PREPARATION OF LEUCITE POWDERS WITH CONTROLLED PARTICLE SIZE DISTRIBUTION

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Leucite ceramics having high fracture toughness and suitable thermal expansion being useful for making ceramic-fused-to-metal restorations represents a very promising material for dental applications. The aim of our work is to replace existing technologies based on the crystallization from a melt by preparation of a composite material in which leucite and glassy matrix are synthesised separately. Both these phases are subsequently homogenised and sintered in a dentist laboratory. This technology ensures reproducible control of leucite ceramics microstructure, which is requited to improve its fracture toughness and persistence. In the present study preparation of leucite powders with controlled particle size distribution was investigated. Leucite was prepared by ion exchange of analcime, the degree of ion exchange was determined by XRD and XRF analysis. As the properties of analcime employed for the reaction are critical for resulting leucite, the effect of process parameters and starting compositions on the particle size, shape and structure was studied.

INTRODUCTION

Leucite - potassium alumino-silicate ($KAlSi_2O_6$) is the major crystalline phase in most high-expansion dental porcelains used for ceramic-fused-to-metal restorations. Leucite was initially introduced into dental porcelains to raise the composite coefficient of thermal expansion to match that of casting alloys when cooled [1]. In addition in last few years it was found that the presence of leucite, owing to its martensitic tetragonal-cubic transition behaviour, also improves values of fracture toughness and persistence of a final dental product.

Leucite structure comprises a framework of corner sharing (Al, Si)O_4 tetrahedra, arranged in fourfold, sixfold and eightfold rings. The sixfold rings are arranged axially, forming structural channels. Such a channel arrangement is typical of feldspathoids and some of zeolites. In comparison with feldspars and other framework structures without channels, they show many possibilities for structural modification, including framework distortion or ionic mobility.

Naturally occurring leucite crystallises in the cubic form. On cooling below the temperature of about 630°C, there is a phase transition to a tetragonal form. The conversion of cubic leucite into the tetragonal modification involves deformation of the sixfold rings, i.e. channels distortion, which is accompanied by slight movements of the K^+ ions. The transformation is martensitic, it proceeds by slipping and twinning mechanism, during which the atoms retain their neighbours and move over a distance that is smaller than their original mutual one [2].

The demand for leucite ceramics having high fracture toughness arose the necessity to develop a new suitable technology of its preparation. Preparation procedures of leucite ceramics were up to now proceeded from a classical technology of dental porcelain based on a crystallisation from a melt. However, nucleation and crystal growth are very slow processes and consequently the thermal treatment requires very long time, tens of hours or even several days. In addition using this procedure it is very difficult to control final microstructure of material, especially homogenous distribution of particles in a glassy matrix [3]. On the contrary a perspective line seems to be the preparation of composite material in which leucite and glassy matrix are synthesised separately. Both these phases are subsequently homogenised and sintered in a dentist laboratory after application on metal framework [4]. This technology ensures reproducible control of leucite ceramics microstructure, which is requited to improve its fracture toughness and persistence.

The aim of this research was to explore a suitable technology leading to the preparation of leucite powders with controlled particle size distribution.

EXPERIMENTAL

Preparation of leucite powders proceeded in two steps. The first step comprises synthesis of analcime ($NaAlSi_2O_6{\cdot}H_2O$) in hydrothermal conditions. The effect of the process parameters (reaction temperature and time) and starting compositions of the reaction mixture (source materials, silica/aluminium ratio, OH^- concentration, and water concentration) on the particle size, shape and structure was studied. Starting sols were made up by mixing aluminate and silicate solutions, which were prepared separately by dissolving silica and aluminium sources in a sodium hydroxide solution under the permanent stirring. Thoroughly homogenized synthesis mixtures were treated hydrothermally in a teflon-lined stainless steal autoclave.

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-ray powder diffraction method (XRD, Philips). Particle size and their distribution were observed by optical microscopy (Olympus BX 51) and determined by image analyser (LUCIA). Particle size and morphology analysis were completed by scanning electron microscopy (SEM, Philips XL 30 CP).

