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## **X-Ray Patterns Identification of Crystallized Sodium Disilicates Mixtures**

The amorphous sodium disilicate transformation into a crystallized product proceeds on several paths, finally resulting a mixture of crystalline  $\alpha$ ,  $\beta$ ,  $\delta$ ,  $\gamma$  polymorphs. The identification of individual crystalline phases is impaired by the overlapping of X-ray patterns corresponding to various polymorph species. A quite different way from the classical Rietveld method of X-ray diffraction data analysis is proposed: qualitative and quantitative identification of polymorph phases is approached as a classification problem with satisfactory results using two types of neural nets. A backpropagation network with post-processing of the outputs and a neural net based on the adaptive resonance theory have been applied with equivalent results. In comparison with Rietveld method, this original approach can be considered a short-cut technique requesting no fundamental data. The reason of this work is to be a background support in assessment procedures concerning the quantitative evaluation of interdependence between the crystallization parameters and the desired composition of the solid phase mixture.

Keywords: XRD analysis, DSC analysis,  $\text{Na}_2\text{Si}_2\text{O}_5$ , neural nets, pattern recognition, pattern classification

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### **1. Introduction**

The sodium disilicate can be amorphous or crystallized in one of the four polymorphs known as  $\alpha$ ,  $\beta$ ,  $\gamma$ ,  $\delta$ - $\text{Na}_2\text{Si}_2\text{O}_5$ . Beside  $\delta$ - $\text{Na}_2\text{Si}_2\text{O}_5$ , which is a genuine layered silicate,  $\beta$  and  $\gamma$ - $\text{Na}_2\text{Si}_2\text{O}_5$  are approaching layered silicates crystal structure and properties [GRUND]. The thermodynamically stable polymorph,  $\alpha$ - $\text{Na}_2\text{Si}_2\text{O}_5$ , differs in all the aspects from the other polymorphs [PANT et al.]. The interest in layered and unlayered sodium disilicates raised since they proved to be valuable co-builders minded to substitute tripolyphosphates (mainly responsible for the so called "eutrophication" process) in detergent formulations.

A wide range of sodium silicates, with general formula  $(\text{Na}_2\text{O})_x(\text{SiO}_2)_y(\text{H}_2\text{O})_z$ , have been tested and developed to full commercial scale as multifunctional builders [RIECK, BOITTIAUX et al., SOERENSON et al., BAUER, WILKENS].

The sodium disilicate polymorphs are fairly characterized, but the recrystallization kinetics of the metastable phases from the amorphous is not well known. Some attempts to obtain a single enriched  $\beta$ ,  $\gamma$  or  $\delta$  phase have been carried out.

The first step of crystalline sodium disilicates preparation consists in drying out the silicate solution to amorphous product, followed by a second step which imply a thermal processing of the amorphous phase to one of the stable or metastable  $\text{Na}_2\text{Si}_2\text{O}_5$  polymorphs.

The solubility of the stable phase,  $\alpha$ - $\text{Na}_2\text{Si}_2\text{O}_5$ , in water is close to zero. The three low pressure metastable polymorphs  $\beta$ ,  $\gamma$  and  $\delta$ - $\text{Na}_2\text{Si}_2\text{O}_5$  are easily soluble in cold/warm water. The metastable phases transform into  $\alpha$ - $\text{Na}_2\text{Si}_2\text{O}_5$  with different kinetics controlled by heating rate and impurities. Some experimental data grant a multistage process with parallel transitions to more than one metastable phase. Some impurities may induce particular polymorph crystallization, but rather a mixture of crystalline structures is recrystallized during the amorphous calcination in 600 to 700°C temperature range.

