Z. Kristallogr. Suppl. **26** (2007) 531-536

X-ray phase analysis in leucite systems

J. Maixner[1*], A. Kloužková[2], M. Mrázová[3], M. Kohoutková[3]

[1]Central Laboratories, Institute of Chemical Technology, Prague, CZ,
[2]Department of Glass and Ceramics, Institute of Chemical Technology, Prague, CZ
[3]Laboratory of Inorganic Materials, Institute of Inorganic Chemistry of AS CR and Institute of Chemical Technology, Prague, CZ
[*] Contact author; e-mail: maixnerj@vscht.cz

Keywords: cubic leucite, phase transformation, X-ray powder diffraction, Rietveld analysis

Abstract. X-ray powder diffraction analysis was used to determine quantitatively the amount of cubic and tetragonal forms of hydrothermally prepared Cs ion-exchanged leucite. The X-ray powder patterns exhibit severe overlap of reflections, since both forms have very similar unit cell parameters. Therefore Rietveld analysis occurred to be the best method to achieve this aim. Furthermore the concentrations of Cs^+- ions present in both forms were elucidated from the refinement of mixed sites occupations and from the precise determination of the unit cell parameters. It was proved that the hydrothermally synthesised Cs - leucite is formed by spherolites having particle size of 2 μm and consisting of crystallites in tens of nm scale as the result of X-ray line broadening analysis.

Introduction

Leucite ($KAlSi_2O_6$) is the dominating crystalline phase in most feldspathic dental porcelains used for ceramic-fused-to-metal restorations [1]. It was found that 15 – 30 % leucite increased the thermal expansion coefficient of the base glass from 10.7 × 10-6 /°C to the 13-15 × 10-6 /°C range for porcelain bonding and also approximately two times the flexural strength of feldspathic porcelain [2, 3]. The mineral leucite can be incorporated into the dental porcelain either from the incongruent melting of feldspar or it can be added as a synthetic powder.

Leucite crystallises at high temperatures in the cubic form, with entries in ICSD [4] having space groups *Ia*-3 (n.206) or *Ia*-3*d* (n.230). On cooling below approximately 625°C, there is a phase transition to a tetragonal form, which has space group $I4_1/a$ (n.88). Conversion of cubic leucite into the tetragonal modification involves deformation of the sixfold rings, i.e. the channels distortion is accompanied by slight movements of the K^+ ions. The transformation is martensitic, that means anisotropic, athermal, with speed of sound diffusion in solids and exhibits temperature hysteresis [5]. It proceeds by a slipping and twinning mechanism, during which the atoms retain their neighbours and move over a distance that is smaller than their original mutual one. Martensitic temperature M_s is not constant, for example in the case of hydrothermally prepared leucite it is 550 °C [6]. For dental porcelains this transformation occurs between 400 – 600 °C. High amount of tetragonal leucite crystals may be the reason for developing large flaws within the glass matrix that would lead to a decrease of the mechanical properties. Potentially, Cs stabilized cubic leucite could be added to leucite porcelains to increase the crystalline content without increasing flaw size and frequency [2, 3]. However, it is first necessary to develop a suitable and reproducible technology of leucite preparation and partially stabilize its high temperature cubic modification. This can be achieved by the ion - exchange (K^+, Cs^+) of analcime ($NaAlSi_2O_6 \cdot H_2O$) as a precursor prepared by hydrothermal synthesis [7].

The aim of this study is the quantitative determination of the amount of cubic modification of Cs - leucite, the estimation of the Cs^+ - ions concentration present in both forms and the evaluation of crystallite size by profile analysis. Particle size and morphology analyses were completed by scanning electron microscopy (SEM).

Experimental

Synthesis of partially stabilized cubic leucite.

Preparation of leucite powders proceeded in two steps, both in hydrothermal conditions: 1) synthesis of analcime ($NaAlSi_2O_6 \cdot H_2O$) [7], and 2) preparation of Cs - leucite performed by ion exchange of analcime.

