PREPARATION AND CHARACTERIZATION OF ANALCIME POWDERS BY X-RAY AND SEM ANALYSES

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Analcime ($NaAlSi_2O_6 \cdot H_2O$) powders having controlled particle size distribution were designed [1, 2] as a potential precursor for the fabrication of leucite ($KAlSi_2O_6$) dental ceramics retaining high fracture toughness and the thermal expansion coefficient adjusted those of metals. The purpose of this study is to investigate the synthesis of analcime and the effect of principal factors influencing its crystallisation. Analcime powders were prepared by hydrothermal synthesis in a Teflon-lined stainless steel autoclave. The role of the composition of the reaction mixture (raw materials, OH^- concentration, and water content), reaction temperature and time were studied. Prepared analcime was in form of homogenous powders with the uniform particle size at intervals 1-5 μm depending on process parameters.

INTRODUCTION

Analcime is a zeolite (and feldspathoid) having a complex aluminosilicate framework that is common to all leucite-type feldspathoids. The framework is based on corner sharing $(Al,Si)O_4$ tetrahedra, arranged in fourfold, sixfold and eightfold rings. The sixfold rings are arranged axially, forming structural channels parallel to 111 [1]. Such a channel arrangement shows many possibilities for structural modification, including framework distortion, channel collapse, and ionic mobility. Due to the similarities in structure, analcime can serve as a precursor for the synthesis of leucite [2, 3]. The latter might become an essential component of composite dental materials designed to exhibit high fracture toughness.

Leucite ceramics used in stomatology is prepared from highly viscous alkaline alumosilicate glasses containing leucite as a main crystalline phase [4-7]. Nucleation and leucite crystals growth from a melt are very slow processes and consequently the thermal treatment requires very long time. In addition using this procedure it is very difficult to control final microstructure of a material, especially leucite particles size and their homogenous distribution in a glassy matrix.

Nowadays it is assumed that preparation technology of composite materials would be more suitable for the fabrication of leucite ceramics having controlled microstructure realized by homogenous dispersion of leucite particles in a glassy matrix [8]. The principal of this new technology is based on a separate synthesis of leucite and matrix, both with controlled particle size distribution. Final microcomposite is obtained by sintering of these two phases. This technology ensures reproducible control of leucite ceramics' microstructure, which is requited to improve its fracture toughness and persistence. The fundamental step for an extensive use of this technology consists in the reproducible synthesis of leucite. A viable route is ion-exchange, using analcime ($NaAlSi_2O_6 \cdot H_2O$) as a precursor. As the particle size and shape do not change during the ion-exchange to leucite, the synthesis of analcime represents the most important part of the preparation.

In this paper we report on the synthesis of analcime in hydrothermal conditions. Special attention was paid to the investigation of the reaction parameters - reaction temperature and time, composition of the reaction mixture (raw materials, OH^- concentration, and water content), with the ultimate goal of efficiently controlling the synthesis procedure, i.e. the phase composition of the reaction product, its particle size and particle size distribution.

EXPERIMENTAL

Starting sols were made by mixing aluminate and silicate solutions, which had been prepared separately by dissolving silica and aluminium raw materials in a sodium hydroxide solution while being stirred permanently. Thoroughly homogenized synthesis mixtures were treated hydrothermally in a Teflon-lined stainless steal autoclave (figure 1). The reaction products were thoroughly washed in boiling distilled water; vacuum filtered and dried in an oven at 100°C.

Phase composition was identified by X'Pert PRO powder diffractometer using parafocusing Bragg-Brentano geometry using CuK_{α} radiation (λ = 1.5418 A, U = 40 kV, I = 30 mA). The particle size and their distribution were observed by optical microscopy (Olympus BX 51) and determined by image analyser (LUCIA). The particle size and morphology analysis was performed using scanning electron microscopy (SEM, Philips XL 30 CP).

