

Thermal Transformations in the System NaF-CaF₂-AlF₃ and X-Ray Diffraction Control of Ca-Containing Electrolytes for Aluminum Production

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ABSTRACT

The details of ternary fluoride crystallization in the system NaF-CaF₂-AlF₃ have been specified. The phases NaCaAlF₆, Na₂Ca₃Al₂F₁₄ and NaAlF₄ have been obtained by high-temperature synthesis. Their thermal transformations have been studied using high-temperature X-ray diffraction. The occurring transformations can be considered in a quasibinary system CaF₂-NaAlF₄, where at T = 745°C - 750°C invariant equilibrium is established with the phases CaF₂-NaCaAlF₆-Na₂Ca₃Al₂F₁₄-(NaAlF₄). The compounds NaCaAlF₆ and Na₂Ca₃Al₂F₁₄ are stable in different temperature ranges. The phase NaCaAlF₆ was fixed by rapid quenching from the melt. It decomposes at heating before 640°C yielding Na₂Ca₃Al₂F₁₄ and NaAlF₄. Direct and inverse transformations between NaCaAlF₆ and Na₂Ca₃Al₂F₁₄ occur in the bulk samples of the electrolyte. A thermal treatment procedure was proposed for the solid electrolyte sample to get a sample corresponding to the composition of the melt and providing high phase crystallinity for the purposes of quantitative X-ray phase diffraction analysis.

Keywords: Aluminum Production; Electrolyte Composition; Ternary System NaF-AlF₃-CaF₂; XRD Electrolyte Composition Control

1. Introduction

Calcium fluoride combined with the excess of aluminum fluoride is the most widely used additive for decreasing the operation temperature in an electrolysis bath in aluminum production [1]. The additives significantly influence the electrolysis efficiency, however its concentrations considerably change in the course of electrolysis due to the high temperature and volatility of the electrolyte components [2]. Therefore, the technology of aluminum production implies monitoring the bath composition and applies to periodical electrolyte correction. For this purpose several hundred electrolyte samples are taken and analyzed every day in a aluminum smelter [1, 3]. At present the electrolyte is analyzed by X-ray powder diffraction technique (XRD). Analysis is made using a cooled solid sample after the sampling procedure. The sample composition is presented by a number of crystal phases: Na₃AlF₆ (cryolite), Na₅Al₃F₁₄ (chiolite), CaF₂,

NaCaAlF₆ and Na₂Ca₃Al₂F₁₄. The quantitative XRD analysis provides the concentration of each present phase. Converted into the concentrations of the fluoride components (NaF, AlF₃, CaF₂) the phases give a technological parameter—cryolite ratio—CR = (NaF(mole)/AlF₃(mole)).

The quantitative phase determination in electrolytes containing calcium fluoride presents a methodological problem. In the course of the crystallization calcium fluoride forms three phases: CaF₂ (fluorite), NaCaAlF₆ and Na₂Ca₃Al₂F₁₄ (calcium cryolites). Since calcium fluoride is able to bind aluminum fluoride and sodium fluoride during the process of crystallization, it is necessary both to determine its chemical concentration and to measure the content of each calcium-containing phase (NaCaAlF₆ and Na₂Ca₃Al₂F₁₄). It has been mentioned in literature that the correlation between the calcium phases changes depending both on the electrolyte composition and sampling procedure [3-5]. The phase NaCaAlF₆ is very poorly crystallized, decreasing the accuracy of its measurement by the XRD method including the application of the

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Rietveld technique [6]. As it is difficult to determine calcium concentration using only the XRD method, the X-ray fluorescence (XRF) measurement of the total calcium content is added to the X-ray analysis scheme used in industry [3]. Practically, when calculating CR it is considered that the calcium-containing phases (NaCaAlF_6 and $\text{Na}_2\text{Ca}_3\text{Al}_2\text{F}_{14}$) are present in the solid sample in equal amounts. In reality, the situation is different giving a deviation in the analysis results. Higher accuracy in the analysis can be achieved on the basis of a detailed investigation of the phase transformation during sampling.