Analcime was synthesised in hydrothermal conditions at 200°C for 2h in a Teflon lined stainless steal autoclave. Starting sols were prepared from fine-ground amorphous silica powder (SiO_2, Polskie Odczynniki Chemiczne Gliwice, PL), sodium hydroxide solution (NaOH, Lachema, CZ) and aluminium powder (Al, Lachema, CZ). After this hydrothermal treatment, the content of the autoclave was washed with boiling distilled water, vacuum filtered and dried in an oven at 100°C.

Tetragonal K-leucite was prepared by ion exchange of analcime (Na^+ ions for K^+ ions) from 4M solution of KCl in autoclave at 200 °C for 4 hours [8].

Cs - leucites were prepared by dual ion exchange of analcime. The synthesis was performed in hydrothermal conditions at 200 °C. First ion exchange proceeded in 4M CsCl for 4h. For second ion exchange a 4M KCl solution was used. The reaction time was modified to obtain the desired amount of cubic form in the final product. After the hydrothermal treatment, the content of the autoclave was washed, vacuum filtered and dried at 100 °C.

X-ray fluorescence, powder diffraction and scanning electron microscopy analyses

An ARL 9400 XP sequential WD-XRF spectrometer was used to perform the XRF measurements. The powders to be analyzed were pressed into pellets about 5 mm thick and diameter of 40 mm without any binding agent and covered with 4 mm supporting polypropylene film. The time of measurement was about 15 min. The data were evaluated with the standardless software Uniquant 4.

Powder XRD data were collected at room temperature with an X'Pert PRO θ–θ powder diffractometer using CuK_α radiation ($\lambda = 1.5418$ Å, U = 40 kV, I = 30 mA) in parafocusing Bragg-Brentano geometry. Data were scanned with an ultrafast X'Celerator detector over the angular range 15 - 90°(2θ) with a step size of 0.0167°(2θ) and a counting time of 100s $step^{-1}$. Texture free samples were prepared by back-load technique thanks to the spherical particle morphology (Fig. 2). Data evaluation, including Rietveld refinement, was performed with the software package HighScore Plus [9].

The morphology and particle size analysis of the synthesised samples were determined using SEM (Philips XL 30 CP). The images were scanned at different magnifications (20 000x, 10 000x and 2500x) to demonstrate the homogeneity and particle size distribution in the whole sample and to show the morphology of the single grains.

Rietveld analysis

All structural parameters were refined with the Rietveld refinement procedure. The starting models for tetragonal (t - leucite) and cubic leucite (c - leucite) were taken from ICSD:

T - leucite (ICSD n.9826): Space group $I4_1/a$ (n.88) with cell edges – a = 13.090 Å and c = 13.750 Å. All atoms occupy the general positions 16 f – K^+ and Cs^+ at (0.3660, 0.3645, 0.1147) with 0.5 occupancy for both atoms; Al1, Si1 at (0.0579, 0.3964, 0.1666), Al2, Si2 at (0.1676, 0.6115, 0.1283), Al3, Si3 at (0.3924, 0.6418, 0.0860) with respective occupancies 0.32 and 0.68, and the framework oxygens O1 at (0.1318, 0.3131, 0.1100), O2 at (0.0921, 0.5107, 0.1303), O3 at (0.1453, 0.6798, 0.2275), O4 at (0.1333, 0.6841, 0.0354), O5 at (0.2900, 0.5772, 0.1205) and, finally, O6 at (0.4826, 0.6174, 0.1667).

C - leucite (ICSD n.78709): Space group Ia-3 (n.206) with a = 13.574 Å . K^+ and Cs^+ occupy the special position 16c (x,x,x; with x = 0.12508) both with 0.5 initial occupancy. All other atoms occupy general positions (48e) – Si at (0.1248, 0.6621, 0.5878), Al at (0.1248, 0.6621, 0.5878), O1 at (0.4670, 0.3836, 0.1452) and O2 at (0.1317, 0.7194, 0.1024).

The refinement procedure was divided into three steps:

1) All atomic positions, occupancies and atomic displacement parameters were kept fixed. Background was modelled by linear interpolation between background intensity points and Pearson VII function was used to describe individual line profiles. Scale factors, unit cell parameters, U and W line profile parameters for both phases and zero shift were refined.