In the second step leucite was prepared by ion exchange of analcime. Analcime powders having particle size of 3-4 μm were used for the reaction. 1 g of a sample was treated with 20 ml of a KCl solution in hydrothermal conditions. Reaction temperature, time and molarity of KCl solution were modified to obtain the optimal conditions of the synthesis. After the hydrothermal treatment, the content of the autoclave was washed, vacuum filtered and dried in an oven at 100°C. Phase identification was carried out with X-ray diffractometr. The degree of ion-exchange was determined by chemical analysis using X-ray fluorescence analysis (XRF, Thermo ARL 9400XP). SEM was used to observe morphological changes of the particles.

RESULTS AND DISCUSSION

Synthesis of analcime

Table 1 illustrates the influence of reaction time and temperature on product s final phase composition and particle size. It is evident that long reaction time as well as higher temperature enhances analcime crystallisation. At temperature of 200°C only two hours were required to synthesize pure analcime. On the other hand at 150°C required reaction time was four hours and at 100°C crystallization of analcime was not observed even after 24 hours. Figure 1 illustrates crystallization process at temperature of 150°C. After one-hour treat-

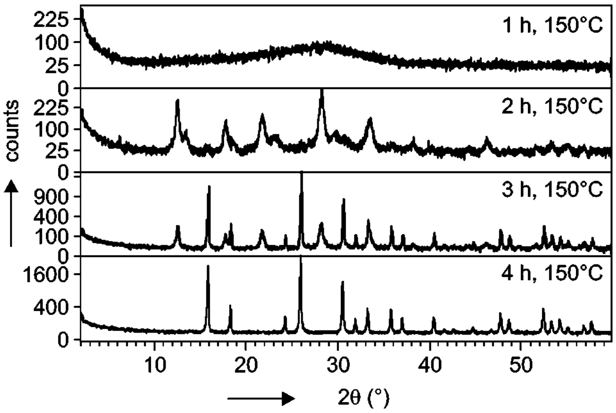

Figure 1. XRD patterns of samples representing crystallization process of analcime at 150°C.

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)
Source mat. - SiO_2, Al SiO_2/Al_2O_3 - 4,8 H_2O/SiO_2 - 16 NaOH molarity - 4M	100	6	amorphous	~ 18
		15	$Na_{3,6}Al_{3,6}Si_{12,4}O_{32}.14H_2O$	~ 11
		24	$Na_{3,6}Al_{3,6}Si_{12,4}O_{32}.14H_2O$	~ 10
	150	1	amorphous	~ 9
		2	$Na_{3,6}Al_{3,6}Si_{12,4}O_{32}.14H_2O$	~ 10
		3	analcime $Na_{3,6}Al_{3,6}Si_{12,4}O_{32}.14H_2O$	~ 6
		4	analcime	~ 5
		15	analcime	~ 5
		24	analcime	~ 6
	200	1	analcime $Na_{3,6}Al_{3,6}Si_{12,4}O_{32}.14H_2O$	~ 5
		2	analcime	~ 3
		15	analcime	~ 4
		24	analcime	~ 4

ment no crystalline phase was identified in the reaction product. As the first arose zeolite P - sodium aluminium silicate hydrate ($Na_{3,6}Al_{3,6}Si_{12,4}O_{32}\cdot 14H_2O$). This metastable phase later gradually dissolved and analcime started to crystallize. After four hours of the hydrothermal reaction only analcime was presented in the product. In terms of particle size, it was observed that the particle size decreases with increasing temperature; no significant changes were observed with increasing reaction time.

Source 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 the deceleration of the analcime synthesis, as zeolite P and residual Al_2O_3 respectively were detected in the reaction product. SEM images of obtained products (figure 2) demonstrate the influence of source materials on their homogeneity and morphology. It can be seen that only composition based on amorphous SiO_2 powder as the silica source and Al or $Al(HO)_3$ as the aluminium sources are suitable for the synthesis of homogeneous analcime powders.

Crystallisation of analcime was found very tolerant of silica/aluminium and water/silica ratio. The effect of SiO_2/Al_2O_3 was monitored for rates in the range from 3 to 6 (table 3). All the studied ratios were found suitable for the synthesis of analcime. Even particle sizes of spot samples did not show strong differences. On the other hand water/silica ratio in the entering reaction mixture influences resulting particle size - the higher H_2O/SiO_2 ratio the smaller particles (table 4).

