



SYNTHESIS OF SODALITE FROM NEPHELINE FOR CONDITIONING CHLORIDE SALT WASTES

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Politecnico di Milano – Milano, Italy

IPRC 2012, Fontana, Wisconsin, USA



**Synthesis of
LiK.SODALITE
through Pressureless
Consolidation process**

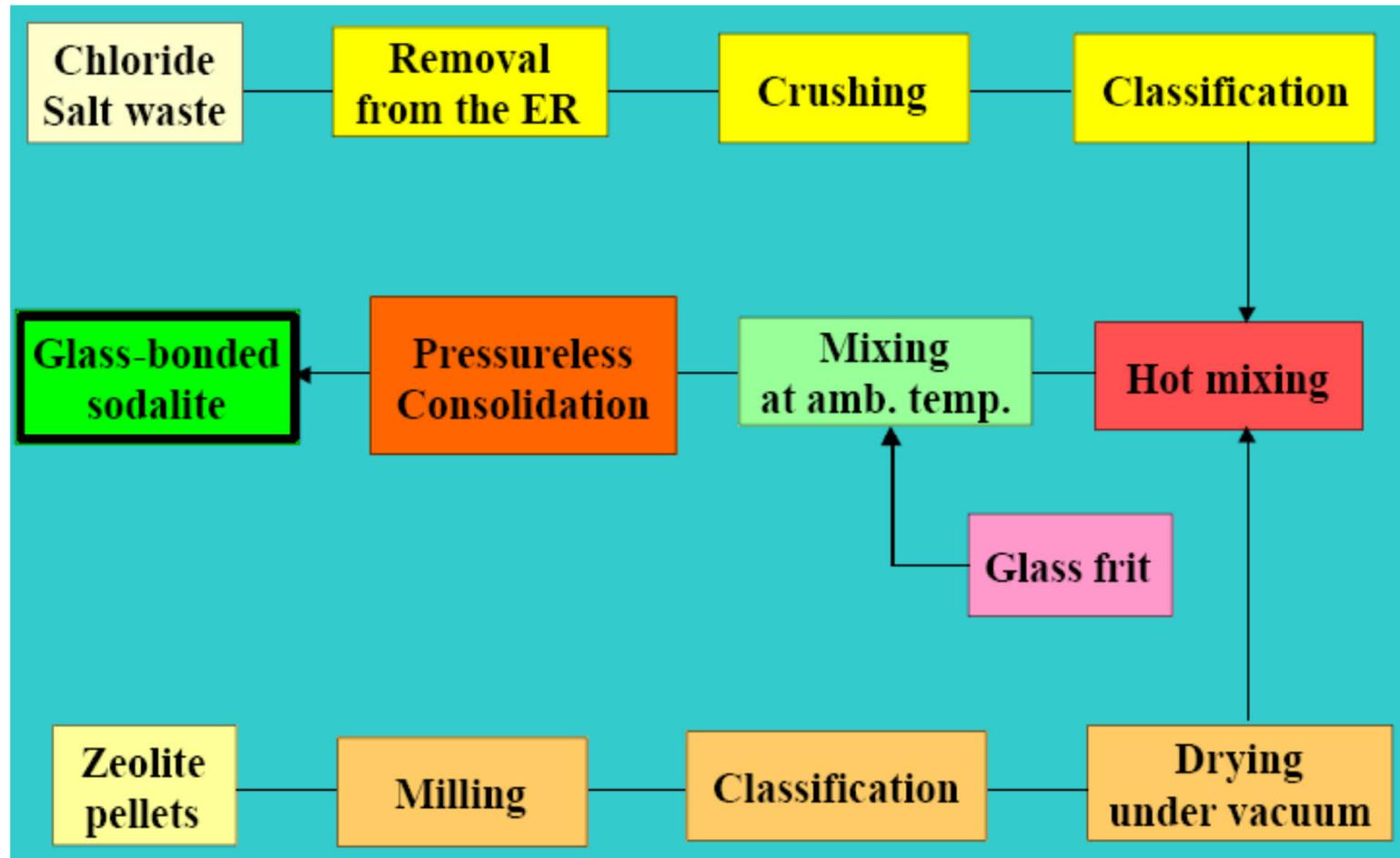




SYNTHESIS of SODALITE

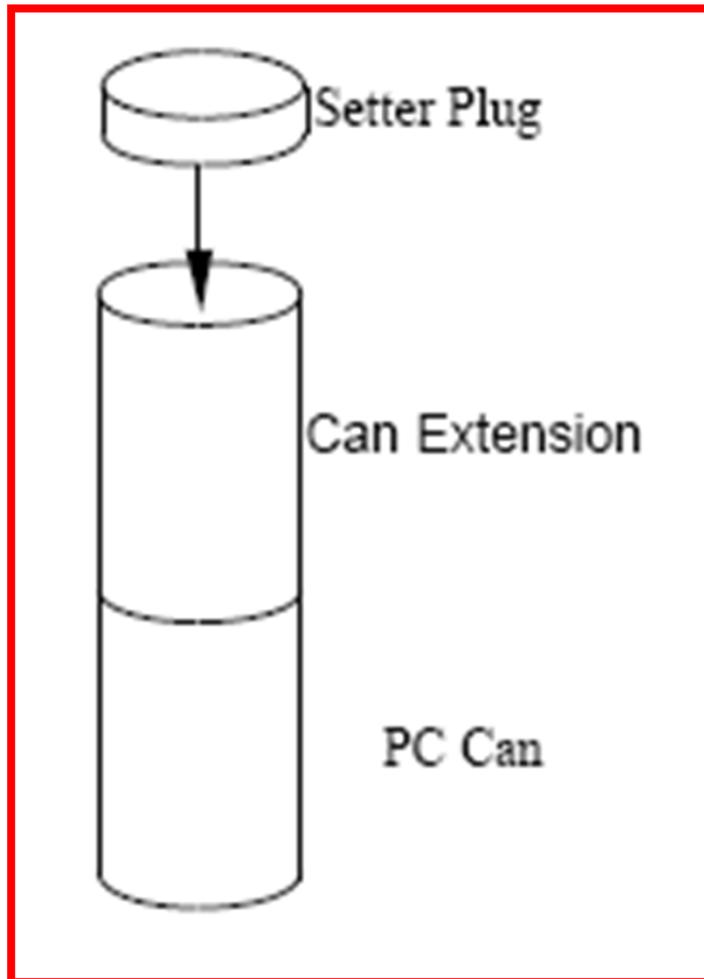


PC Process at ANL

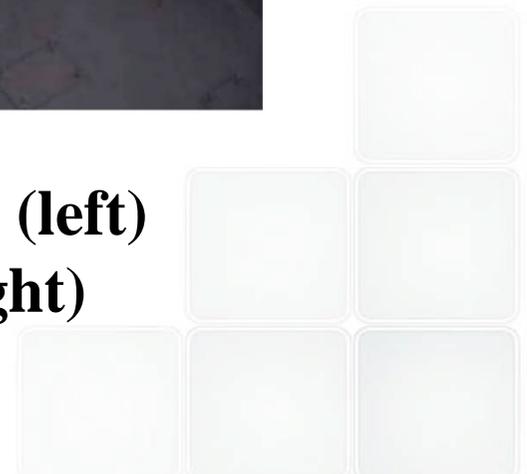


Process flow diagram for Pressureless Consolidation process at ANL

PC Process
at ANL

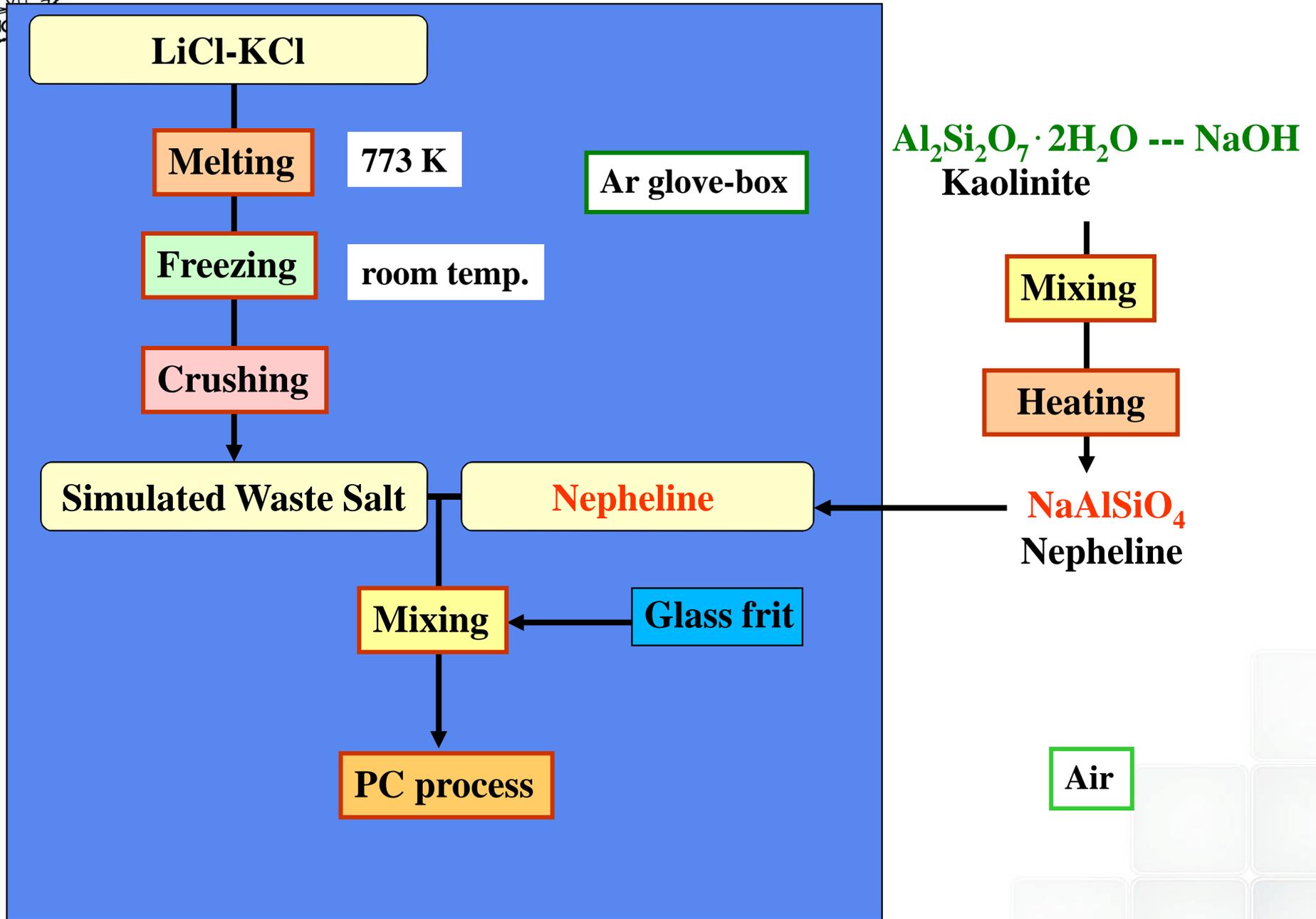


**Pressureless Consolidation Can Assembly (left)
and Production-scale CWF furnace (right)**





SYNTHESIS of SODALITE



SYNTHESIS of SODALITE



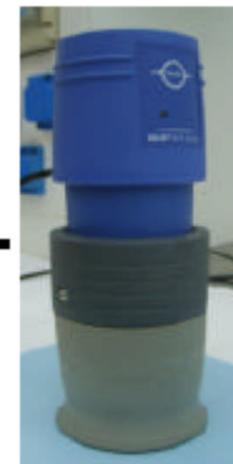
**Kaolinite
+ NaOH**



700°C



700°C



Synthesis of nepheline

SYNTHESIS of SODALITE



Mixing and grinding of nepheline with LiCl-KCl

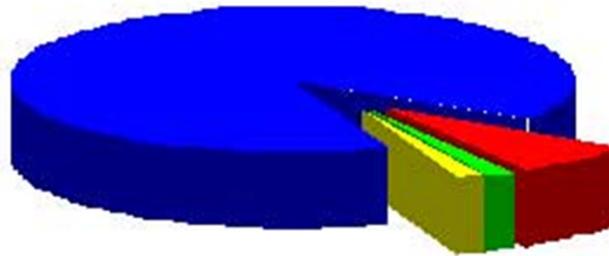


SYNTHESIS of SODALITE



Eutectic : LiCl - KCl
90 %

ALCl (AL = Rb, Cs)
1,5 %



LnCl₃ (Ln = lanthanides)
7 %

ALECl₂ (ALE = Sr, Ba)
1,5 %

Reference composition of chloride salt wastes



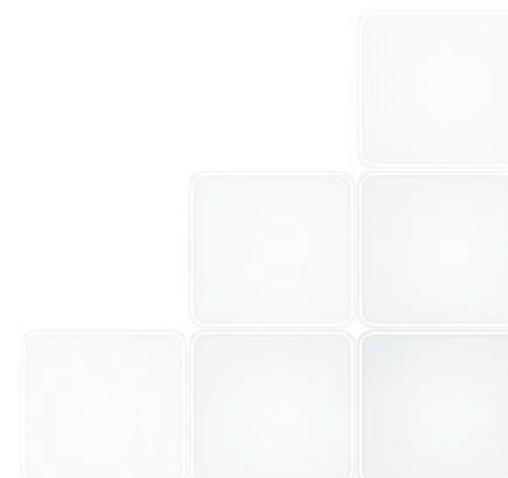


SYNTHESIS of SODALITE

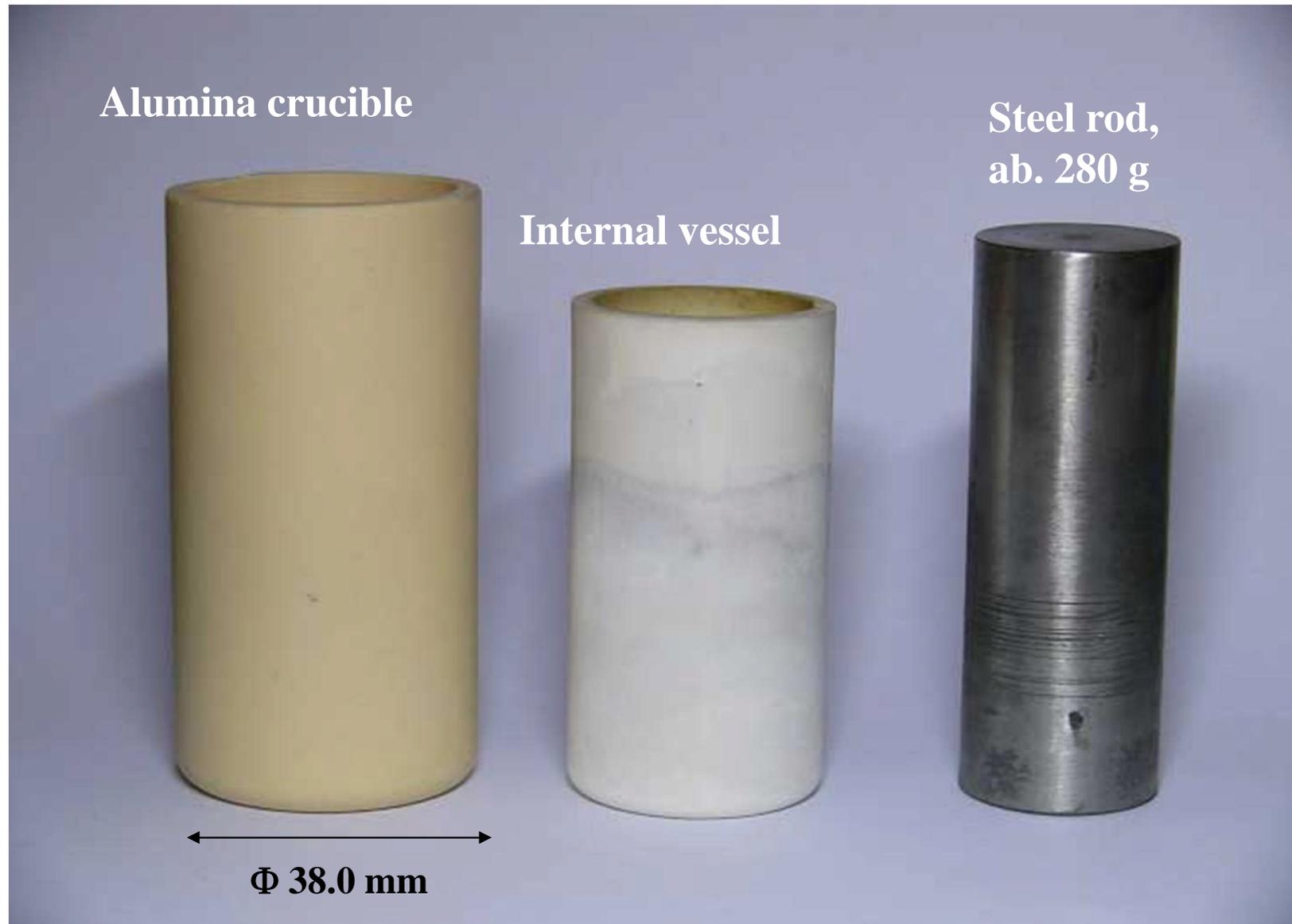


Composition of glass frit

Component	Wt%
Al₂O₃	2.0
CaO	11.5
Fe₂O₃	0.23
K₂O	2.0
MgO	2.0
Na₂O	13.0
SiO₂	71.3

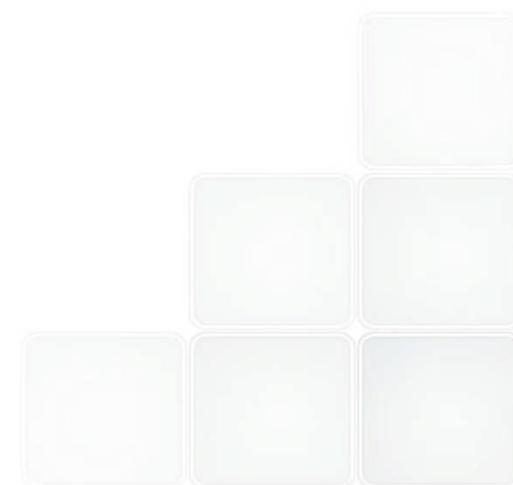


SYNTHESIS of SODALITE



Components used for labo. scale Pressureless Consolidation experiments

SYNTHESIS of SODALITE



SYNTHESIS of SODALITE



Sodalite pellet after a Pressureless Consolidation experiment



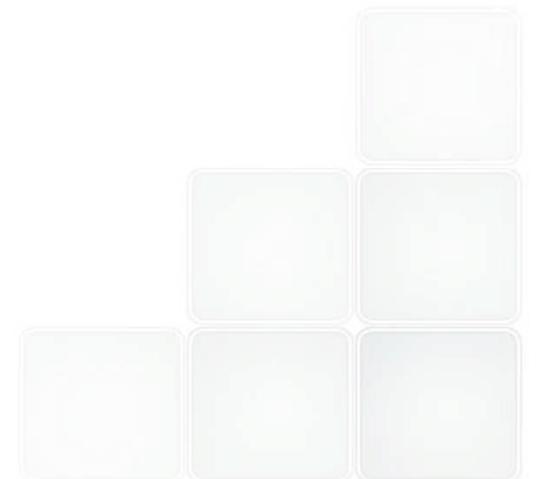


SYNTHESIS of SODALITE

Experiments with a common glass frit

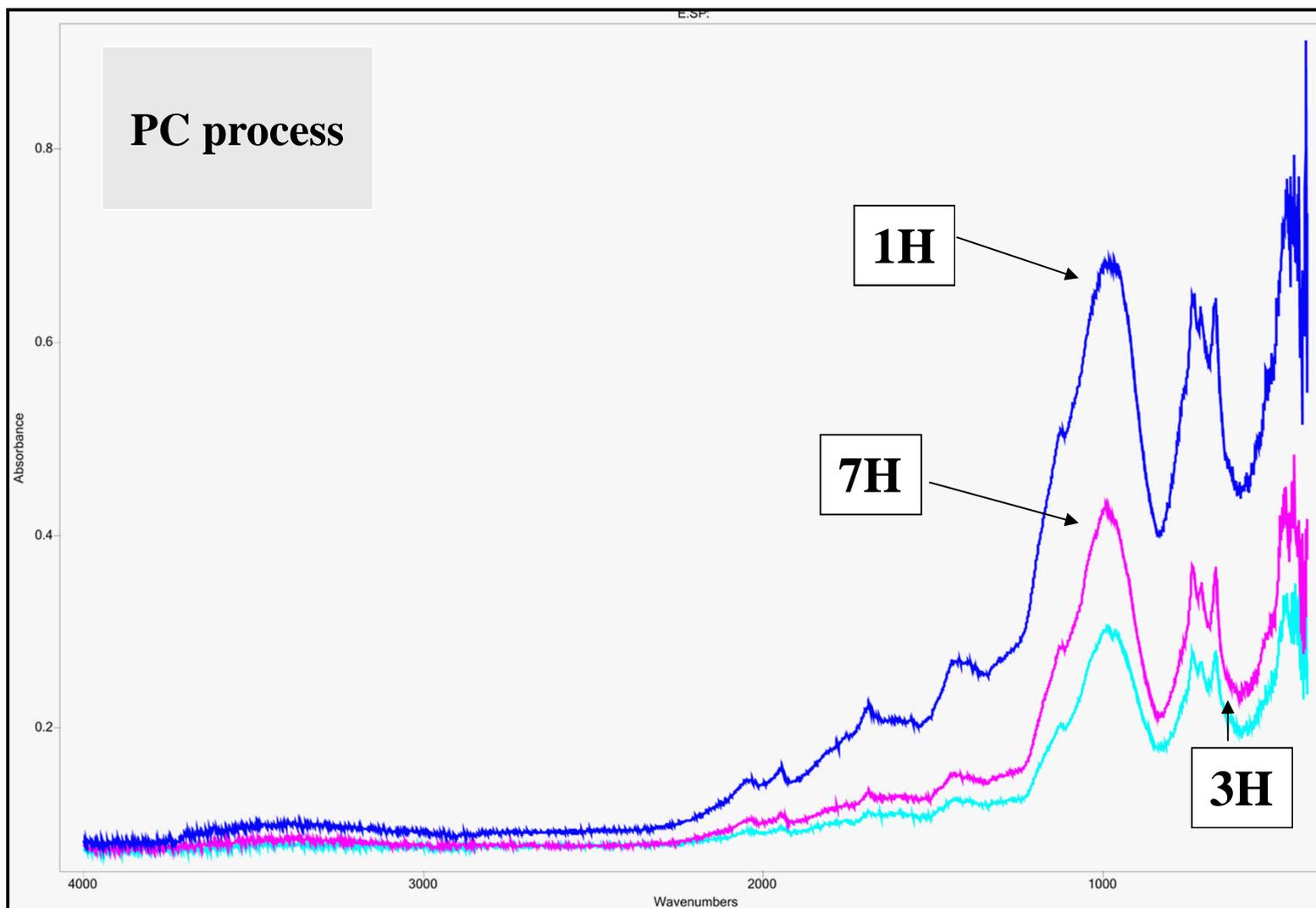
Density of the final product:

2.122 g/cc





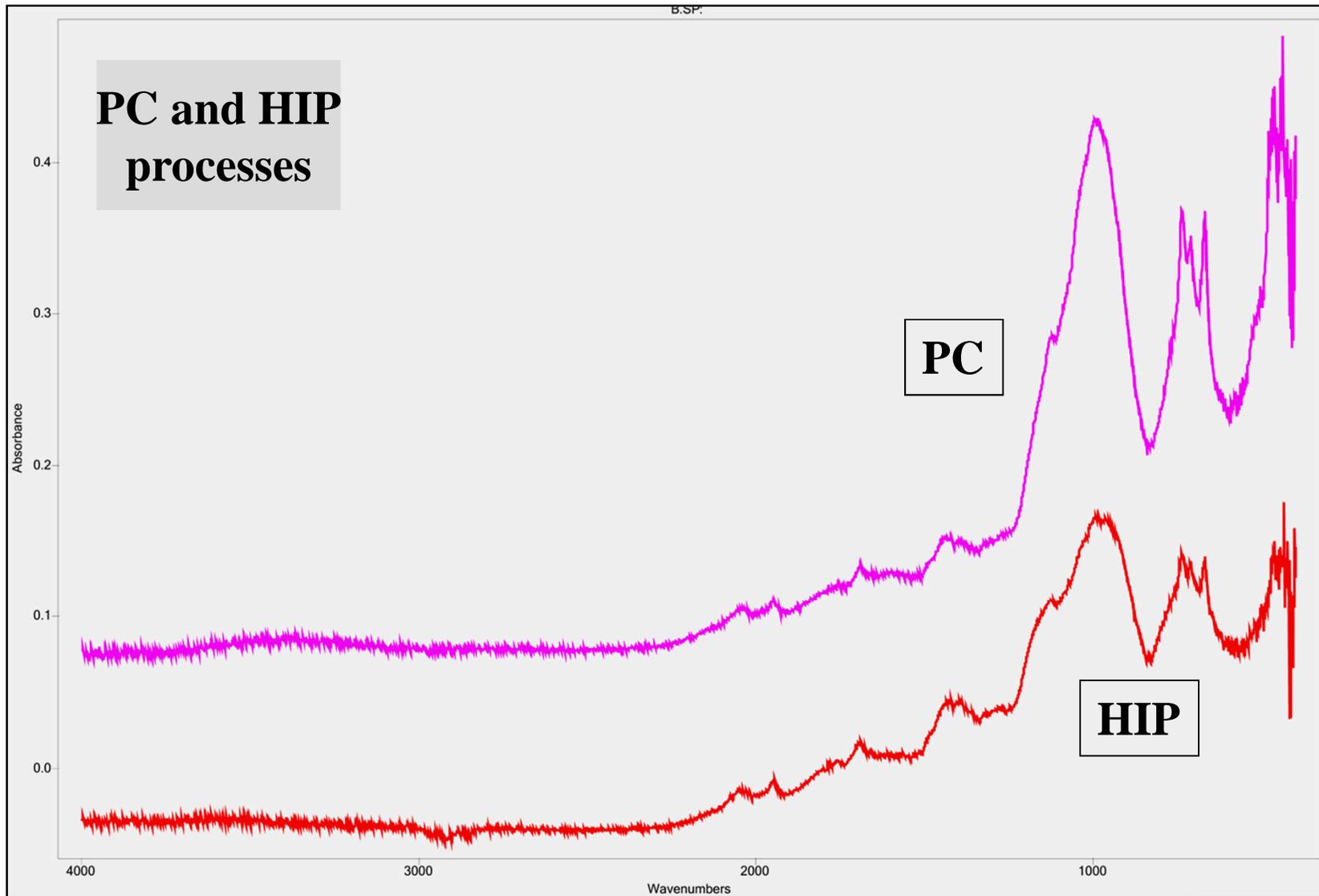
SYNTHESIS of SODALITE



FTIR spectra at increasing time of reaction



SYNTHESIS of SODALITE



Comparison of FTIR spectra



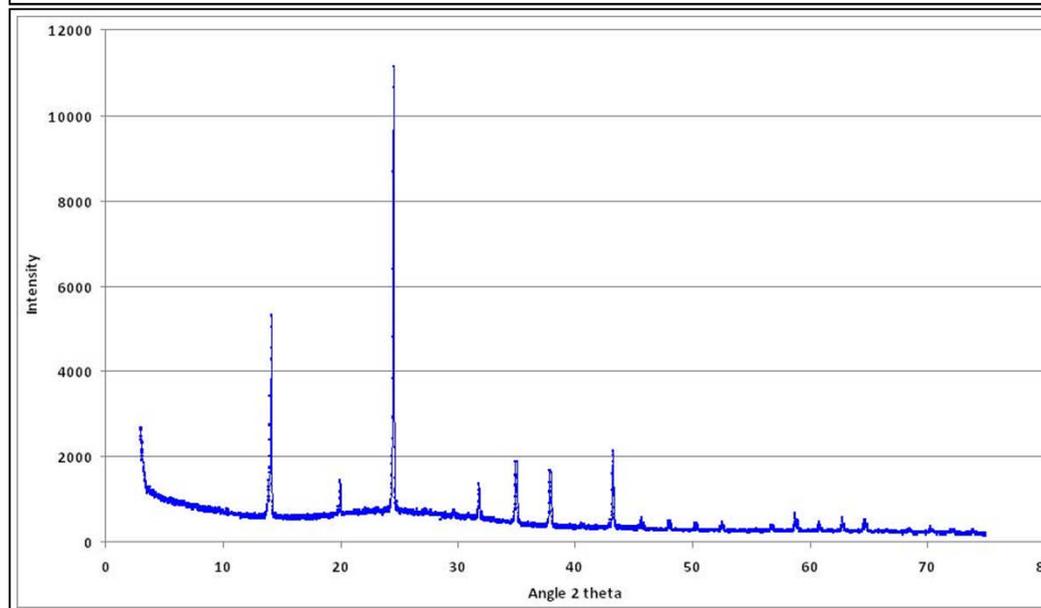
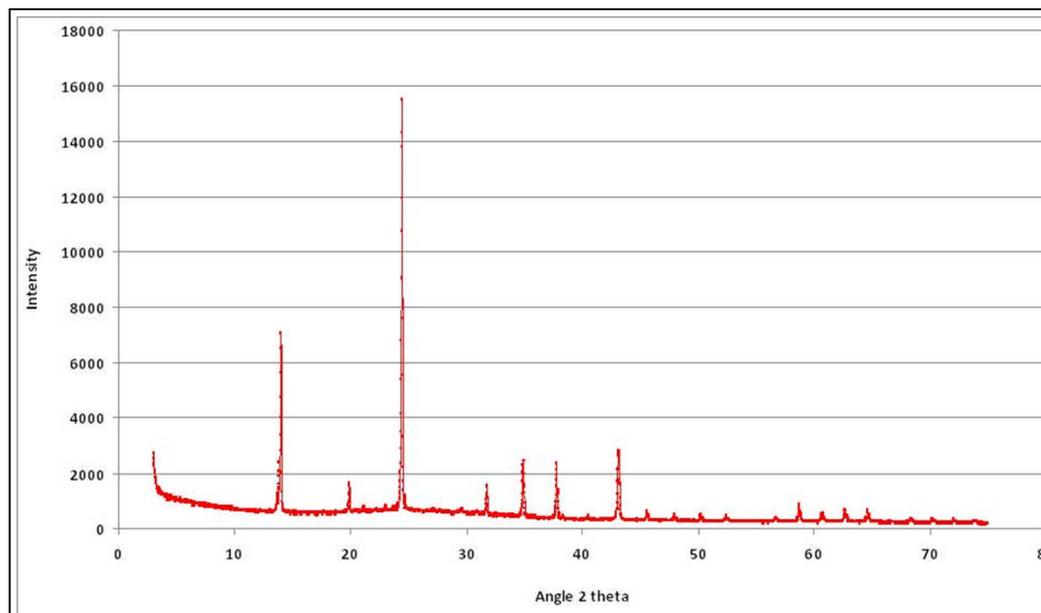
SYNTHESIS of SODALITE



LiK.SOD.HIP

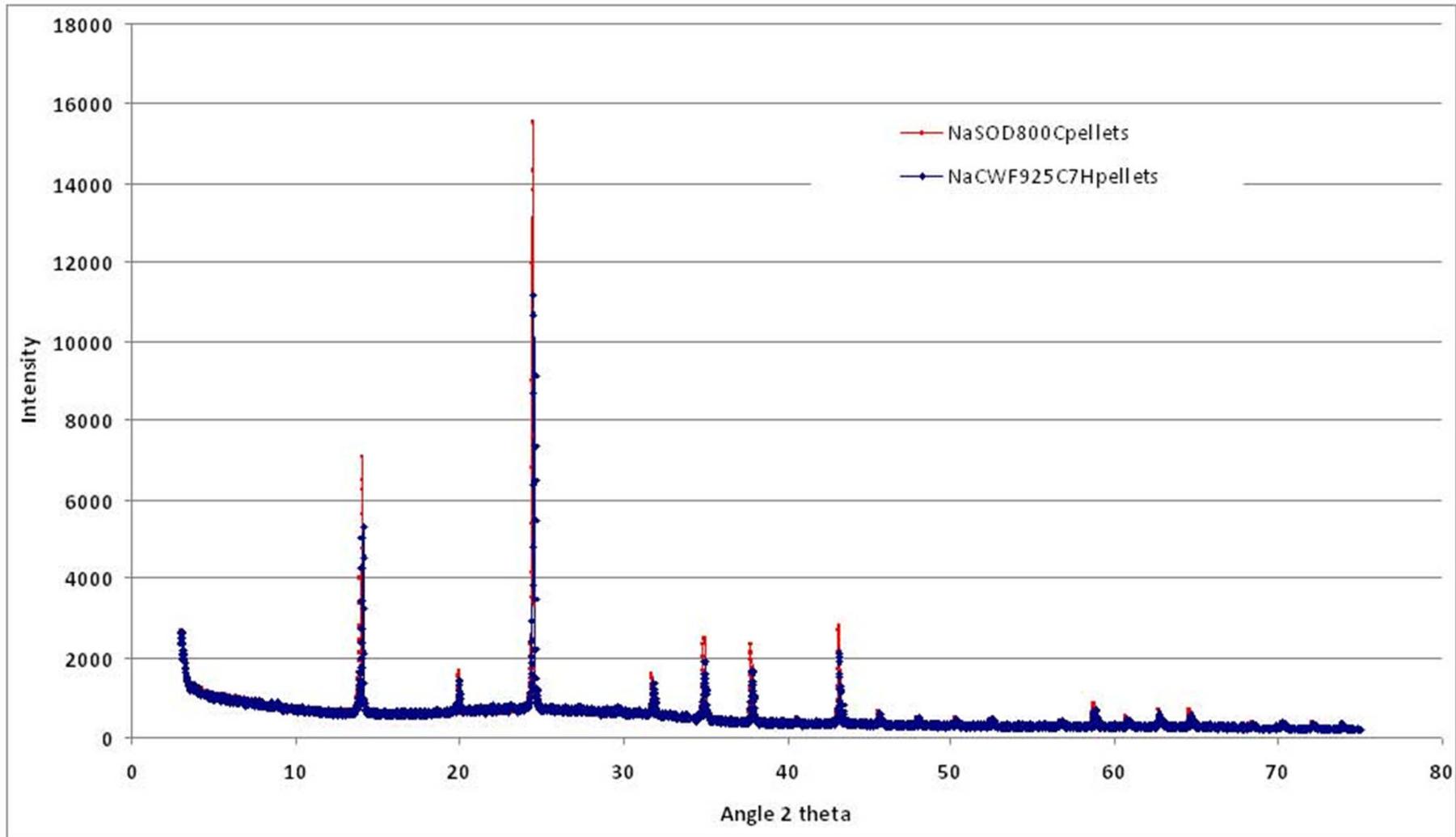
**Comparison of
XRD spectra**

LiK.SOD.PC





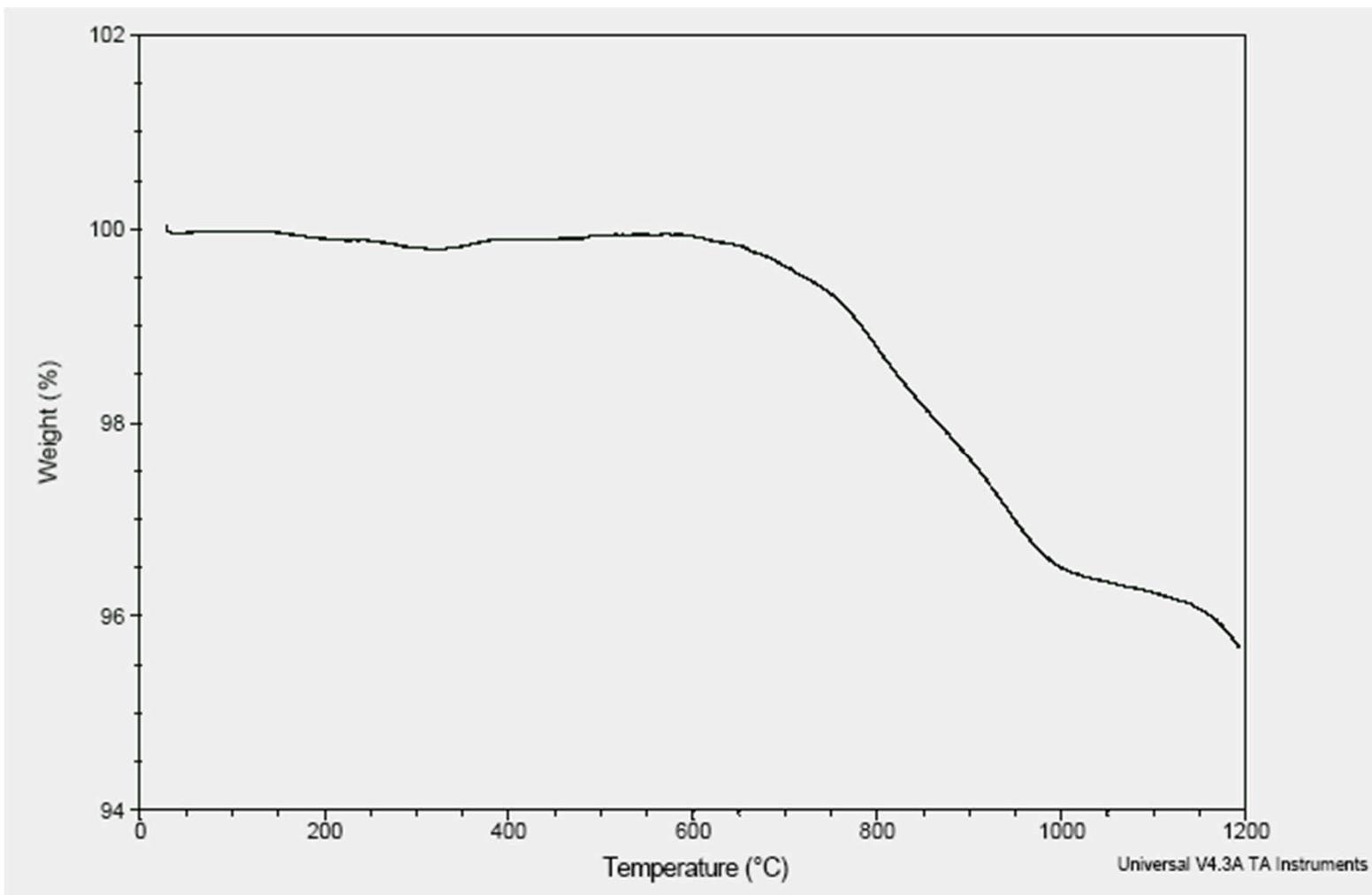
SYNTHESIS of SODALITE



Overlapping of XRD spectra: **PC process**; **HIP process**

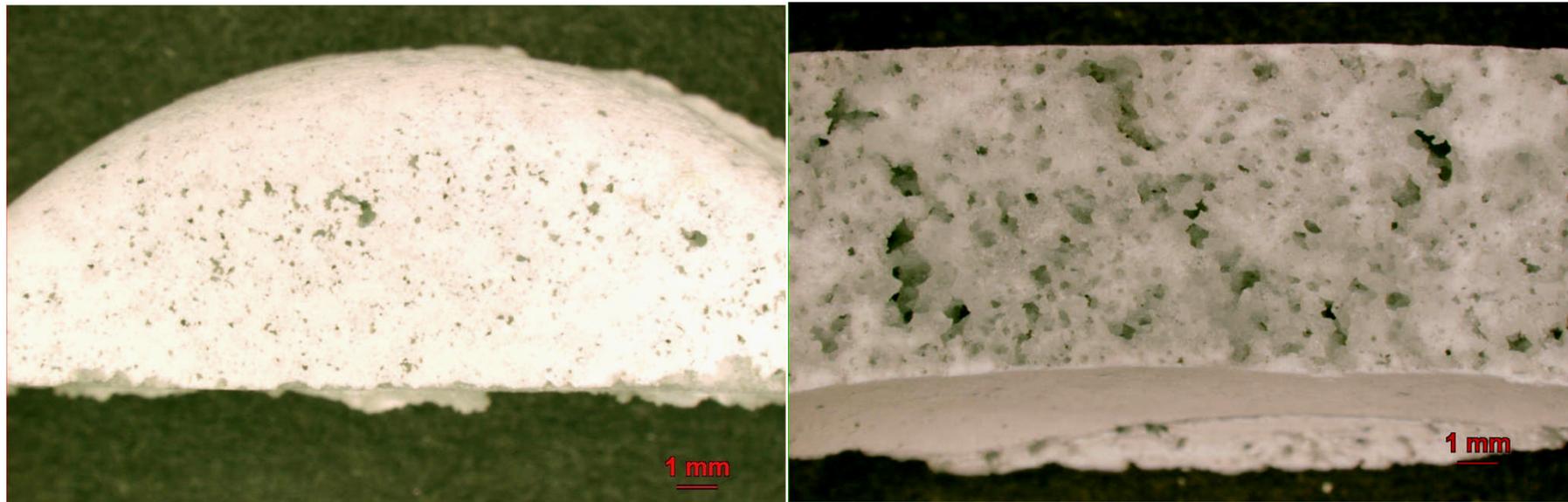


SYNTHESIS of SODALITE

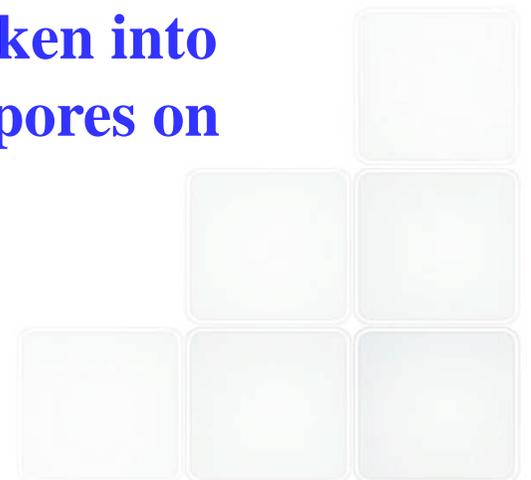


TGA of SODALITE from PC process

SYNTHESIS of SODALITE



Stereomicroscopy pictures of the product broken into two pieces, showing homogeneous matrix and pores on both top and side surface

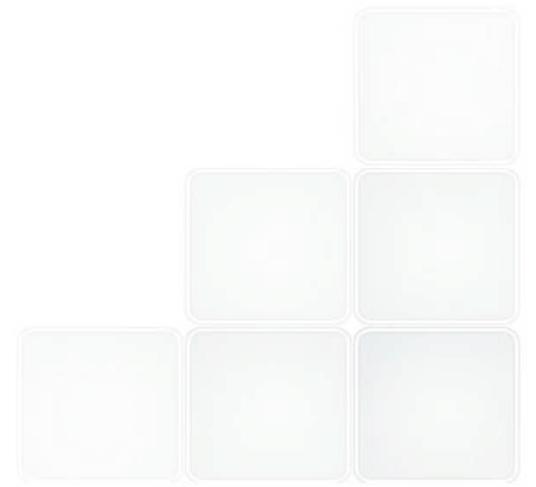




SYNTHESIS of SODALITE



Experiments with a borosilicate glass





SYNTHESIS of SODALITE



Composition of borosilicate glass

Component	Wt%
Al_2O_3	7.5
B_2O_3	19.3
CaO	1.3
K_2O	0.4
Li_2O	0.0
Na_2O	6.5
SiO_2	63.1



SYNTHESIS of SODALITE



Components used for labo. scale Pressureless Consolidation experiments



SYNTHESIS of SODALITE



$d^{20C} = 2.122 \text{ g/cc}$

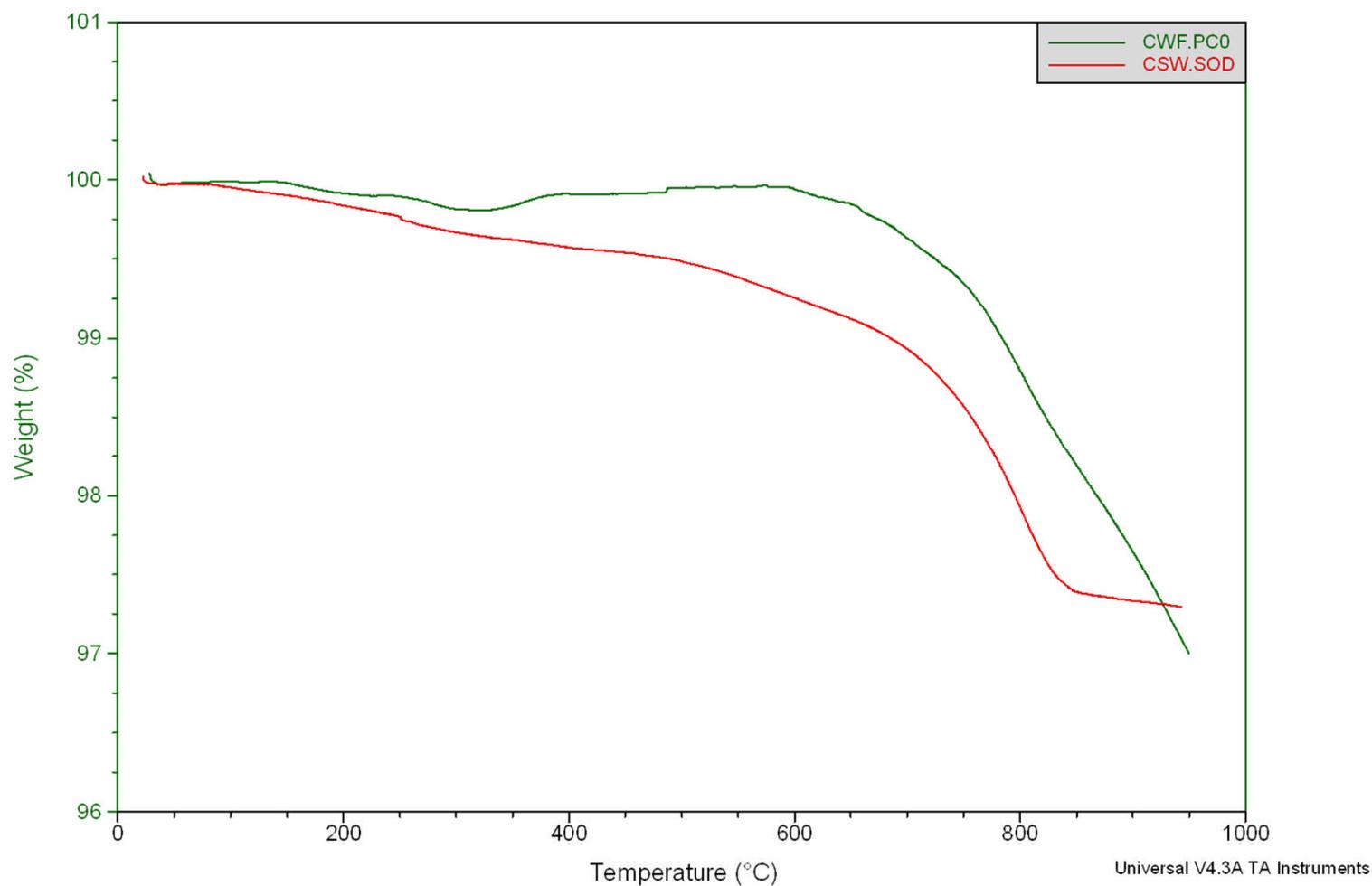


$d^{20C} = 2.430 \text{ g/cc}$

Comparison of samples obtained from glass frit (left)
and borosilicate glass (right)