2) K^+ and Cs^+ ions were constrained to share the same site coordinates, the same atomic displacement parameter and complementary occupancies. Their coordinates and occupancies were refined and the atomic displacement parameter was kept fixed. All corresponding Al and Si atoms in the framework were constrained to share the same site coordinates with one common atomic displacement parameter for all Al, Si atoms and complementary occupancies. Their coordinates were refined, but occupancies and atomic displacement parameter were kept fixed. The O atoms in the framework were not refined.

3) For size/strain analysis the Si standard (with no micro strain and no size broadening) was measured, refined and saved as size-strain standard in the HighScore Plus software. In this way the instrumental broadening parameters were available for further use in size/strain refinements of prepared leucite samples. Two methods supposing either only size broadening or size and strain broadening were applied. Both gave similar results for crystallite size, and negligible microstrain (0.2 - 0.5 %) for the second approach. Therefore line broadening in our samples is mainly due to the small size of the leucite crystallites (between 30 – 40 nm for c - leucite and 50 – 70 nm for t – leucite).

Results and discussion

Partially stabilised cubic leucites were prepared by dual ion exchange of the synthesised analcime. The reaction time of the second ion exchange was modified to obtain the desired amount of cubic form in the final product: sample B - 5h, C - 8h and D - 72h. Sample A representing tetragonal K – leucite was prepared by single ion exchange of analcime. Chemical and phase composition of the products prepared by tuning the above mentioned synthesis procedure are shown in Table 1.

Figure 1 shows the X-ray powder diffraction patterns for tetragonal K - leucite (A), for partially stabilised mixtures of t - and c - leucite (3.84 mol % Cs_2O - B and 5.22 mol% Cs_2O – C) and for fully stabilised c-leucite (9.52 mol% Cs_2O - D).

Table. 1 Chemical and phase composition of the products by XRF and XRD [weight %]

Sample	Na_2O	Al_2O_3	SiO_2	K_2O	Cs_2O	t - leuc.	c -leuc.	R_{wp} [%]
A	1.0 (6)	27.7(2)	50.6(3)	20.6(2)	0.00	100	0	5.26
B	1.1 (6)	25.1(2)	45.6(3)	14.6(1)	13.2(2)	54 (1)	46 (1)	7.15
C	1.1 (6)	24.2(2)	44.2(3)	12.7(1)	17.5(2)	38 (1)	62 (1)	4.63
D	1.1 (1)	23.0(2)	40.2(3)	6.1 (1)	25.4(2)	0	100	7.31

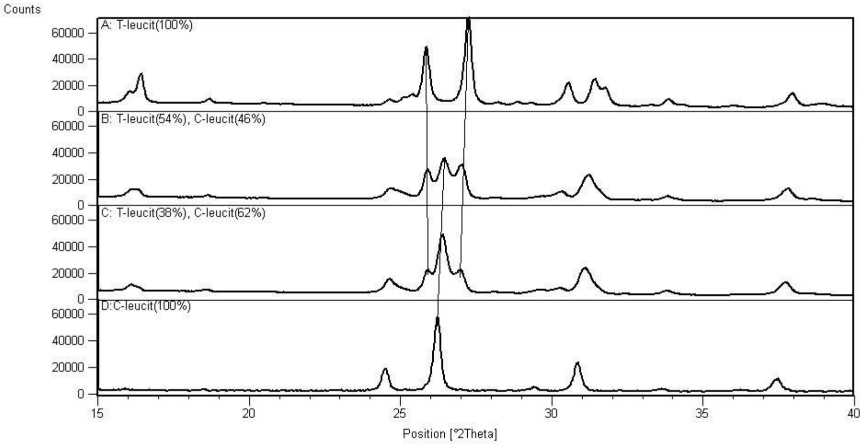

Figure 1. X-ray powder diffraction patterns of the products of ion-exchange from analcime: A t- leucite (100 %), B t - leucite (54 %) and c – leucite (46 %), C t- leucite (38 %) and c- leucite(62 %) , D c- leucite (100 %).

Prepared samples were in form of homogenous powders with uniform particle size ~ 2 μm and shape (Fig. 2). SEM images revealed that these particles are spherolites composed by much smaller particles. As confirmed by X-ray line profile analysis, the particle size is in the interval 30 – 70 nm.

