

THE DIELECTRIC PROPERTIES OF PLAGIOCLASE FELDSPARS

DIELEKTRIČNE LASTNOSTI PLAGIOKLAZNIH FELDSPAROV

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The effect of Na^+ substitution by Ca^{2+} on the octahedral site, and the simultaneous substitution of Al^{3+} for Si^{4+} on the tetrahedral site, in a plagioclase feldspar $\text{Na}_x\text{Ca}_{1-x}\text{Al}_{2-x}\text{Si}_{2+x}\text{O}_8$ solid solution on the sintering characteristics, crystal structure and dielectric properties was studied. The structural investigations showed that the end-members, albite $\text{NaAlSi}_3\text{O}_8$ ($x = 1$) and anorthite $\text{NaAl}_2\text{Si}_2\text{O}_8$ ($x = 0$), started to form at 800°C and 1200°C , respectively. The temperature of the plagioclase-phase formation was found to decrease with Na concentration. The sintering temperatures showed a similar trend and were about 200°C higher. The dielectric measurements in the radio-frequency region revealed that the compositions with Na ($x \geq 0.8$) exhibit increased conductivity, which is reflected in higher dielectric losses. Furthermore, Na-containing feldspars showed lower Q_{xf} (quality factor x frequency) values and permittivity in the microwave region compared to the anorthite, which has a $Q \times f$ of 19300 and a permittivity of 7.2 (measured at 9.9 GHz).

Keywords: low-temperature cofired ceramic (LTCC) technology, plagioclase feldspars, anorthite, albite, low-permittivity substrate material

Proučevali smo vpliv zamenjave Na^+ s Ca^{2+} na oktaedrskem mestu in istočasne substitucije Al^{3+} s Si^{4+} na tetraedrskem mestu na karakteristiko sintranja, kristalno strukturo in dielektrične lastnosti trdnih raztopin $\text{Na}_x\text{Ca}_{1-x}\text{Al}_{2-x}\text{Si}_{2+x}\text{O}_8$ ($0 \leq x \leq 1$) plagioklaznih feldsparov. Strukturne raziskave so pokazale, da se albít ($x = 1$) in anortit ($x = 0$) pričneta tvoriti pri 800°C oz. 1200°C . Temperatura tvorbe plagioklazne faze se niža z vsebnostjo natrija. Temperature sintranja kažejo podobno tendenco in so okrog 200°C višje. Dielektrične meritve plagioklaznih trdnih raztopin z $x \geq 0.8$ v radio frekvenčnem območju so pokazale povečano prevodnost, kar se izraža kot višje dielektrične izgube. Trdne raztopine kažejo manjši vrednosti $Q \times f$ in dielektričnosti v mikrovalovnem frekvenčnem območju v primerjavi z anortitom, ki ima $Q \times f$ 19300 in dielektričnost 7,2, izmerjeno pri 9,9 GHz.

Ključne besede: tehnologija nizkosinterabilne-sočasno-sintrane keramike, plagioklazni glinenci, anortit, albít, nizkodielektrični substratni materiali

1 INTRODUCTION

Current developments in microwave circuits are oriented towards the miniaturization and integration of passive components in 3D modules using low-temperature cofired ceramic (LTCC) technology. There is a growing need in LTCC technology for low-temperature-sinterable-substrate materials with even higher Q values and a temperature-stable permittivity of less than 12. In recent years many studies on developing LTCC substrates have dealt with ceramics based on anorthite ($\text{CaAl}_2\text{Si}_2\text{O}_8$)^{1,2}, cordierite ($\text{MgAl}_2\text{Si}_{2.5}\text{O}_9$)³ and anorthite-cordierite^{4,5,6} prepared from either finely ground minerals (kaolinite, dolomite, calcite)^{1,4,6} or recrystallized from glass powder². In spite of controlling the particle size of the minerals used the complete crystallization of the anorthite phase has never been achieved below 1200°C ¹. However, C.L. Lo et al.² did manage to crystallize anorthite with the help of a TiO_2 nucleating agent at 950°C by recrystallizing glass powders with a median particle size of $0.4\text{ }\mu\text{m}$. The glass powders in this study were prepared by ball-milling the ground powders, which were obtained by quenching the melt of oxides with the stoichiometric composition of anorthite². Both methods of synthesis, from minerals

and via recrystallization, led to ceramics with some amount of glassy phase, which increases the dielectric losses. Dense, glass-free ceramic anorthite would be expected to have lower dielectric losses.

