, the maximum quantity of Li₃Na₃Al₂F₁₂ that can be formed is 0.36 g (12.5% (w/w)).

3.1.1. Effect of temperature

In Fig. 2, the diffractograms of solids obtained after the leaching of β-spodumene at temperatures between 25 and 75 °C and HF 10% (v/v) are shown.

From the diffractograms of Fig. 2, it can be observed that the relative intensity of cryolithionite (Li₃Na₃Al₂F₁₂; JCPDS 22-416) diffraction lines decrease when the reaction temperature increases. This is due to the fact that in most of the precipitation reactions, the increase in temperature leads to an increased solubility of precipitated compounds (Putnis et al., 2003; Stephen et al., 1962).

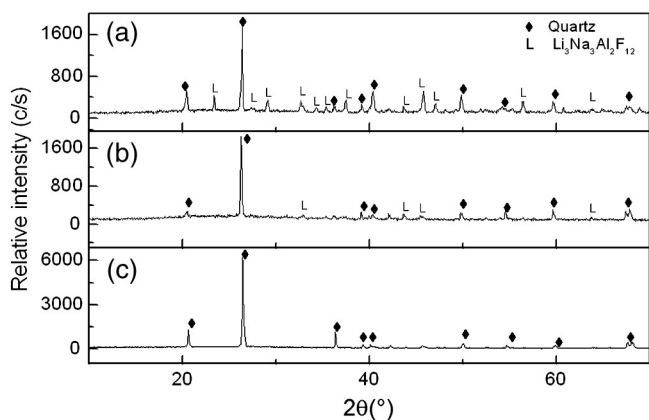


Fig. 2. Diffractograms of the synthesized solids through route I) at different temperatures: (a) 25 °C; (b) 50 °C and (c) 75 °C.

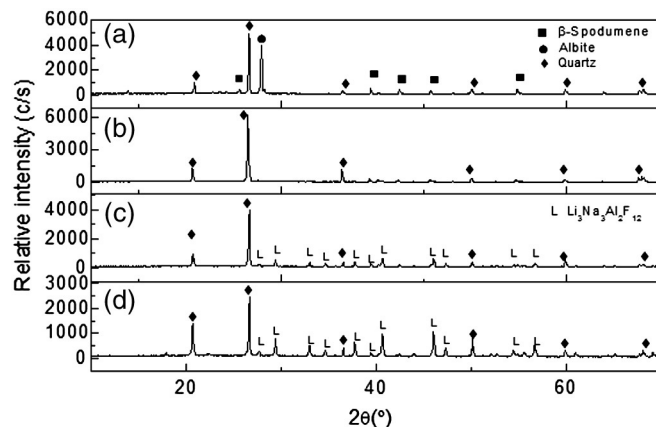


Fig. 3. Diffractograms of the synthesized solids through route I) for different concentrations of HF: (a) 5% (v/v); (b) 10% (v/v); (c) 15% (v/v) and (d) 20% (v/v).

3.1.2. Effect of HF concentration

Fig. 3 shows the diffractograms of the solids obtained after the leaching of β-spodumene at 75 °C and a reaction time of 120 min, with different concentrations of HF.

In Fig. 3, it can be inferred that when HF concentration increases, dissolution of β-spodumene present in the ore occurs, and furthermore it enhances the intensity of diffraction lines corresponding to Li₃Na₃Al₂F₁₂ structure (Fig. 3(c) and (d)).

At concentrations of HF below the stoichiometric (Fig. 3(a)) the formation of the compound Li₃Na₃Al₂F₁₂ is not observed because the dissolution of albite, which provides Na⁺ ions required for the formation of Li₃Na₃Al₂F₁₂, is not achieved. At HF concentrations of 10% (v/v) (Fig. 3(b)) the presence of Li₃Na₃Al₂F₁₂ is not detected as already described in Section 3.1.1. It is worth mentioning that the formation of Na₂SiF₆ and Na₃AlF₆ was not observed. This is due to low pH conditions and low sodium content in solution, which did not allow the precipitation of these compounds (Kumar et al., 2010).

3.1.3. Effect of NaCl addition

Fig. 4 shows the diffractograms of the solids obtained after the leaching of β-spodumene at 75 °C, reaction time of 120 min and HF 15% (v/v) with different Na⁺ concentrations. For comparative purposes, the diffractogram of the formed products through route I) without NaCl is shown in Fig. 4(a).