In order to find out experimental conditions, which lead to the formation of a particular polymorph, the solid phase analysis is of a paramount importance. The interpretation of the X-ray diffraction data can generally prove the entity of a certain crystalline polymorph. This type of analysis is rather difficult to be achieved when several polymorphs are simultaneously present. The classical procedure of X-ray diffraction data analysis is Rietveld method [RIETVELD 1967, RIETVELD 1969]. The basis of this method is the equation:

$$y_{ic} = y_{ib} + \sum_p \sum_{k=k_1^p}^{k_2^p} G_{ik}^p I_k \quad (1)$$

where  $y_{ic}$  is the net intensity calculated at point  $i$  in the pattern,  $y_{ib}$  is the background intensity,  $G_{ik}$  is a normalised peak profile function,  $I_k$  is the intensity of the  $k$ -th Bragg reflection,  $k_1, k_2$  are the reflections contributing intensity to point  $i$ , and the superscript  $p$  corresponds to the possible phases present in the sample. The intensity  $I_k$  is given by the expression:

$$I_k = S M_k L_k |F_k|^2 A_k E_k \quad (2)$$

where  $S$  is the scale factor,  $M_k$  is the multiplicity,  $L_k$  is the Lorentz-polarisation factor, and  $F_k$  is the structure factor:

$$F_k = \sum_{j=1}^n f_j \exp [2\pi i (h_r^t r_j - h_k^t B_j h_k)] \quad (3)$$

where  $f_j$  is the scattering factor or scattering length of atom  $j$ , and  $h_k, r_j$  and  $B_j$  are matrices representing the Miller indices, atomic coordinates and anisotropic thermal vibration parameters, respectively, and the superscript  $t$  indicates matrix transposition. The factor  $P_k$  is intended to describe the effects of preferred orientation. The factor  $A_k$  is the absorption correction and  $E_k$  an extinction correction.

The positions of the Bragg peaks from each phase are determined by their respective set of cell dimensions, in conjunction with a zero parameter and the wavelength (or diffractometer constants) provided. All of these parameters may be refined simultaneously with the profile and crystal structural parameters. For *TOF* the position of the Bragg peak is calculated using:

$$TOF = DC d_k + DA + ZERO \quad (4)$$

where  $d_k$  is the  $d$  spacing of the  $k$ -th reflection,  $DC$  is the diffractometer constant and is dependent on the path length of the instrument,  $DA$  is a variable correction factor and  $ZERO$

is the zero point value. The wavelength (or diffractometer constant) is refinable, but some or all of the cell dimensions must be fixed to avoid divergences in the least squares procedure. When more than one wavelength is used in a histogram, such as  $K_{a1}$  and  $K_{a2}$ , the second wavelength is automatically tied to the first so that  $I_1/I_2$  is constant. The ratio of the intensities for two possible wavelengths is absorbed in the calculation of  $|F_k|^2$ , so that only a single scale factor for each phase is required.

From this very short description, it is obvious that the Rietveld method needs a lot of fundamental data, not very easy available, especially for polymorphs.

In the present paper an algorithm of short identification grounded on artificial neural networks is approached. The networks are trained to recognize different X-ray patterns in a mixture of polymorph phases or the approximated composition of such a mixture. Based on this algorithm an experimental study on  $\text{Na}_2\text{Si}_2\text{O}_5$  crystallization was carried out in order to define some appropriate experimental conditions that can lead to an enriched  $\beta\text{-Na}_2\text{Si}_2\text{O}_5$  phase.

## 2. Experimental Setup

An experimental study of disilicate crystallization under different experimental conditions was carried on in order to identify a pilot technology for  $\beta\text{-Na}_2\text{Si}_2\text{O}_5$  enriched product. Reagent grade  $\text{SiO}_2$  and  $\text{NaOH}$ , as well as technical grade disilicate solution were used to produce amorphous phase. The molar ratio  $\text{SiO}_2/\text{Na}_2\text{O}$  was varied in the range 1.9 – 2.1. Other samples, in which 0.005 – 0.030 mol  $\text{CaO}$  or/and  $\text{MgO}$  replace  $\text{Na}_2\text{O}$  in the disilicate formula, were also prepared. The amorphous materials were ground to less than  $63\mu\text{m}$  particle size and heated up to  $600\text{-}700^\circ\text{C}$  for 15 - 60 minutes. The crystalline product structures were semiquantitatively ascertained from X-ray diffraction data and from Differential Scanning Calorimetry (DSC) analysis.

