A structural and dielectric characterization of $Na_xCa_{1-x}Al_{2-x}Si_{2+x}O_8$ (x=0 and 1)

Marjeta Macek Krzmanc, Matjaz Valant, Danilo Suvorov
Advanced Materials Department, Jožef Stefan Institute, Ljubljana, Slovenia

Abstract

Albite and anorthite, the end-members of the plagioclase feldspar structural family ($Na_xCa_{1-x}Al_{2-x}Si_{2+x}O_8$), were synthesized under sub-solidus conditions using the solid-state reaction technique. The structural investigations revealed that both the plagioclase-phase formation and sintering temperature decreased from the anorthite ($CaAl_2Si_2O_8$; x=0), which started to form at 1000°C and sintered at 1300°C, to the albite ($NaAlSi_3O_8$; x=1), which started to form at 800°C and sintered at 1000°C.

Dielectric measurements in the microwave (MW) frequency region revealed that a high temperature (1500°C) and an extended heat-treatment time were needed to obtain low-loss anorthite ceramics (Qxf=10000 GHz-19000 GHz). In contrast, the albite attained Qxf=11200 GHz at a lower temperature (1025°C). A temperature coefficient of resonant frequency (τ_f) close to zero (-5 ppm/°C) was another advantage of the albite over the anorthite, which exhibited τ_f=-130 ppm/°C. The dielectric measurements also revealed that a slow cooling rate considerably improved the Qxf values of the anorthite and albite.

Keywords: Albite, B: X-ray methods, C: dielectric properties, E: powders-solid state reaction
E: Sintering

Introduction

Rapid developments in the electronics industry have created needs in low-temperature cofired-ceramic (LTCC) technology for low-temperature-sinterable-substrate materials with even higher Q values and a temperature-stable permittivity of less than 12. The currently used low-permittivity LTCC substrates still contain some glassy phase, which is added either for lowering the sintering temperature or remains in the system due to incomplete recrystalization.[1] It is known that most glasses have high dielectric losses, and because of this the amount of glass in the dielectric material is very important, since this will considerably affect the dielectric losses of the final material. The lowest dielectric losses would be expected in glass-free ceramics that are prepared by synthesizing under sub-solidus conditions.

In addition to cordierite ($Mg_2Al_4Si_5O_{18}$) and celsian ($BaAl_2Si_2O_8$), anorthite ($CaAl_2Si_2O_8$) is regarded as a promising low-permittivity substrate material. Based on their structure, anorthite and celsian belong to the large group of feldspars, which comprise alkali feldspars **(**$Na_xK_{1-x}AlSi_3O_8$**)**, plagioclase feldspars ($Na_xCa_{1-x}Al_{2-x}Si_{2+x}O_8$) and $K_xBa_{1-x}Al_{2-x}Si_{2+x}O_8$ solid solutions. The feldspar crystal structure is composed of a three-dimensional framework of corner-shared tetrahedra, where each tetrahedron is centered by a Si^{4+} or an Al^{3+}. Each oxygen atom is located at the corners of the tetrahedra and links two tetrahedra. The charge balance due to the Al^{3+} substitution for Si^{4+} is maintained by the addition of an interstitial alkali or alkaline-earth ion.

Although the feldspar group is large, no other materials (with the exception of anorthite[2] or celsian[1]) have been investigated for microwave dielectric applications. Based on the structural similarity with anorthite the other plagioclase solid solutions, $Na_xCa_{1-x}Al_{2-x}Si_{2+x}O_8$, seem to be

worth investigating. The literature on plagioclase feldspars is vast.[3-7] Due to their abundance in the earth's crust the plagioclase feldspars have attracted particular attention from mineralogists. Their investigations were, however, made difficult by the sluggish kinetics of ordering, the small differences in the X-ray scattering efficiencies of Al and Si and a structure complicated by different Al/Si ordering across the solid solubility range. X-ray diffraction (XRD) and transmission electron microscopy (TEM), which were most frequently used in studying feldspars, gave information about an average long-range structure. However, the experimental and theoretical studies showed the importance of considering both the short-range order (SRO) and long-range order (LRO) in examinations of the thermodynamic properties of feldspars.[5-7] It is known that the T-O distance (T = Si, Al) and the lattice angle γ are the most sensitive to the element (Si or Al) that occupies the tetrahedral site.[3, 8] The calculations of T-O distance were frequently used for a determination of Al and Si distribution in a triclinic albite ($C\bar{1}$), which has four different crystallographic sites for the tetrahedrally coordinated atoms (Si and Al), called T10, T1m, T20 and T2m.[3, 8-9] The low albite is completely ordered with all the Al located on T10 sites (Al occupancy of the sites: T10 = 1, T1m = T20 = T2m = 0). The slightly disordered albite is named intermediate albite ($0.25<T10<1$). In highly disordered high albite the Al atoms occupy all four T sites with a preference for the T10 site.