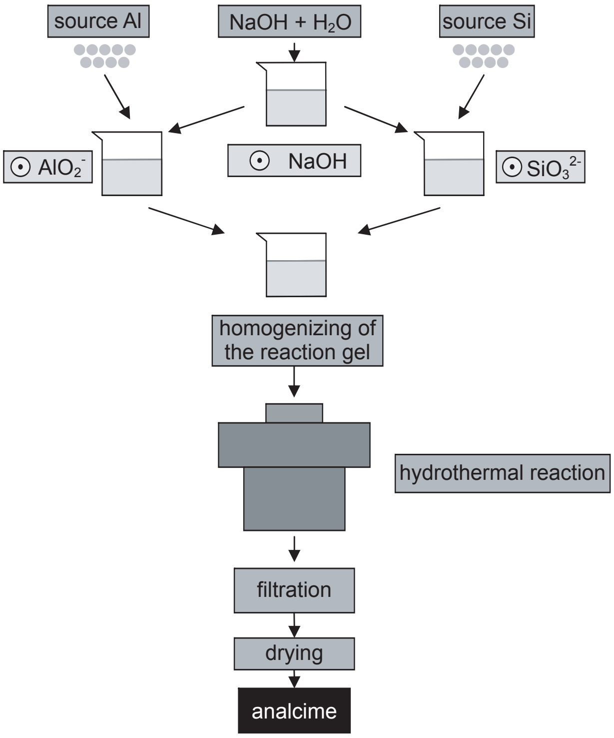

Figure 1. Scheme of the preparation procedure of analcime.

Influence of reaction temperature and time

Long reaction time as well as higher temperatures enhances analcime crystallisation (table 1). At 200°C only two hours were required to synthesize pure analcime. On the other hand, at 150°C a reaction time of four hours was required and at 100°C the crystallization of analcime was not observed even after 24 hours.

Figure 2 illustrates the crystallization process at 150°C. After one-hour treatment no crystalline phase was identified in the reaction product. The first reaction product was zeolite P1 (Na) - sodium aluminium silicate hydrate ($Na_6Al_6Si_{10}O_{32}\cdot 12H_2O$). Later in the process, this metastable phase dissolved gradually and at the same time analcime started to crystallize. After four hours of the hydrothermal reaction the only substance present in the product was analcime.

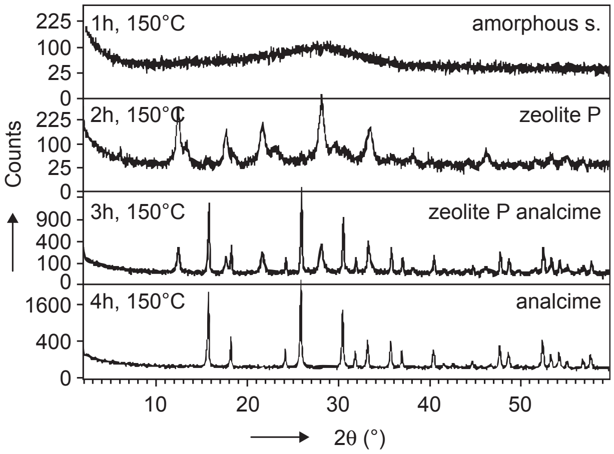

Figure 2. XRD patterns of samples representing the crystallization process of analcime at 150°C.

Table 1. Resulting phase compositions and particle sizes as a function of the process parameters.

Starting composition	Reaction temperature (°C)	Reaction time (h)	Phase composition	Particle size (µm)
Raw mat. - SiO_2, Al SiO_2/Al_2O_3 - 4,8 H_2O/SiO_2 - 16 NaOH molarity - 4M	100	2	amorphous	~ 5-20
		15	$Na_{6.4}Al_{6.4}Si_{9.6}O_{32}\cdot 4{,}6H_2O$ zeolite P	~ 11
		24	$Na_{6.4}Al_{6.4}Si_{9.6}O_{32}\cdot 4{,}6H_2O$ zeolite P	~ 10
	150	1	amorphous	~ 9
		2	zeolite P	~ 10
		3	zeolite P analcime	~ 6
		4	analcime	~ 5
		15	analcime	~ 5
		24	analcime	~ 4
	200	1	zeolite P analcime	~ 5
		2	analcime	~ 3
		15	analcime	~ 4
		24	analcime	~ 4

As to particle size, it was observed that it changes with increasing temperature (figure 3). These changes can be mainly attributed to changes of phase compositions of the reaction products. On the other hand scanning electron microscopy showed no significant changes in particle size or shape at the identical phase composition of the product.