Typical DSC diagrams are displayed in Fig. 1 and Fig. 2. Fig. 3 shows some of the X-ray diffraction spectra.

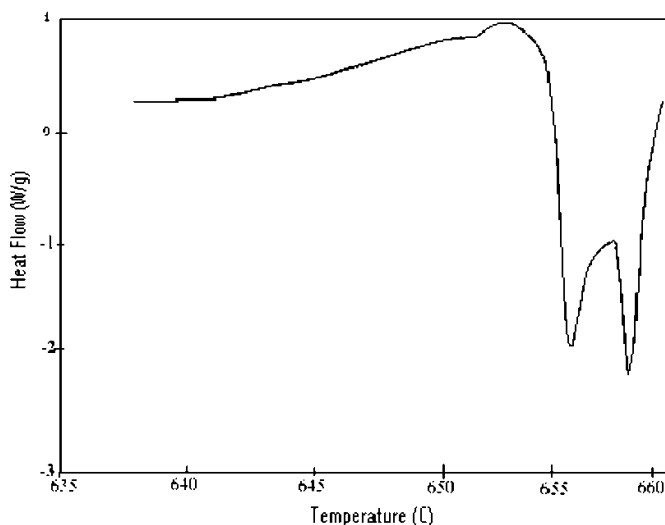


Fig. 1: DSC diagram for pure  $\text{Na}_2\text{Si}_2\text{O}_5$

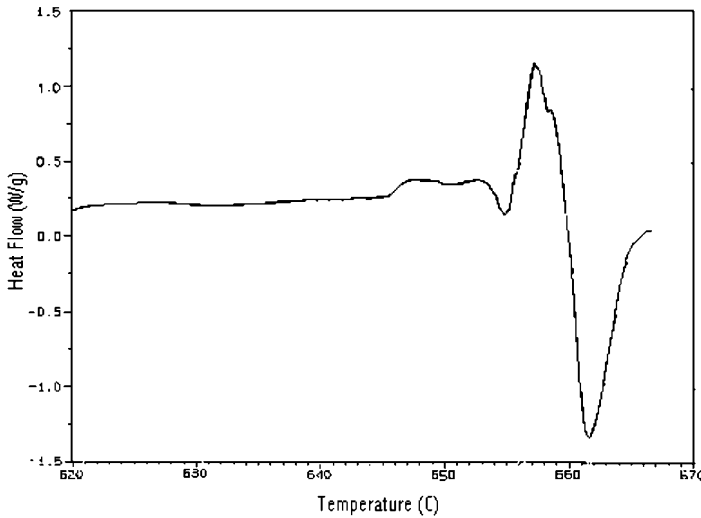


Fig. 2: DSC diagram for  $\text{Na}_2\text{SiO}_3$  with 0.03m CaO + 0.03m MgO replacing Na<sub>2</sub>O in the disilicate formula

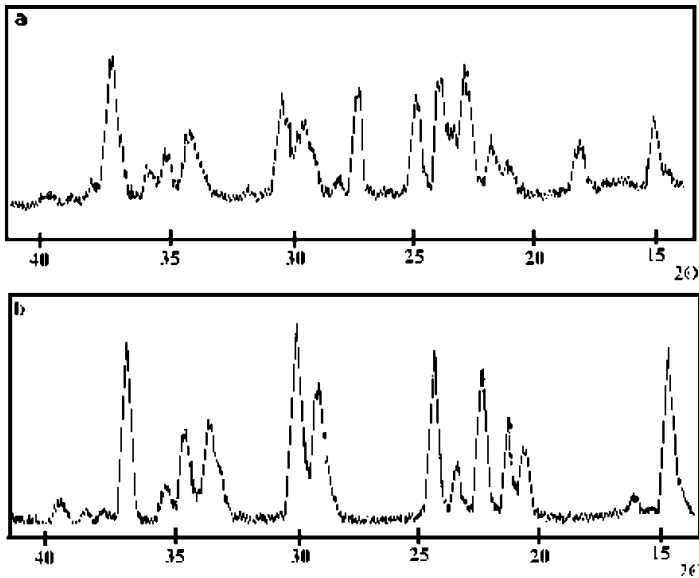


Fig. 3: X-ray diffraction patterns for pure  $\text{Na}_2\text{SiO}_3$  (a) and  $\text{Na}_2\text{SiO}_3$  with 0.03m CaO + 0.03m MgO replacing Na<sub>2</sub>O in the disilicate formula (b)