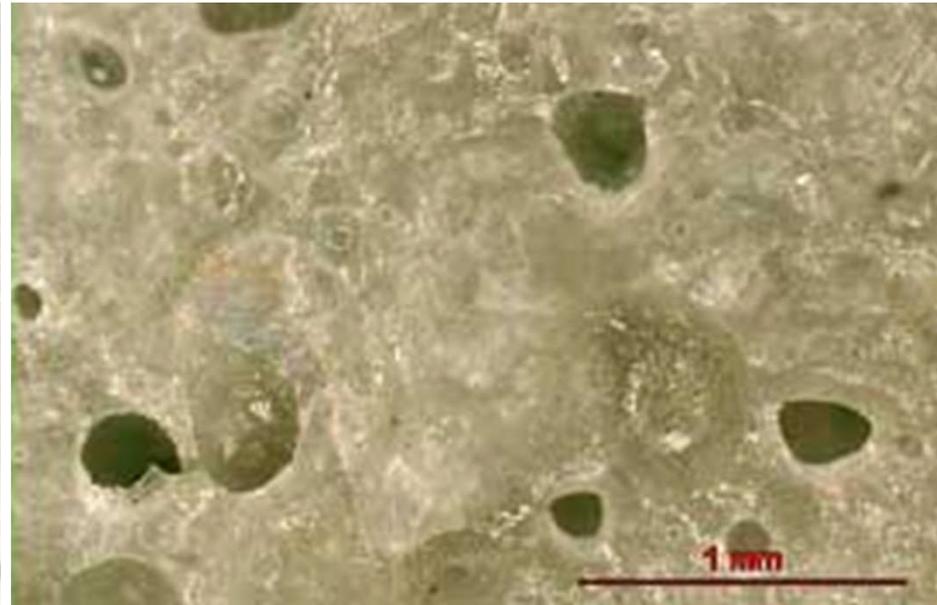
SYNTHESIS of SODALITE



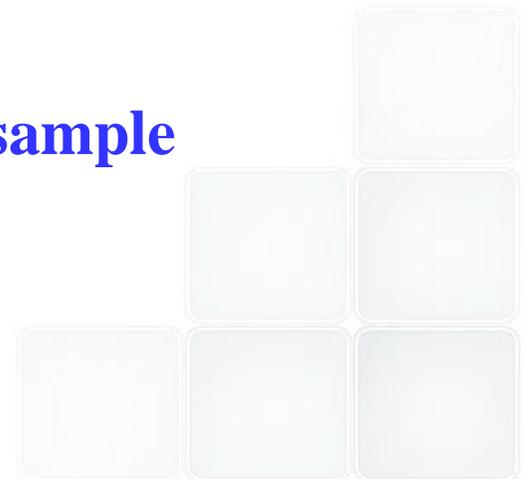
Thermal analysis of **LiK.SOD.BG**
and **LiK.SOD.GF**



SYNTHESIS of SODALITE

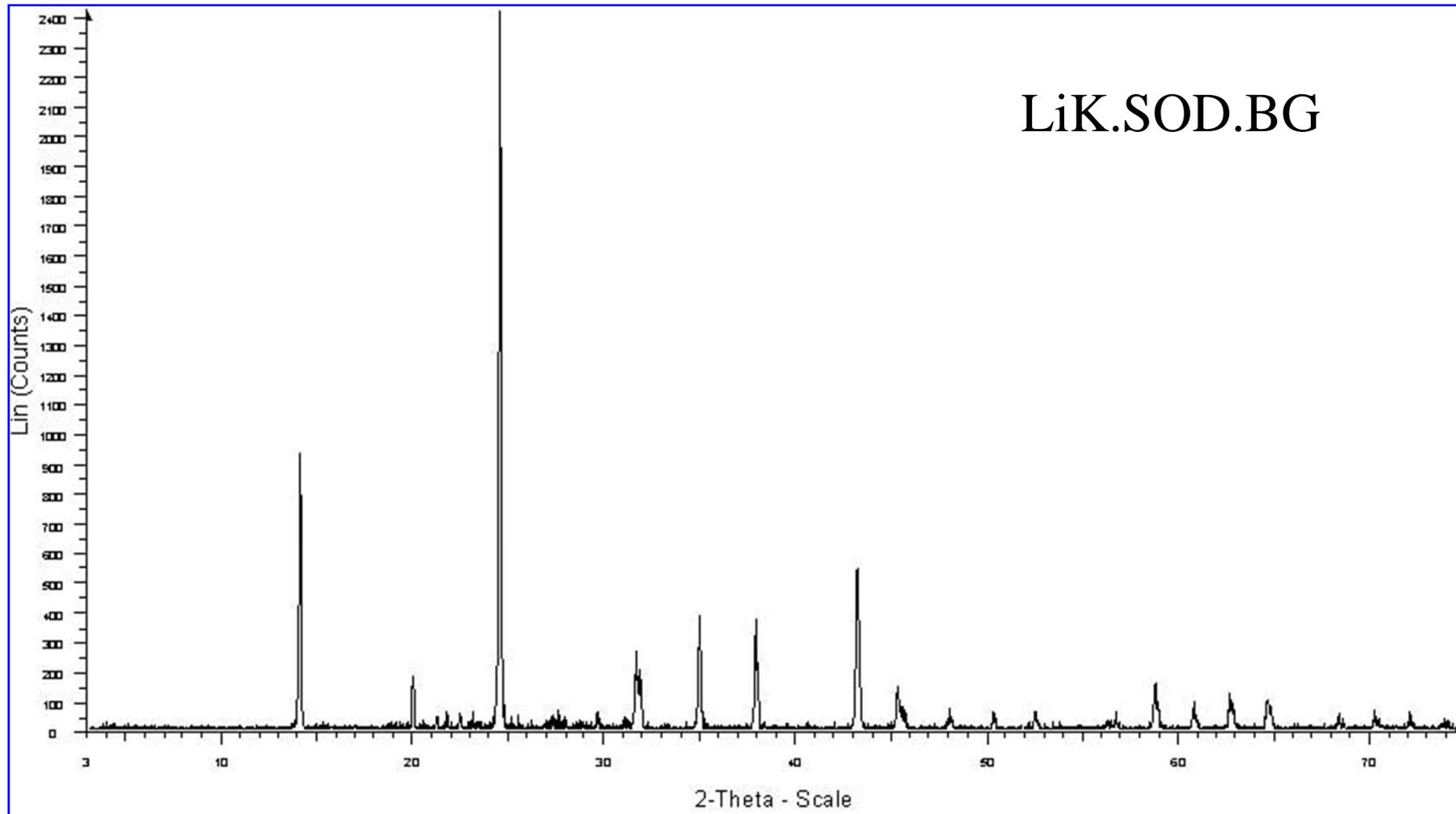


Pictures at the stereomicroscopy of a SOD.BG sample



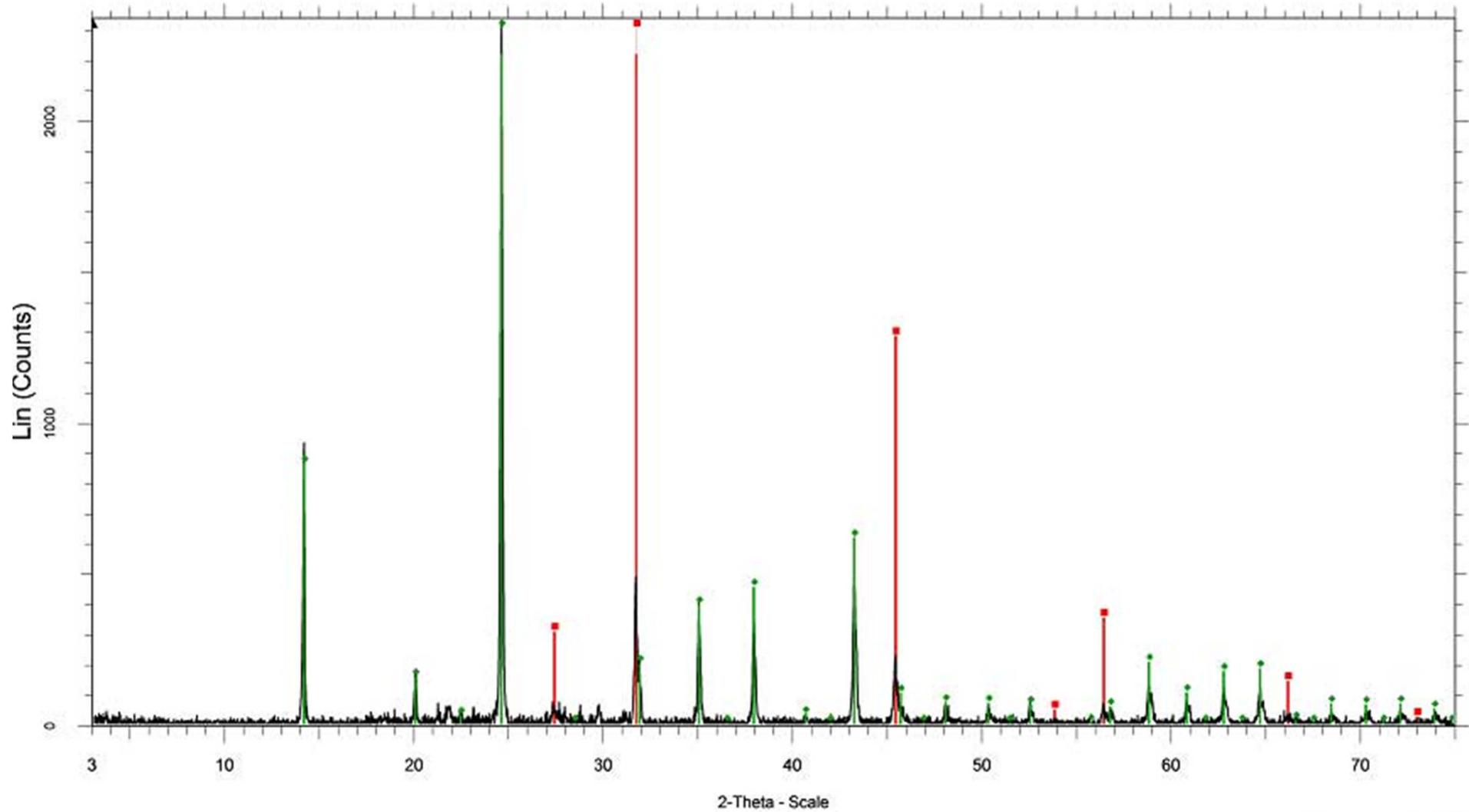


SYNTHESIS of SODALITE



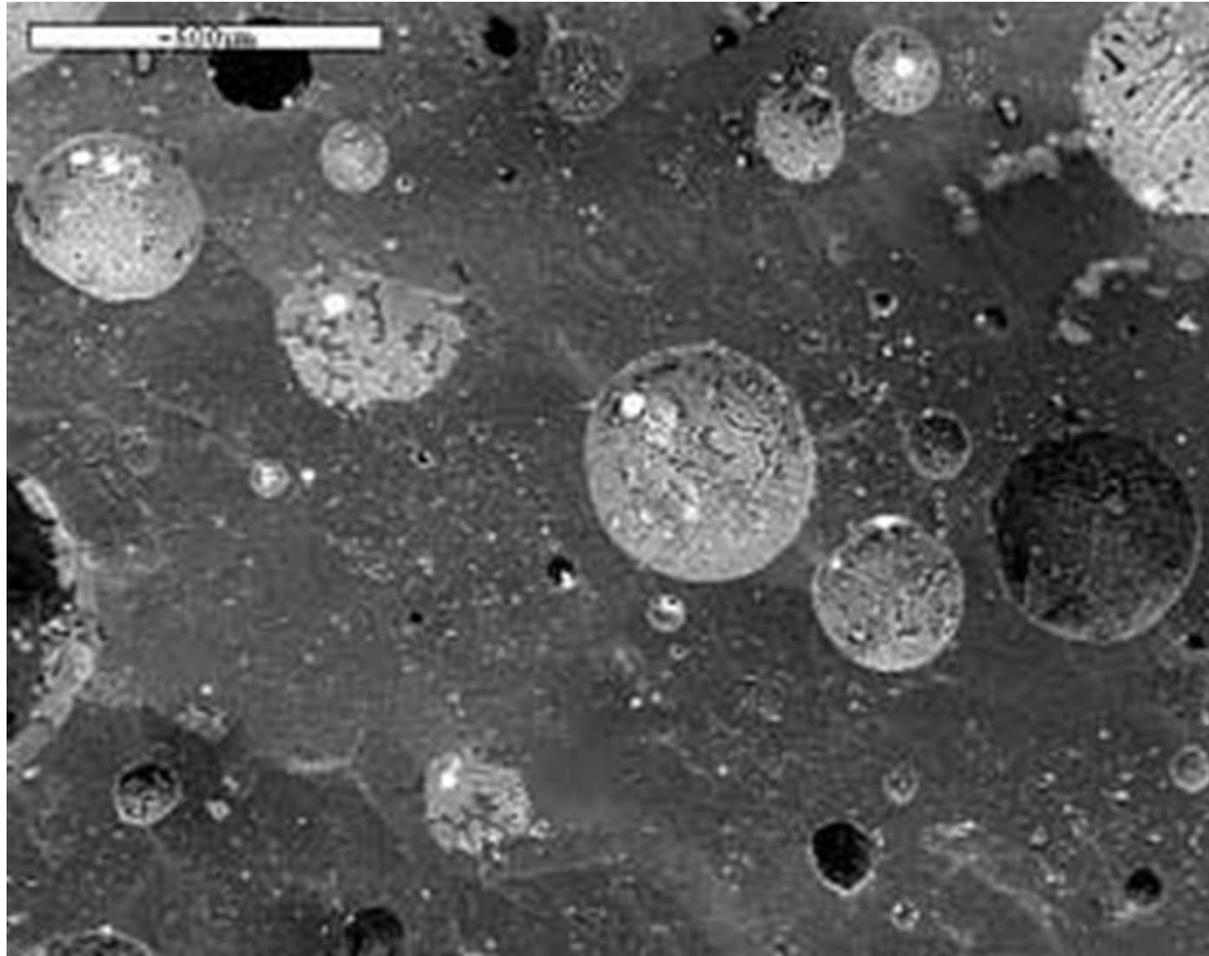


SYNTHESIS of SODALITE

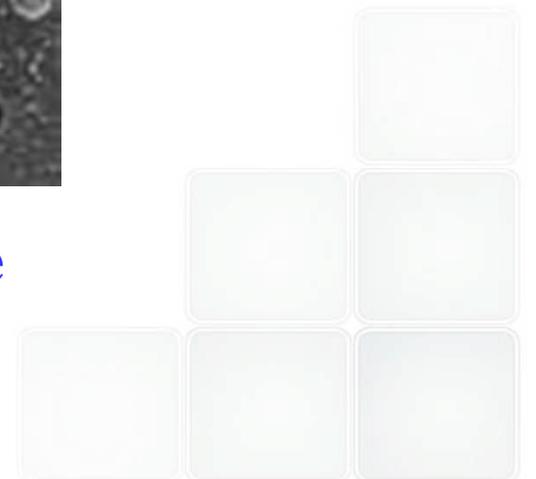


LiK.SOD.BG: peaks of sodalite and alite

SYNTHESIS of SODALITE



SEM picture of a LiK.SOD.BG sample

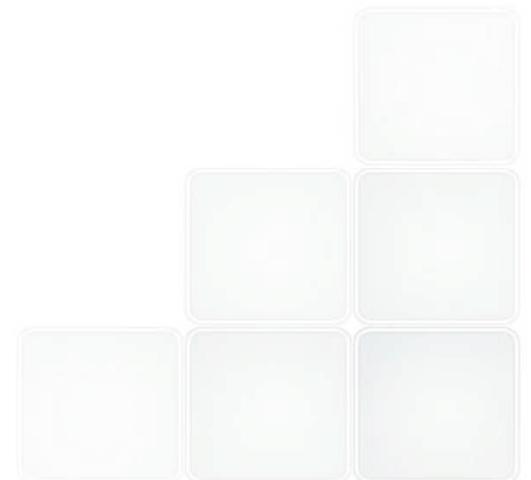


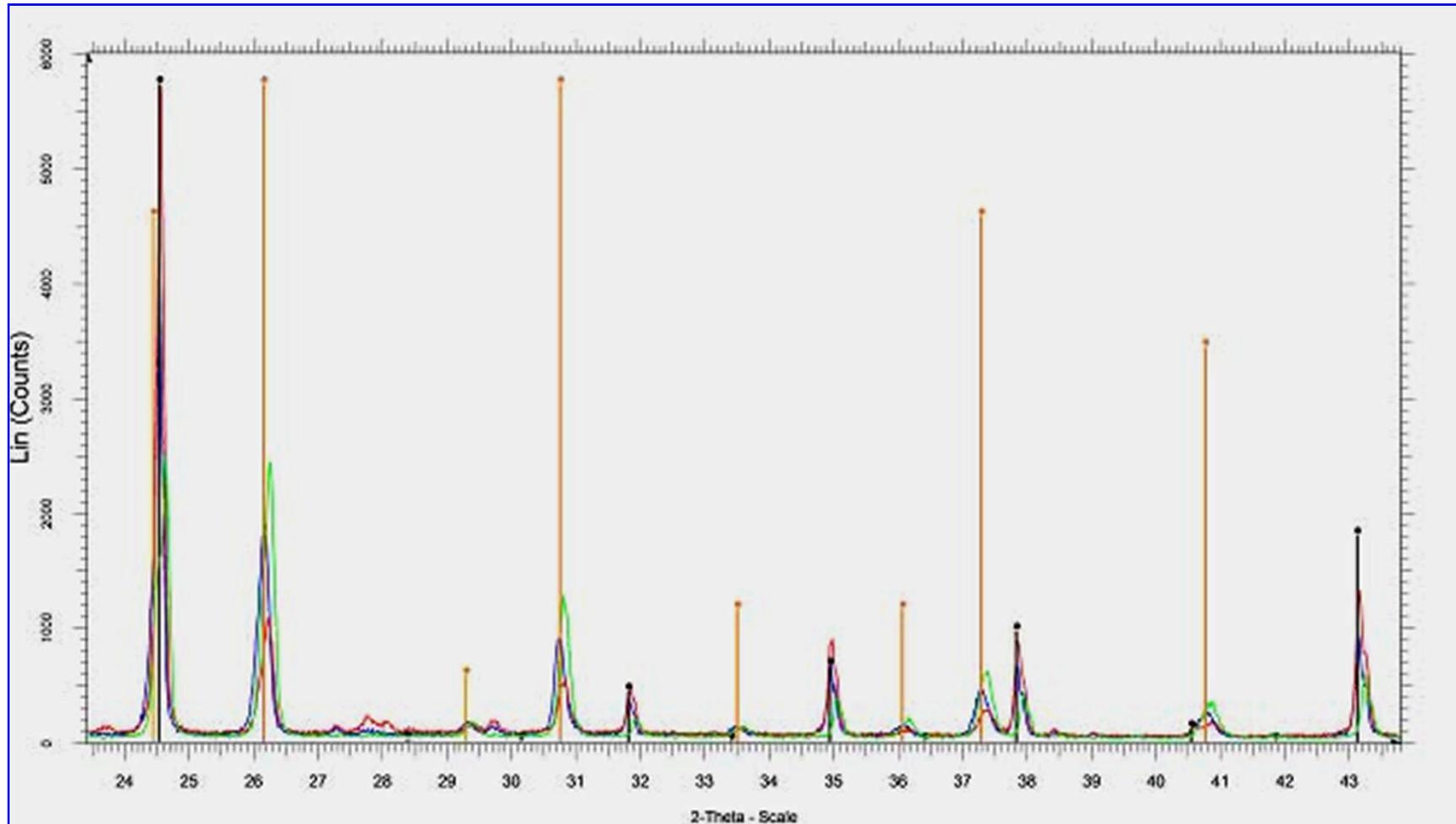


SYNTHESIS of SODALITE



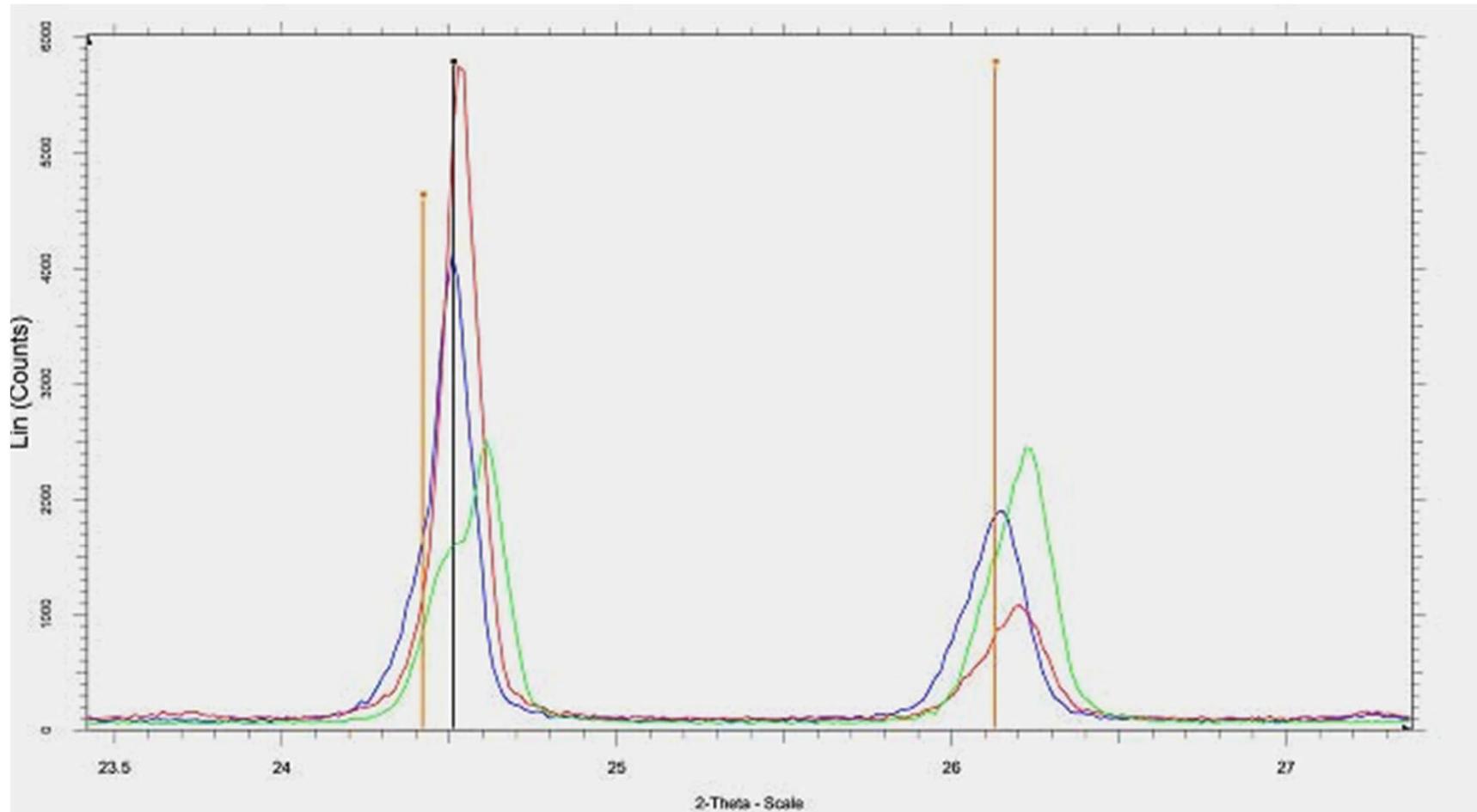
Studies with Cs, Sr, and Nd





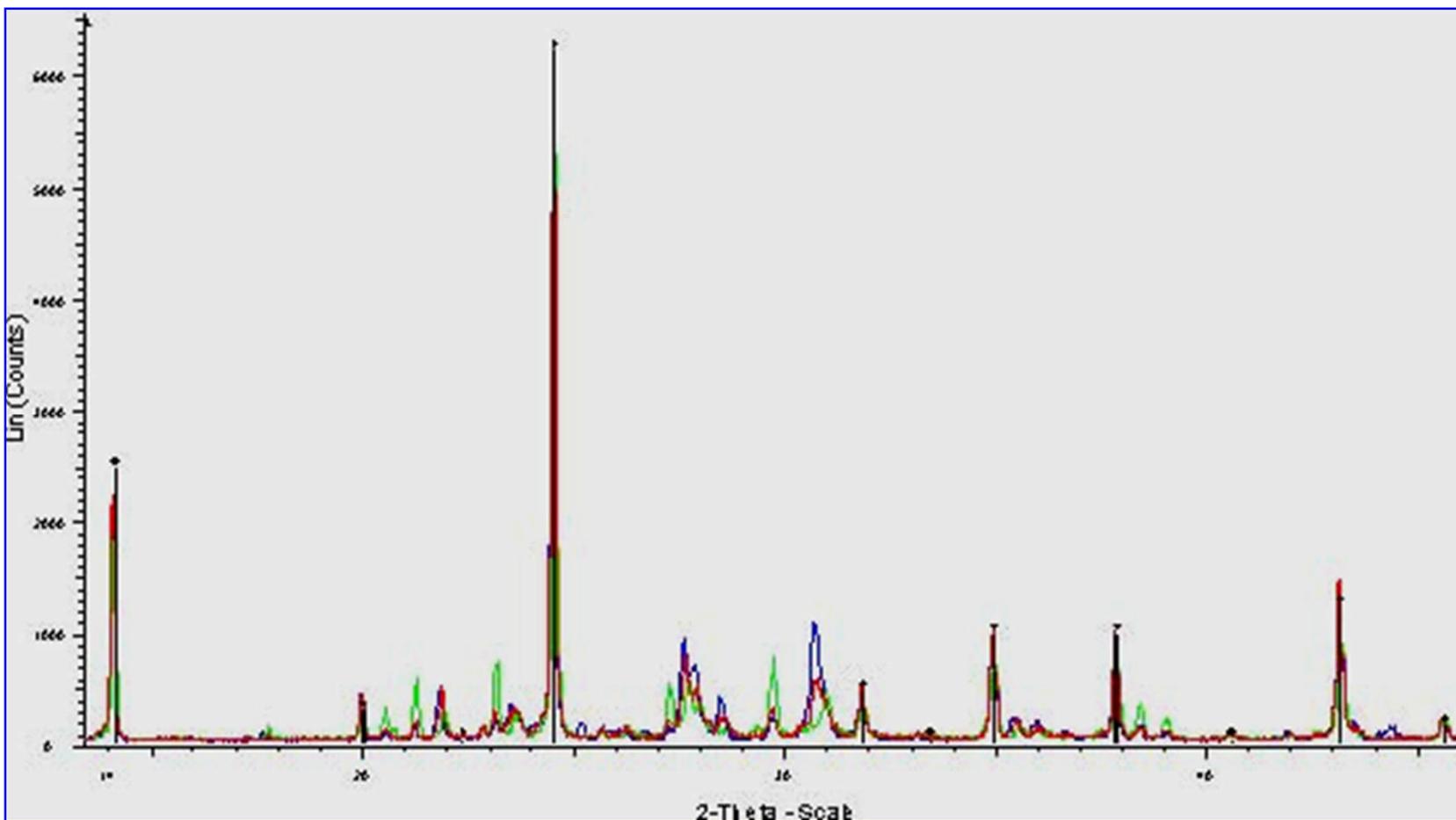
**XRD spectra of the samples 100Cs.SOD (green line),
50Cs.SOD (blue line) and 25Cs.SOD (red line)**