Influence of raw materials

Raw materials used for the synthesis and corresponding final phase compositions are listed in table 2. Using colloidal SiO_2 sol as the silica source and Al_2O_3 as the aluminium source led to a deceleration of the analcime synthesis, as zeolite P1 and residual Al_2O_3,

Table 2. Review of raw materials and corresponding final phase compositions.

Starting composition	Raw materials	Reaction time (h)	Phase composition	Particle size (µm)
	amorph. SiO^2	2	analcime	~ 3-4
	Al	24	analcime	~ 4
	Colloidal SiO_2 sol	2	analcime zeolite P	~ 10-30
	Al	24	analcime	~ 15-20
SiO_2/Al_2O_3 - 4,8	Fumed SiO_2	2	analcime	~ 2-20
H_2O/SiO_2 - 16	Al	24	analcime	~ 25-30
NaOH molarity - 4M	Amorph. SiO_2	2	analcime	~ 8-16
Temperature - 200°C	$Al_2O_3\cdot 2SiO_2$	24	analcime	~ 5-7
	Amorph. SiO_2	2	analcime Al_2O_3	~ 3-12
	Al_2O_3	24	analcime Al_2O_3	~ 5-20
	Amorph. SiO_2	2	analcime	~ 7
	$Al(OH)_3$	24	analcime	~ 4