Fig. 4(a) and (b), where masses of Na⁺ were less than the stoichiometric ones (<0.53 g Na⁺, Na⁺/Li⁺ < 1) calculated from reactions (1), (2) and (3), shows the presence of Li₃Na₃Al₂F₁₂ and quartz. The comparison of both diffractograms shows that when the content

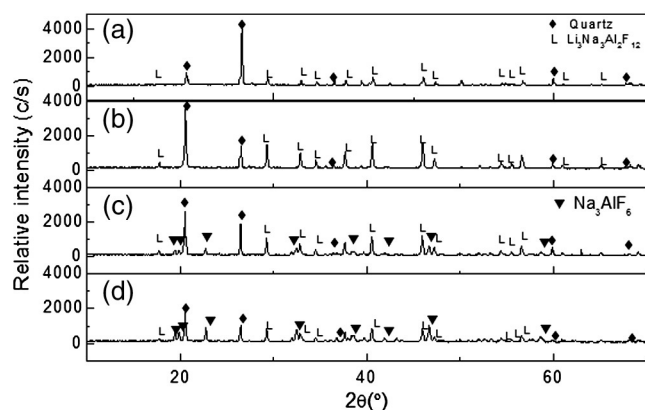


Fig. 4. Diffractograms of the synthesized solids through route I) and different quantities of NaCl: (a) without NaCl; (b) 1 g; (c) 3 g and (d) 5 g.

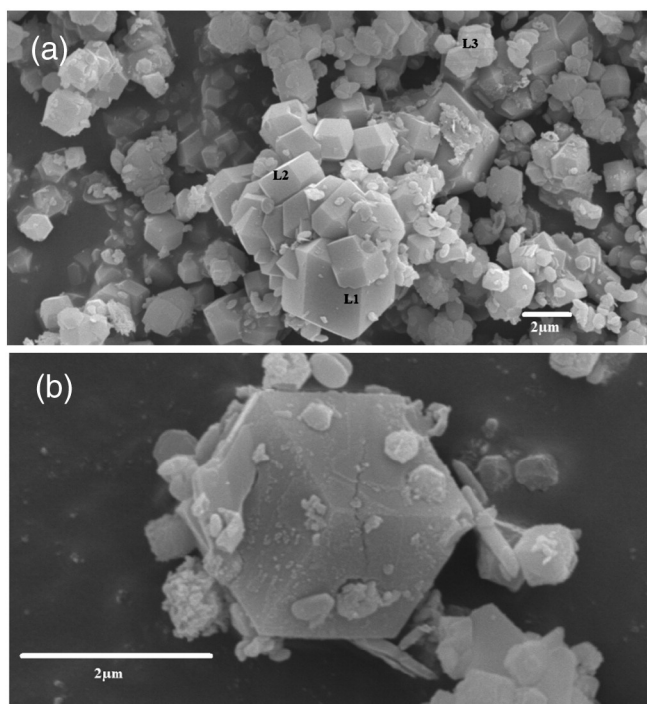


Fig. 5. SEM micrographs with different magnifications of the synthesized solid through route I).

of Na^+ increases, the relative intensities of the peaks corresponding to $\text{Li}_3\text{Na}_3\text{Al}_2\text{F}_{12}$ increase. This indicates an increase in the mass of the solid precipitate.

Fig. 4(c) shows that, at masses higher than the stoichiometric ones (1.2 g Na^+ , $\text{Na}^+/\text{Li}^+ > 1$), $\text{Li}_3\text{Na}_3\text{Al}_2\text{F}_{12}$ and quartz accompanied by Na_3AlF_6 (ICDD 01-082-0227) were obtained. This can be attributed to the increase in Na^+ mass above the stoichiometric value required to form $\text{Li}_3\text{Na}_3\text{Al}_2\text{F}_{12}$. This augment leads to a partial replacement of Li^+ ions for Na^+ ions according to reaction (4) (Garton and Wanklyn, 1967).



Fig. 4(d) shows the increase in the relative intensity of Na_3AlF_6 diffraction lines and the decrease in $\text{Li}_3\text{Na}_3\text{Al}_2\text{F}_{12}$ diffraction lines produced by the increase in Na^+ content. This is expected, because more quantity of Na^+ leads to a greater Li^+ replacement (reaction (4)).

3.1.4. Characterization of the synthesized solid through route I)

Fig. 5 and Table 2 show the SEM micrographs and results of the EPMA analysis of the precipitates obtained with 15% (v/v) HF and a reaction time of 120 min at 75 °C.

In the micrographs of Fig. 5, crystals with a well defined cubic structure can be observed. Through EPMA analysis (Table 2), it can be corroborated that the percentages in weight corresponding to each element coincide with the stoichiometry of the compound $\text{Li}_3\text{Na}_3\text{Al}_2\text{F}_{12}$ identified by XRD. The presence of oxygen in the solids can be attributed to the existence of water, due to the fact that these compounds are highly hygroscopic.