The first description of the phase relations in the system $\text{NaF-AlF}_3\text{-CaF}_2$ was published by Fedotyev and Ilyinsky in 1912 [1]. Pfund and Zimmerman [7] established the phase NaCaAlF_6 , which melts incongruently. A diagram fragment limited to the compounds $\text{Na}_3\text{AlF}_6\text{-AlF}_3\text{-CaF}_2$ was reported by Craig and Brown [8]. They found that several phases could be crystallized from the melt: CaF_2 , Na_3AlF_6 , $\text{Na}_5\text{Al}_3\text{F}_{14}$, Ca_2AlF_7 , CaAlF_5 , AlF_3 , NaCaAlF_6 , $\text{NaCaAl}_2\text{F}_9$. Later Baggio [9] made a correction and found out that the real composition of the phase $\text{NaCaAl}_2\text{F}_9$ corresponded to $\text{Na}_2\text{Ca}_3\text{Al}_2\text{F}_{14}$. It was confirmed by crystal structure investigations [10-12]. Anufrieva and co-authors [13] reported a diagram of the system $\text{NaF-AlF}_3\text{-CaF}_2$, where seven phases crystallize including three congruently melting phases: Na_3AlF_6 , NaAlF_4 , CaAlF_5 , and four incongruently melting ones: $\text{Na}_5\text{Al}_3\text{F}_{14}$, NaCaAlF_6 , $\text{NaCaAl}_2\text{F}_9$, Ca_2AlF_7 . On the basis of the thermal analysis data, Baggio [9] established that NaCaAlF_6 existed in three polymorphous modifications with the transition temperatures 610°C and 722°C . The solid solutions in the wide ranges were not observed in the system [14,15]. Recently, it has been established that the phases NaCaAlF_6 and $\text{Na}_2\text{Ca}_3\text{Al}_2\text{F}_{14}$ have different temperature ranges of stability [1,16].

In this paper, the conditions for the ternary phase crystallization in the system $\text{NaF-CaF}_2\text{-AlF}_3$ have been specified. The individual phases NaCaAlF_6 , $\text{Na}_2\text{Ca}_3\text{Al}_2\text{F}_{14}$ and NaAlF_4 have been synthesized. Their thermal transformations have been studied using high-temperature X-ray diffraction technique. A thermal treatment procedure for the solid electrolyte sample has been proposed to get a sample corresponding to the composition of the melt and providing high phase crystallinity for the purposes of quantitative X-ray phase diffraction analysis.

2. Experiment

2.1. Synthesis of NaCaAlF_6 and $\text{Na}_2\text{Ca}_3\text{Al}_2\text{F}_{14}$

Individual crystal phases NaCaAlF_6 and $\text{Na}_2\text{Ca}_3\text{Al}_2\text{F}_{14}$ were synthesized from stoichiometric mixtures of a chemical grade AlF_3 (99%), NaF (99%) and CaF_2 (98%) at high temperature solid-state sintering. The detailed description of the synthesis is presented in [1]. The phase

NaAlF_4 was obtained by condensation of vapors arising above the melt NaCaAlF_6 , the synthetic details are described in [16].

2.2. Synthesis of Calcium-Containing Electrolytes

Three samples of a calcium-containing electrolyte with CR 1.9, 2.4, 2.7 and CaF_2 concentration equal to 8% (mas.) labeled as E1, E2, E3 were synthesized from the mixtures of the fluorides AlF_3 , NaF , and CaF_2 . The 10 g fluoride mixture was loaded in a platinum crucible closed with a cap and melted in a furnace at about 960 to 1000°C for 20 min depending on the CR value and then cooled in air.

2.3. X-Ray Diffraction Analysis (XRD Analysis)

X-ray diffraction patterns were scanned by an X'Pert Pro (Panalytical) diffractometer, equipped with a PIXel detector with a graphite monochromator. $\text{CuK}\alpha$ -radiation was used. The scans were made in the range from 10° to 80° , with a step of 0.026° (2Θ) and the total scanning time being 12 min. The samples were prepared by direct loading into a cuvette of 27 mm in diameter.

2.4. High Temperature X-Ray Studies

High temperature X-ray studies were carried out using an X'Pert Pro (Panalytical) Diffractometer with a high temperature chamber NTK1200N "Anton Paar" in vacuum. The sample was prepared in a platinum cuvette of 10 mm in diameter. The sample weight was about 200 mg. The temperature of the sample was increased and decreased at a rate of $50^\circ/\text{min}$ to a certain temperature and then an X-ray diffraction pattern was taken in the range from 5 to 80° (2Θ) for 5 min. Then, the process was repeated at the next temperature stage. The X-ray data were processed with the help of High Score Plus software (Panalytical) [17].

3. Results and Discussion

Figure 1 presents a composition triangle of the system $\text{NaF-CaF}_2\text{-AlF}_3$, with the area of the "industrial electrolytes" being marked.

