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Tailoring of $K_{0.8}Al_{0.7}Fe_{0.15}Si_{2.25}O_6$ Leucite Based Dental Ceramic Material

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THIS PAPER IS DEDICATED TO DR. SVETOZAR MUSIĆ ON THE OCCASION OF HIS 70TH BIRTHDAY

Abstract: Potassium based ceramic materials composed from leucite in which 5 % of Al is exchanged with Fe and 4 % of hematite was synthesized by mechanochemical homogenization and annealing of K_2O-SiO_2-Al_2O_3-Fe_2O_3 mixtures. Synthesized material was characterized by X-ray Powder Diffraction (XRPD) and Scanning Electron Microscopy coupled with Energy Dispersive X-ray spectroscopy (SEM/EDX). The two methods are in good agreement in regard to the specimen chemical composition suggesting that a leucite chemical formula is $K_{0.8}Al_{0.7}Fe_{0.15}Si_{2.25}O_6$. Rietveld structure refinement results reveal that about 20 % of vacancies exist in the position of K atoms.

Keywords: leucite, dental ceramic material, structure, synthesis, ball milling.

INTRODUCTION

AN OPTIMIZATION of a material properties *i.e.* material tailoring for industrial applications is an imperative for successful applications. Detailed knowledge of a material structure is one step ahead to the final solution. Alkaline metal based ceramic materials are widely used in industry as: electroceramic components,[1] matrixes for fluorescent screens,[2,3] thermo-refractory materials,[4,5] electromagnetic windows,[1,5] dental ceramics[6] *etc*. So far, investigations of many alkaline ceramic materials, although started from the beginning of the last century, reveal unexplained properties and unsolved parts of a material structure.

Leucite, $KAlSi_2O_6$ is common mineral in some volcanic rocks in which it crystallizes with a cubic crystal structure at high temperature (ca. 900 °C). Upon cooling to 700–600 °C, it transforms into a tetragonal modification which is stable at room temperature, and forms characteristic polysynthetic twin lamellae. The transformation is reversible.[7] Structurally it belongs to feldspathoids - tectosilicates characterized with Al-Si framework structure. Voids within framework are partly filled with K atoms, Figure 1.

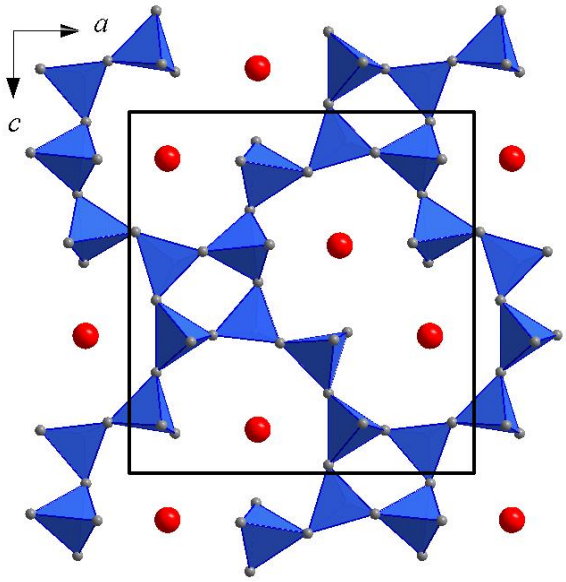

Figure 1. Polyhedral representation of one pseudolayer in leucite $KAlSi_2O_6$ structure. Blue tetrahedra represent SiO_4 and AlO_4 units while red spheres represent K atoms.

Leucite crystalizes as euhedral pseudocubic crystals in tetragonal $I4_1/a$ space group. Characteristic unit cell parameters are: a = 13.056 Å, c = 13.751 Å ($a : c$ = 1 : 1.053). Inside the unit cell there are 16 asymmetric units (Z = 16). Common impurities in natural leucites are: Ti, Fe, Mg, Ca, Ba, Na, Rb, and Cs. Impurities concentrations are rather small in natural leucites. However, leucite structures exist even after complete exchange of Al with Fe.[7]