Based on its structure, anorthite belongs to the feldspars, which are the most abundant minerals in the earth's crust. The feldspar crystal structure is composed of a three-dimensional framework of corner-shared SiO_4 tetrahedra with each Si^{4+} ion being surrounded by four oxygen ions and each oxygen ion shared between two Si^{4+} ⁷. Si^{4+} is frequently substituted by Al^{3+} , and the charge balance is maintained by the addition of an interstitial alkali metal or alkaline-earth ions. In plagioclase feldspars with the general formula $\text{Na}_x\text{Ca}_{1-x}\text{Al}_{2-x}\text{Si}_{2+x}\text{O}_8$ ($0 \leq x \leq 1$) Na^+ is replaced by Ca^{2+} on the octahedral sites and the charge is compensated by a simultaneous substitution of Al^{3+} for Si^{4+} on the tetrahedral sites.

Due to the structural similarity between anorthite ($x = 0$) and albite ($\text{NaAlSi}_3\text{O}_8$, $x = 1$) the dielectric properties of albite and the plagioclase solid solutions seem to be worth investigating. Based on the lower melting point of the albite (1118°C)⁸ compared to the anorthite (1553°C)⁸, the sintering temperatures of the albite and

the plagioclase solid solutions are expected to be closer to the LTCC requirements. In this study we have prepared glass-free feldspars and characterized their dielectric properties, and in order to reach the low sintering temperatures required for LTCC technology the plagioclase family was investigated as well.

2 EXPERIMENTAL PROCEDURE

The $\text{Na}_x\text{Ca}_{1-x}\text{Al}_{2-x}\text{Si}_{2+x}\text{O}_8$ ($0 \leq x \leq 1$) solid solutions were synthesised using the solid-state reaction technique. Stoichiometric mixtures of reagent-grade oxides (Al_2O_3 , 99.99%, alfa Aesar, SiO_2 , 99.9%, Alfa Aesar, Na_2CO_3 , 99.5% Alfa Aesar and CaCO_3 , 99.99% Alfa Aesar) were homogenized and pre-reacted under subsolidus conditions for 10 h. The pre-reaction and sintering temperatures depended on the composition and varied from 600 °C to 1300 °C and from 1050 °C to 1400 °C, respectively. Prior to sintering the pre-reacted powders were ball-milled in ethanol with yttrium-doped zirconium-oxide balls.

The x-ray powder-diffraction (XRD) studies were performed with a Bruker AXS D4 Endeavor diffractometer using $\text{Cu K}\alpha$ radiation. XRD data were collected from $10^\circ < 2\theta < 70^\circ$ with a step of 0.04 or 0.02, a counting time of 1 s or 4 s, and a variable V20 slit.

The radio-frequency (RF) dielectric measurements were performed at frequencies (f) from 1 kHz to 1 MHz on silver-plated disk capacitors using a high-precision LCR meter (Agilent 4284 A). The temperature dependence of the dielectric properties was measured from -80 °C to 150 °C by placing the samples in an environmental chamber (Delta Design, Delta 9039) and monitoring the temperature with a copper-constantan (T-type) thermocouple. The microwave (MW) dielectric properties were characterized using the closed air-cavity method with a network analyzer (HP 8719C). Permittivity and quality factor (Q) values were calculated at the resonant conditions (TE_{018} mode) from the S_{11} -reflection coefficient as proposed by Kajfež et al.⁹. To determine the temperature dependence of resonant frequency the test cavities were inserted into a temperature-controlled chamber. The dielectric characteristics of the samples were analyzed in the temperature range from 20 °C to 60 °C.

