Tailoring of $\text{K}_{0.8}\text{Al}_{0.7}\text{Fe}_{0.15}\text{Si}_{2.25}\text{O}_6$ Leucite Based Dental Ceramic Material

Aleksandar Kremenović,1,* Martin Fabián,2 Predrag Vulić,1 Čedomir Jovalekić,3 Jarošlav Briančin2

1 Laboratory of Crystallography, Faculty of Mining and Geology, University of Belgrade, Đušina 7, 11001 Belgrade, Serbia
2 Institute of Geotechnics, Slovak Academy of Sciences, Watsonova 45, 04001 Košice, Slovakia
3 Institute for Multidisciplinary Studies, University of Belgrade, Kneza Vladišava 1, 11001 Belgrade, Serbia
* Corresponding author’s e-mail address: akremenovic@rgf.bg.ac.rs

RECEIVED: March 17, 2016 * REVISED: March 23, 2016 * ACCEPTED: March 23, 2016

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 $\text{K}_2\text{O}-\text{SiO}_2-\text{Al}_2\text{O}_3-\text{Fe}_2\text{O}_3$ 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 $\text{K}_{0.8}\text{Al}_{0.7}\text{Fe}_{0.15}\text{Si}_{2.25}\text{O}_6$. 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

A N 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, $\text{KAlSi}_2\text{O}_6$ 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 polycrystalline 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 $\text{KAlSi}_2\text{O}_6$ structure. Blue tetrahedra represent $\text{SiO}_4$ and $\text{AlO}_4$ units while red spheres represent K atoms.
Leucite crystallizes as euheural pseudocubic crystals in tetragonal 4/6 space group. Characteristic unit cell parameters are: \(a = 13.056 \, \text{Å}, \quad c = 13.751 \, \text{Å} \) (\(a : c = 1 : 1.053\)). Inside the unit cell there are 16 asymmetric units (\(Z = 16\)). Common impurities in natural leucites are: Ti, Fe, Mg, Ca, Ba, Na, Nb, 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).

**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 \(KAl_2Fe_2O_3Si_2O_6\). 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-filled proportional counter. The divergence and receiving slits were 1 ° and 0.1 mm, respectively. The scanning range was 4–90 ° in 2\(\theta\), with a step of 0.03 ° and a scanning time of 22 s per step. The determination of the structural parameters of the \(K_{0.8}Al_{2.2}Fe_{0.2}Si_{2.2}O_{10.8}\) 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).

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

| Crystal data |  |
|--------------|---|
| Chemical formula | \(K_{0.8}Al_{2.2}Fe_{0.2}Si_{2.2}O_{10.8}\) |
| \(M_r\) | 217.74 |
| Crystal system, space group | Tetragonal, 4/6 |
| Temperature / K | 295 |
| \(a, c / \text{Å}\) | 13.1334(3), 13.7343(4) |
| \(V / \text{Å}^3\) | 2368.99(9) |
| \(Z\) | 16 |
| Radiation type | Cu K\(\alpha\), Cu K\(\beta\) radiation, \(\lambda = 1.540562, 1.544390 \, \text{Å}\) |
| Specimen shape | Irregular |

**Refinement**

| Difference | TCH pseudo-Voigt |
| Factors and goodness of fit | \(R_p = 11.00, R_{wp} = 14.10, R_{exp} = 9.64, R_{fact} = 6.11, \chi^2 = 2.15\) |
| No. of data points | 2868 |
| No. of parameters | 45 |
| No. of restraints | 10 |

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Croat. Chem. Acta 2016, 89(1), 101–104 DOI: 10.5562/cca2860
Table 2. Fractional atomic coordinates x, y and z, isotropic displacement parameters $U_{iso}$ / Å$^2$ and site occupation parameters Occ. for $K_{1.5}Al_{2.5}Fe_{0.5}Si_{1.5}O_{8}$. Estimated standard deviations are in parenthesis.