SYNTHESIS of SODALITE



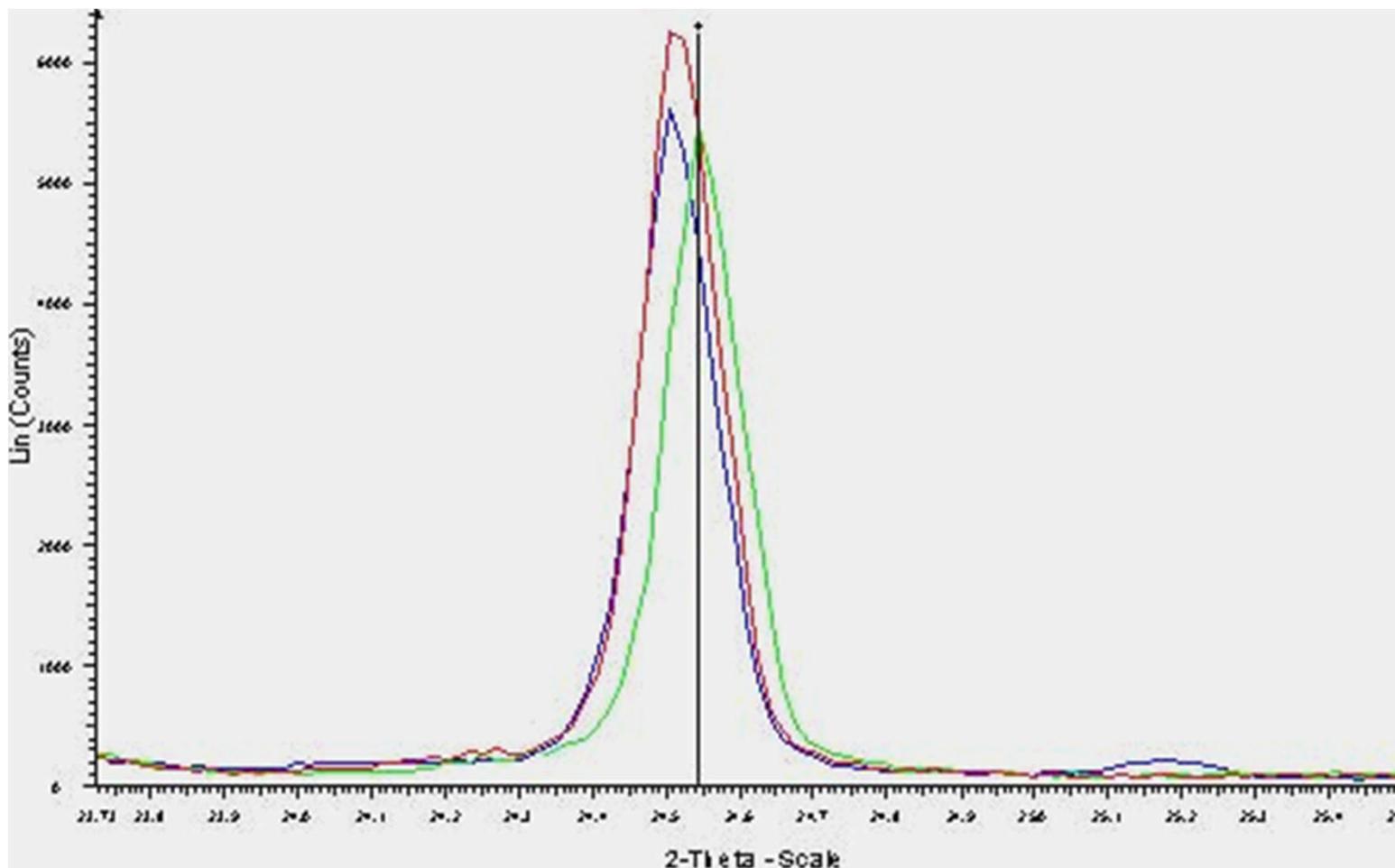
Comparison among the XRD spectra of the samples 100Cs.SOD (green line), 50Cs.SOD (blue line) and 25Cs.SOD (red line) and the sodalite (black vertical line) and pollucite (yellow vertical line) phases present in the spectral library

SYNTHESIS of SODALITE

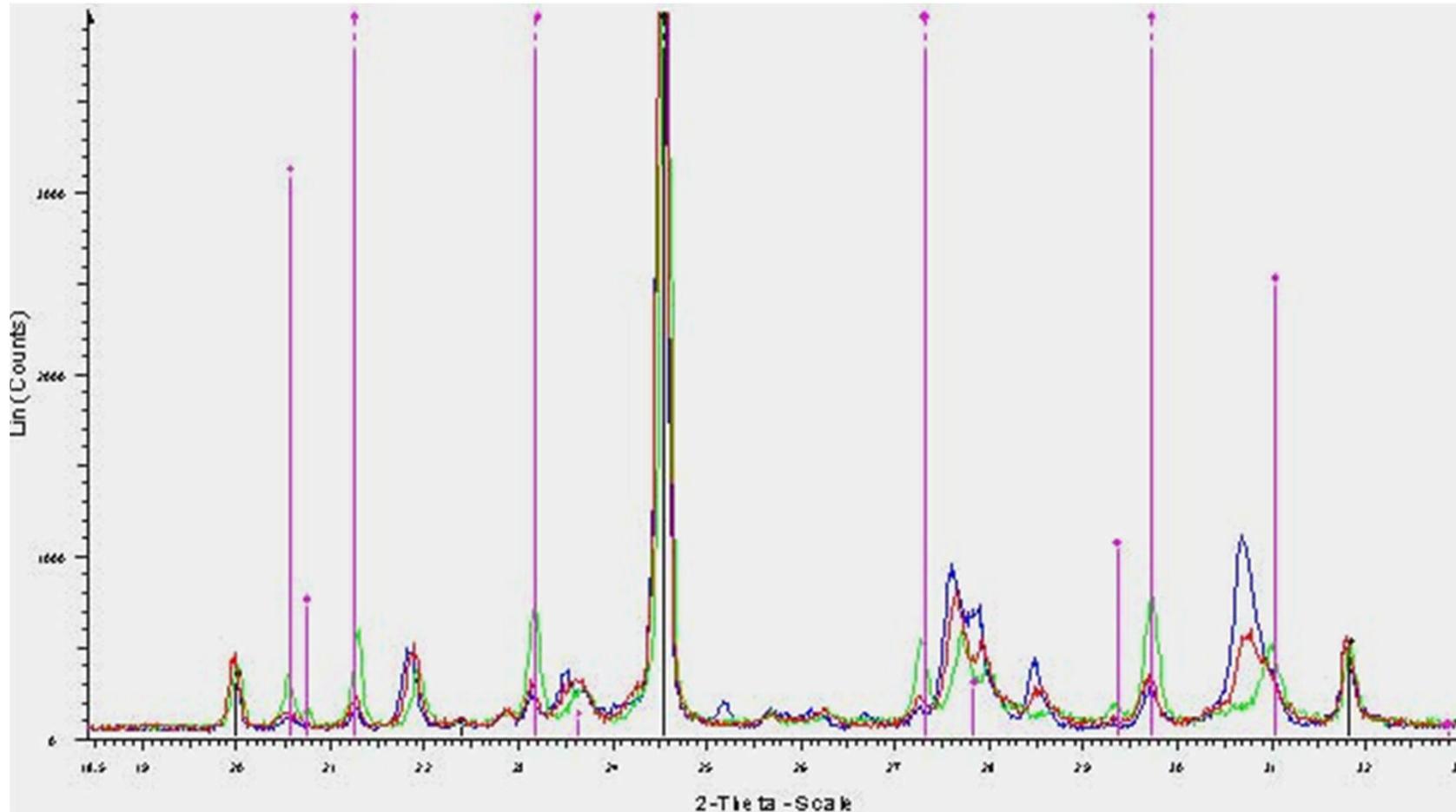


**XRD spectra of the samples 100Sr.SOD (blue line),
50Sr.SOD (red line) and 25Sr.SOD (green line)**

SYNTHESIS of SODALITE

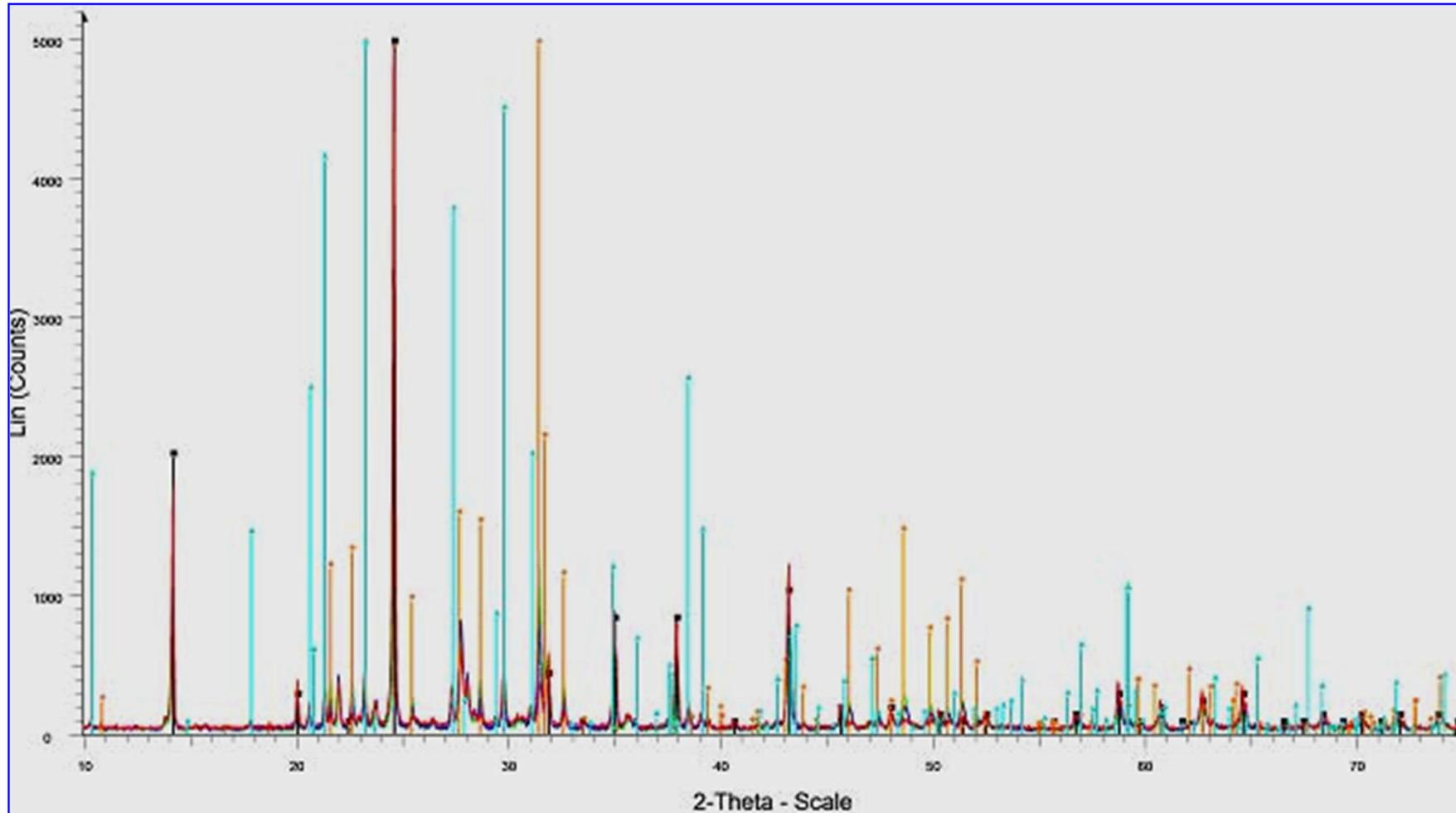


Comparison among the main peak of the sodalite phase from the library and the profiles of the samples 100Sr.SOD (blue line), 50Sr.SOD (red line) and 25Sr.SOD (green line)



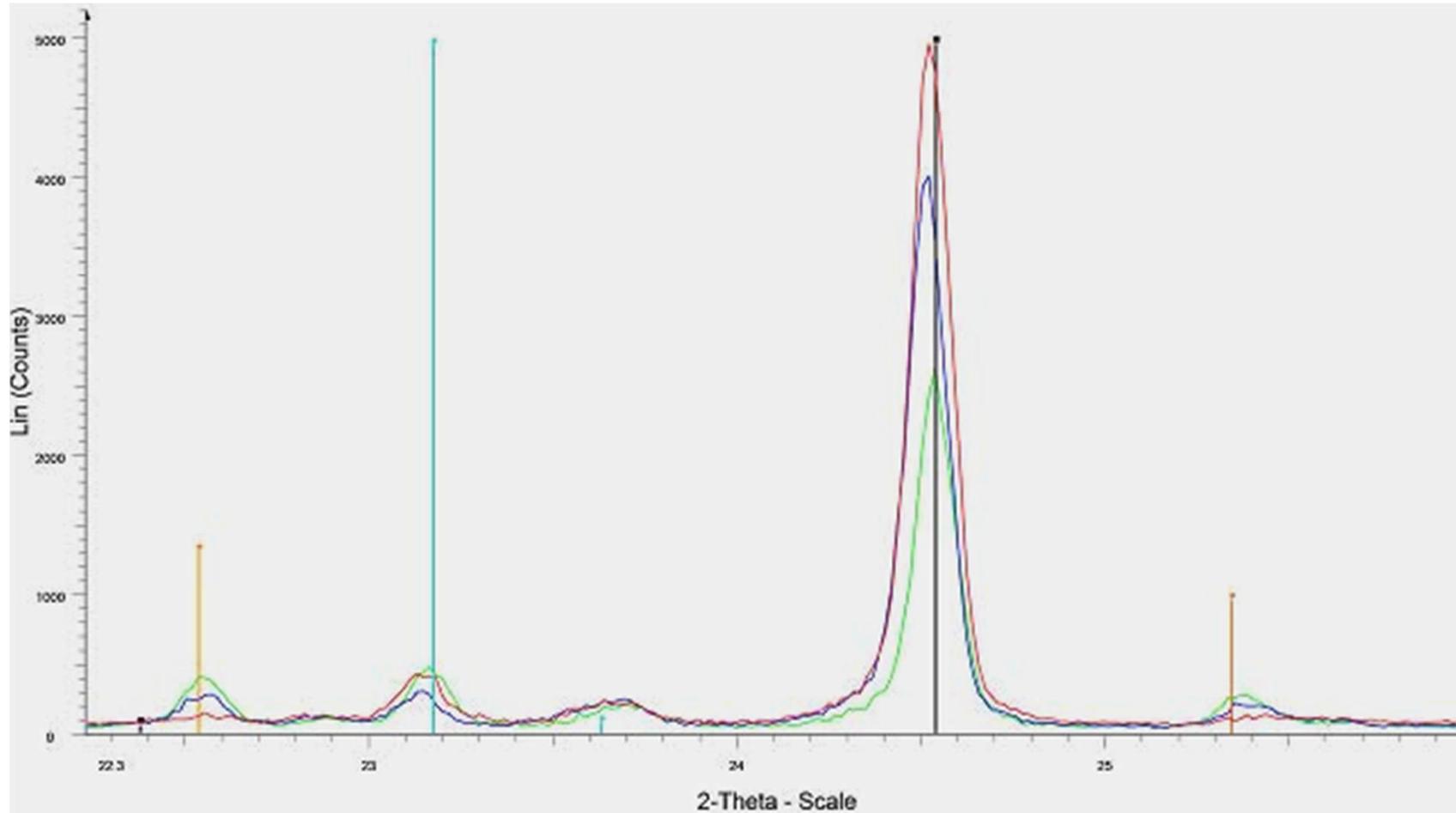
Presence of nepheline (pink vertical line) in the samples 100Sr.SOD (blue line), 50Sr.SOD (red line) and 25Sr.SOD (green line)

SYNTHESIS of SODALITE



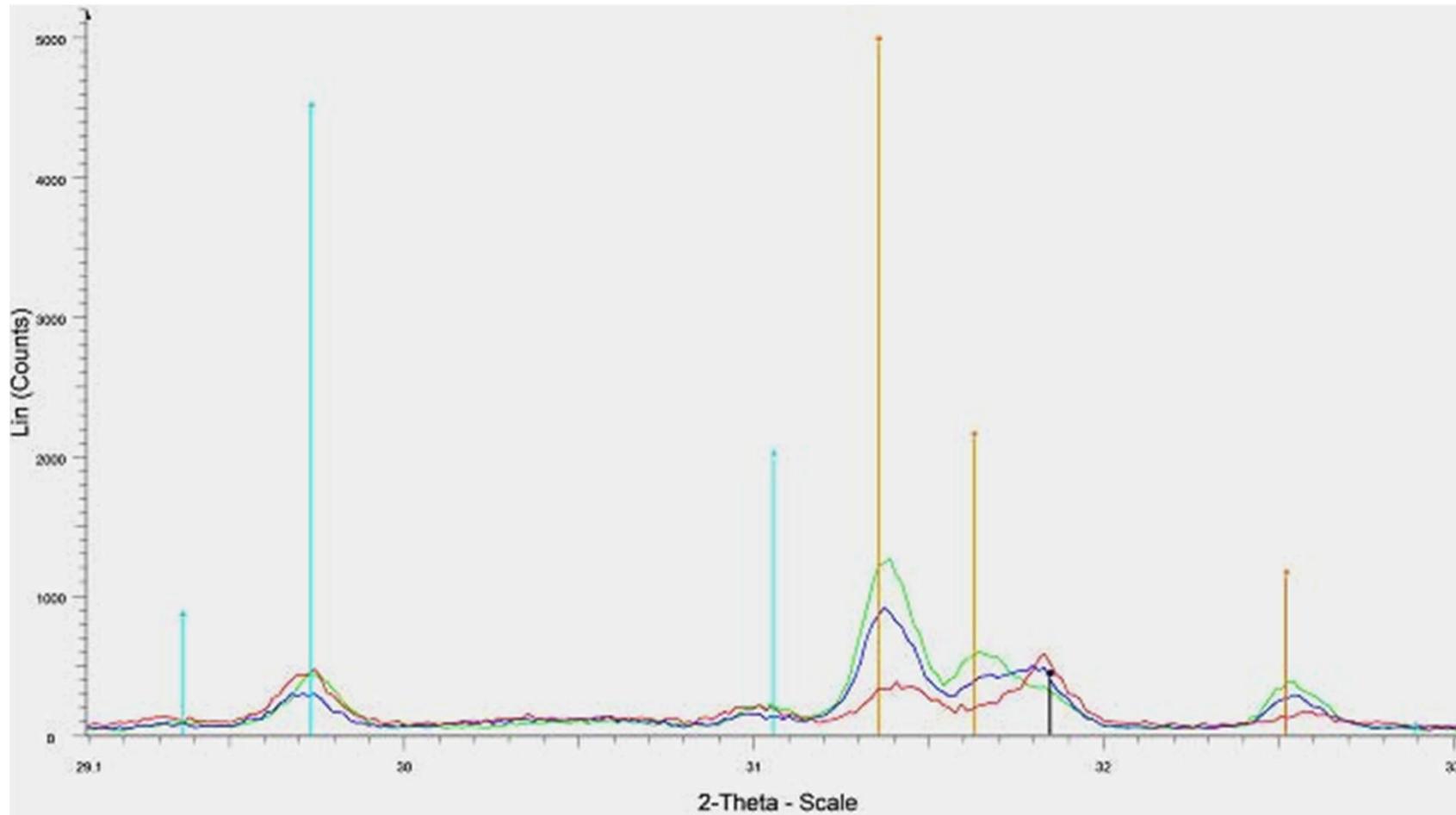
**XRD spectra of the samples 100Nd.SOD (green line),
50Nd.SOD (blue line) and 25Nd.SOD (red line)**

SYNTHESIS of SODALITE



Comparison among the XRD spectra of the samples 100Nd.SOD (green line), 50Nd.SOD (blue line) and 25Nd.SOD (red line) and the main peak of sodalite (black vertical line) at $2\theta = 24.54$ present in the spectral library

SYNTHESIS of SODALITE



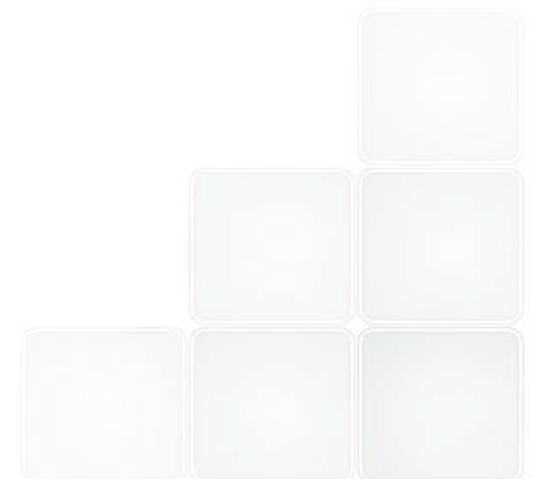
Comparison among the XRD spectra of the samples 100Nd.SOD (green line), 50Nd.SOD (blue line) and 25Nd.SOD (red line) and the main peak of calcium neodymium oxide silicate (yellow vertical line) at $2\theta = 31.36$ present in the spectral library



SYNTHESIS of SODALITE



Static leach tests according to ASTM C1285-02 (reapproved 2008)





SYNTHESIS of SODALITE



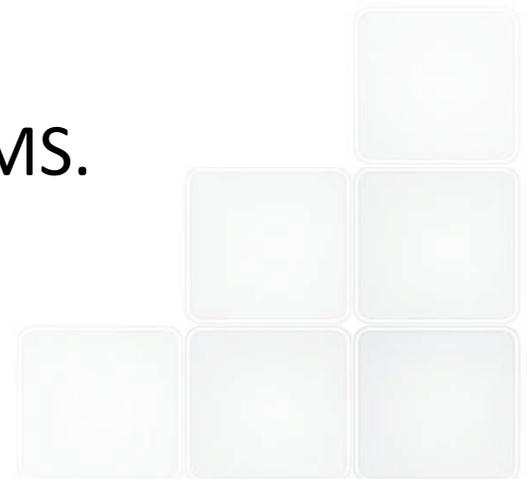
Test vessel	PFA TFE-fluorocarbon vessel rated to > 0.5 MPa
Test duration	1-7-15-30-90-150 days \pm 2%
Leachant	Ultrapure water
Condition	Static
Minimum sample mass	\geq 1 g
Particle size	63 to 125 μm
Leachant volume	20 cm³/g
Temperature	23 \pm 2° C, 90 \pm 2°
Atmosphere	Air



SYNTHESIS of SODALITE



- The glass waste form was crushed and sieved to 63 - 125 μm ;
- 1 g of sized and cleaned material is placed in the appropriate vessel with 20 mL of ultrapure water;
- The vessel is sealed and kept at a constant temperature for the chosen test duration;
- The vessel is cooled to ambient temperature;
- The pH is measured on an aliquot of the leachate together with its temperature;
- The leachate is filtered and analysed by ICP-MS.