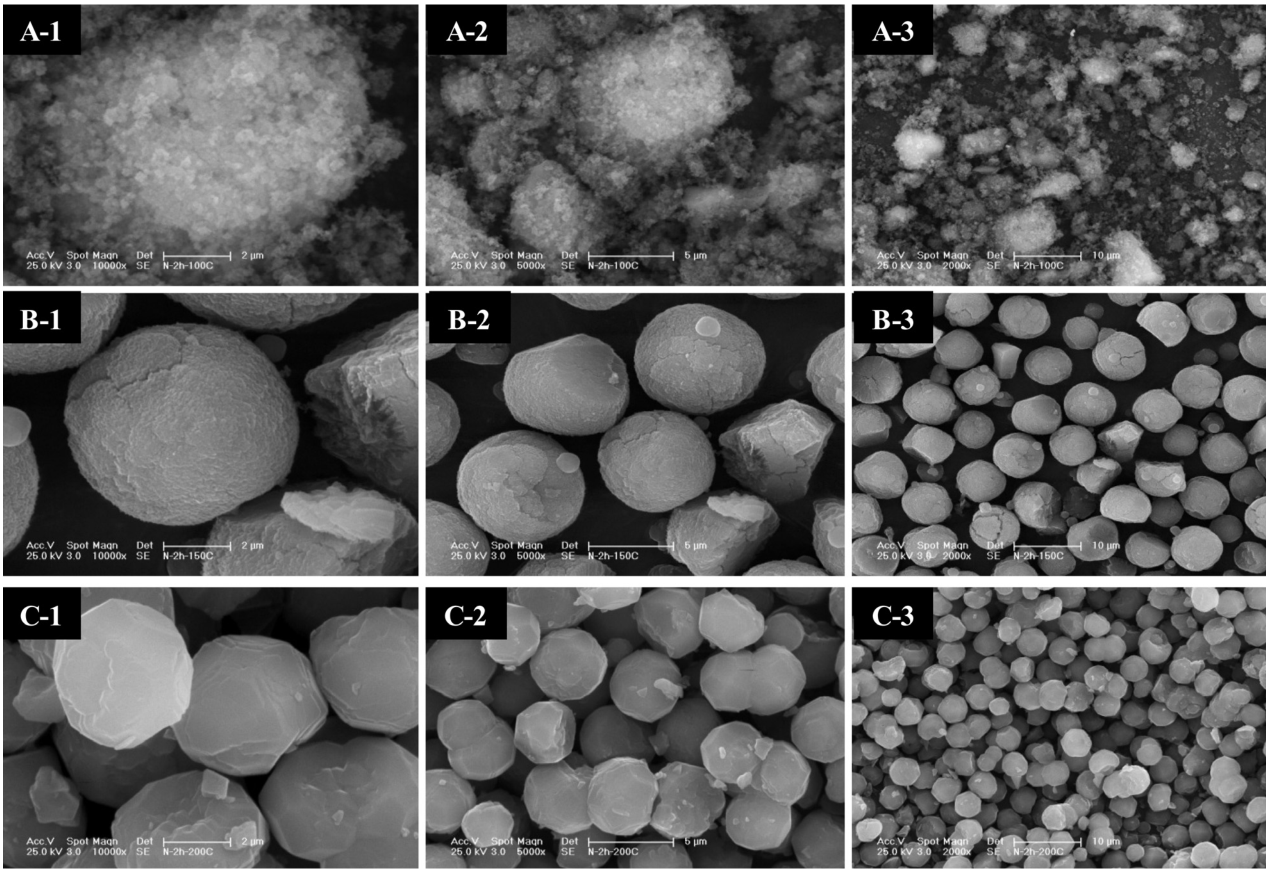

Figure 3. SEM images of products prepared by 2 hours of hydrothermal synthesis at 100°C (A), 150°C (B) and 200°C (C).

respectively, were detected in the reaction product. Compositions based on amorphous SiO_2 powder as the silica source and Al or $Al(HO)_3$ as the aluminium sources were found to be suitable for the synthesis of homogeneous analcime powders.

Table 3. Resulting phase compositions and particle sizes as a function of the NaOH molarity.

Starting composition	NaOH molarity	Phase composition	Particle size (µm)
Raw mat. - SiO_2, Al SiO_2/Al_2O_3 - 4,8 H_2O/SiO_2 - 16 Temp. - 200°C Time - 24 h	1M	amorphous	~ 5 - 15
	2M	analcime	~ 8
	3M	analcime	~ 6
	4M	analcime	~ 4
	5M	analcime faujasite-Na	~ 3
	6M	faujasite-Na	~ 1

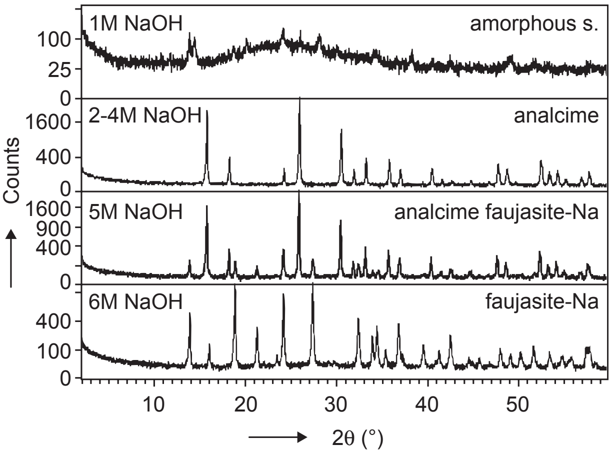

Figure 4. XRD of samples illustrating the role of NaOH.

Table 4. Resulting phase compositions and particle sizes as a function of the H_2O/SiO_2 ratio.

Starting composition	H_2O/SiO_2 ratio	Phase composition	Particle size (µm)
Raw mat. - SiO_2, Al SiO_2/Al_2O_3 - 4,8 NaOH - 4M Temp. - 200°C Time - 24 h	6	amorphous	~ 1-10
	8	$NaAlSi_2O_6.H_2O$ zeolite P	~6-8
	10	$NaAlSi_2O_6.H_2O$	~ 5-6
	12	$NaAlSi_2O_6.H_2O$	~4-5
	14	$NaAlSi_2O_6.H_2O$	~ 5
	16	$NaAlSi_2O_6.H_2O$	~ 3-4
	18	$NaAlSi_2O_6.H_2O$	~ 4
	20	$NaAlSi_2O_6.H_2O$	~ 3
	22	$NaAlSi_2O_6.H_2O$	~ 3-4
	24	$NaAlSi_2O_6.H_2O$	~ 1-2
	26	$NaAlSi_2O_6.H_2O$ $Na_{14}Al_{12}Si_{13}O_{51}\cdot 6H_2O$	~ 3
	28	$NaAlSi_2O_6.H_2O$ $Na_{14}Al_{12}Si_{13}O_{51}\cdot 6H_2O$	~ 3