The optical properties of the leucite glass-ceramic make it one of the most appropriate materials for the fabrication of dental restorations. The leucite has almost the same refractive index as the glass. Therefore, the translucency is never hindered by the crystallization of the leucite in the glass. Leucite based glass-ceramics has ability to match the colour of the natural tooth. Addition of other chemical elements, like iron, could slightly change the colour of the dental ceramic to desirable hue. Another advantage of the leucite based glass-ceramic materials in dental industry is that due to low thermal expansion coefficient its stability during fusion is remarkable.[6]

In order to tailor potassium based ceramic materials with good properties for dental industry we have synthesized them by mechanochemical homogenization and annealing of K_2O-SiO_2-Al_2O_3-Fe_2O_3 mixtures. Our main goal was to synthesize leucite in which 10 % of Al is exchanged with Fe and to characterize it by X-ray Powder Diffraction (XRPD) and Scanning Electron Microscopy coupled with Energy Dispersive X-ray spectroscopy (SEM/EDX).

Table 1. Experimental details for XRPD data collection. Estimated standard deviations are in parenthesis.

Crystal data	
Chemical formula	$K_{0.8}Al_{0.7}Fe_{0.15}Si_{2.25}O_6$
M_r	217.74
Crystal system, space group	Tetragonal, $I4_1/a$
Temperature / K	295
a, c / Å	13.1334(3), 13.7343(4)
V / Å^3	2368.99(9)
Z	16
Radiation type	Cu Kα_1, Cu Kα_2 radiation, λ = 1.540562, 1.544390 Å
Specimen shape	Irregular
Data collection	
Diffractometer	Brucker D8 Advance
Specimen mounting	packed powder pellet
Data collection mode	Reflection
Scan method	Step
2θ values	$2\theta_{min}$ = 4.000 °, $2\theta_{max}$ = 90.010 °, $2\theta_{step}$ = 0.030 °
Refinement	
Profile function	TCH pseudo-Voigt
Background function	linear extrapolation between points; 15 points were determined by visual estimation and refined
R factors and goodness of fit	R_p = 11.00, R_{wp} = 14.10, R_{exp} = 9.64, R_{Bragg} = 6.11, χ^2 = 2.15
No. of data points	2868
No. of parameters	45
No. of restraints	10

Computing details: Data collection: D8 Software;[11] program used to refine structure: FULLPROF;[8] molecular graphics: *DIAMOND*.[12]

EXPERIMENTAL DETAILS

Sample Preparation

The starting compounds were SiO_2, Al_2O_3, K_2CO_3 and Fe_2O_3. They were mixed in appropriate molar ratio according to the stoichiometric formula $KAl_{0.9}Fe_{0.1}Si_2O_6$. Mechanochemical treatment was performed during one hour in a planetary ball mill (Fritsch Pulverisette 5) equipped with tungsten carbide bowls (250 ml in volume) and balls (10 mm in diameter). The mass of the powder was 10 g and the balls-to-powder mass ratio was 20 : 1. The milling was done in air atmosphere without any additives. The angular velocity of the supporting disc and vial was 32.2 and 40.3 rad s^{-1}, respectively. The intensity of milling corresponded to an acceleration of about 10 times the gravitational acceleration. The milling vessels were opened for removing of the CO_2 which evaporate during milling. After milling the obtained powders were pressed in pellets under pressure of 50 MPa and sintered at temperature of 1100 °C for 24 hours. Than specimens were milled again but not opened for removing of the CO_2. At the end specimens were pressed in pellets under pressure of 50 MPa and sintered at 1100 °C for 24 hours.

Experimental Techniques and Methods

For the collection of the XRPD data a D8 Advance (Bruker, Germany) X-ray powder diffractometer was used. The diffractometer was equipped with a Cu-tube and a Xe-filed proportional counter. The divergence and receiving slits were 1 ° and 0.1 mm, respectively. The scanning range was 4–90 ° in 2θ, with a step of 0.03 ° and a scanning time of 22 s per step. The determination of the structural parameters of the $K_{0.8}Al_{0.7}Fe_{0.15}Si_{2.25}O_6$ was carried out using the Rietveld method implemented in the FullProf program package.[8]

SEM images were recorded using a MIRA3 FE-SEM microscope (TESCAN, Czech Republic) equipped with an EDX detector (Oxford Instruments, UK).

Table 2. Fractional atomic coordinates *x*, *y* and *z*, isotropic displacement parameters U_{iso} / Å^2 and site occupation parameters Occ. for $K_{0.8}Al_{0.7}Fe_{0.15}Si_{2.25}O_6$. Estimated standard deviations are in parenthesis.