| Atom   | x      | y      | z      | $U_{iso}$ | Occ.  |
|--------|--------|--------|--------|-----------|-------|
| $T_1$  | 0.0569(3) | 0.39418(7) | 0.1629(4) | 2.3(2)    | 0.98(3) |
| $T_1$  | 0.0569(3) | 0.39418(7) | 0.1629(4) | 2.3(2)    | 0.98(3) |
| $T_2$  | 0.1669(6) | 0.61073(6) | 0.12622(6) | 2.3(2)    | 0.97(3) |
| $T_2$  | 0.1669(6) | 0.61073(6) | 0.12622(6) | 2.3(2)    | 0.97(3) |
| $T_3$  | 0.39087(5) | 0.6410(1) | 0.09021(9) | 2.3(2)    | 0.97(2) |
| $T_3$  | 0.39087(5) | 0.6410(1) | 0.09021(9) | 2.3(2)    | 0.97(2) |
| O      | 0.1324(1) | 0.3128(1) | 0.1101(2) | 2.3(2)    | 1.0     |
| O      | 0.0937(7) | 0.5087(6) | 0.132(1)  | 2.3(2)    | 1.0     |
| O      | 0.1506(4) | 0.673(1)  | 0.2281(9) | 2.3(2)    | 1.0     |
| O      | 0.127(1)  | 0.6723(8) | 0.2088(9) | 2.3(2)    | 1.0     |
| O      | 0.2870(3) | 0.5724(3) | 0.113(2)  | 2.3(2)    | 1.0     |
| O      | 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 $KAlSi_2O_8$. Few low intensity peaks in the pattern belong to hematite. Quantitative phase analysis indicated that only 4(1)% of hematite is in the specimen. An amorphous phase could not be recognized by XRPD 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 mechanochemical treatment is possible. That could be another reason for the unit cell difference compared to the reference material. Moreover, the Rietveld refinement results (Figure 2, Tables 1–3) show that about 5% of Al is exchanged with Fe and that 20% of vacancies exist in the position of K atoms. Chemical formula of synthesized compound recalculated from site occupation parameter values is $K_{0.8}Al_{2.5}Fe_{0.5}Si_{1.5}O_{8}$. Table 2. However, estimated standard deviations of site occupation parameters are relatively high suggesting that they are not reliable for calculation 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. 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, $K_{0.8}Al_{2.5}Fe_{0.5}Si_{1.5}O_{8}$ 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, $K_{0.8}Al_{2.5}Fe_{0.5}Si_{1.5}O_{8}$ 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 $K_{0.8}Al_{2.5}Fe_{0.5}Si_{1.5}O_{8}$. 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$_1$    | 3.07(1)              |
| $T_1-O_2$  | 1.637(9)             | K-O$_1$    | 3.06(2)              |
| $T_1-O_3$  | 1.63(1)              | K-O$_1$    | 3.04(2)              |
| $<T_1-O>$  | 1.626                | K-O$_1$    | 3.00(1)              |
| $T_2-O_3$  | 1.665(8)             | K-O$_3$    | 3.00(2)              |
| $T_3-O_3$  | 1.64(1)              | <K-O>      | 3.065                |
| $T_3-O_3$  | 1.61(1)              |            |                      |
| $T_3-O_3$  | 1.643(5)             |            |                      |
| $T_3-O_3$  | 1.652                |            |                      |
| $T_3-O_3$  | 1.69(1)              |            |                      |
| $T_3-O_3$  | 1.665(6)             |            |                      |
| $T_3-O_3$  | 1.633(2)             |            |                      |
| $T_3-O_3$  | 1.691(3)             |            |                      |
| $<T_3-O>$  | 1.670                |            |                      |
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.

Acknowledgment. The Serbian Ministry of Science has financially supported this work through grant Nos. 176016, 45015. The Swiss National Science Foundation has financially supported this work under contract No. SCOPES IZ73Z0_127961. M.F. and J.B. thankVEGA (2/0097/13) and APVV (14-0103) for support of their work.

REFERENCES

[1] I. G. Talmy, D. A. Haught, E. J. Wuchina, Proceedings of Sixth International SAMPE Electronics Conference, USA, 1992, 687.
[2] W. B. Im, Y. Kim, D. Y. Yeon, Chem. Mater. 2006, 18, 1190.
[3] A. Kremenović, Ph. Colomban, B. Piriou, D. Massiot, P. Florian, J. Phys. Chem. Solids 2003, 64, 2253.
[4] A. Kremenović, P. Norby, R. Dimitrijević, V. Dondur Phase Transitions 1999, 68, 587.
[5] A. Kremenović, P. Norby, R. Dimitrijević, V. Dondur Phase Transitions 2004, 77, 955.
[6] E. El-Meliegy, R. van North, Glasses and Glass Ceramics for Medical Applications, Springer, London, 2012, p.p. 167–192.
[7] R. A. Lange, I. S. E. Carmichael, J. F. Stebbins, Am. Mineral. 1986, 71, 937.
[8] J. Rodriguez-Carvajal, FULLPROF, Abstracts of the Satellite Meeting on Powder Diffraction of the XVth Congress of the IUCr, Toulouse, France, 1990, p. 127.
[9] F. Mazzi, E. Galt, G. Gottardi, Am. Mineral. 1976, 61, 108.
[10] R. L. Blake, R. E. Hessevick, T. Zoltai, L. W. Finger, Am. Mineral. 1966, 51, 123.
[11] Bruker D8 Software, Bruker AXS Inc., Madison, Wisconsin, USA, 2005.
[12] K. Brandenburg, H. Putz, DIAMOND, Crystal Impact GbR, Bonn, Germany, 2005.