SYNTHESIS of SODALITE



Normalized Release

$$NL_i = \frac{c_i}{f_i \cdot (SA/V)}$$

Normalized Release Rate

$$NR_i = \frac{c_i}{f_i \cdot (SA/V) \cdot t}$$

Percentage of release

$$(\sum a_i / a_0) \cdot 100$$

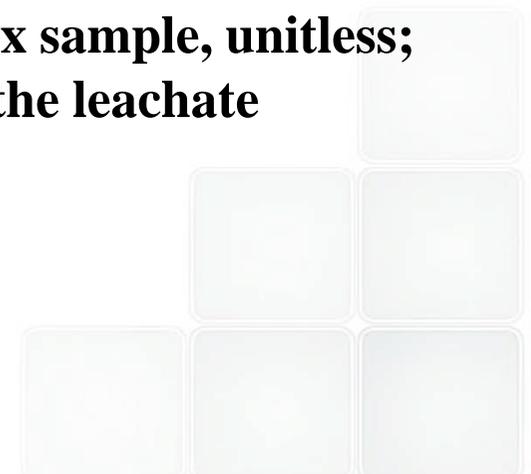


SYNTHESIS of SODALITE



$$NL_i = \frac{c_i}{f_i \cdot (SA/V)}$$

- NL_i = **normalized release, g · m⁻²**;
 c_i = **concentration of element “i” in the leachate, g / L**;
 f_i = **fraction of element “i” in the unleached waste matrix sample, unitless**;
 SA/V = **surface area of the waste matrix sample divided by the leachate volume, m² / L**



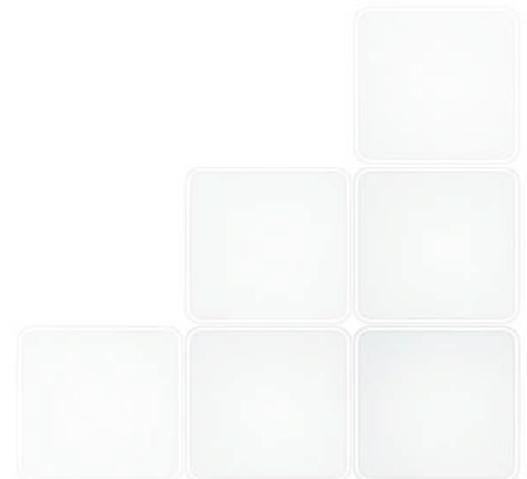


SYNTHESIS of SODALITE



$$NR_i = \frac{c_i}{f_i \cdot (SA/V) \cdot t}$$

- NR_i = **normalized release rate, $g \cdot m^{-2} \cdot day^{-1}$;**
- c_i = **concentration of element “i” in the leachate, g / L ;**
- f_i = **fraction of element “i” in the unleached waste matrix sample, unitless;**
- SA/V = **surface area of the waste matrix sample divided by the leachate volume, m^2 / L ;**
- t = **time duration of test in days.**





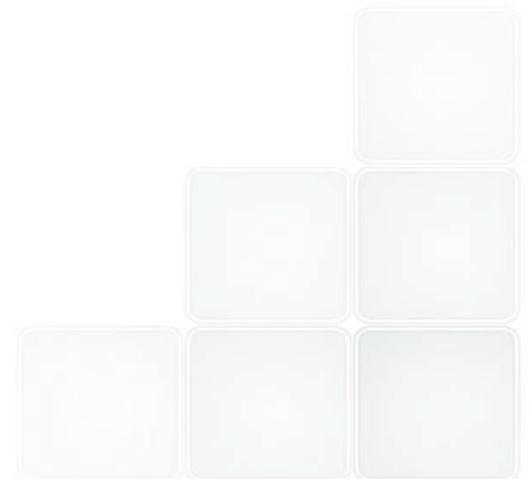
SYNTHESIS of SODALITE



$$\left(\sum a_i / a_0 \right) \cdot 100$$

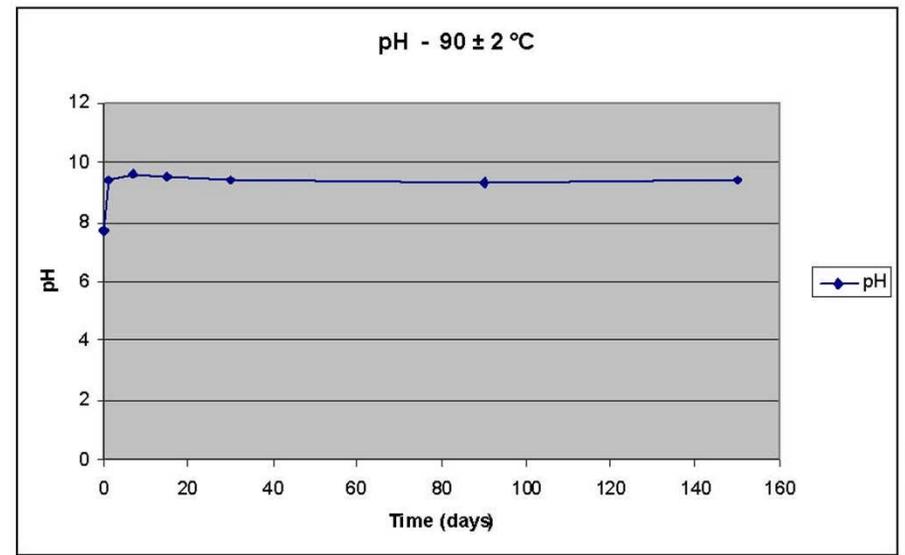
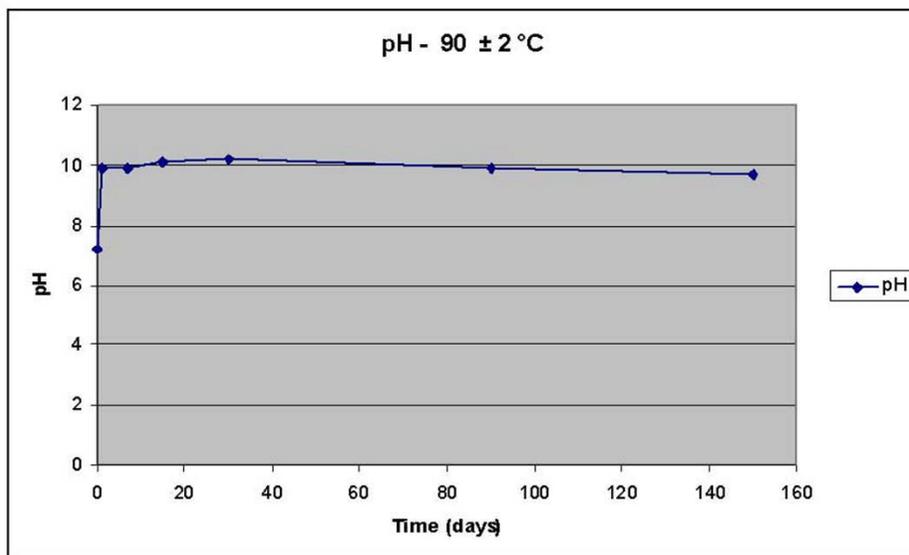
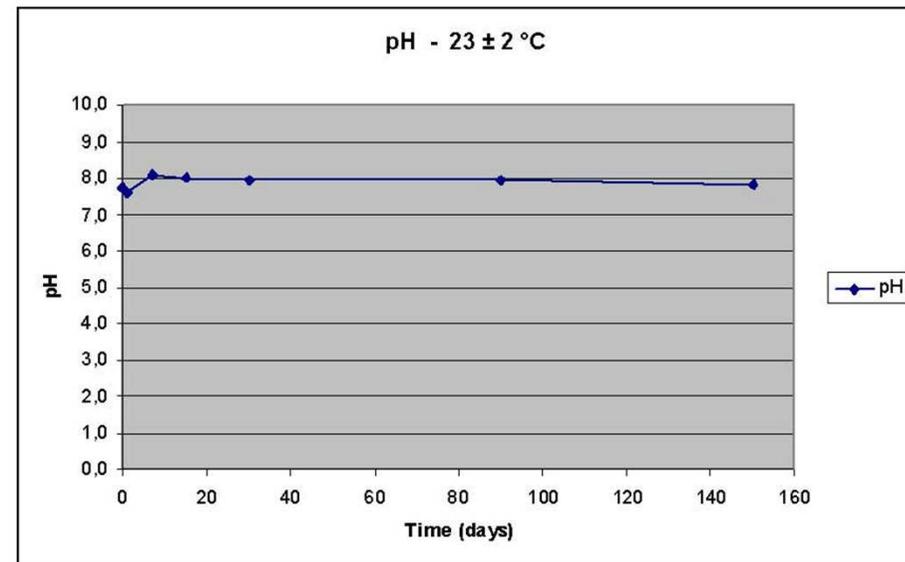
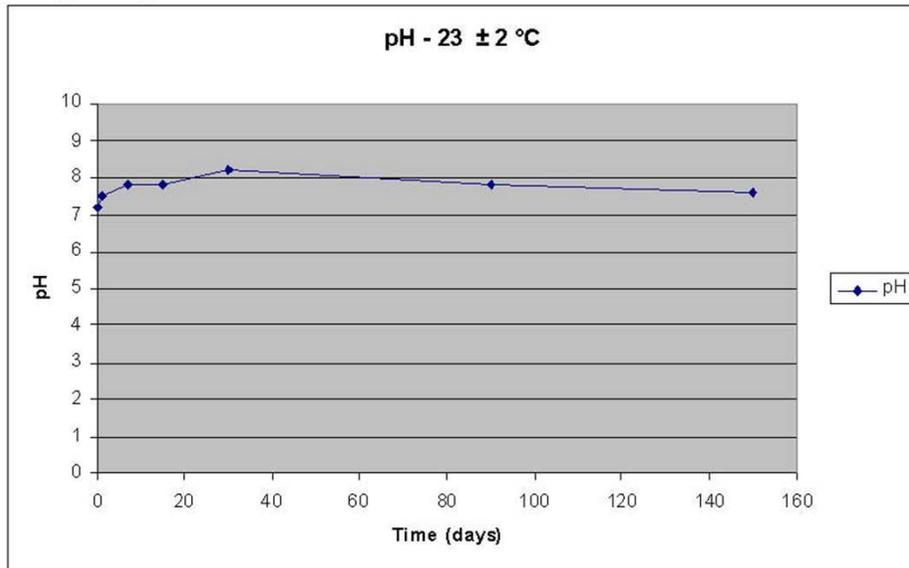
Percentage of release

- a_i = weight in kilograms of each constituent leached during each leaching interval
- a_0 = weight in kilograms of the i th constituent initially present in the sample.