### 3. Modeling

The fringe intensities in a X-ray diffraction pattern are given as relative values:  $i_q = (I_q / I_{max}) * 100$ , where  $I_q$  is the fringe intensity at scattering angle  $q$  and  $I_{max}$  is the maximum fringe intensity in the entire pattern. For pure substances, obtained under controlled crystallization experiments, the X-ray patterns are known. When several polymorphs are involved, the identification of a particular pattern in industrial crystallized samples is rather difficult. This fact is due to the overlapping fringes at certain scattering angles. An additive

rule has been assumed [FILIPESCU et al. 1996] in order to provide an appropriate significance of the cumulated fringe intensity:

$$I_{\mathbf{q}} = \sum_{k=1}^m I_{\max,k} * i_{\mathbf{q},k} * w_k \quad (5)$$

where:  $I_{\max,k}$  is the maximum absolute fringe intensity in the X-ray pattern of the polymorph  $k$ ,  $i_{\mathbf{q},k}$  is the relative fringe intensity corresponding at scattering angle  $\mathbf{q}$  for the same polymorph  $k$ ,  $w_k$  is the mass fraction of polymorph  $k$ , and  $m$  is the number of phases in the solid mixture.

### 3.1. X-Ray Patterns Identification with a Backpropagation Neural Net

#### 3.1.1. Qualitative Identification of Polymorphs

The qualitative identification of polymorphs has been made by considering 15 classes which represent all solid mixtures that can be made up from the four sodium disilicate polymorphs: 4 classes stand for the pure components  $\alpha$ ,  $\beta$ ,  $\gamma$ , or  $\delta$ - $\text{Na}_2\text{Si}_2\text{O}_5$ , 6 classes for the binary mixtures, 4 classes for the ternary mixtures and one class subsumes the mixtures of all four phases. Each class is characterized by the scattering angles where peaks are to be expected in the X-ray pattern of the phases involved in the mixture. Taking any of the possible four polymorphs mixture as a distinct class where the composition is not known, the relative fringe intensity has not been introduced as a characteristic of the pattern.

The total number of scattering angles for all four phases, where significant peaks emerge is 35. A backpropagation neural network (BPNN) with 35 input nodes was built up. The nodes correspond to the specific scattering angles in increasing order. The inputs to these nodes have binary values (0 or 1). The value "1" singles out an existing peak in the X-ray pattern and the value "0" a missing peak. The number of output nodes is equal to the number of classes, 15, and also have binary representation. If the pattern matches the one described by the class  $k$ , then the output of node  $k$  will take the value "1", and the other nodes will take the output "0". When the continuous output values were postprocessed to binary vectors (0 or 1), "the winner takes all" principle [WASSERMAN] was applied. In this way the classification algorithm avoids ambiguous responses.

The network was trained to recognize simulated data sets corresponding to all the above mixtures X-ray patterns. A correct classification of all learning data sets was realized with a BPNN characterized by 12 nodes in one hidden layer, hyperbolic tangent transfer function and  $\delta$  learning rule with cumulative update of weights. The test data consist in some simulated modified patterns, very close to the genuine ones, with two or three displaced and/or random missing peaks. These changes may occur in some specific experimental conditions. These patterns were classified with an error of 8%.

#### 3.1.2. Quantitative Identification of Polymorphs

Furthermore, a BPNN was built up for the quantitative identification of X-ray diffraction patterns pertaining binary mixtures of  $\alpha$  and  $\beta$ - $\text{Na}_2\text{Si}_2\text{O}_5$  polymorphs and ternary mixtures of  $\alpha$ ,  $\beta$  and  $\delta$ - $\text{Na}_2\text{Si}_2\text{O}_5$  polymorphs. The number of input nodes stands for the main diffraction

angles of the polymorph patterns, in increasing order. The numerical input signals to these nodes are the relative fringe intensities evaluated by rel. (5). The number of output nodes is equal to the number of ascertained classes, where each class represents a given concentration of the polymorph mixture.