Although albite belongs to the same structural family as anorthite its dielectric properties in the microwave (MW) frequency region have not yet been investigated. The main objective of our work was to study the influence of sintering temperature and cooling rate on the dielectric properties of the plagioclase end-members. The dielectric losses strongly depend on the degree of order, which in plagioclases was determined by the thermal history and cooling rate.

On the basis of different heat treatments we indirectly try to correlate the dielectric losses with the ordering in anorthite and albite.

Experimental

The albite and anorthite were synthesized under sub-solidus conditions using the solid-state reaction technique. The albite was synthesized from reagent-grade compounds, Na_2CO_3, Al_2O_3 and SiO_2, which were homogenized and then pre-reacted at 700°C, 800°C and 900°C. The synthesis of albite was completed by sintering powders with a median particle size of 0.7 μm at 1000–1070°C. To achieve a small particle size the powders were milled in ethanol with yttrium-doped zirconium-oxide balls with a diameter of 3 mm and 0.8 mm. For the synthesis of anorthite the stoichiometric mixture of $CaCO_3$, Al_2O_3 and SiO_2 was pre-reacted at 1000°C, 1100°C and 1200°C. Similar to albite, the anorthite powder was milled prior sintering at 1300–1500°C. After sintering, the samples were cooled quickly or slowly with a controlled cooling rate (0.5°C/min). Fast cooling means uncontrolled cooling in an oven by natural convection, conduction and radiation to room temperature.

The XRD studies were performed with a Bruker AXS D4 Endeavor diffractometer using Cu Kα radiation. The DIFFRAC plus TOPAS R program was used for determining the lattice parameters of the albite with a Rietveld structural refinement of the powder XRD data. Microstructural studies of the samples were conducted with a scanning electron microscopy (SEM) (JEOL, JXA 840A) coupled with energy-dispersive X-ray spectroscopy (EDX) and software (Series II X-ray microanalyzer, Tracor Nothern, Middleton, WI).

The radio-frequency (RF) dielectric measurements were performed at frequencies (f) from 1 kHz to 1 MHz on In/Ga-plated disk capacitors using a high-precision LCR meter (Agilent

4284 A). The MW dielectric properties were characterized using the closed air-cavity method with a network analyzer (HP 8719C). Permittivity (ε) and quality factor (Q) values were calculated at the resonance conditions ($TE_{01\delta}$ mode) from the S_{11}-reflection coefficient as proposed by Kajfež et al..[10] To determine the temperature coefficient of resonant frequency (τ_f) the test cavities were inserted into a temperature-controlled chamber. The dielectric characteristics of the samples were analyzed in the temperature range from 20ºC to 60ºC.

Results and Discussion

Solid-state synthesis and structure of albite and anorthite

The reactions that occurred during the heat treatments were followed by XRD analysis, which showed that the albite formed at approximately 200°C less than the anorthite. **Albite:** The pre-reaction at 700 °C of the sample with the nominal composition of albite led to the partial crystallization of SiO_2, the decomposition of Na_2CO_3 and the formation of $Na_2Si_2O_5$ and nepheline. The greater part of the Al_2O_3 remained unreacted at this temperature. In addition to the nepheline, the albite started to form at 800°C. During sintering at 1000 °C≤ T≤1070 °C, the nepheline and Al_2O_3 phases completely disappeared and the synthesis of the albite was completed (Fig. 1). The degree of ordering in albite can be estimated from the lattice angle γ or simply from the distance between the diffraction lines corresponding to the 131 and $1\bar{3}1$ crystal planes ($\Delta131=2\Theta(131)-2\Theta(1\bar{3}1)$). Both the γ angle and the Δ131 parameter are a measure of the difference between the Al occupancy of the T10 site and the average Al occupancy over the other T-sites. The value 90.260° of the lattice angle γ for the albite sample, which was obtained with a Rietveld structural refinement of the powder XRD data, showed good agreement with the results for high albite obtained by other researchers (γ=90.115°-90.257°).[3] The Δ131 parameter of 1.937 additionally confirmed the high albite structure, which was also expected from the temperatures of the synthesis and the sintering.