Atom	*x*	*y*	*z*	U_{iso}	Occ.
T_1 = Si,Al	0.0569(3)	0.39418(7)	0.1629(4)	2.3(2)	0.98(3)
T_1 = Fe	0.0569(3)	0.39418(7)	0.1629(4)	2.3(2)	0.02(3)
T_2 = Si,Al	0.16869(6)	0.61073(6)	0.12622(6)	2.3(2)	0.97(3)
T_2 = Fe	0.16869(6)	0.61073(6)	0.12622(6)	2.3(2)	0.03(3)
T_3 = Si,Al	0.39087(5)	0.6410(1)	0.09021(9)	2.3(2)	0.97(2)
T_3 = Fe	0.39087(5)	0.6410(1)	0.09021(9)	2.3(2)	0.03(2)
O_1	0.1324(1)	0.3128(1)	0.1101(2)	2.3(2)	1.0
O_2	0.0937(7)	0.5087(6)	0.132(1)	2.3(2)	1.0
O_3	0.1506(4)	0.673(1)	0.2281(9)	2.3(2)	1.0
O_4	0.127(1)	0.6723(8)	0.0288(9)	2.3(2)	1.0
O_5	0.2870(3)	0.5724(3)	0.113(2)	2.3(2)	1.0
O_6	0.4827(1)	0.6171(1)	0.1670(1)	2.3(2)	1.0
K	0.372(1)	0.3604(9)	0.120(1)	2.3(2)	0.78(1)

RESULTS AND DISCUSSION

Collected XRPD pattern corresponds to reference leucite $KAlSi_2O_6$.[9] Few low intensity peaks in the pattern belong to hematite.[10] Quantitative phase analysis indicated that only 4(1) % of hematite is in the specimen. An amorphous phase could not be recognized by XPRD analysis. Therefore, it is reasonable to assume that part of Fe is incorporated into leucite structure. Obtained unit cell parameters for leucite (a = 13.1334(3) Å and c = 13.7343(4) Å; $a : c$ = 1 : 1.046) are different from the reference (a = 13.09(1) Å and c = 13.75(1) Å; $a : c$ = 1 : 1.050) indicating that Fe partly exchanges Al during synthesis procedure. Vacancy creation during mechanochemial treatment is possible. That could be another reason for the unit cell difference compared to the reference material. Moreover, the Rietvled refinement results (Figure 2, Tables 1–3) show that about 5 % of Al is exchanged with Fe and that ca. 20 % of vacancies exist in the position of K atoms. Chemical formula of synthesized compound recalculated from site occupation parameter values is $K_{0.8}Al_{0.7}Fe_{0.15}Si_{2.25}O_6$, Table 2. However, estimated standard deviations of site occupation parameters are relatively high suggesting that they are not reliable for recalculation of leucite chemical formula. Ionic radii for Si^{4+}, Al^{3+} and Fe^{3+} are 0.26, 0.39, and 0.49 Å respectively. Therefore, interatomic distance values are more reliable than site occupation parameters indicating that T_1 atomic site is mostly occupied with Si while T_2 and T_3 are occupied with Si, Al and Fe. Atomic site T_3 contains more Al and Fe than other two *T* sites, as given in Table 3. Interatomic distances, as well as overall temperature parameters, are in good agreement with literature data.[9] Obtained accuracy parameter values are reasonable, indicating reliable refinement, as shown in Table 1.

Morphology of as-prepared sample was determined by SEM analyses. Leucite, $K_{0.8}Al_{0.7}Fe_{0.15}Si_{2.25}O_6$, occurs in microspherical forms, approximately 0.5–1 μm in size, Figure 3a. Semi-quantitative chemical composition of the synthesized compound calculated from the EDX results, Figures 3b and 3c, $K_{0.8}Al_{0.7}Fe_{0.15}Si_{2.25}O_6$ is in good agreement with XRPD results. Moreover, elemental mapping shows that all constituent elements are uniformly distributed over the as-prepared sample confirming its homogeneity.