Table 2
EPMA analysis of the marked particles in Fig. 4(a) in atom %.

Particle	%F	%Na	%Al	%O
L ₁	47	18	25.5	9.5
L ₂	44	19	26	11
L ₃	48	17	24	10

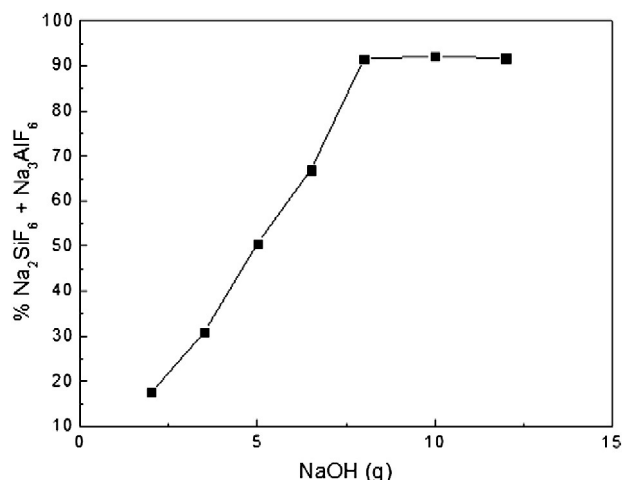


Fig. 6. Effect of NaOH addition on the recovery of Na_3AlF_6 and Na_2SiF_6 from the leach liquor of β -spodumene dissolution.

3.2. Synthesis through route II)

The reaction proposed for obtaining a mixture of the compounds Na_2SiF_6 and Na_3AlF_6 is the following [3, 4]:

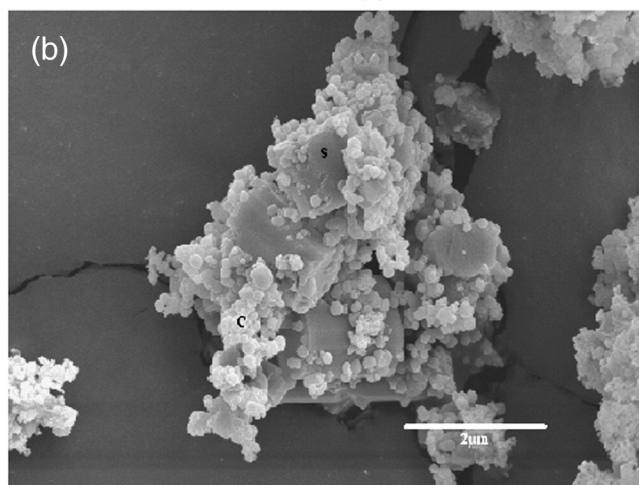
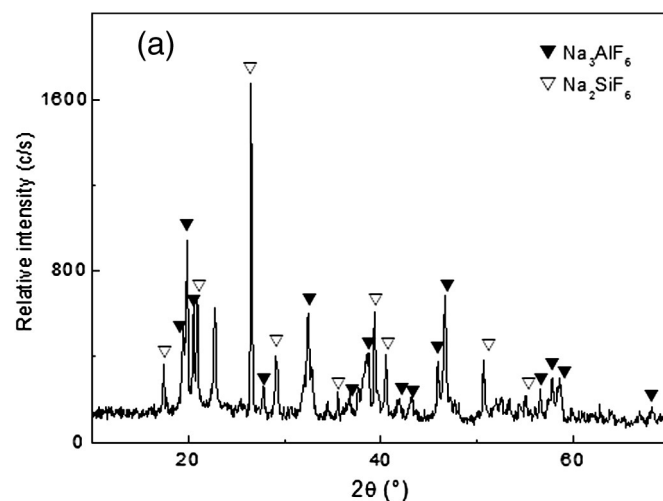
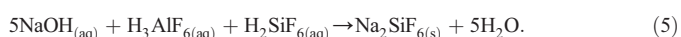


Fig. 7. Characterization by DRX and SEM of the synthesized solids by route II), with 8 g of NaOH.

Table 3
EPMA analysis of the particles marked in Fig. 8 in atom %.

Particle	%F	%Na	%Al	%Si	%O
C	36	38	20	–	6
S	39	37	–	25	–

3.2.1. Effect of NaOH addition

The results of the effect of NaOH mass in the recovery percentage of Na₃AlF₆ and Na₂SiF₆ from the leach liquors of β-spodumene dissolution process (mass of the ore 5 g, HF 10% (v/v), 120 min and 75 °C) are shown in Fig. 6.