3 RESULTS AND DISCUSSION

3.1 Synthesis of feldspar ceramics

In the pre-reacted sample with the stoichiometry of albite that was fired at 700 °C various crystal phases such as SiO_2 , Al_2O_3 and $\text{Na}_2\text{Si}_2\text{O}_5$ were present. An initial crystallization of the albite took place at 800 °C; however, these three phases were still present in smaller amounts. The level of albite formation was enhanced when the firing temperature was increased to 1050 °C

(Figure 1a). In contrast, the other end-member of the plagioclase feldspars, the anorthite, formed at a much higher temperature. At 1100 °C the prereacted sample with the stoichiometry of anorthite was composed of SiO_2 , Al_2O_3 , CaAl_2O_4 and $\text{Ca}_2\text{Al}(\text{AlSi})\text{O}_7$ phases. The anorthite crystallized at 1200 °C (**Figure 1b**). Y. Kobayashi et al.¹ also showed that a complete crystallization of anorthite prepared from kaolin and calcites took place at 1200 °C. However, the anorthite ceramics from this experiment also contained a small amount of glassy phase that originated from the starting chemical composition, which was shifted away from the single-phase anorthite.

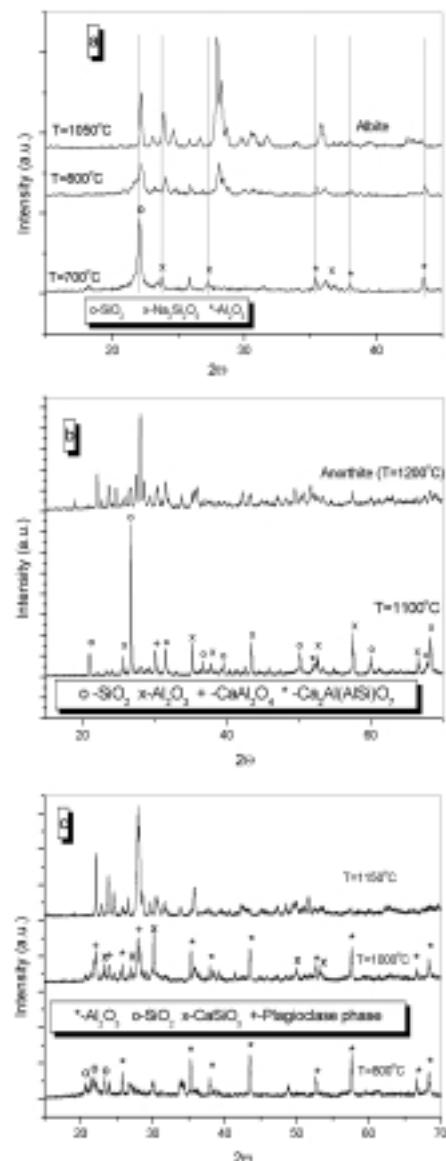


Figure 1: XRD patterns for the samples with stoichiometric compositions of (a) $\text{NaAlSi}_3\text{O}_8$, (b) $\text{CaAl}_2\text{Si}_2\text{O}_8$ and (c) $\text{Na}_{0.6}\text{Ca}_{0.4}\text{Al}_{1.4}\text{Si}_{2.6}\text{O}_8$, fired for 10 hours at different temperatures

Slika1: Rentgenski spektre vzorcev s stehiometričnimi sestavami (a) $\text{NaAlSi}_3\text{O}_8$, (b) $\text{CaAl}_2\text{Si}_2\text{O}_8$ in (c) $\text{Na}_{0.6}\text{Ca}_{0.4}\text{Al}_{1.4}\text{Si}_{2.6}\text{O}_8$, ki so bili žgani 10 ur pri različnih temperaturah