Table 2 includes the unit cell parameters and the occupancy values of four selected samples marked A, B, C, D and the corresponding data taken from ICDD [10] for t-K-leucite (PDF card 38-1423), t-Cs-leucite (PDF card 85-1628), high-temperature c-K-leucite (PDF card 76-2298) and c-pollucite (PDF card 88-0055).

Table. 2 Lattice parameters and occupancies for (K^+,Cs^+) mixed sites.

Sample	a_t [Å]	c_t [Å]	a_c [Å]	t- K_{occ}	t- Cs_{occ}	c- K_{occ}	c- Cs_{occ}
A-K-leuc.	13.062(1)	13.744(1)	-	1	0	-	-
B-Cs-leuc.	13.196(2)	13.749(3)	13.477(2)	0.77(3)	0.23(3)	0.77(3)	0.23(3)
C-Cs-leuc.	13.218(1)	13.751(3)	13.496(2)	0.73(3)	0.27(3)	0.75(3)	0.25(3)
D-Cs-leuc.	-	-	13.570(1)	-	-	0.56(3)	0.44(3)
t-K-leuc.	13.06	13.75	-	1	0	-	-
t-Cs-leuc.	13.65	13.72	-	0	1	-	-
c-K-leuc.	-	-	13.46	-	-	1	0
c-polluc.	-	-	13.66	-	-	0	1

The respective radii of K^+ and Cs^+ are 1.33 and 1.65 Å. From the ICDD data it is seen that the a_t parameter of t - leucite is very sensitive to K^+, Cs^+ ion exchange, while c_t remains almost unchanged. Also, the a_c parameter of c - leucite shows significant but smaller change than a_t of t - leucite. The degree of ion exchange estimated from the variations of the unit cell parameters using the ideal Vegard's law and obtained as occupancy factors for the measured samples A, B, C, D are in good agreement and agree with the XRF analysis. The unit cell parameters and the occupancies of the K^+, Cs^+ site clearly demonstrate the partial K^+, Cs^+ ion exchange and the fact that K^+, Cs^+ ion exchange can partially or fully stabilize high-temperature c - leucite at room temperature.

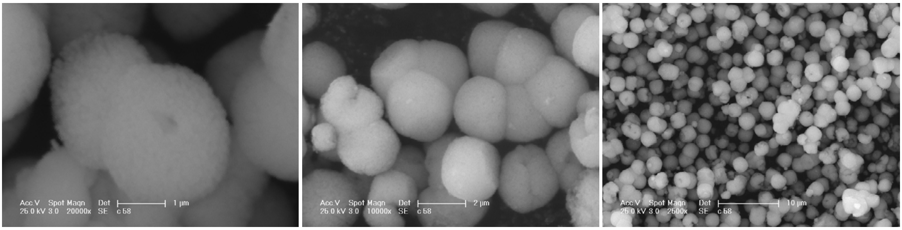

Figure 2. SEM images of D -Cs -leucite product (magnification of 20 000x, 10 000x, 2500x)

Concluding remarks

XRPD analysis showed that partially stabilized Cs - leucite powders prepared by dual ion exchange of analcime correspond to crystalline Cs - leucite in both tetragonal and cubic forms.

XRF analysis was used to estimate the degree of ion - exchanges (K^+, Cs^+) in the samples – it cannot explain ion - exchanges (K^+, Cs^+) in separate phases. The method is fast and reliable in the stage of tuning the synthesis procedure.

SEM was used to study the grain morphology and size distribution. The final products are spherolites about 2 µm large consisting of particles of tens nm scale. This was supported by XRPD giving 50 nm as average crystallite size.

Finally, Rietveld quantitative analysis was used to determine the phase content of t - leucite and c - leucite, as well as the degree of (K^+, Cs^+) exchanged in t - leucite and c -leucite by refining the occupancies and measuring the unit cell parameters and their comparison with the literature data.

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Acknowledgements. The authors are very grateful to S. Bakardjieva for her kind assistance with SEM. This work was supported by Grant MSM 6046137302 and was a part of the project No 2A-1TP1/063, "New glass and ceramic materials and advanced concepts of their preparation and manufacturing", realized under financial support of the Ministry of industry and trade.