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

Starting composition	Source materials	Phase composition
SiO_2/Al_2O_3 = 4,8 H_2O/SiO_2 = 16 NaOH molarity - 4M Temperature - 200°C Time - 2h	Amorph. SiO_2 powder Al	analcime
	Colloidal SiO_2 sol Al	analcime $Na_{3,6}Al_{3,6}Si_{12,4}O_{32}.14H_2O$
	Fumed SiO_2 Al	analcime
	Amorph. SiO_2 powder $Al_2O_3.2SiO_2$	analcime
	Amorph. SiO_2 powder Al_2O_3	analcime Al_2O_3
	Amorph. SiO_2 powder $Al(OH)_3$	analcime

Table 3. Effect of SiO_2/Al_2O_3 ratio on analcime particle size.

Starting composition	SiO_2/Al_2O_3 ratio	Phase composition	Particle size (μm)
	3	analcime	~ 3-4
Source mat. - SiO_2, Al	3,5	analcime	~ 7
H_2O/SiO_2 - 16	4	analcime	~ 5
NaOH molarity - 4M	4,5	analcime	~ 5
Temperature - 200°C	5	analcime	~ 5
Time - 24h	5,5	analcime	~ 6
	6	analcime	~ -2-3

Table 4. Effect of H_2O/SiO_2 ratio on analcime particle size.

Starting composition	H_2O/SiO_2 ratio	Phase composition	Particle size (μm)
Source mat. - SiO_2, Al SiO_2/Al_2O_3 - 4.8 NaOH molarity - 4M Temperature - 200°C Time - 24h	10	analcime	~ 6
	12	analcime	~ 5
	14	analcime	~ 5
	16	analcime	~ 4
	18	analcime	~ 4
	20	analcime	~ 3