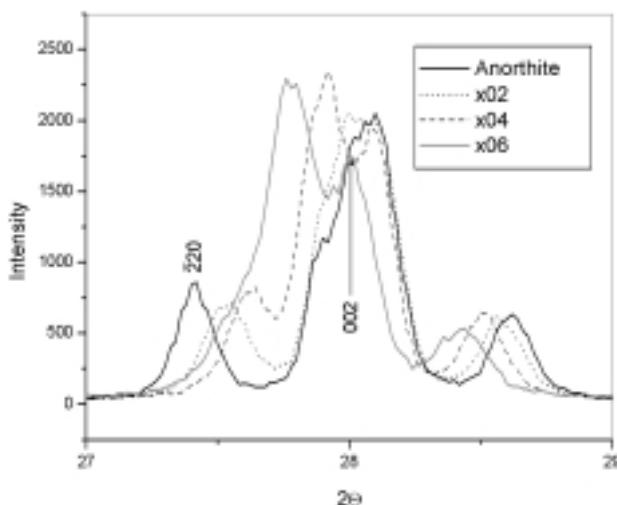


Figure 2: XRD patterns of the anorthite, $\text{Na}_{0.2}\text{Ca}_{0.8}\text{Al}_{1.8}\text{Si}_{2.2}\text{O}_8$ (curve x02), $\text{Na}_{0.4}\text{Ca}_{0.6}\text{Al}_{1.6}\text{Si}_{2.4}\text{O}_8$ (curve x0.4) and $\text{Na}_{0.6}\text{Ca}_{0.4}\text{Al}_{1.4}\text{Si}_{2.6}\text{O}_8$ (curve x0.6) samples, fired at 1400°C , 1250°C , 1200°C and 1150°C , respectively

Slika 2: Rentgenski posnetki vzorcev anortita, $\text{Na}_{0.2}\text{Ca}_{0.8}\text{Al}_{1.8}\text{Si}_{2.2}\text{O}_8$ (krivulja x 02), $\text{Na}_{0.4}\text{Ca}_{0.6}\text{Al}_{1.6}\text{Si}_{2.4}\text{O}_8$ (krivulja x 0.4) and $\text{Na}_{0.6}\text{Ca}_{0.4}\text{Al}_{1.4}\text{Si}_{2.6}\text{O}_8$ (krivulja x 0.6), ki so bili žgani pri 1400°C , 1250°C , 1200°C oziroma pri 1150°C

The $\text{Na}_x\text{Ca}_{1-x}\text{Al}_{2-x}\text{Si}_{2+x}\text{O}_8$ ($0 < x < 1$) solid solutions formed at $800 - 1200^\circ\text{C}$, and the formation temperature of the solid-solution phases decreased with increasing Na content. The XRD results in Figure 1c show the crystallization of a $\text{Na}_{0.6}\text{Ca}_{0.4}\text{Al}_{1.4}\text{Si}_{2.6}\text{O}_8$ solid solution. Besides Al_2O_3 , CaSiO_3 and SiO_2 phases, the plagioclase phase was also present at 1000°C . At 1150°C , however, only the plagioclase phase was detected (Figure 1c).

The XRD spectra of pre-reacted powders with the nominal composition $\text{Na}_x\text{Ca}_{1-x}\text{Al}_{2-x}\text{Si}_{2+x}\text{O}_8$ ($0 \leq x \leq 0.6$) confirmed the formation of plagioclase solid solutions. The most intense peak in the XRD spectra of the plagioclase phase shifted to a lower 2θ value with increasing Na concentration. At the same time the $\bar{2}20$ peak shifted to a higher 2θ value. In the $\text{Na}_{0.6}\text{Ca}_{0.4}\text{Al}_{1.4}\text{Si}_{2.6}\text{O}_8$ sample the 002 peak appeared as a result of the change in the space group from $\bar{\text{I}}\bar{1}$ to $\bar{\text{C}}\bar{1}$, whereas the $\bar{2}20$ peak could not be discerned from the most intense peak (Figure 2).