SYNTHESIS of SODALITE



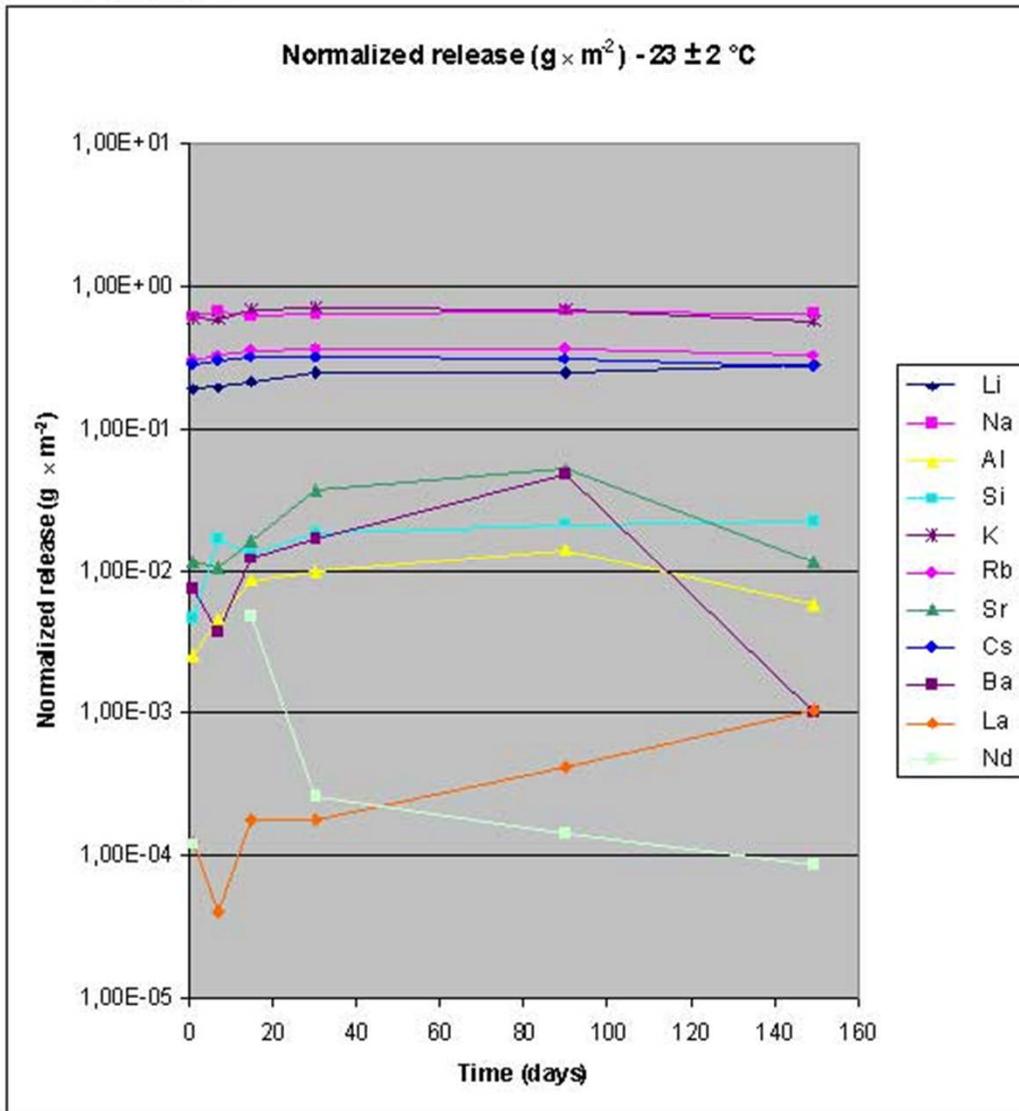
LiK.SOD.GF

LiK.SOD.BG

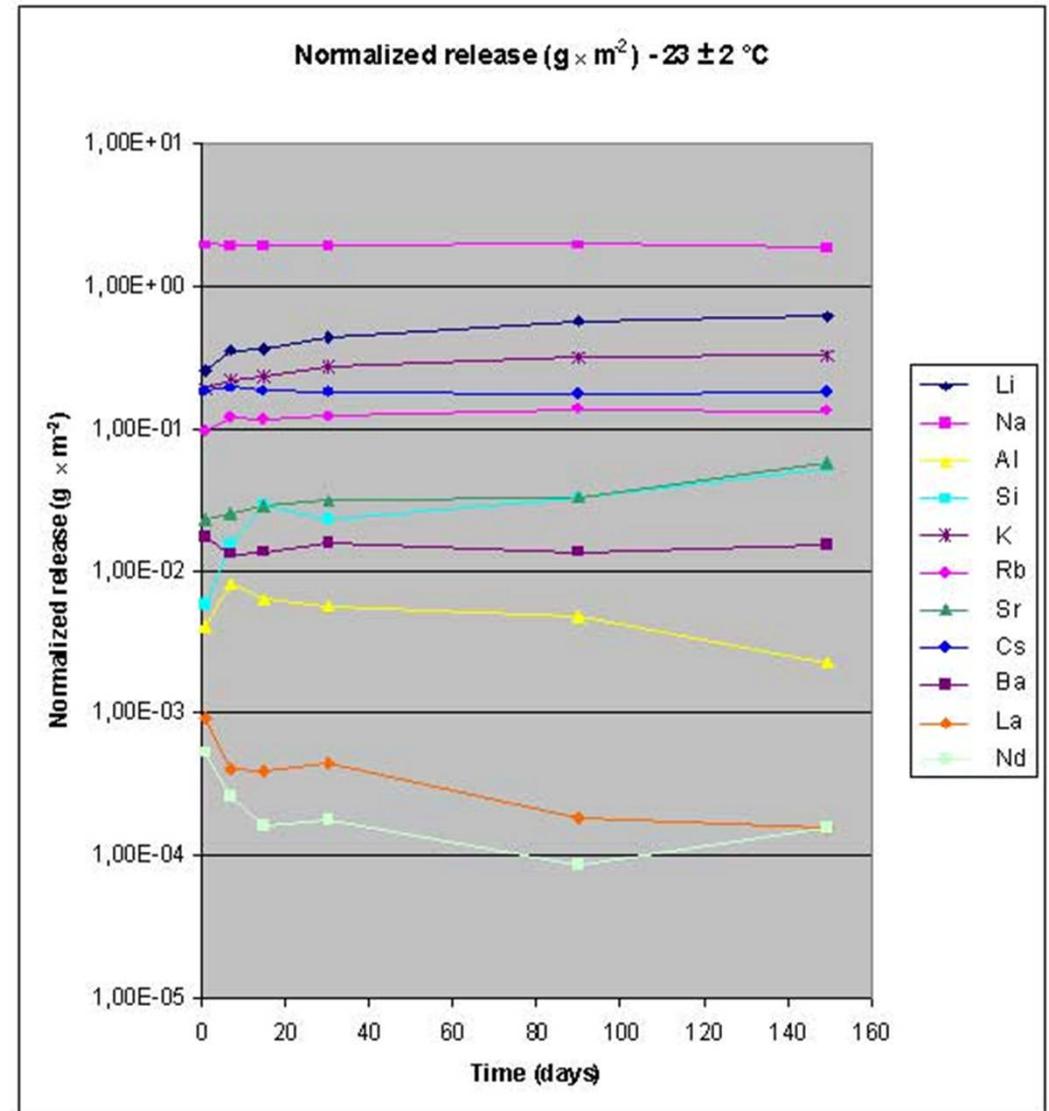
Trend of pH at 23 and 90° C



SYNTHESIS of SODALITE



LiK.SOD.GF

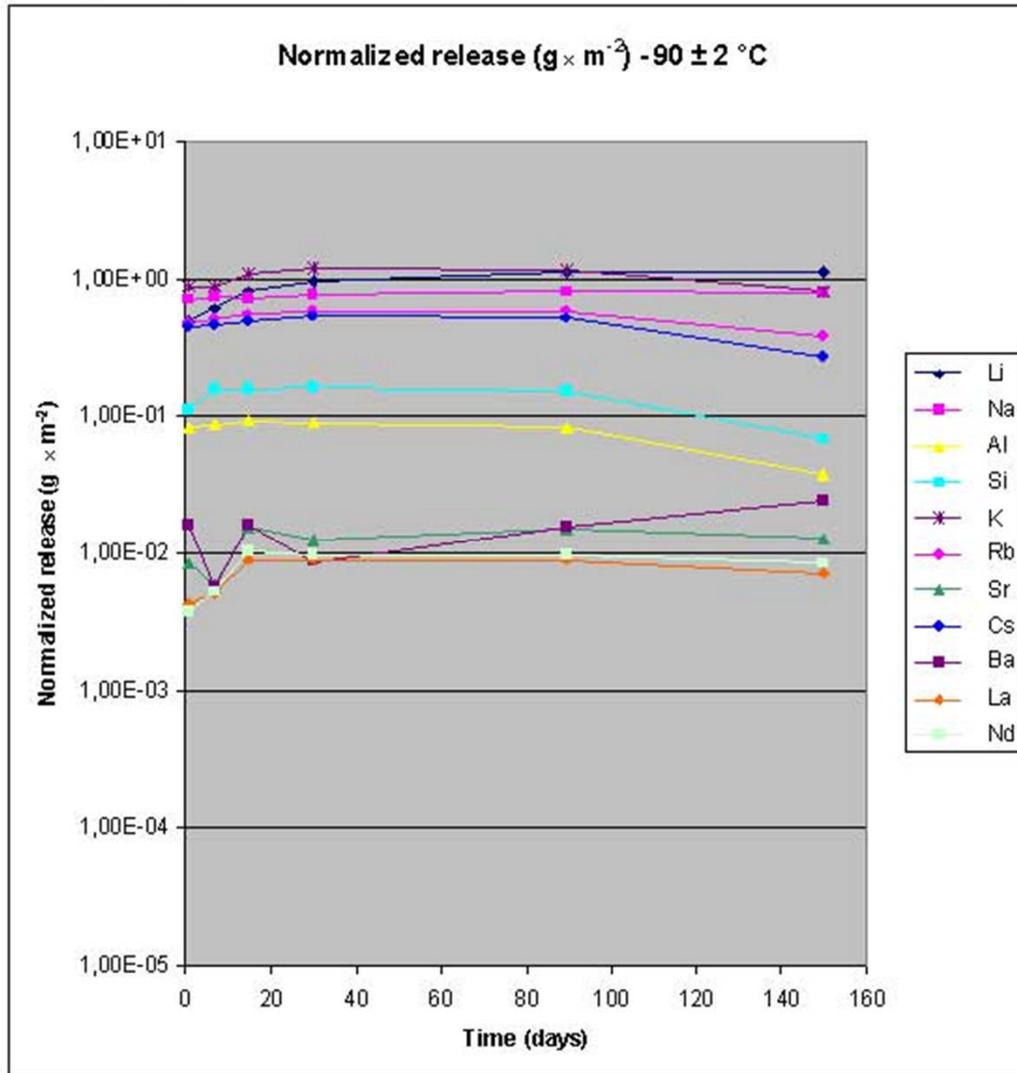


LiK.SOD.BG

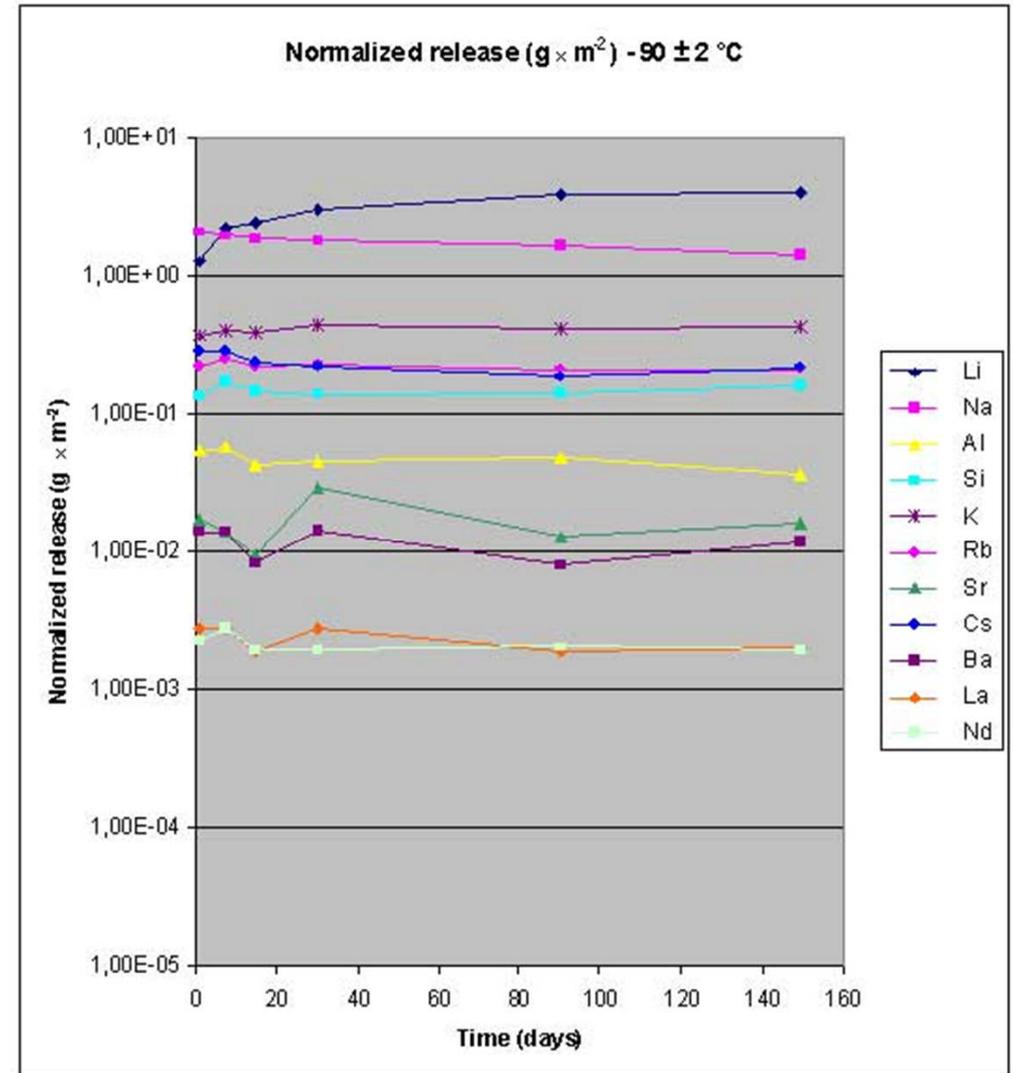
Normalized release at 23° C



SYNTHESIS of SODALITE



LiK.SOD.GF

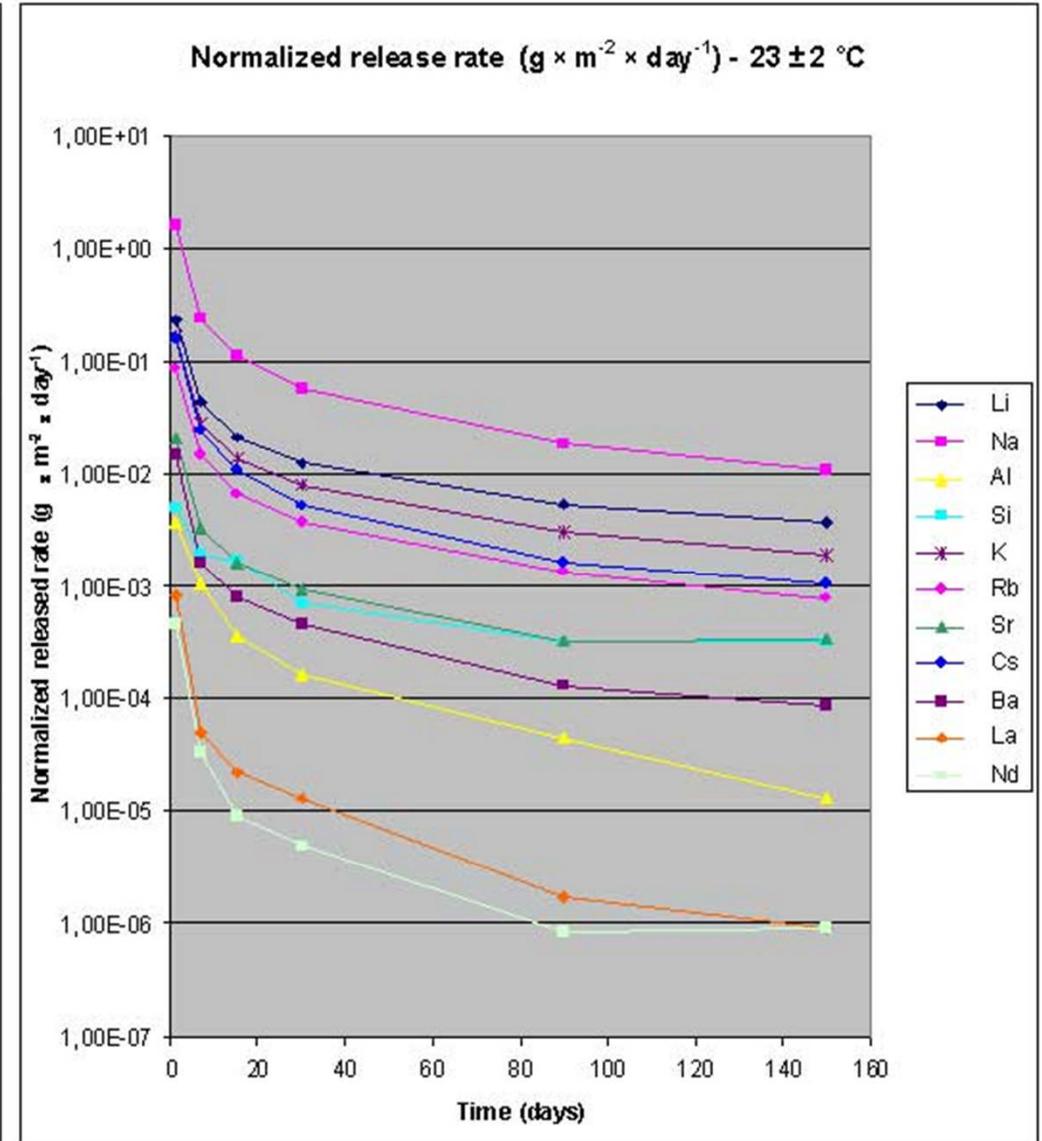
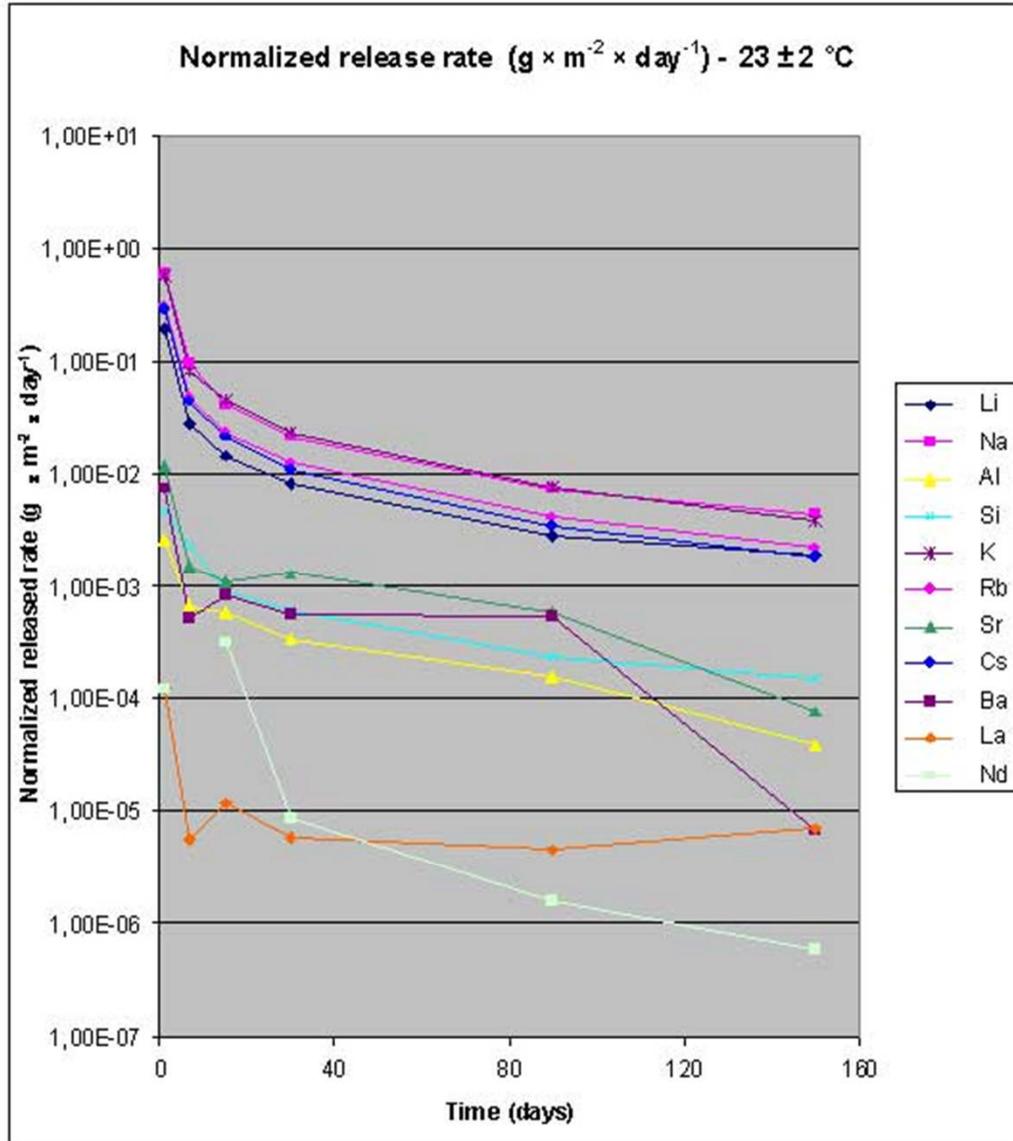