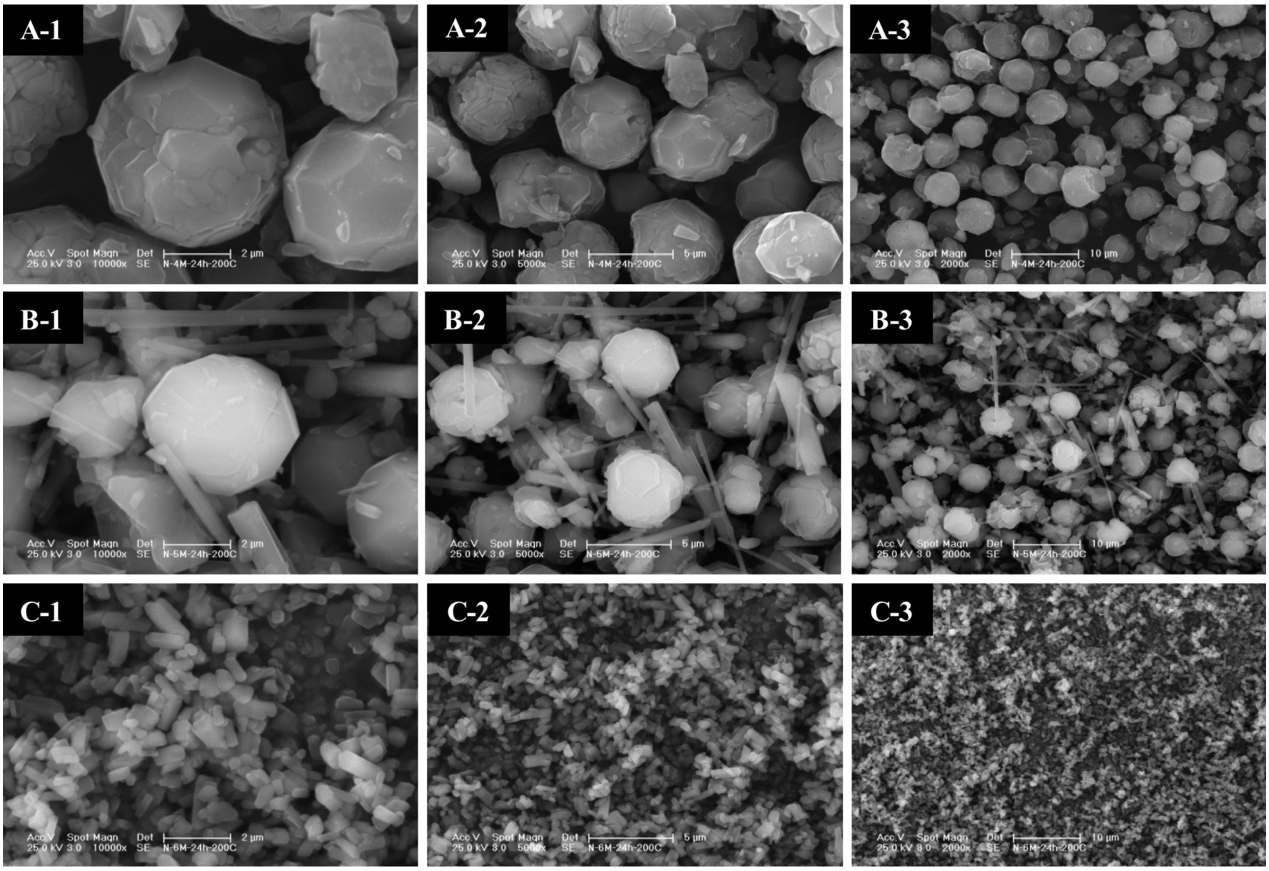

Figure 5. SEM images of analcime (A) prepared from 4M NaOH, sample prepared from 5M NaOH containing spherical particles of analcime and needle - like particles of faujasite (B), faujasite prepared from 6M NaOH (C).