3.2 Chemical compatibility with Ag

Because it is necessary to co-fire a Ag electrode with the LTCC-ceramic layers it is important that the electrode and the ceramics do not react with each other, because this could change the characteristics or even destroy the functionality of the LTCC module. In order to check the compatibility of the compounds and the electrode, a compatibility test involving Ag and anorthite (albite) was performed. The pressed mixtures consisting of homogenized anorthite (albite) and 30 % of Ag powder were fired at 900°C for 5 hours. The XRD spectra of the fired mixtures showed the presence of the

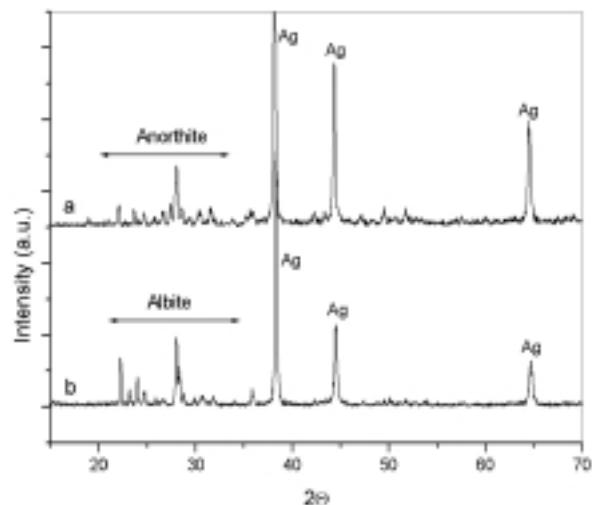


Figure 3: XRD patterns of the mixtures consisting of 70 % anorthite, 30 % Ag (**curve a**) and 70 % albite, 30 % Ag (**curve b**), fired at 900°C for 5 hours

Slika 3: Rentgenski posnetki mešanic, sestavljenih iz 70 % anortita, 30 % Ag (**krivulja a**) in 70 % albita, 30 % Ag (**krivulja b**), ki so bili žgani 5 ur pri 900°C

initial phases, Ag and anorthite, (Figure 3, curve a) and Ag and albite, (Figure 3, curve b), which confirmed that there was no reaction between the Ag and the anorthite (albite) for conditions relevant to LTCC technology.

3.3 Dielectric properties

The permittivities of the albite and the $\text{Na}_x\text{Ca}_{1-x}\text{Al}_{2-x}\text{Si}_{2+x}\text{O}_8$ ($0 < x < 1$) solid solutions measured at 1MHz were slightly lower than that of the anorthite (Table 1), which could be expected from the smaller ion polarizability of Na^+ compared to Ca^{2+} . The dielectric

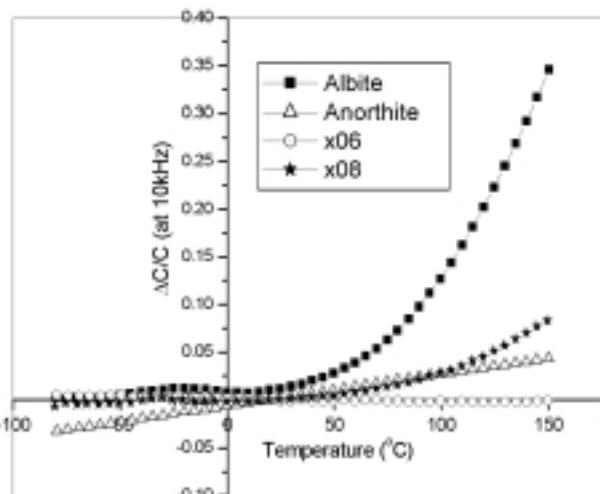


Figure 4: Temperaturna odvisnost $\Delta C/C$, izmerjena pri 10 kHz za albit, anortit, $\text{Na}_{0.8}\text{Ca}_{0.2}\text{Al}_{1.2}\text{Si}_{2.8}\text{O}_8$ (krivulja x 08) in $\text{Na}_{0.6}\text{Ca}_{0.4}\text{Al}_{1.4}\text{Si}_{2.6}\text{O}_8$ (krivulja x 06)