The presence of four and, sometimes, five phases in the electrolyte samples contradicts to the Gibbs's phase rule and indicates the non-equilibrium conditions of their formation. The system peculiarity is the location of the ternary phases in the section of $\text{CaF}_2\text{-NaAlF}_4$. This allows one to confine the possible electrolyte composition field by the triangle $\text{CaF}_2\text{-Na}_3\text{AlF}_6\text{-NaAlF}_4$. The double fluoride phases Ca_2AlF_7 and CaAlF_5 have never occurred in the electrolyte samples and it is a well-grounded argument for marking this triangle field.

3.1. NaCaAlF₆ and Na₂Ca₃Al₂F₁₄

It was experimentally found that the pure phase NaCaAlF₆ could only be obtained at a temperature above 710°C but lower than 740°C (the melting temperature). The pure phase Na₂Ca₃Al₂F₁₄ was synthesized at 500°C - 620°C. The phases NaCaAlF₆ and Na₂Ca₃Al₂F₁₄ were investigated by high-temperature X-ray diffraction in a multi-stage heating procedure in vacuum. The X-ray diffraction data for both compounds were obtained at 100°C, 300°C, 400°C, 500°C, 550°C, 570°C, 600°C. Some of the X-ray

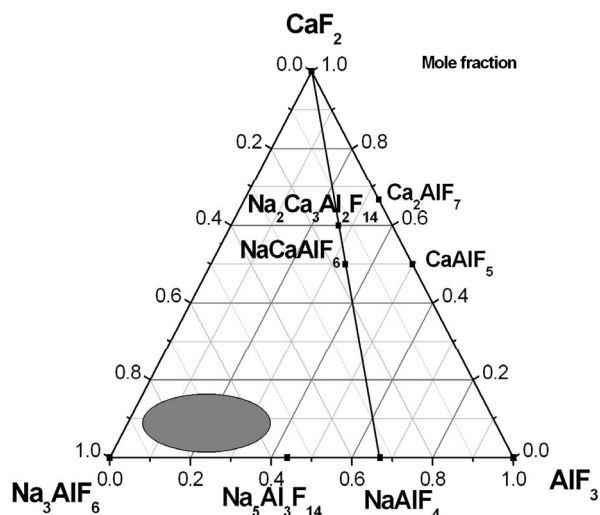


Figure 1. Composition triangle of the system NaF-CaF₂-AlF₃. The field of the “industrial electrolyte” composition is marked by the color spot.

diffraction patterns for NaCaAlF₆ are presented in **Figure 2**. More detailed information can be found in [18].

Below 400°C the phase NaCaAlF₆ undergoes structural transformation ($\alpha \rightarrow \beta$) without changing the composition. At 500°C the decay begins followed by the appearance of peaks of Na₂Ca₃Al₂F₁₄ and CaF₂ at the X-ray powder pattern.

The phase Na₂Ca₃Al₂F₁₄ appears to be stable in vacuum approximately up to 600°C and then decomposes into two products: CaF₂ and Na₃AlF₆, which were observed in the X-ray diffraction pattern (**Figure 3**). There was no evidence obtained of the expected solid state decomposition into NaCaAlF₆ and CaF₂ in the thin sample in vacuum. The final products belong to the binary system CaF₂-Na₃AlF₆ of the eutectic type with the melting temperature being 945°C [14]. The phase transformation β -Na₃AlF₆ \rightarrow α -Na₃AlF₆ occurs in the system at cooling.

The high-temperature experiments have demonstrated that calcium-containing phases have different temperature intervals of stability. The phase NaCaAlF₆ is metastable in normal conditions. Its relaxation in the conditions of low pressure and the thin sample, which do not prevent diffusion, begins at 500°C and follows into Na₂Ca₃Al₂F₁₄. No reverse transformation was observed under the experimental conditions. The observed conversion can be explained by engaging the volatile unstable phase NaAlF₄ according to the following equations:

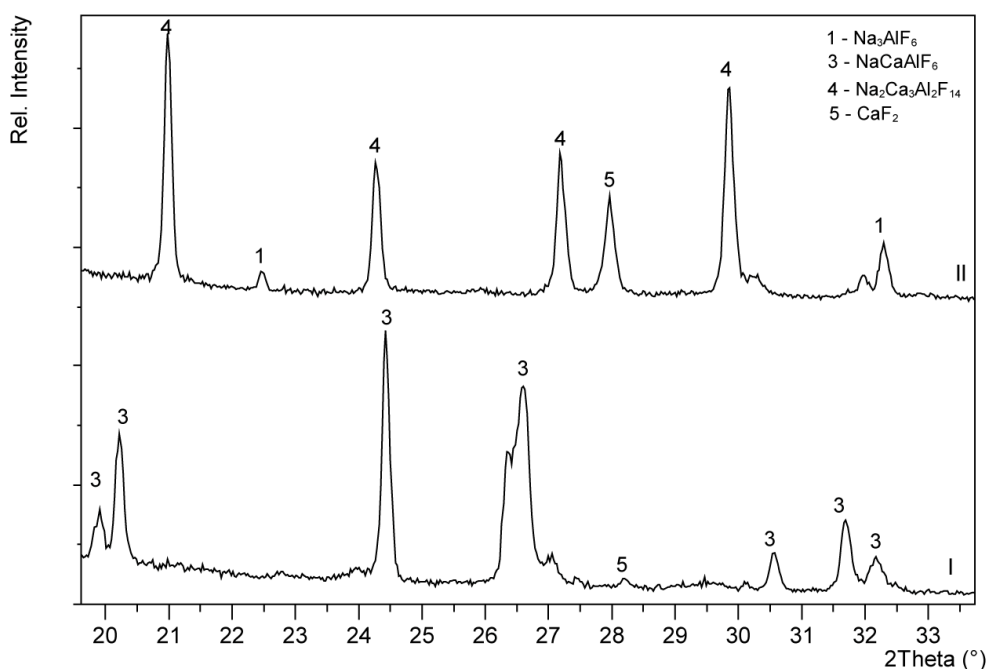


Figure 2. X-ray diffraction patterns from the high-temperature series for the sample with the initial content of NaCaAlF₆. (I) —at 25°C, NaCaAlF₆; (II)—at 500°C for 1 h, Na₂Ca₃Al₂F₁₄, CaF₂, Na₃AlF₆.

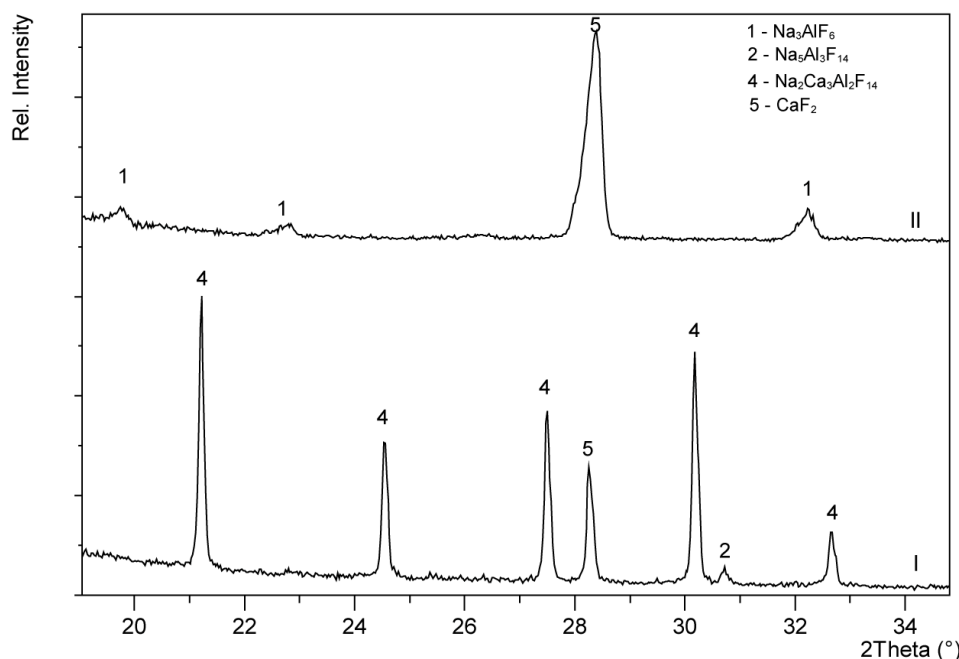
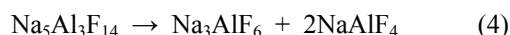
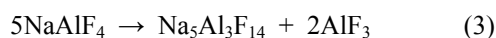


Figure 3. X-ray diffraction patterns from the high-temperature series for the sample with the initial content of $\text{Na}_2\text{Ca}_3\text{Al}_2\text{F}_{14}$. (I)—at 25°C , $\text{Na}_2\text{Ca}_3\text{Al}_2\text{F}_{14}$; (II)—at 600°C , CaF_2 and $\beta\text{-Na}_3\text{AlF}_6$.