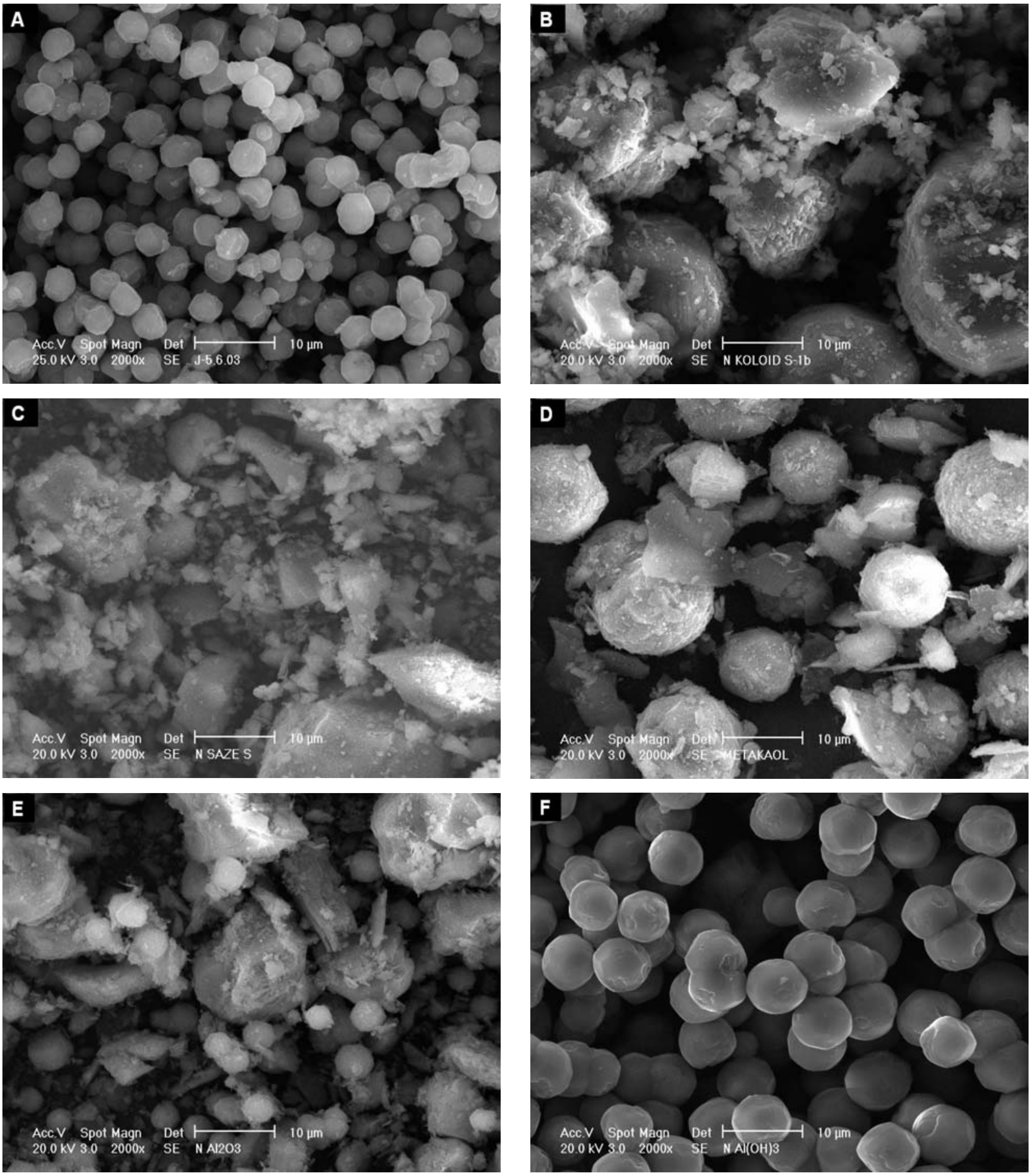

Figure 2. SEM micrographs of analcime grains - A: prepared from SiO_2, Al, - B: colloidal SiO_2 sol, Al, - C: fumed SiO_2, Al, - D: SiO_2, $Al_2O_3.2SiO_2$, - E: SiO_2, Al_2O_3, - F: SiO_2, $Al(OH)_3$.

The role of initial molarity of sodium hydroxide solution was monitored in samples listed in table 5. From the results it is perceptible that NaOH molarity significantly effects both phase composition and particle size of the resulting product. It was proved that the particle size decreases with increasing molarity of the solution. Figure 3 represents XRD spectra of above-mentioned samples, i.e. spectrum of amorphous substance prepared from 1M NaOH, next of analcime synthesized from 2-4M NaOH, in the sample using 5M NaOH two different crystalline phases were identified - analcime, faujasite-Na ($Na_{14}Al_{12}Si_{13}O_{51}\cdot 6H_2O$), and the last is the spectrum of faujasite-Na prepared from 6M NaOH.

Preparation of leucite by ion-exchange of analcime

Reaction conditions and corresponding degrees of ion-exchange are stated in table 6. The results show that the percentage of prepared leucite considerably increases with increasing molarity of KCl solution and with increasing reaction temperature. Hydrothermal treatment at 200°C for 3 hours in a 4M KCl solution was sufficient to transform analcime to leucite completely.

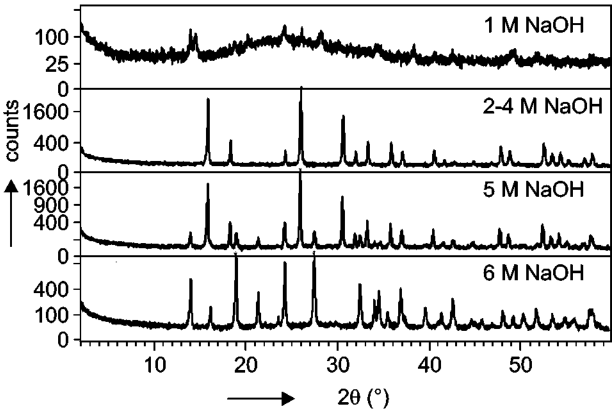

Figure 3. XRD patterns of samples illustrating the role of NaOH molarity in the analcime synthesis.

Figure 4 illustrates the ion-exchange process from starting analcime till final leucite at temperature 200°C. Lower part of the image demonstrates a confrontation of the peak list of the prepared leucite with that of a reference pattern - Leucite, syn, 38-1423.

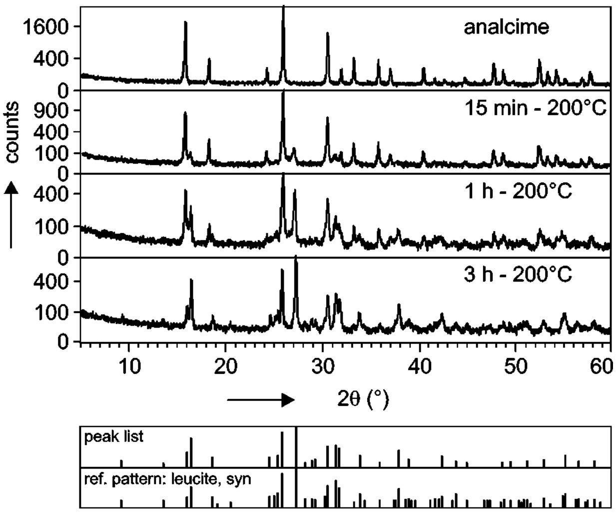

Figure 4. XRD patterns of samples representing ion-exchange process. Lower part - a confrontation of the peak list of the prepared leucite with that of a reference pattern - Leucite, syn, 38-1423.