It may be inferred from the analysis of Fig. 6 that the recovery of Na₃AlF₆ and Na₂SiF₆ increases when augmenting the amounts of NaOH. The maximum value of recovery achieved was 92% (w/w) with 8 g of NaOH. This amount of NaOH corresponds to the stoichiometric value calculated from reaction (5).

3.2.2. Characterization of the synthesized solid through route II

The results of XRD and SEM characterization of the solids synthesized by this route are shown in Fig. 7.

In Fig. 7(a) the appearance of diffraction lines that correspond to the structure of Na₂SiF₆ (ICDD 96-901-1051) and Na₃AlF₆ can be observed, this agrees with the proposed reaction (5).

The presence of Li₃Na₃Al₂F₁₂ was not observed because Na⁺ replaces Li⁺ and leads to the formation of cryolite, reaction (4). Cryolite was formed at concentrations of Na⁺ higher than the stoichiometric ones for reaction (4) (Garton and Wanklyn, 1967; Kumar et al., 2006, 2010).

In Fig. 7(b) the presence of two types of particles, well differentiated by their morphology, can be observed. Some of them have hexagonal shape (S) with a slight growth in one of their axes which gives the appearance of hexagonal bars. Others are found around the first ones as small particles of irregular shape (C).

The results of the characterization by EPMA of the synthesized solids is shown in Table 3.

The EPMA analysis performed on each one of the particles marked in Fig. 7(b) shows that their stoichiometry coincide with the products of reaction (5), (C) corresponds to Na₃AlF₆ and (S) to Na₂SiF₆. The oxygen in the particle identified with (C) corresponds to the presence of water, due to its hygroscopicity, as mentioned before.

3.3. Synthesis through route III

The reactions proposed for the synthesis of Na₃AlF₆, Na₂SiF₆ and Li₃Na₃Al₂F₁₂ are the following:

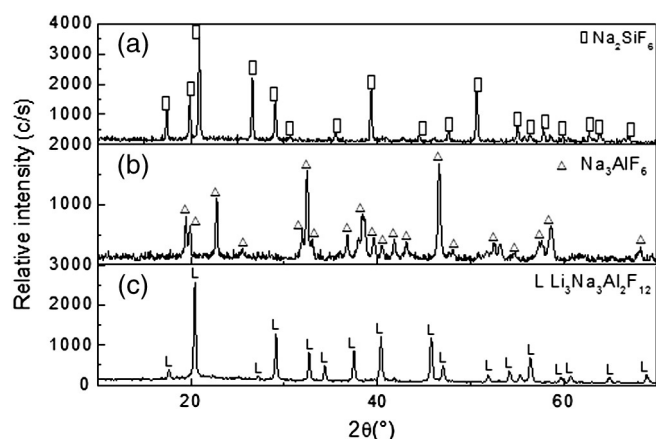
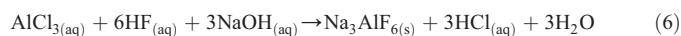
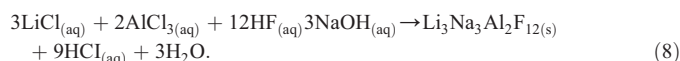
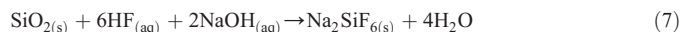


Fig. 8. Diffractograms of the synthesized solids through route III: (a) reaction (6); (b) reaction (7) and (c) reaction (8).



Characterizations of each synthesized compounds carried out by XRD and SEM are shown in Figs. 8 and 9, respectively.

Diffractograms in Fig. 8 indicate that the formation of the solids Na₃AlF₆, Na₂SiF₆ and Li₃Na₃Al₂F₁₂ has taken place according to reactions (6), (7) and (8), respectively, without other phases detected as impurities.

In Fig. 9(a), (b) and (c) three types of particles without well defined crystalline structures, can be observed. This can be attributed to the fact