The most expected decay reaction was not observed experimentally:



The calcinations of the bulk samples at atmospheric pressure confirm these transformations of the calcium-containing phases.

3.2. NaAlF_4

Experimental evidence for the participation of NaAlF_4 in the above processes was obtained by the calcinations of NaCaAlF_6 in a flow of an inert gas. The experimental details are described in [16]. The solids condensed from the gas present a mixture of colorless fibrous crystals stable in air. The XRD analysis confirmed that the obtained substance was NaAlF_4 . The thermal stability of NaAlF_4 was studied by high-temperature X-ray diffraction and thermal analysis. The phase appears to be metastable in normal conditions. It is observed at heating in air up to 390°C and, then the exothermic solid state decomposition occurs giving $\text{Na}_5\text{Al}_3\text{F}_{14}$ and AlF_3 .

3.3. Calcium-Containing Electrolytes

As it was obtained from the X-ray diffraction data the prepared electrolyte samples were composed from the following phases: Na_3AlF_6 , $\text{Na}_5\text{Al}_3\text{F}_{14}$, NaCaAlF_6 , $\text{Na}_2\text{Ca}_3\text{Al}_2\text{F}_{14}$, and CaF_2 . The phase NaCaAlF_6 , domi-

nated in the sample E3 ($\text{CR} > 2.6$), and the phase $\text{Na}_2\text{Ca}_3\text{Al}_2\text{F}_{14}$ —in the samples E1 and E2 ($\text{CR} < 2.3$).

The presence of two and sometimes three calcium containing phases in the sample is a consequence of non-equilibrium crystallization. The phase NaCaAlF_6 does not completely transform into $\text{Na}_2\text{Ca}_3\text{Al}_2\text{F}_{14}$ and in normal conditions remains metastable. It explains the broadened peaks on the X-ray diffraction pattern due to the crystalline degradation. According to the phase diagram of the system $\text{NaF-AlF}_3\text{-CaF}_2$ proposed by Anufrieva with the co-authors [13], in the samples with $\text{CR} \sim 2$ at cooling process after the formation of cryolite, the peritectic reaction occurs with the formation of $\text{Na}_5\text{Al}_3\text{F}_{14}$ (chiolyte), and then NaCaAlF_6 . At the crystallization of the electrolytes with CR near 3 the cryolite crystallization is followed by a peritectic reaction with the formation of NaCaAlF_6 .

This distinction can be the reason for NaCaAlF_6 prevailing in the electrolyte samples with $\text{CR} > 2.7$. The transformation of NaCaAlF_6 into $\text{Na}_2\text{Ca}_3\text{Al}_2\text{F}_{14}$ at cooling results in NaAlF_4 yielding. The active volatile molecules of NaAlF_4 interact with the components of the electrolyte, in particular, with Na_3AlF_6 , giving chiolyte. The decay of NaCaAlF_6 occurs in the samples with varying degrees of completeness. This explains the variation of the phase composition for the samples with the same chemical content. However, from the analytical point of view a definite relation between the phase and elemental content is considered as the basis for the accuracy and precision, especially in the technological control in alu-

minum production. One of the ways to get correspondence between the phase and elemental analysis is to analyze thermodynamically stable phases in the sample. This is why the conditions of the thermal treatment by calcination in air were investigated in the temperature range from 560°C to 710°C.

It was found that the phase compositions of the samples thermally treated at a temperature of 710°C, 610°C, 560°C were different. Thus, calcium ions in the sample E1, calcinated at 710°C were preferably collected in NaCaAlF₆. In the samples heated at 610°C and 560°C calcium ions were predominantly in Na₂Ca₃Al₂F₁₄ (Figure 4).

Since the treated samples were in the solid state, the formation of Na₂Ca₃Al₂F₁₄ below 600°C can be interpreted as the decay described by Equation (1). The released phase NaAlF₄ interacts with cryolite, Equation (4). The described results were repeated with the samples E2 and E3. Thus, the experiments show that a sample regardless of its CR can be transformed into the equilibrium state. The high phase crystallinity suitable for further quantitative X-ray diffraction analysis was another important effect.