Table 3. Selected interatomic distances (expressed in Å) for $K_{0.8}Al_{0.7}Fe_{0.15}Si_{2.25}O_6$. Estimated standard deviations are in parenthesis.

connection	interatomic distance	connection	interatomic distance
T_1-O_1	1.628(4)	K- O_1	3.22(1)
T_1-O_1	1.611(4)	K- O_2	3.07(1)
T_1-O_2	1.637(9)	K- O_3	3.06(2)
T_1-O_4	1.63(1)	K- O_4	3.04(2)
<T_1-O>	1.626	K- O_5	3.00(1)
T_2-O_2	1.665(8)	K- O_6	3.00(2)
T_2-O_3	1.64(1)	<K- O>	3.065
T_2-O_4	1.66(1)		
T_2-O_5	1.643(5)		
<T_2-O>	1.652		
T_3-O_3	1.69(1)		
T_3-O_5	1.665(6)		
T_3-O_6	1.633(2)		
T_3-O_6	1.691(3)		
<T_3-O>	1.670		

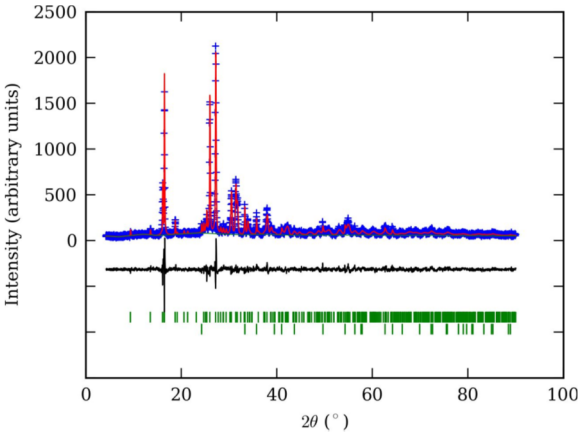

Figure 2. Final Rietvled plot for $K_{0.8}Al_{0.7}Fe_{0.15}Si_{2.25}O_6$ leucite based ceramic material. Blue crosses denote observed step intensities; the red line represents the corresponding calculated values. The difference curve between observed and calculated values is given at the bottom (black line). Vertical green bars represent diffraction line positions; upper bars correspond to $K_{0.8}Al_{0.7}Fe_{0.15}Si_{2.25}O_6$ leucite, lower to hematite.

All obtained results, which are in good agreement, suggest that synthesis was quite successful. In the future, a synthesis should be slightly changed in order to obtain pure leucite enriched with Fe, *i.e.* without hematite.

CONCLUSIONS

Potassium based ceramic material with promising properties for dental industry was tailored by mechanochemical homogenization and annealing of K_2O-SiO_2-Al_2O_3-Fe_2O_3 mixtures. Chemical and mineral compositions, as well as crystal structures, were investigated by X-ray Powder Diffraction (XRPD) and Scanning Electron Microscopy coupled with Energy Dispersive X-ray spectroscopy (SEM/EDX). Obtained results, which are in good agreement, suggest that synthesis was quite successful. In the future, a synthesis should be slightly changed in order to obtain pure leucite enriched with Fe, *i.e.* specimen without hematite.

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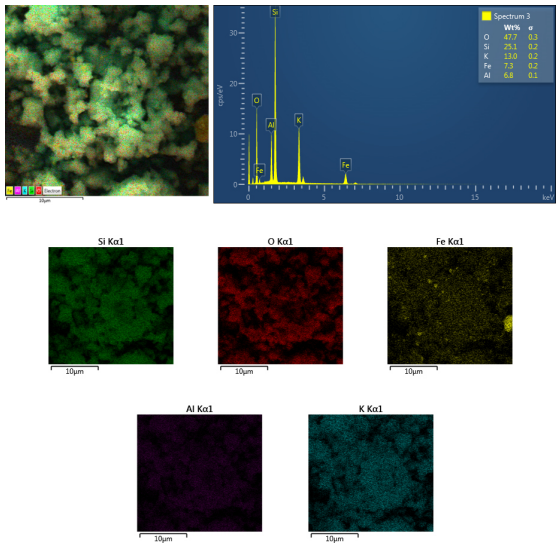

Figure 3. Scanning electron micrograph (a), EDX analysis (b) and elemental mapping (c) for $K_{0.8}Al_{0.7}Fe_{0.15}Si_{2.25}O_6$ leucite based ceramic material.

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