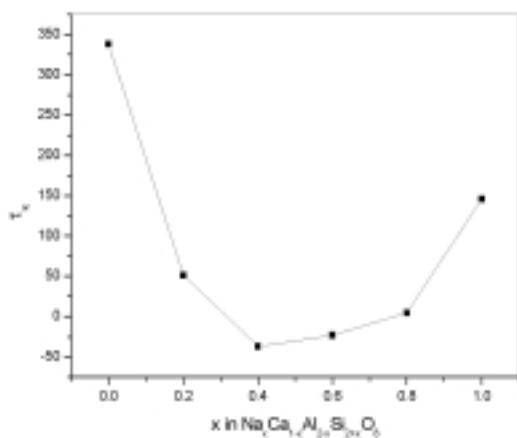


Figure 5: The temperature coefficient of permittivity (τ_k) at 1MHz for various compositions $\text{Na}_x\text{Ca}_{1-x}\text{Al}_{2-x}\text{Si}_{2+x}\text{O}_8$ ($0 \leq x \leq 1$)

Slika 5: Temperaturni koeficient dielektričnosti pri 1MHz za različne sestave $\text{Na}_x\text{Ca}_{1-x}\text{Al}_{2-x}\text{Si}_{2+x}\text{O}_8$ ($0 \leq x \leq 1$)

losses were low for all the compositions ($\tan \delta \leq 5 \cdot 10^{-4}$). In comparison with the other plagioclase feldspar, the albite and $\text{Na}_{0.8}\text{Ca}_{0.2}\text{Al}_{1.2}\text{Si}_{2.8}\text{O}_8$ exhibited slightly higher dielectric losses at 1MHz (**Table 1**), most likely a result of the increased conductivity, which is particularly so for the albite. The increased conductivity was observed from the measurements of the temperature dependence of capacitance as an increase in the capacitance (C) at higher temperatures and lower frequencies (1 kHz, 10 kHz), which occurs due to the presence of mobile charge carriers that cause a space-charge polarization (**Figure 4**). The albite, and to a lesser extent also the $\text{Na}_{0.8}\text{Ca}_{0.2}\text{Al}_{1.2}\text{Si}_{2.8}\text{O}_8$, showed an increased conductivity, whereas the compositions with a lower Na content did not (**Figure 4**).

The temperature dependence of permittivity (τ_k) of the solid solutions was much lower than those of the anorthite and albite (**Figure 5**). This is atypical behavior for isostructural solid solutions and might be a consequence of phase transitions along the solid solubility range. The dielectric properties of plagioclase

feldspars measured in the MW region are listed in **Table 2**. The permittivities closely correspond to those measured at RFs, and meet the requirements for LTCC substrates. The temperature dependence of resonant frequency (τ_f) was negative and very low, especially for the solid solutions with $x = 0.4, 0.6$ and 0.8 (**Table 2**). The τ_f of an anorthite ceramic synthesized in this study was lower than the τ_f of commercial anorthite-based LTCC tapes ($\tau_f = -80 \text{ ppm}$)¹⁰ and comparable with the τ_f of the recrystallized anorthite reported by C.L. Lo et al. ($\tau_f = \text{from } -60 \text{ ppm}/^\circ\text{C} \text{ to } -30 \text{ ppm}/^\circ\text{C}$)². In addition, the measured Qxf value is similar to those measured by C.L. Lo et al. (25000 GHz), but 10 times higher than that of commercial tapes ($\approx 2000 \text{ GHz}$). The $Q \times f$ -values of the albite and the plagioclase solid solutions (4500-11100 GHz) were 2 to 4 times smaller than the $Q \times f$ -value of the anorthite (19300 GHz), but still much higher than that of the commercial anorthite-based tapes (**Table 2**).