The identification of the binary  $\alpha+\beta$  mixture composition was achieved assuming 21 classes characterized by mass fraction of  $\alpha\text{-Na}_2\text{Si}_2\text{O}_5$  between 0 and 1 with a concentration step of 0.05. The BPNN for binary mixtures had 18 input nodes and 21 output nodes. For ternary mixtures the number of classes increases as well as the number of the main diffraction angles which characterize a given mixture. Consequently, a BPNN with 26 input nodes and 37 output nodes was built up. The output nodes correspond to a number of classes characterized by mass fraction of the three polymorphs with a concentration step of 0.1. The output nodes were post-processed to binary vectors as it was described above. The value "1" of the response of an output node discloses a particular concentration class.

The neural nets for quantitative identification of polymorphs were trained using the hyperbolic transfer function, the  $\delta$  learning rule and cumulative update of weights. Meaningful identification results were obtained for one hidden layer with 10 nodes for binary mixtures and respectively for one hidden layer with 15 nodes for ternary mixtures. The neural networks properly recognized all the classes.

For both binary and ternary mixtures the test data covered 60 simulated sets accounting for intermediate mass fractions, other than those included in the learning stage. These patterns were satisfactory encompassed in the nearest learned concentration class (10% error for binary mixtures and 13 % error for ternary mixtures). These errors occurred are caused mainly by the relatively high concentration steps. For more accurate results a lower concentration step should be considered.

For an experimental X-ray pattern of a prepared mixture containing 50%  $\alpha$  and 50%  $\beta\text{-Na}_2\text{Si}_2\text{O}_5$ , the BPNN indicated 55%  $\alpha\text{-Na}_2\text{Si}_2\text{O}_5$  and 45%  $\beta\text{-Na}_2\text{Si}_2\text{O}_5$ . For the mentioned concentration step of 5% this result can be considered reasonable.

### 3.2. X-Ray Patterns Identification with a Neural Net based on Adaptive Resonance Theory

A neural net based on adaptive resonance theory (ART) is a vector classifier [WASSERMAN]. It is an auto-associative net that accepts an input vector and classifies it into one of a number of categories. These categories depend upon which of a number of stored patterns it most resembling. Its classification decision is indicated by the single recognition layer that fires. If the input vector does not match any stored pattern, a new category is created by storing a pattern alike the input vector. Once a stored pattern is found to match the input vector within a specified tolerance (the vigilance), that pattern is adjusted to look still more alike the input vector. No stored pattern is ever modified if it does not match the current input pattern within a given vigilance. Thus, the opposition between stability and plasticity is conciliated: new patterns can create additional classification categories, but a new pattern cannot cause any change to the existing memory unless close matching.

ART [CARPENTER et al., GROSSBERG] is divided into two paradigms: ART-1 is designed to accept only binary input vectors, whereas ART-2 can classify both binary and continuous inputs. In the present work an ART-1 network was built up to identify binary  $\alpha$  and  $\beta$ -

Na<sub>2</sub>Si<sub>2</sub>O<sub>5</sub> mixtures X-ray diffraction patterns. The inputs of the net correspond to the binary representations of the main 18 signals of the pattern. The order of the signals was chosen in accordance with the increasing values of the incidence angle. The signals, which consist in cumulative percentages of relative intensity, were represented in a binary form by their discretization into increments of 10 percent. If the signal is assimilated as a column, the fields corresponding to the signal were coded with +1, and the fields above it with -1 (e.g. the signal 0.34 was coded as: 1,1,1,1,-1,-1,-1,-1,-1,-1). In this way the number of input nodes is 180. The network was trained with 21 patterns of binary  $\alpha$  and  $\beta$ - Na<sub>2</sub>Si<sub>2</sub>O<sub>5</sub> mixtures, with mass/mole fraction ranging between 0 and 1, and a discretization step of 0.05. All these patterns were generated using the above mentioned addition rule. According with concentration classes, the number of output nodes is 21. The architecture of the ART-1 network is illustrated in Fig. 4.