LiK.SOD.BG

Normalized release at 90°C



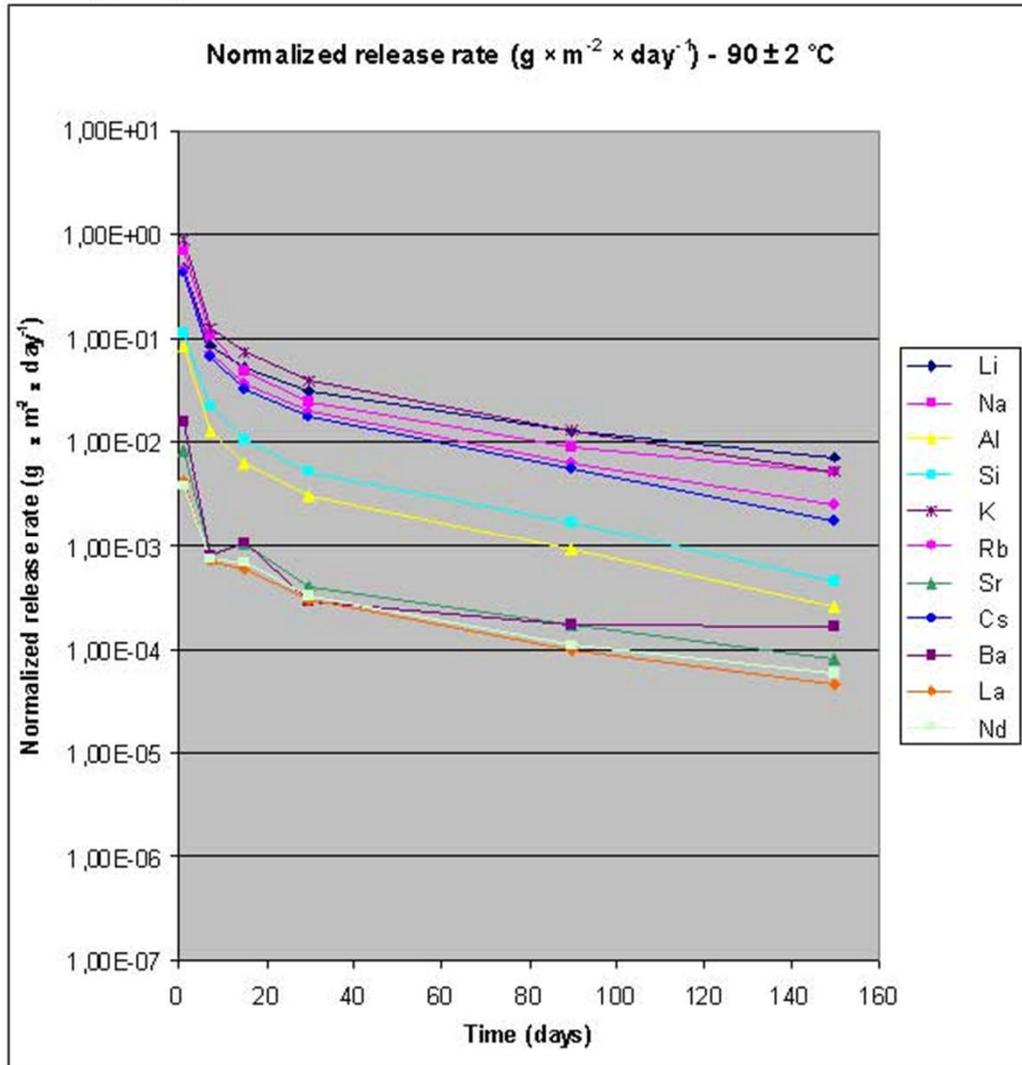
SYNTHESIS of SODALITE



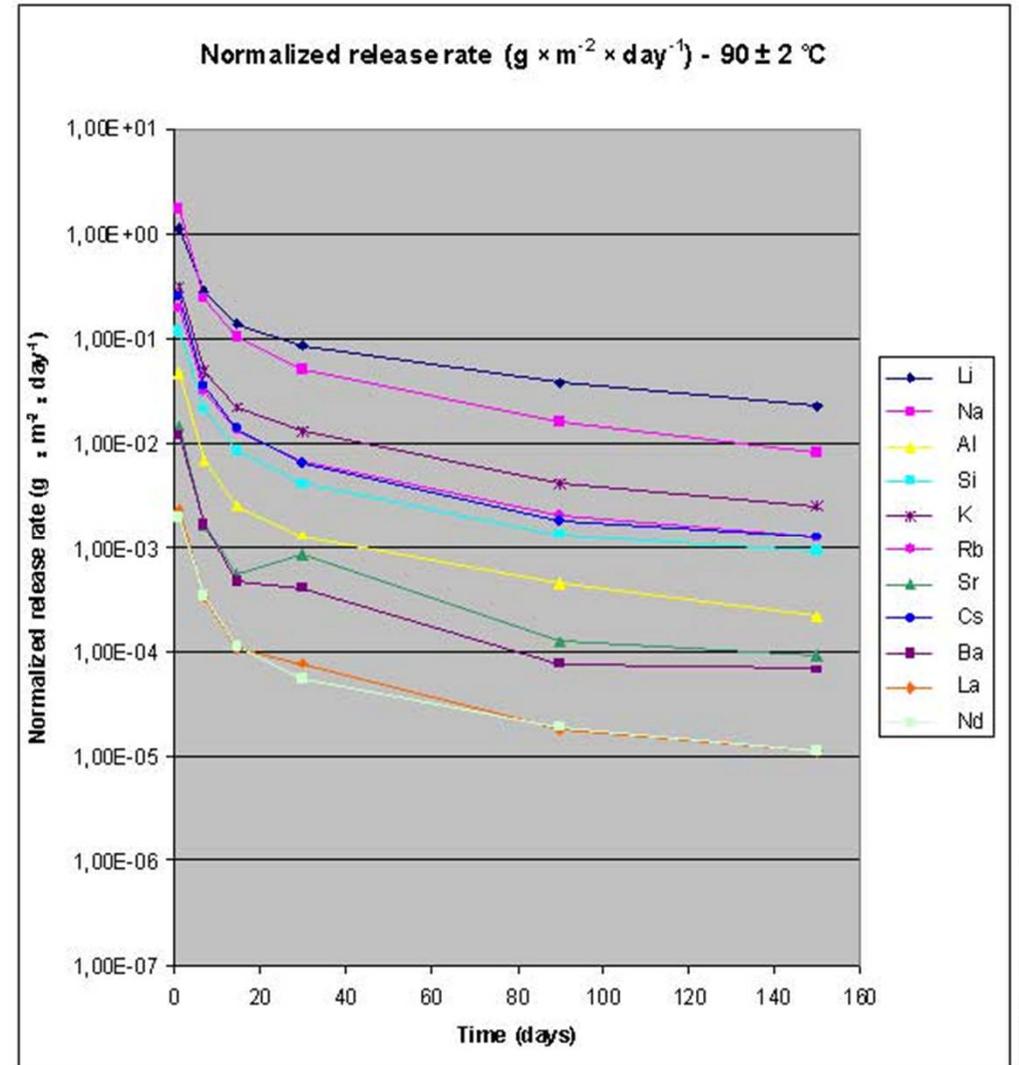
LiK.SOD.GF

LiK.SOD.BG

Normalized release rate at 23°C

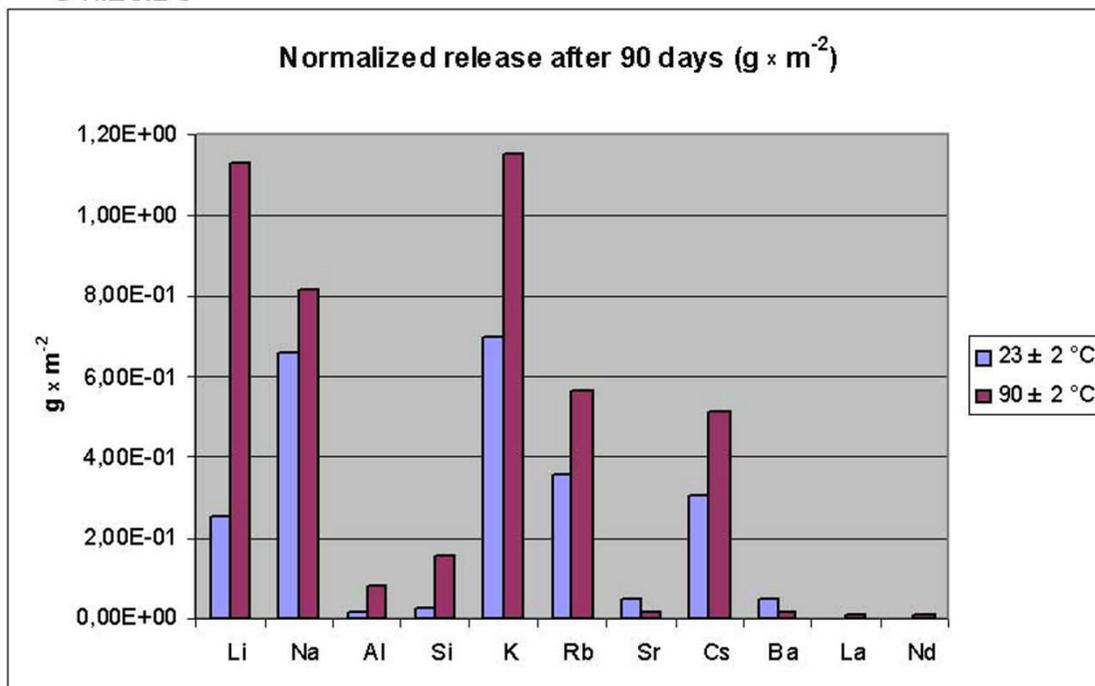


LiK.SOD.GF



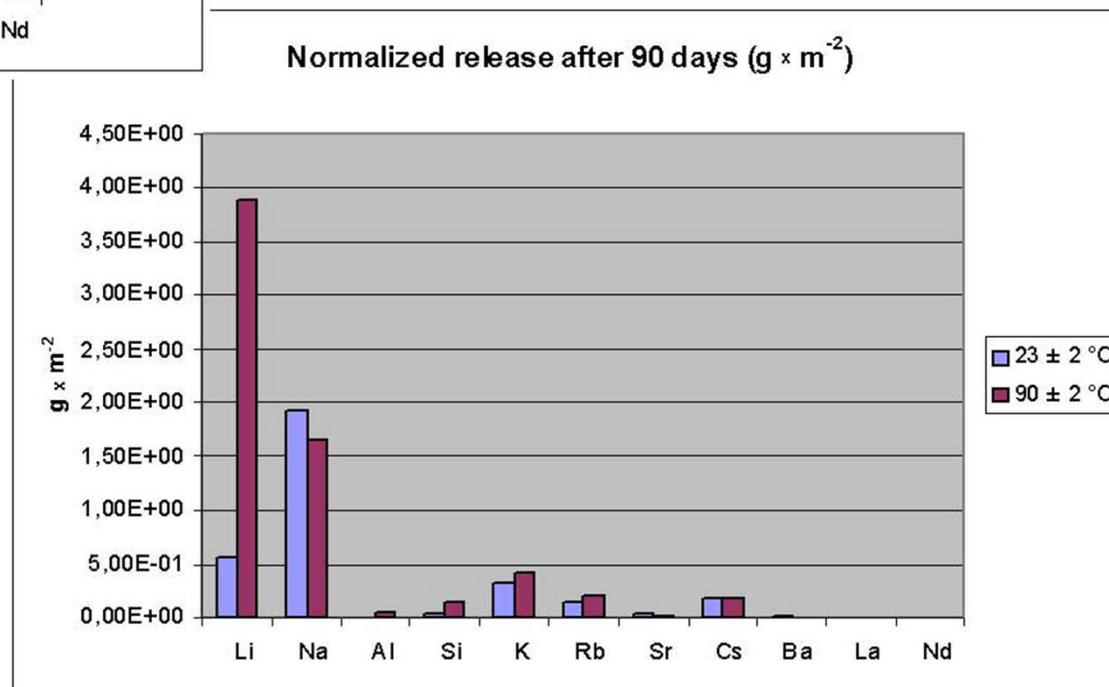
LiK.SOD.BG

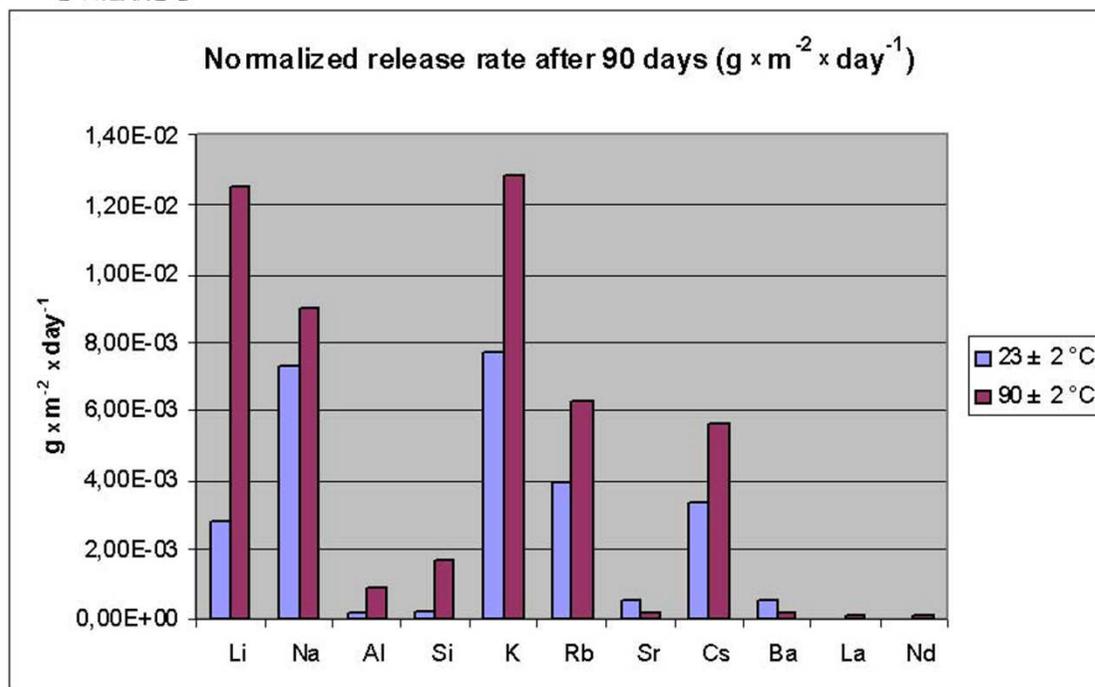
Normalized release rate at 90°C



LiK.SOD.GF

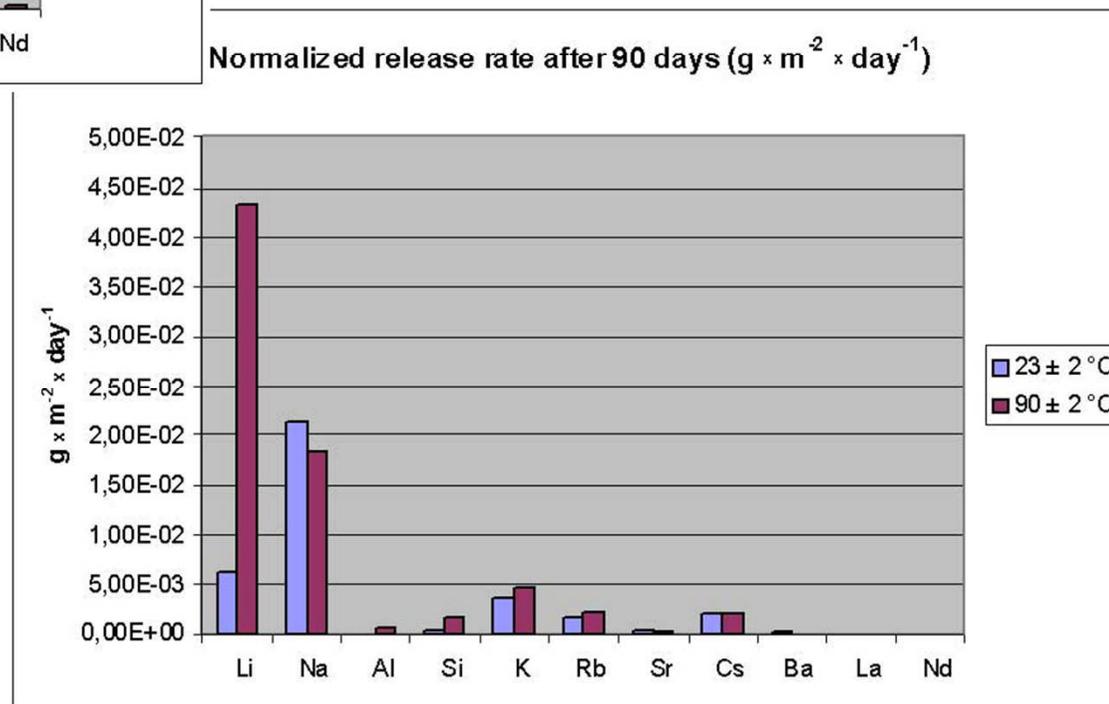
LiK.SOD.BG





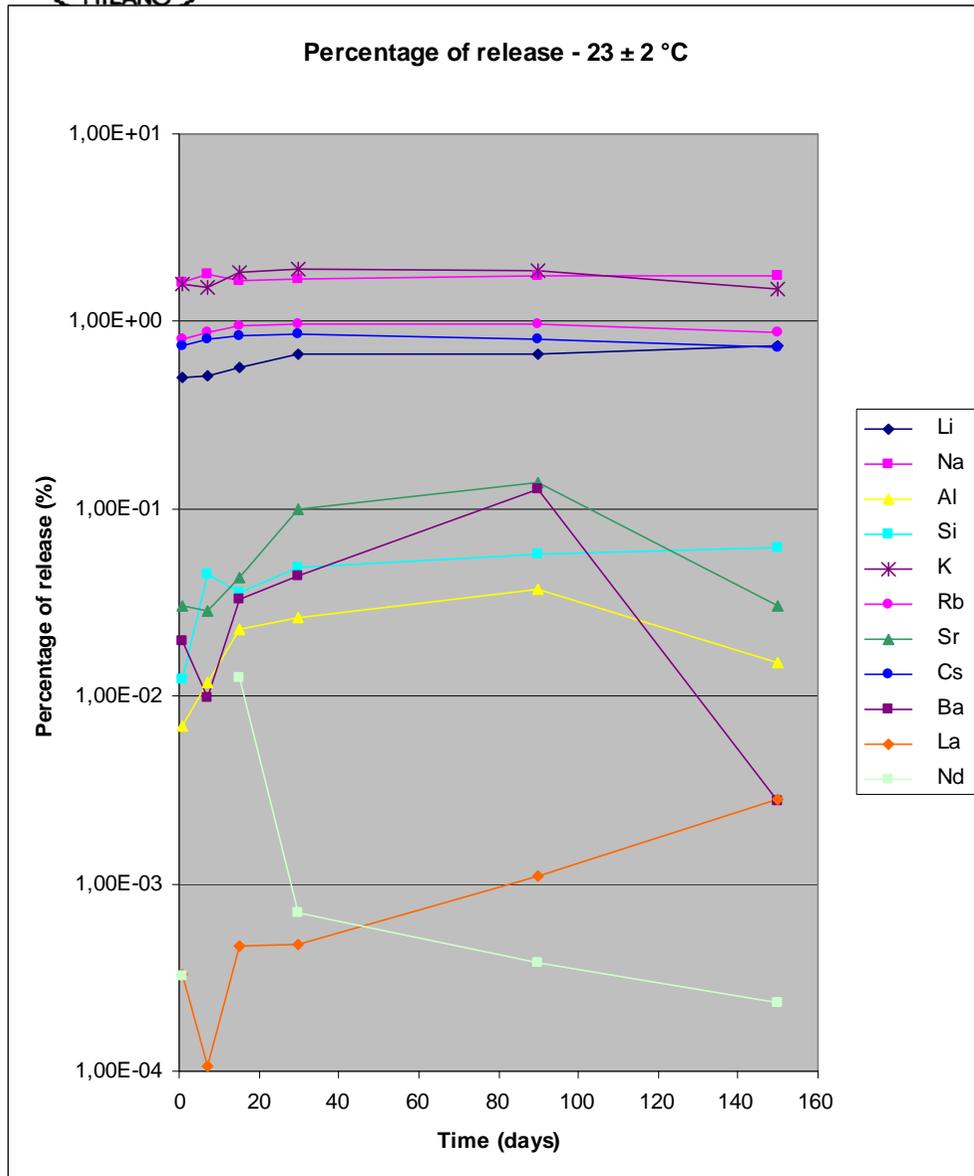
LiK.SOD.GF

LiK.SOD.BG

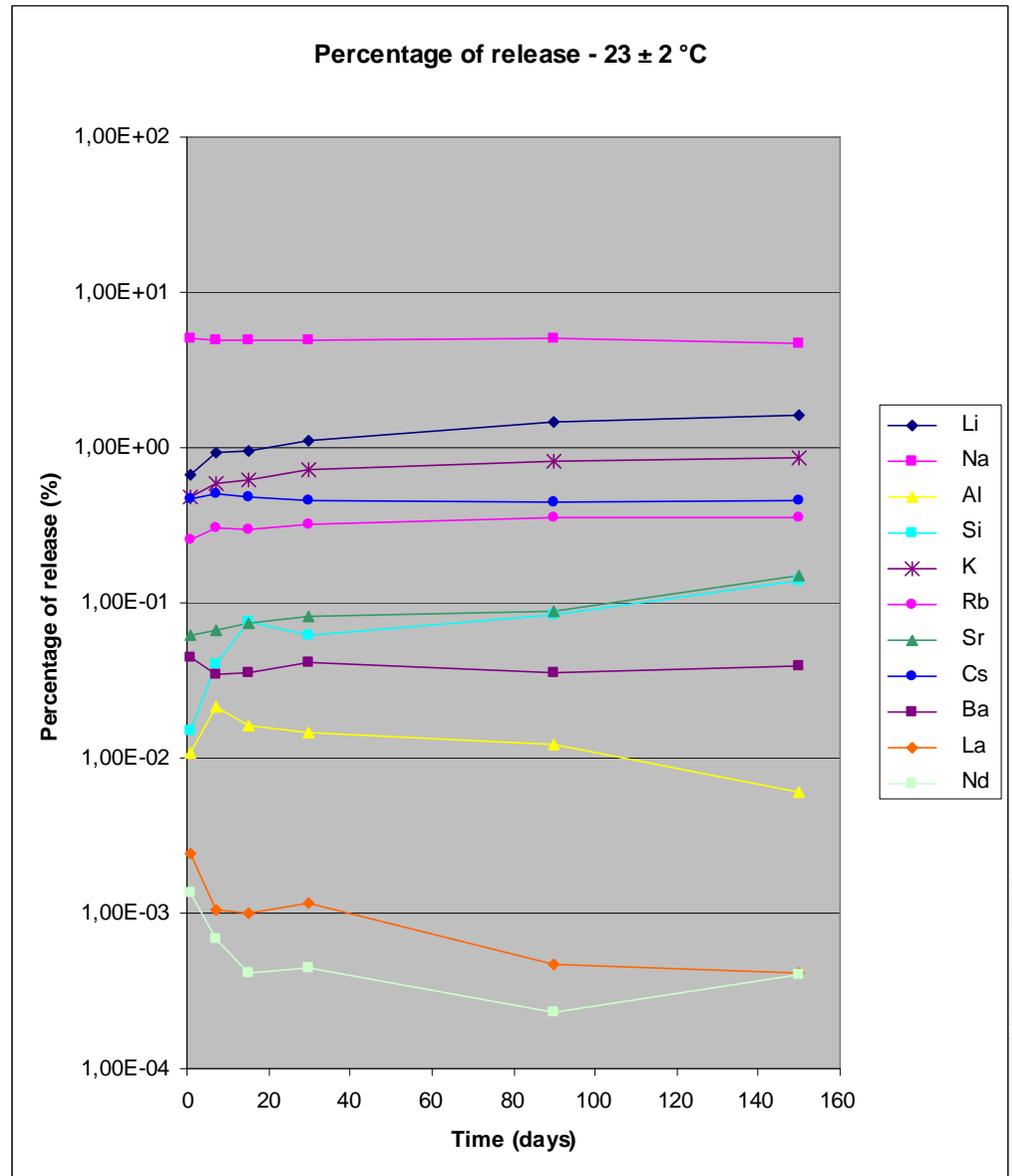




SYNTHESIS of SODALITE



LiK.SOD.GF

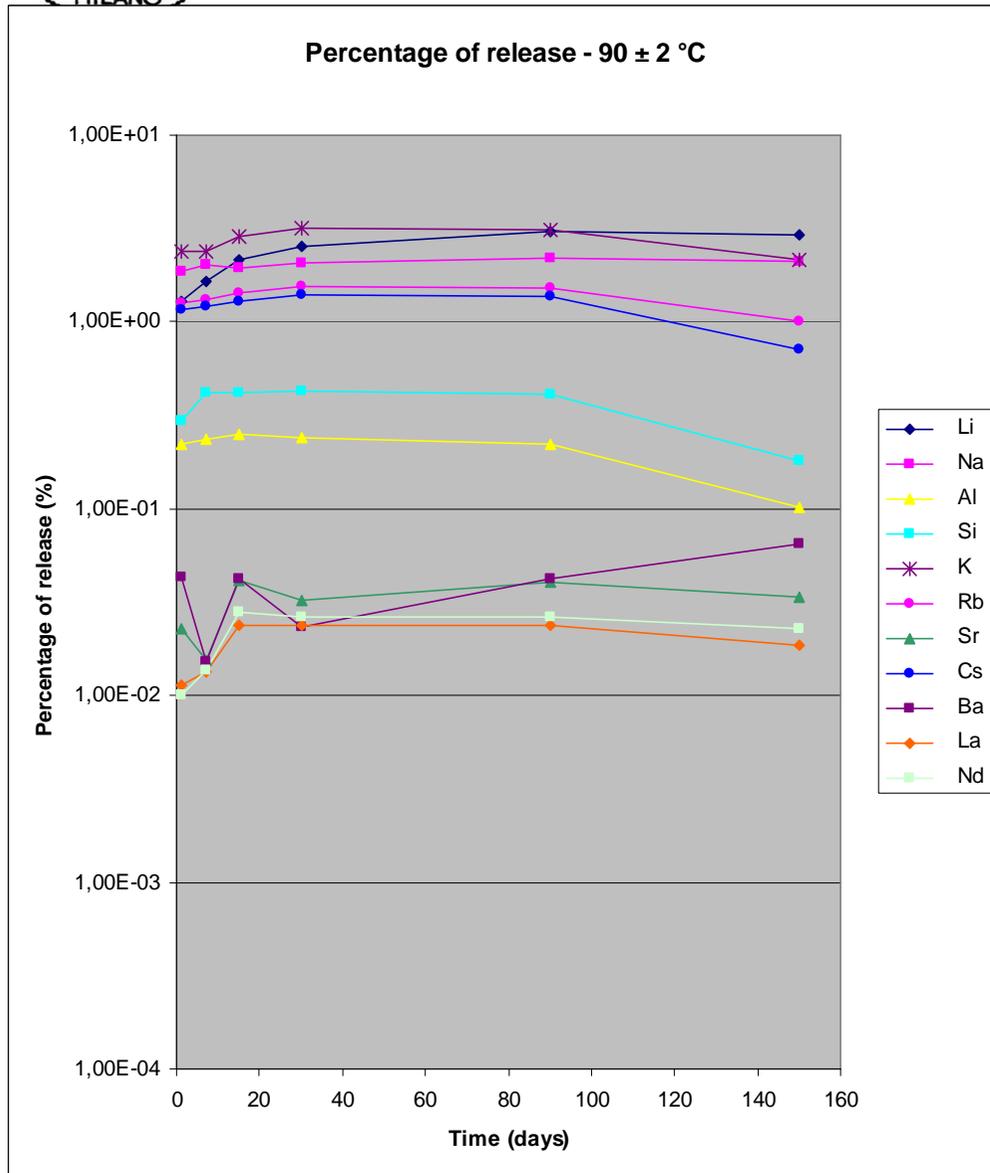


LiK.SOD.BG

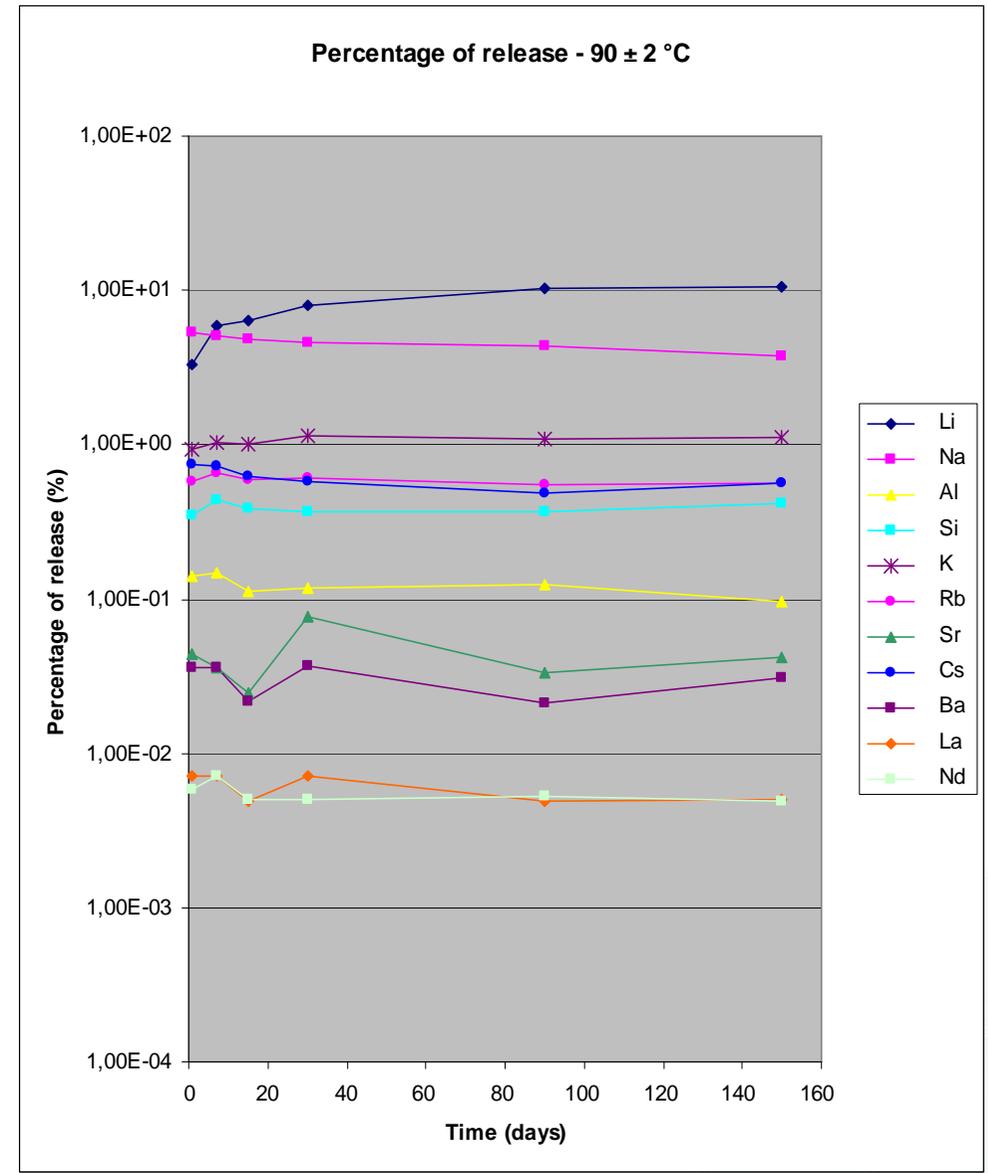
% of release at 23° C



SYNTHESIS of SODALITE

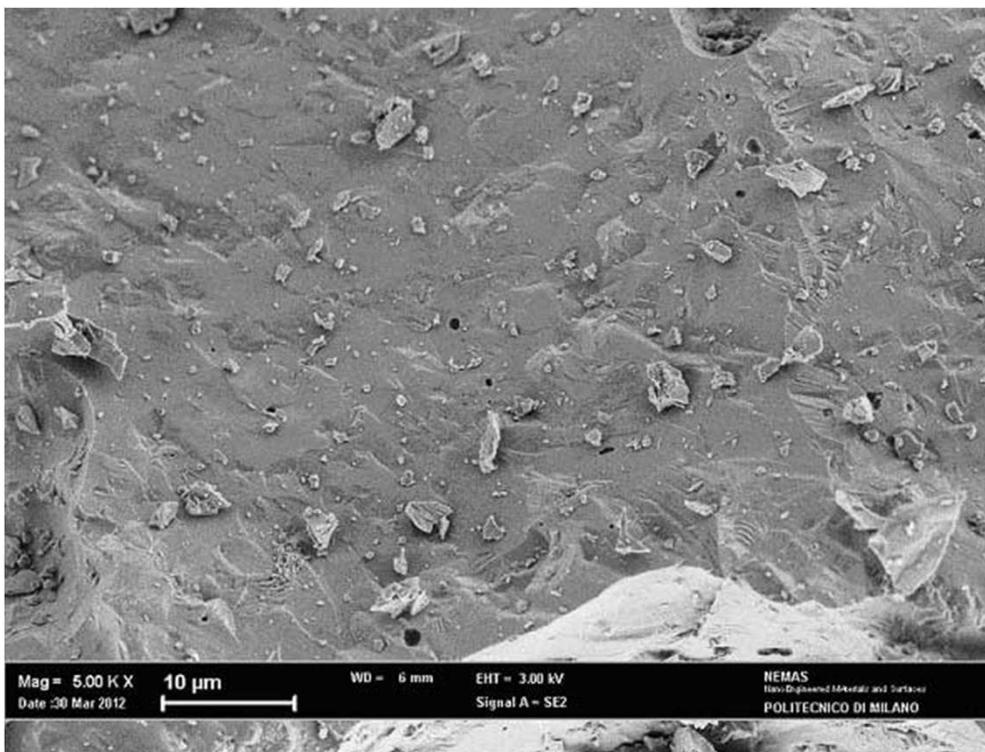


LiK.SOD.GF

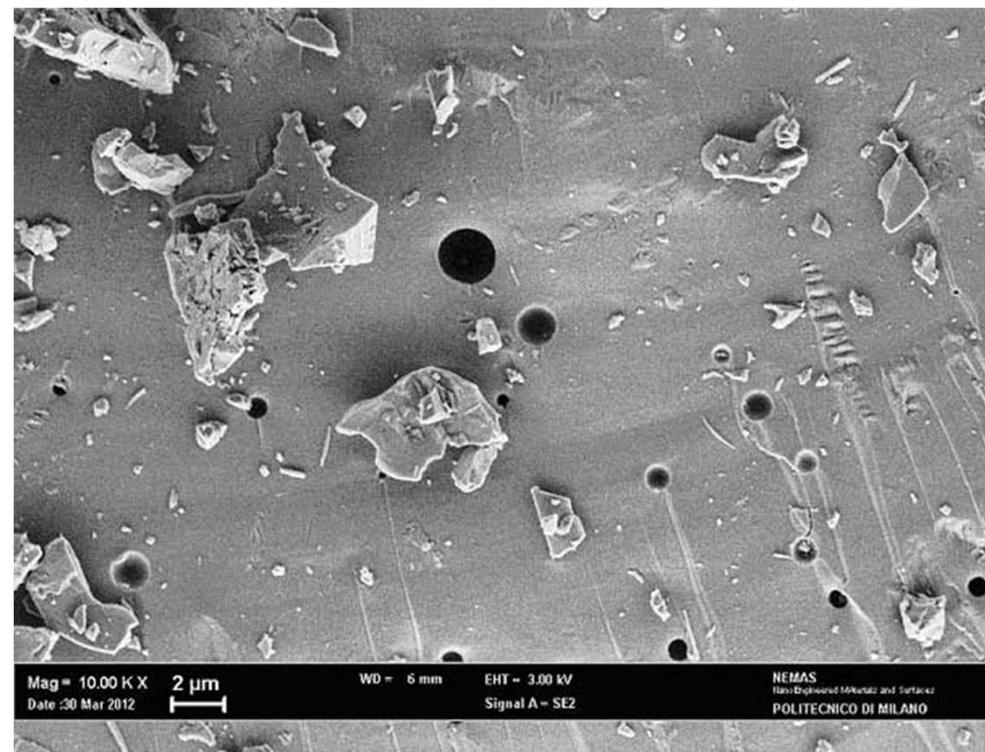


LiK.SOD.BG

% of release at 90° C



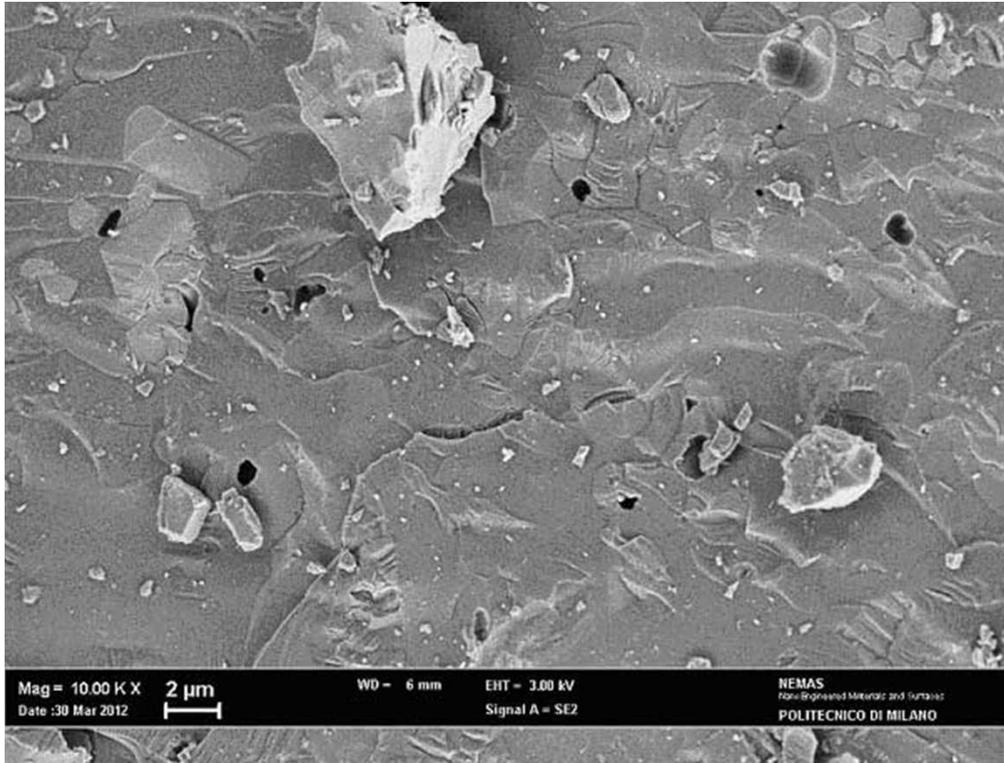
LiK.SOD.GF



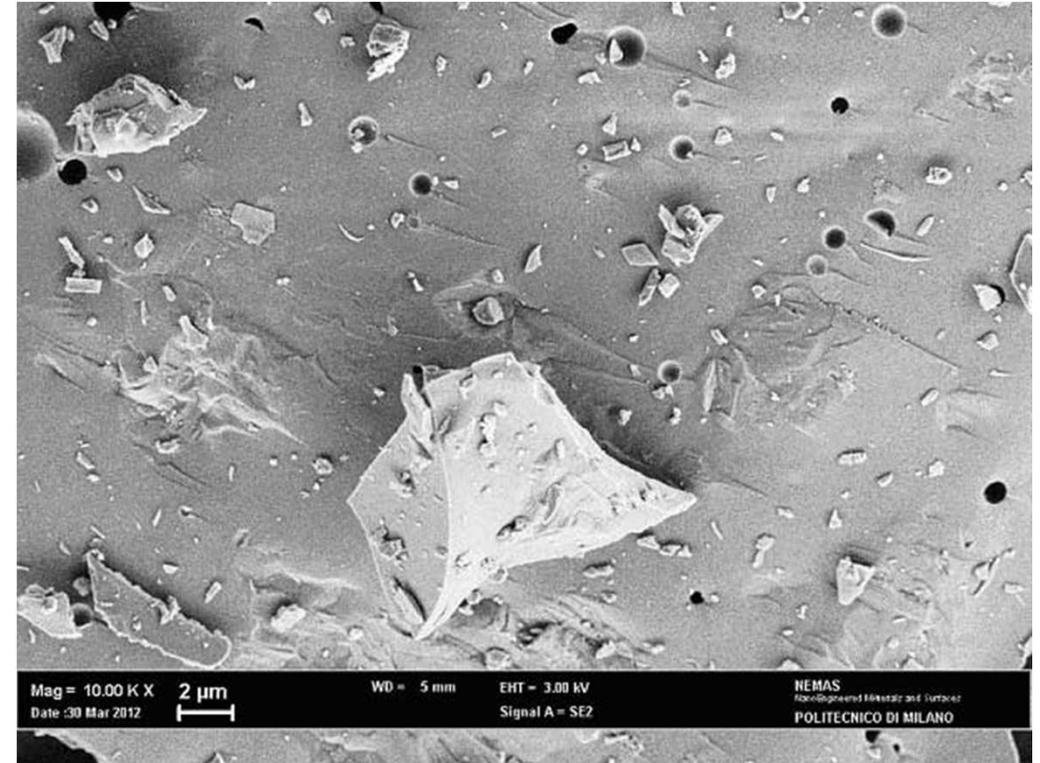
LiK.SOD.BG

90 days of leaching at 23° C





LiK.SOD.GF



LiK.SOD.BG

90 days of leaching at 90° C





SYNTHESIS of SODALITE



Normalized release after 7 day leaching at 90° C Comparisons among leach tests

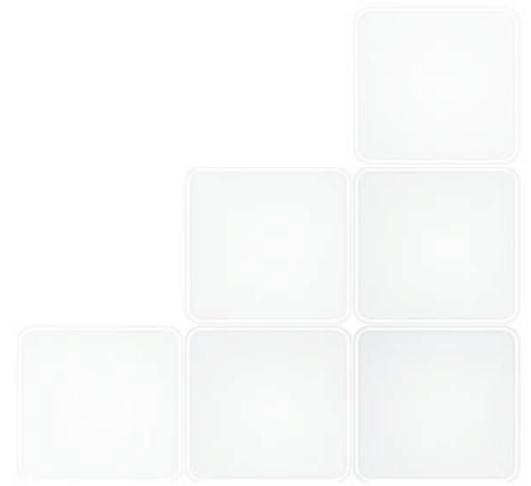
Element	Normalized Release, g · m ⁻²		
	<i>ANL</i>	<i>This study, LiK.SOD.GF</i>	<i>This study, LiK.SOD.BG</i>
Al	0.06	0.09	0.06
Si	0.05	0.09	0.10
Li	0.66	0.61	2.23
Na		0.75	1.94
K		0.89	0.40
B	0.25	---	0.49



SYNTHESIS of SODALITE



XRD spectra after leaching

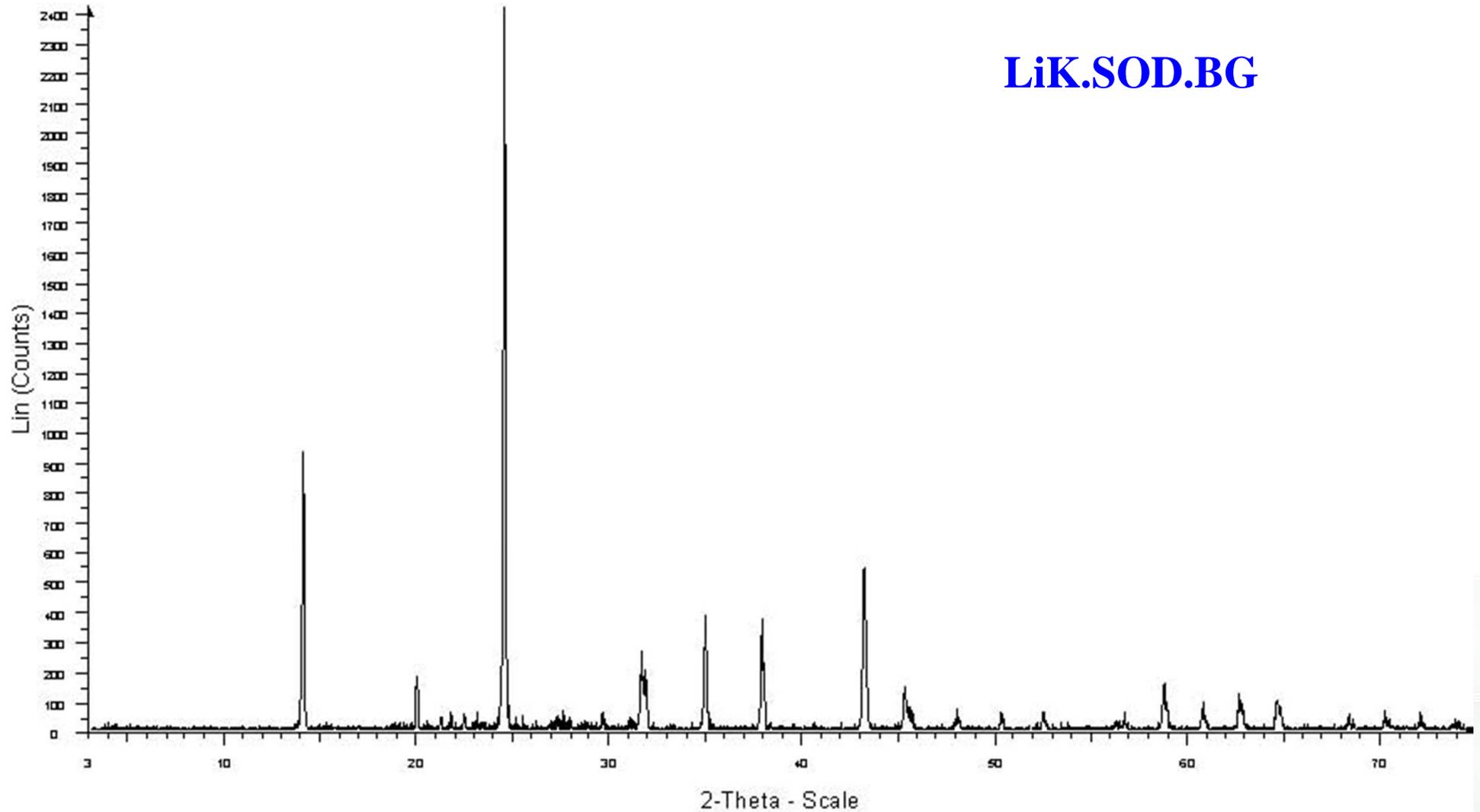




SYNTHESIS of SODALITE



LiK.SOD.BG