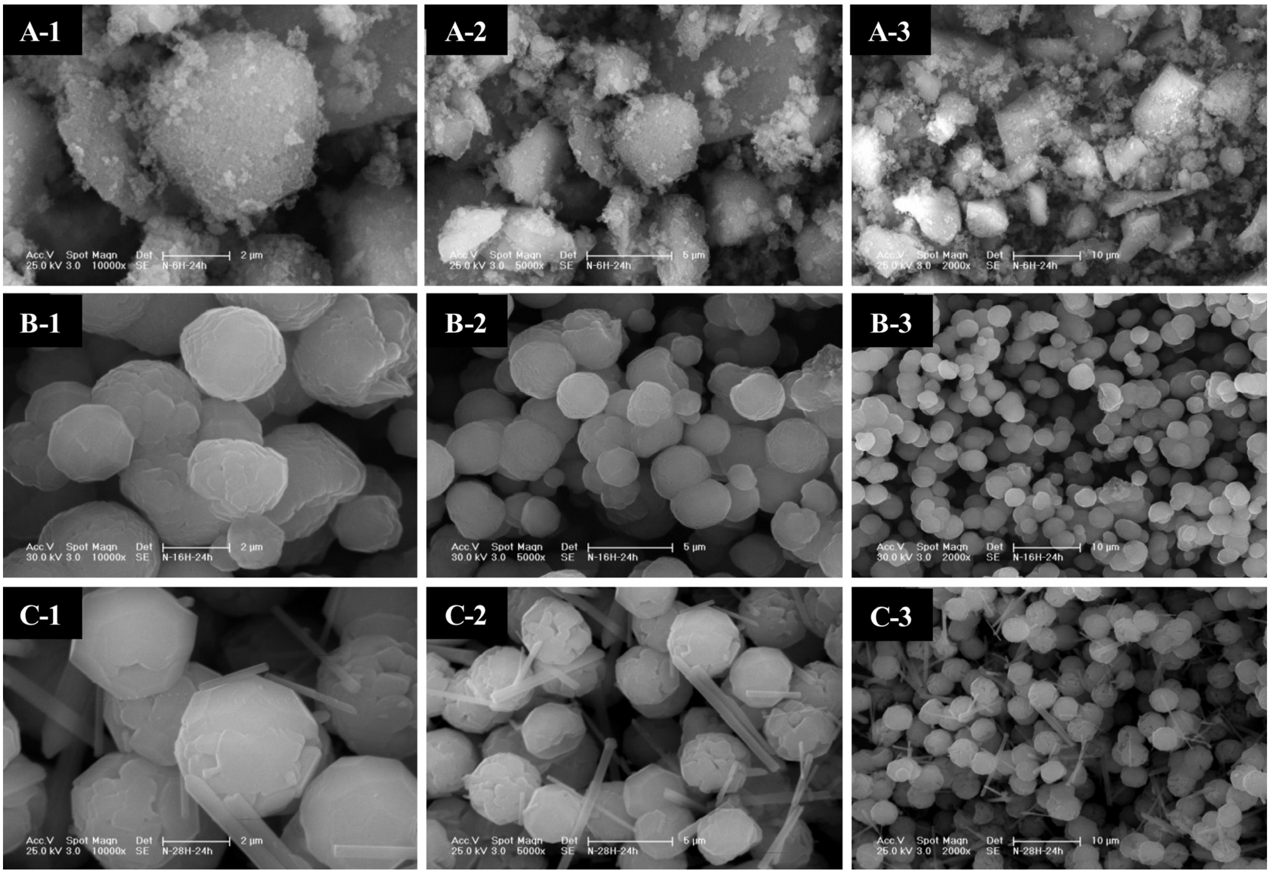

Figure 6. SEM images of samples prepared from reaction mixtures with H_2O/SiO_2 = 6 (A), 16 (B) and 28 (C).