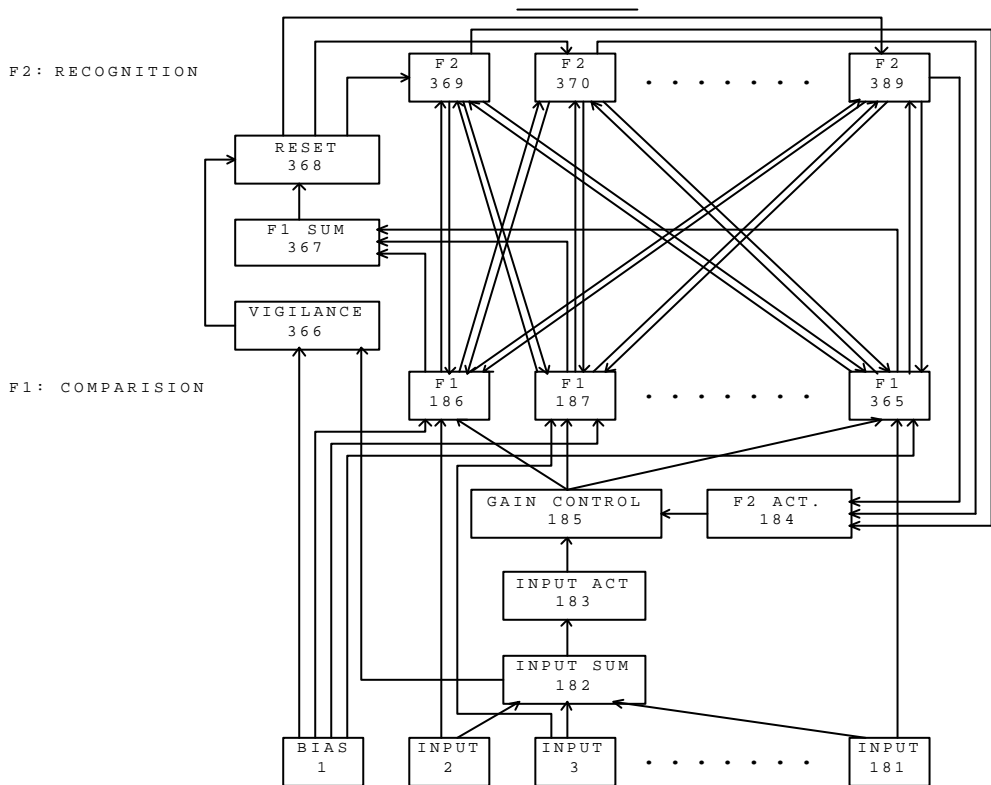


Fig. 4: The architecture of ART-1 network

The ART-1 learning strategy is implemented in the comparison and recognition layers named F1 and respectively F2 in Fig. 4. The blocks Gain Control, Reset, Vigilance, Sum of Inputs, Sum of F1 Layer, and Activation are control functions needed for training and classification. The network performance strongly depends on the adequate selection of learn and recall parameters. Finally, it was obtained a complete classification of 21 patterns

into 21 categories. Due to the fact that this network is an auto-associative one, in comparison with hetero-associative networks (e.g. backpropagation) the duration of training is very short.

The network gave accurate results in the recognition of some generated patterns corresponding to intermediate concentrations of polymorphs. All these patterns were identified and classified to proper categories in the nearest range of the learned value of concentration.

For the equimolar mixture of  $\alpha$ - and  $\beta$ - $\text{Na}_2\text{Si}_2\text{O}_5$  experimental pattern the network indicated 45%  $\alpha$  and 55%  $\beta$ , for the mentioned classification concentration step of 5%. This error margin is satisfactory for our purposes.