4 CONCLUSIONS

Although the dielectric measurements showed that the dense anorthite ceramic exhibited high Qxf value (19300 GHz) and a permittivity low enough for a substrate material, the sintering temperature (1400 °C) was far too high for use in LTCC technology. The temperature of the plagioclase-phase formation and the sintering temperature decreased with an increase in Na concentration from the anorthite to albite end-member. However, the sintering temperature of the albite was still at least 100 °C too high for LTCC technology. Compared to the anorthite, the plagioclase solid solutions showed 2 to 4 times smaller $Q \times f$ -values ($\approx 4500 \text{ GHz}$ $\approx 11100 \text{ GHz}$), but near zero τ_k and τ_f , which is very important for potential LTCC applications. All plagioclase feldspars are chemically compatible with Ag under LTCC processing conditions. Further work must focus on decreasing the sintering temperature below the melting point of Ag without any significant deterioration of the properties. In the event that the sintering temperature can be decreased such a material would

Table 1: Dielectric Properties of Plagioclase Feldspars $\text{Na}_x\text{Ca}_{1-x}\text{Al}_{2-x}\text{Si}_{2+x}\text{O}_8$ at 1MHz

Tabela 1: Dielektrične lastnosti plagioklaznih glinencev $\text{Na}_x\text{Ca}_{1-x}\text{Al}_{2-x}\text{Si}_{2+x}\text{O}_8$ pri 1MHz.

x→	0(Anorthite)	0.2	0.4	0.6	0.8	1(Albite)
ϵ	7.4	6.6	5.9	6.7	5.4	6.6
$\tan \delta$	$<10^{-4}$	$<10^{-4}$	$<10^{-4}$	$<10^{-4}$	$5 \cdot 10^{-4}$	10^{-4}

Table 2: Dielectric Properties of Plagioclase Feldspars $\text{Na}_x\text{Ca}_{1-x}\text{Al}_{2-x}\text{Si}_{2+x}\text{O}_8$ in MW region

Tabela 2: Dielektrične lastnosti plagioklaznih glinencev $\text{Na}_x\text{Ca}_{1-x}\text{Al}_{2-x}\text{Si}_{2+x}\text{O}_8$ v mikrovalovnem področju.

x→	0(Anorthite)	0.2	0.4	0.6	0.8	1(Albite)
ϵ	7.2	5.7	4.9	5.7	5.1	5.9
τ_f (ppm/ $^\circ\text{C}$)	-30	-44	-14	-12	-12	-21
$Q \times f$ (GHz)	19300	4500	7900	11100	8000	4900
f_0 (GHz)	9.9	10.4	10.5	10.4	10.6	10.4

exhibit superior properties to existing commercial LTCC tapes.

5 REFERENCES

- ¹ Y. Kobayashi, E. Kato, J. Am. Ceram. Soc., 77 (1994) 3, 833-834
- ² C.-L. Lo, J.-G. Duh, B.-S., Chiou, W-H Lee, J. Am. Ceram. Soc., 85 (2002) 9, 2230-2235
- ³ K. Sumi, Y. Kobayashi, E. Kato, J. Am. Ceram. Soc., 82 (1999) 3, 783-785
- ⁴ M. R. Boudchicha, S. Achour, A. Harabi, J. Mater. Sci. Lett., 20 (2001) 215-217
- ⁵ J-H. Jean, J.-I.Shen, Jpn. J. Appl. Phys. 35 (1996) 3942-3946
- ⁶ A. Harabi, M. R. Boudchicha, N. Aklouche, S. Achour, Engineering Materials 206-213 (2002), 111-114
- ⁷ R. A. McCauley, J. Mater. Sci., 35 (2000) 3939-3942
- ⁸ J. F. Schairer, J. Am. Ceram. Soc., 40 (1957) 7, 232
- ⁹ D. Kajfez, E.J.Hwan, IEEE Trans. MTT-32, (1984) 666-670
- ¹⁰ S. X. Dai, R. F. Huang, D.L. Wilcox . J. Am. Ceram. Soc., 85 (2002) 4, 828-832