The obtained results were tested using the samples of an industrial electrolyte. The milled samples were placed into an open crucible and calcinated in a furnace at temperatures of from 450°C to 650°C for a predetermined time. The experiments showed that after calcinations at temperatures below 600°C, poorly crystallized NaCaAlF₆ transformed into well-crystallized Na₂Ca₃Al₂F₁₄ (Figure 5). Simultaneously, a slight decrease of Na₃AlF₆ and increase of Na₅Al₃F₁₄ were noted. The calcination of the

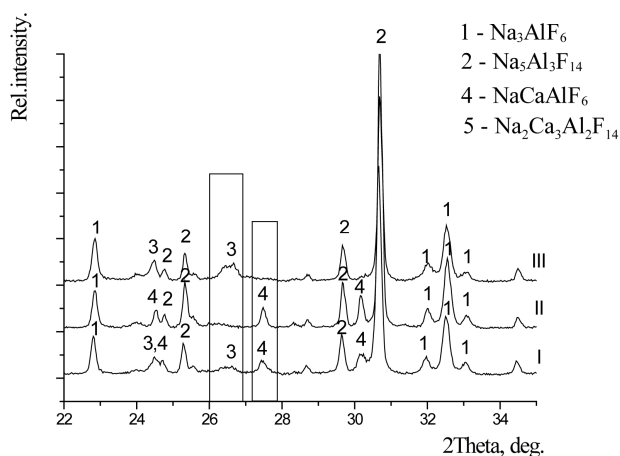


Figure 4. X-ray diffraction patterns from the high-temperature series for the sample of the electrolyte sample E1. (I)—at 25°C, the initial sample cooled in air, calcium ions are distributed into two phases—NaCaAlF₆, Na₂Ca₃Al₂F₁₄; (II)—at 560°C; calcium ions are in Na₂Ca₃Al₂F₁₄; (III)—at 710°C, calcium ions are in NaCaAlF₆. The analytical lines of the phases are highlighted in the rectangles.

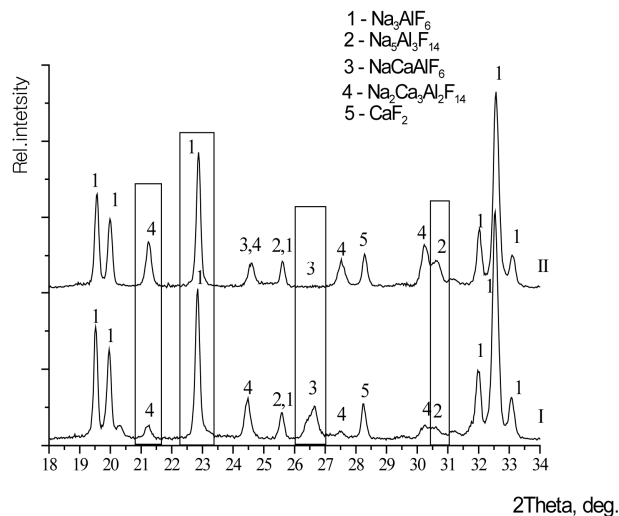


Figure 5. X-ray diffraction patterns of the sample industrial electrolyte (CR—2.54, CaF₂—8.19% (mas.)). (I)—at 25°C, electrolyte sample cooled in air consisted from the phases Na₃AlF₆ (1), Na₅Al₃F₁₄ (2), NaCaAlF₆ (3), Na₂Ca₃Al₂F₁₄ (4), CaF₂ (5); (II)—at 500°C after 30 min. consisted from Na₃AlF₆ (1), Na₅Al₃F₁₄ (2), Na₂Ca₃Al₂F₁₄ (4), CaF₂ (5). The analytical lines of the phases are highlighted in the rectangles.

samples without NaCaAlF₆ at temperatures below 600°C did not induce changes in the X-Ray powder pattern. There was no any significant variation mentioned of the elemental composition of the sample. Thus, the optimal temperature for the thermal treatment is about 600°C. The calcination at a temperature above 600°C results in the presence of NaCaAlF₆.

4. Conclusion

It is found that the interconversion of ternary fluorides NaCaAlF₆ and Na₂Ca₃Al₂F₁₄ occurs in the electrolyte samples at cooling. At sampling the non-equilibrium cooling conditions stops the phase transformation and results in poorly crystallized Ca-containing phases. An additional thermal treatment procedure can be applied to achieve good phase crystallinity without changing the elemental composition. The approach is effective when using XRD analysis for the electrolyte monitoring at aluminum production. The optimal temperature for the thermal treatment is about 600°C which provides the complete transformation of NaCaAlF₆ into Na₂Ca₃Al₂F₁₄.

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