#### 4. Results and Discussion

For each experimental sample, the X-ray diffraction spectrum was analyzed using the BPNN model. The qualitative analyses revealed that all samples were composed only of  $\alpha$  and  $\beta$ -polymorphs. Consequently, for quantitative evaluation the BPNN characterizing binary mixture was used. The relative fringe intensities at the characteristic scattering angles (18 nodes) were used as checking data for the BPNN. Tab. 1 contains the results concerning quantitative evaluations. For each sample a quantitative analysis using common methods of X-ray identification was also performed. The differences between the two methods are just in the range of usually experimental errors (2-15%).

Molar ratio $\text{SiO}_2/\text{Na}_2\text{O}$	Impurities fraction (number of mols replacing $\text{Na}_2\text{O}$ in disilicate formula)	Heating duration (minutes)					
		15		30		60	
		<i>a</i>	<i>b</i>	<i>a</i>	<i>b</i>	<i>a</i>	<i>b</i>
2.05	-	75	62	70	62	70	62
2.00	-	50	55	60	60	60	60
1.93	-	40	40	45	40	45	40
2.05	CaO, MgO, $\text{Fe}_2\text{O}_3$ less than 0.5%	45	40	45	40	50	45
1.93	CaO, MgO, $\text{Fe}_2\text{O}_3$ less than 0.5%	50	55	55	60	55	60
2.00	0.010m CaO+0.010m MgO	90	95	95	95	95	95
2.00	0.020m CaO+0.020m MgO	95	95	95	97	95	97
2.00	0.030m CaO+0.030m MgO	95	95	95	97	95	97

a) Composition identified by the BPNN

b) Composition identified by common methods

Table 1:  $\beta$ - $\text{Na}_2\text{Si}_2\text{O}_5$  content in natrium disilicate samples heated at 640°C.

The data in Tab. 1 show that the  $\beta$ - $\text{Na}_2\text{Si}_2\text{O}_5$  / $\alpha$ - $\text{Na}_2\text{Si}_2\text{O}_5$  ratio in the heated samples depends on the molar ratio and purity, but the presence of usual impurities in technical grade  $\text{Na}_2\text{Si}_2\text{O}_5$  (CaO, MgO,  $\text{Fe}_2\text{O}_3$  smaller than 0.05%) does not increase or decrease the  $\beta$ - $\text{Na}_2\text{Si}_2\text{O}_5$  concentration. The addition of grater quantities of CaO and MgO to substitute  $\text{Na}_2\text{O}$  in disilicate formula leads to a straight increase in  $\beta$ - $\text{Na}_2\text{Si}_2\text{O}_5$  concentration. This behavior suggests the importance of additives as precursor growth, inhibiting agent or simply favoring  $\beta$ - $\text{Na}_2\text{Si}_2\text{O}_5$  heteronucleation. Data in Tab. 1 also show a poor influence of the heating duration on recrystallization yield. This fact may be assigned to the athermal nucleation of

both  $\alpha$ - $\text{Na}_2\text{Si}_2\text{O}_5$  and  $\beta$ - $\text{Na}_2\text{Si}_2\text{O}_5$  precursors during the steady raise of temperature to 600°C, which is followed by a temperature dependent nuclei growth consuming the amorphous phase [FILIPESCU et al. 1999].

## 5. Conclusions

The algorithms advanced for X-ray pattern identification yield a quick matching and classification providing low error margin even when several polymorphs occur in the same sample. Both qualitative identification of polymorph phases and composition evaluation of polymorph mixtures were performed with satisfactory results using backpropagation neural networks with post-processing of the continuous output values to binary vectors.

A neural net based on adaptive resonance theory has given good performances in X-ray pattern identification. This network, being an auto-associative one, presents the supplementary advantage of a very short duration in the training stage.

Once the neural networks trained, the analyses of X-ray diffraction spectra is very simple, even if more than two phases are found in the same sample. This method can be implemented into an expert system for the on-line qualitative and quantitative analysis of polymorph mixtures based on X-ray diffraction spectra interpretation.

X-ray and thermal analysis of the amorphous and crystalline sodium disilicate phases in conjunction with neural network models were used in the identification of a stage sequence in amorphous thermal treatment, able to produce a  $\beta$ - $\text{Na}_2\text{Si}_2\text{O}_5$  enriched material.

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