Influence of OH^- concentration

The role of the initial molarity of sodium hydroxide solution was monitored in samples listed in table 3. The NaOH molarity significantly effects both phase composition and the particle size of the resulting product. It has been proved that the particle size decreases with the increasing molarity of the solution.

Figure 4 represents XRD patterns of the aforementioned samples, i.e. the amorphous substance prepared using 1M NaOH (figure 4 - top), analcime synthesized using 2-4M NaOH (figure 4 - second from top), the mixture of analcime and faujasite-Na ($Na_{14}Al_{12}Si_{13}O_{51}\cdot 6H_2O$) prepared using 5M NaOH (figure 4 - third from top), and the Na-faujasite resulting when 6 M NaOH is used (figure 4 - bottom), cf. also the micrographs on figure 5.

Influence of H_2O/SiO_2 ratio

Starting reaction conditions and resulting phase compositions and particle sizes of prepared samples monitoring the effect of H_2O/SiO_2 ratio in the reaction gel are listed in table 4. The results show that analcime crystallizes in relatively wide range of H_2O/SiO_2 values from 8 to 28 and pure analcime between 10 and 24. Starting reaction gels having low H_2O/SiO_2 ratio lead to deceleration of the hydrothermal reaction. In case of the H_2O/SiO_2 = 8 metastable phase zeolite P1 (Na) - $Na_6Al_6Si_{10}O_{32}\cdot 12H_2O$ was identified in the reaction product analogues to the samples prepared at lower temperatures and shorter times respectively. Product prepared from gel with H_2O/SiO_2 = 6 was even amorphous (figure 6 - A). On the other hand samples prepared from gels having high H_2O/SiO_2 ratios (equal to 26, 28) contained besides analcime also particles of faujasite-Na ($Na_{14}Al_{12}Si_{13}O_{51}\cdot 6H_2O$) (figure 6 - C).

The particle size of prepared analcime powders slightly decreases with increasing H_2O/SiO_2 ratio (table 4).

CONCLUSION

Homogeneous analcime powders with the particle size of approx. 2 μm were prepared under hydrothermal conditions. As a result of the detailed investigation of the synthesis of analcime, i.e. of the effect of process parameters and starting compositions, it is now possible to control the particle size, shape and structure of the reaction product efficiently. The results show that long reaction times as well as higher temperatures lead to enhanced analcime crystallisation. The choice of raw materials affects especially homogeneity and morphology of the product. The initial molarity of sodium hydroxide solution significantly affects both phase composition and the particle size. It has been proved that the particle size decreases with increasing molarity of NaOH solution and H_2O/SiO_2 ratio. Low values of H_2O/SiO_2 ratio in starting reaction gels lead to deceleration of the hydrothermal reaction.

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PŘÍPRAVA A CHARAKTERIZACE ANALCIMOVÝCH PRÁŠKŮ ANALÝZAMI RTG A SEM

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Byl navržen postup syntézy analcimových prášků ($NaAlSi_2O_6 \cdot H_2O$) s řízenou velikostí částic, které jsou vhodným prekurzorem pro přípravu leucitové dentální suroviny. Přítomnost leucitu ($KAlSi_2O_6$) v dentální keramice vede k vyšším hodnotám lomové houževnatosti a koeficientu délkové teplotní roztažnosti oproti klasickému živcovému dentálnímu porcelánu. Cílem této studie bylo vyvinout novou metodu přípravy alnalcimu v hydrotermálních podmínkách a provést analýzu možných faktorů, které ovlivňují průběh jeho krystalizace, tj. složení reakční směsi (volba surovin, koncentrace OH^- iontů, vliv poměru H_2O/SiO_2), reakční teplotu a čas. Bylo prokázáno, že vhodně zvolenými podmínkami syntézy lze tímto způsobem připravit homogenní analcimové prášky s uniformní velikostí částic v rozmezí 1-5 μm.