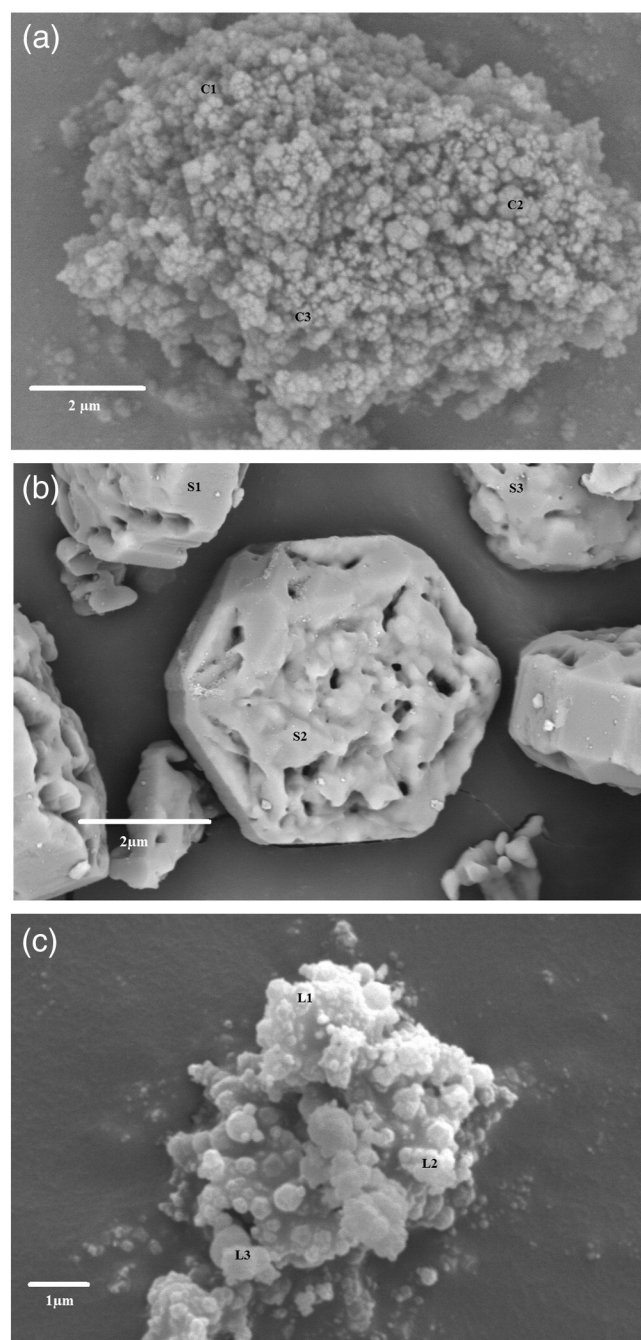


Fig. 9. SEM micrographs of different particles of the synthesized solids by route III: (a) reaction (6); (b) reaction (7) and (c) reaction (8).

Table 4
EPMA analysis of the particles marked in Fig. 10(a), (b), and (c), in atom %.

Figure	Particle	%F	%Na	%Al	%Si	%O
10(a)	C ₁	35	38	21	–	5
	C ₂	33	40	21	–	6
	C ₃	32	39	22	–	7
10(b)	S ₁	41	31	–	27	–
	S ₂	41	33	–	26	–
	S ₃	42	31	–	27	–
10(c)	L ₁	42	26	22	–	10
	L ₂	42	24	26	–	7
	L ₃	42	18	34	–	56

that the time of aging of each precipitate was insufficient for the growth of the nuclei (Putnis et al., 2003).

In Table 4 the results of the EPMA analysis performed on the particles pointed out in Fig. 9 are shown.

Results in Table 4 show that the chemical compositions of the solids obtained coincide with the stoichiometry of the compounds that are expected to be formed according to reactions (6), (7) and (8). Particles marked with (C) in Fig. 9(a) correspond to Na₃AlF₆; those pointed with (S) in Fig. 9(b) correspond to Na₂SiF₆; and particles marked with (L) (Fig. 9(c)) correspond to Li₃Na₃Al₂F₁₂. The presence of oxygen was previously explained in Section 3.1.4.

4. Conclusions

The experimental results obtained show that:

1. The synthesis through route I) leads selectively to the formation of Li₃Na₃Al₂F₁₂ at 75 °C and a HF concentration of 15% (v/v).
2. By controlling the concentration of HF and Na in route I), the precipitation of Li₃Na₃Al₂F₁₂ can be promoted or avoided. The addition of NaCl in route I) leads to an increase in Li₃Na₃Al₂F₁₂ recovery (>90%).

3. The compounds Na₂SiF₆ and Na₃AlF₆ were synthesized together through route II) with a recovery of 92%. This route can be considered a good method for the purification of residual liquids with high fluoride ion content. For example, in the treatment of waste from the leaching of minerals with HF.
4. The compounds Na₃AlF₆, Na₂SiF₆ and Li₃Na₃Al₂F₁₂ were synthesized through route III). Since no presence of other phases was detected after the synthesis, these compounds were used as standards for the characterization by XRD of the solids obtained through routes I) and II).

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