Table 5. Resulting phase compositions and particle sizes as a function of the NaOH molarity.

Starting composition	NaOH molarity	Phase composition	Particle size (μm)
Source mat. - SiO_2, Al SiO_2/Al_2O_3 - 4,8 H_2O/SiO_2 - 16 Temperature - 200°C Time - 24h	1M	amorphous	~ 9
	2M	analcime	~ 7
	3M	analcime	~ 6
	4M	analcime	~ 4
	5M	analcime, faujasite-Na	~ 3
	6M	faujasite-Na	~ 1

Table 6. Effect of SiO_2/Al_2O_3 ratio on analcime particle size.

KCl molarity	Reaction temperature (°C)	Reaction time (h)	Degree of ion-exchange (%)
1M	200	1	33
2M	200	1	49
3M	200	1	63
4M	200	1	24
4M	100	1	35
4M	150	1	52
4M	200	15 min	26
4M	200	30 min	58
4M	200	1	67
4M	200	2	90
4M	200	3	100
4M	200	4	100
4M	200	24	100

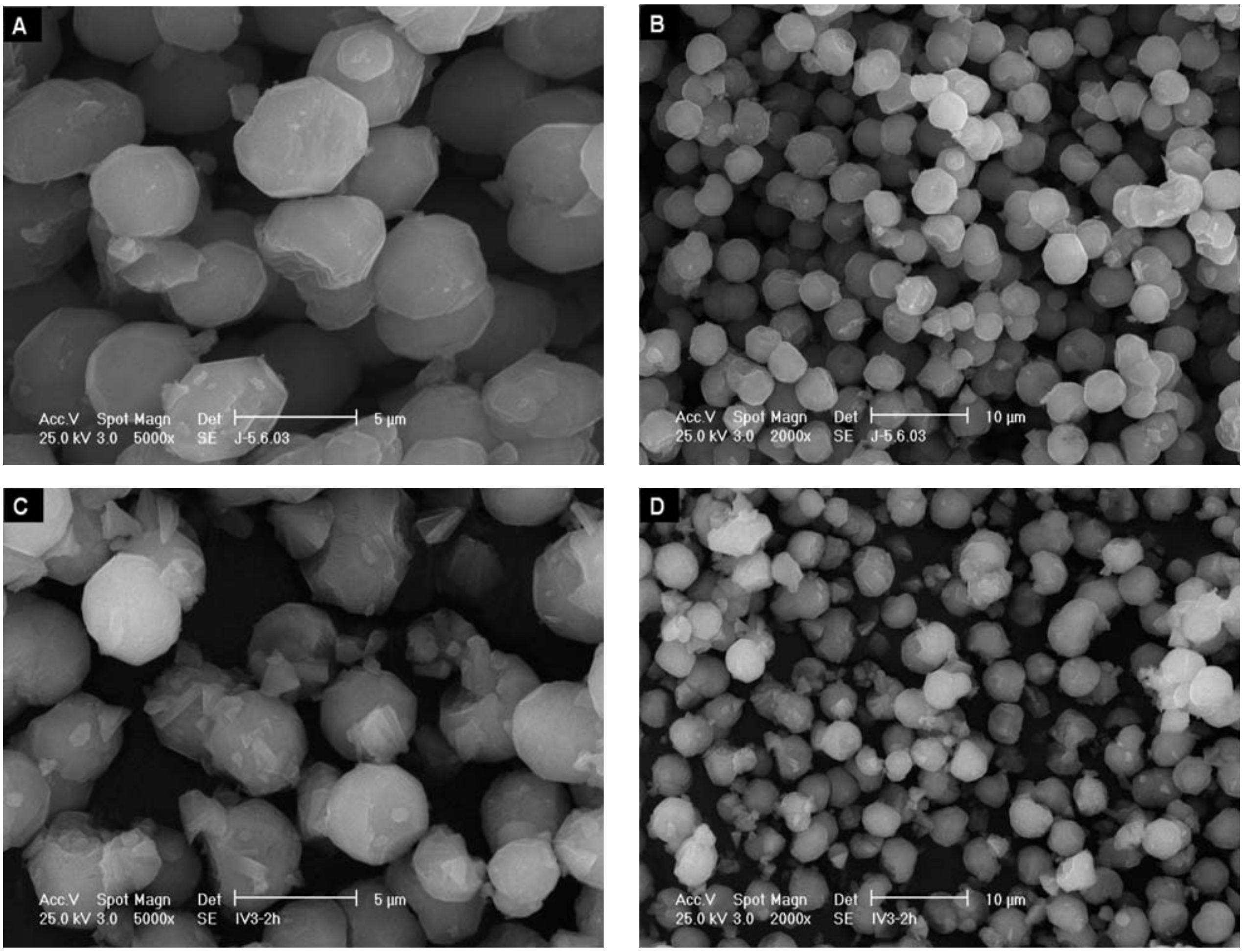

Figure 5. SEM micrographs of analcime (A, B) and resulting leucite (C, D) after 3h of ion-exchange reaction at 200°C.

Scanning electron microscopy of the reacted analcime grains showed no significant changes in their size or shape. On the other hand distinct cracks were observed on grain surfaces leading to disintegration of some particles (figure 5). These cracks are probably due to a transformation from cubic analcime to tetragonal form of leucite accompanied by a significant decrease in solid volume.

CONCLUSIONS

Homogeneous leucite powders with the particle size of 3µm were prepared by ion-exchange of analcime. The reaction proceeded in a solution of KCl in hydrothermal conditions. 3 hours of hydrothermal treatment at 200°C in a 4M KCl solution were sufficient to transform analcime to leucite completely. The particle size and their distribution did not significantly change during the ion-exchange process.

Detailed investigation of the synthesis of analcime, i.e. of the effect of process parameters and starting compositions, made possible to control particle size, shape and structure of the reaction product. Results showed that long reaction time as well as higher temperature enhanced analcime crystallisation. Choice of source materials effected especially homogeneity and morphology of the product. Initial molarity of sodium hydroxide solution significantly effected both phase composition and particle size. It was proved that the particle size decreased with increasing molarity of the NaOH solution and water/silica ratio.