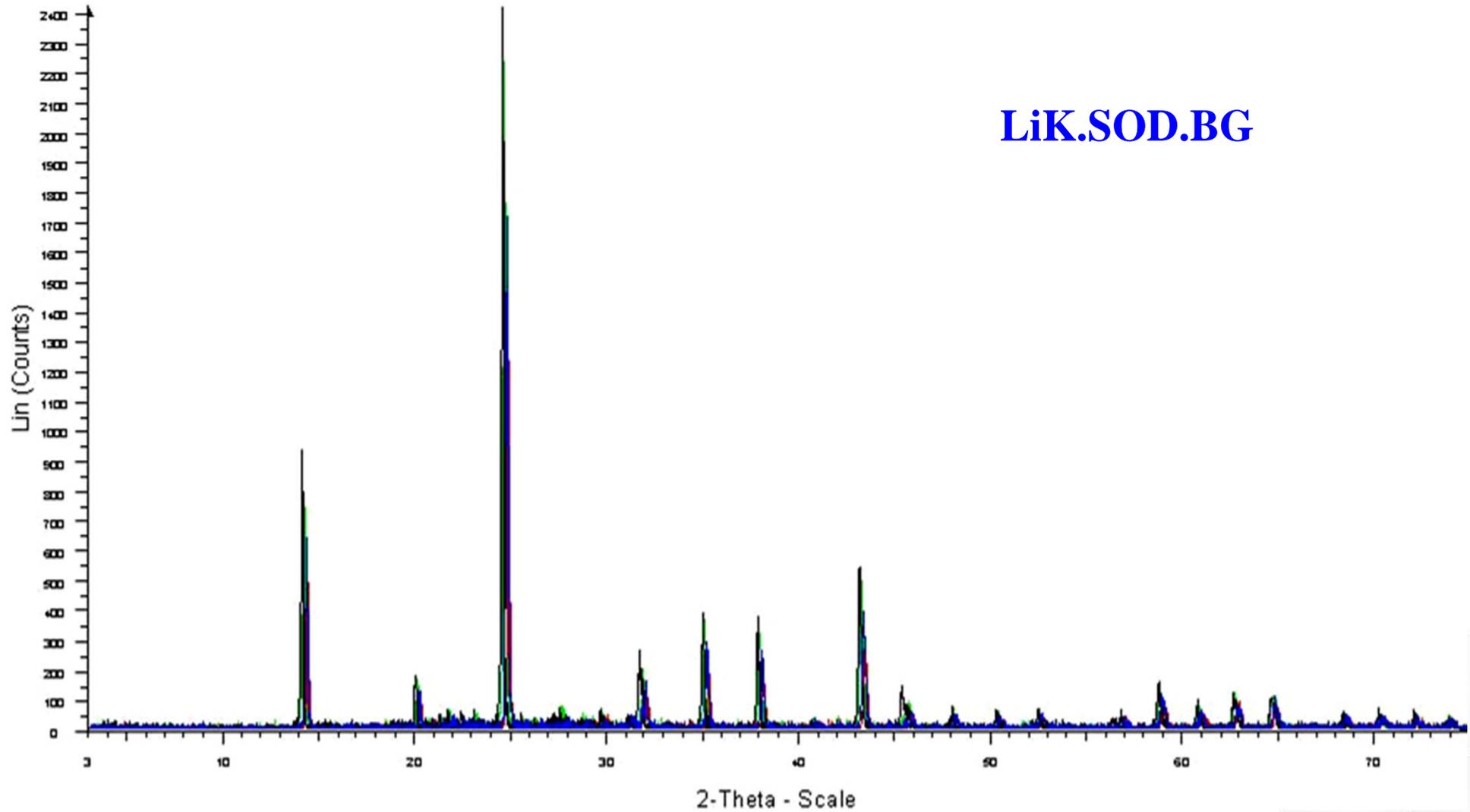
Peaks before leaching



SYNTHESIS of SODALITE



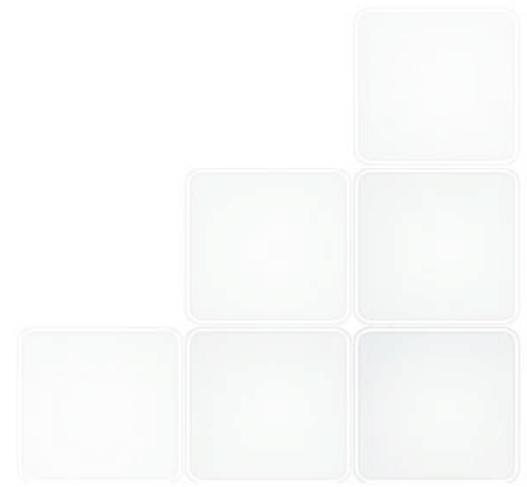
LiK.SOD.BG



Peaks after 7, 10 and 90 days of leaching

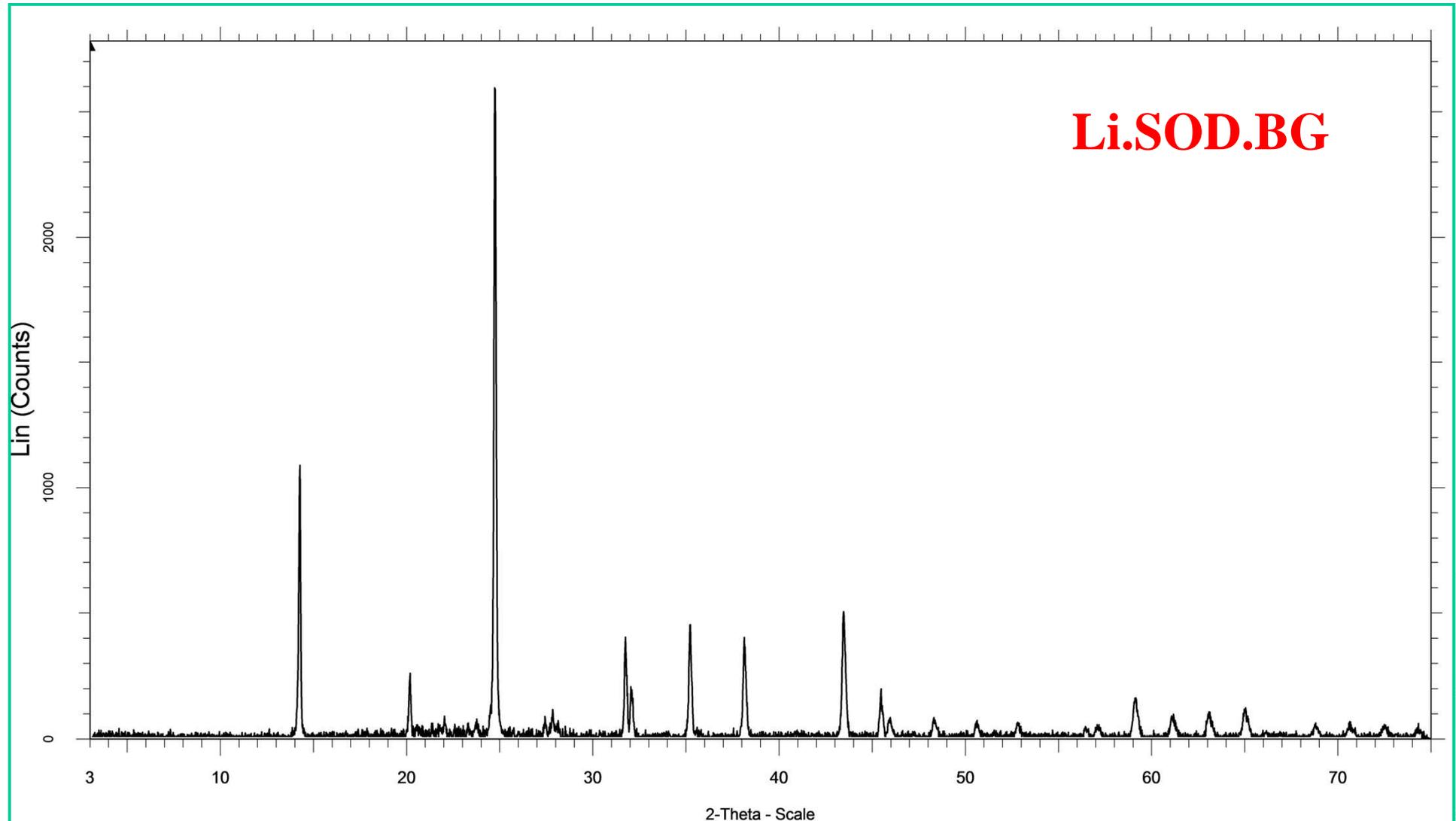


Synthesis of Li.SODALITE through PC process



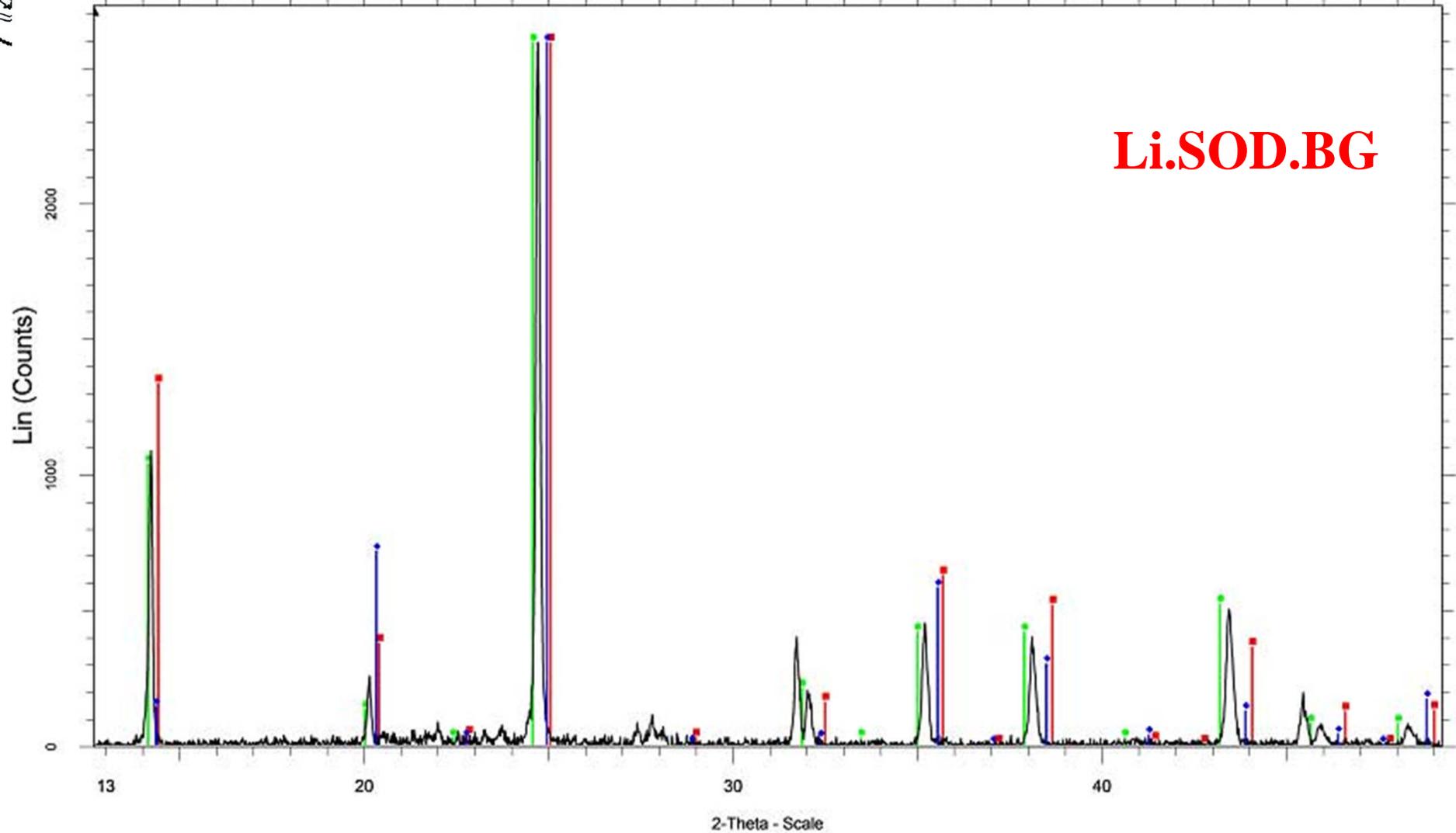


SYNTHESIS of SODALITE





SYNTHESIS of SODALITE



Phase 37-746 Sodalite $\text{Li}_{3.85}\text{Na}_4$;
phase 46-800, Lithium Sodium Aluminium Chlorate Silicate,
 $\text{Li}_{7.4}\text{Na}_{0.6}\text{Al}_6\text{Si}_6\text{O}_{24}(\text{ClO}_4)_2$;
phase 80-625, Sodalite $\text{Li}_{3.85}\text{Na}_{4.15}(\text{AlSiO}_4)_6\text{Cl}_2$.



SYNTHESIS of SODALITE



Normalized release after 7 day leaching at 90° C Comparisons among leach tests

Element	Normalized Release, g · m ⁻²			
	<i>ANL</i>	<i>This study, LiK.SOD.GF</i>	<i>This study, LiK.SOD.BG</i>	<i>This study, Li.SOD.BG</i>
Al	0.06	0.09	0.06	0.09
Si	0.05	0.09	0.10	0.06
Li	0.66	0.61	2.23	1.94
Na		0.75	1.94	1.44
K		0.89	0.40	---
B	0.25	---	0.49	0.22



Conclusions

Experimental work by ENEA and PoliMi demonstrate the feasibility of SODALITE synthesis through the Pressureless Consolidation process, developed by Argonne National Laboratory

Both XRD and FTIR spectra of the product prepared by heating mixed fine powders of chloride salt wastes (8.7%), nepheline (66.3%) and glass frit (25.0%) at 925° C for 7 hours in a little furnace inside an argon atmosphere glove-box correspond to the one of sodalite from the spectral library.

The results of the leach tests depend on the type of glass powder used.