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PŘÍPRAVA LEUCITU S ŘÍZENOU VELIKOSTÍ ČÁSTIC

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Leucit ($KAlSi_2O_6$) je hlavní krystalickou fází ve většině živcových dentálních porcelánů používaných v zubním lékařství pro metalo-keramické náhrady. Přítomnost leucitu v porcelánové matrici zvyšuje hodnotu koeficientu teplotní roztažnosti výsledného kompozitního materiálu a umožňuje tak jeho spájení s kovovou výztuží. Leucitová keramika navíc oproti klasickému živcovému dentálnímu porcelánu vykazuje vyšší hodnoty lomové houževnatosti. Cílem našeho výzkumu je nahradit dosavadní technologii přípravy leucitové keramiky založenou na krystalizaci leucitu z taveniny novou technologií, která by umožnila reprodukovatelné řízení mikrostruktury výsledného leucitového kompozitu. V předkládané práci byla vyvinuta příprava leucitových prášků s řízenou velikostí částic.

Leucit byl získán iontovou výměnou analcimu ($NaAlSi_2O_6 \cdot H_2O$), strukturního analogu leucitu připraveného pro tento účel řízenou hydrotermální syntézou. Jsou zde shrnuty faktory ovlivňující průběh a výsledek hydrotermální syntézy meziproduktu- analcimu, především s ohledem na homogenitu a velikost částic připravených prášků. Následná iontová výměna byla rovněž vedena v hydrotermálních podmínkách, stupeň výměny byl určen XRD a XRF analýzami. Výsledky provedené studie ukazují, že hydrotermální syntézou analcimu (2 hodiny při 200°C) a následným 3 hod. hydrotermálním zahříváním produktu při teplotě 200°C v 4M roztoku KCl lze připravit homogenní leucitové prášky s velikostí částic 3 μm, které jsou vhodným prekurzorem pro přípravu dentálních kompozitních materiálů.