Anorthite: During the first pre-reaction at 1000°C, the formation of gehlenite, wolastonite and a small amount of anorthite took place in addition to the crystallization of SiO_2. With further heat treatment the amount of anorthite phase increased, while the gehlenite, wollastonite and Al_2O_3 decreased. Besides anorthite, Al_2O_3 was still present at 1200°C. Single-phase anorthite was obtained during sintering at 1300–1500°C (Fig. 2).

Dielectric properties

The ordering/disordering processes in albite has been the subject of numerous theoretical and experimental studies.[6-9] In terms of LRO and SRO, the high albite ($C\bar{1}$) structure has no LRO of the anorthite type, but a high degree of SRO, which cannot be determined from the XRD data.[5-7] When comparing the fast-cooled albite samples heat treated at different temperatures, a nearly linear decrease of Qxf values from 8500 GHz to 3100 GHz was observed in the temperature range from 1000°C to 1070°C (Fig. 3). We noticed no significant change of Δ131 parameter and lattice angle γ in this temperature range. According to the Monte-Carlo simulation of Gordillo and Herrero, there was a very small variation of aluminum distribution at the different tetrahedral sites in the temperature range 1000–1070 °C.[9] In addition to this, Meneghinello et al. showed in their study that very long times (several days) were required to attain some differences in the occupation of the tetrahedral sites.[8] Therefore, the absence of change in the Δ131 parameter and the lattice angle γ with temperature was not surprising due to the relatively short heat-treatment time (15 hours) and the small temperature range used in our experiments. In addition to this, the Δ131 parameter and the lattice angle γ reflect an average structure and do not give information about the SRO. The Qxf values of the albite decreased, most probably due to the changes in the SRO, which was supposed to fall with increasing temperature.[7] A slow cooling rate of 0.5°C/min considerably improved the Qxf

values of the albite (Fig.3). The highest Qxf value (11200 GHz) was obtained for albite heat treated at 1025°C, and this value was nearly two times higher than the value (6100 GHz) of the albite sample that was cooled quickly. At 1050°C the improvement of the Qxf value was still considerable, while at 1070°C the slow cooling rate only slightly improved the Qxf value.

Numerous studies of Al/Si ordering in anorthite have revealed that the equilibrium degree of order in anorthite is reached asymptotically.[4-6] The first crystals that form during the heating of the anorthite glass have no LRO and essentially the $C\bar{1}$ symmetry.[4] However, a considerable degree of SRO in these crystals was determined with the help of ^{29}Si MAS NMR spectroscopy.[5] With further annealing the size of the ordered domains increased, so developing the LRO structure with $I\bar{1}$ symmetry.[4, 5] Our dielectric measurements were in accordance with this asymptotic approach to the ordered state. The anorthite sintered at 1300°C for 15 hours and then cooled quickly exhibit Qxf =5500 GHz. When the sintering temperature was increased to 1400°C and 1500°C the Qxf values were increased to 6300 GHz and 8400 GHz, respectively. An additional improvement of Qxf values was obtained with slow, 0.5°C/min controlled cooling (Fig. 3) or extended heat-treatment times, when the Qxf values were of the order of 10000 GHz to 19000 GHz. The increase of ordering with temperature can be expected from the fact that the ordered $I\bar{1}$ structure is stable up to ~2000°C in the absence of melting at 1557°C.[4]

For the analysis of dielectric properties the anorthite and the albite powders were sintered to dense ceramics with the typical remaining level of porosity as shown in Fig. 4. The slightly lower permittivity (ε=5-6) of albite compared to anorthite (ε=7.4) can be expected, firstly, from the smaller ion polarizability of Na^+ in comparison with Ca^{2+} and, secondly, due to the slightly higher porosity of the albite sample.

The measurements of τ_f revealed another important advantage of albite over anorthite, which exhibited τ_f= -130 ppm/°C. In contrast, the τ_f of albite (-5 ppm/°C) sintered at 1000°C is in line with the values (±10ppm/°C) required by LTCC tehnology. A decrease in τ_f (-5 ppm/°C - -24 ppm/°C) in the temperature range 1000–1050°C was followed by a larger decrease to –54 ppm/°C at 1070°C.

The low dielectric losses of the slow-cooled albite and anorthite samples indicated the importance of the slow cooling in the synthesis of the other plagioclase solid solutions with intermediate composition. This will be the subject of our future work

Conclusions

Our investigations of the microwave dielectric properties of albite and anorthite, which were synthesized under sub-solidus conditions, revealed that in some respects albite can compete with anorthite. The sintering temperature decreased from 1300°C for anorthite to 1000°C for albite. While low-loss anorthite ceramics (Qxf=10000 GHz-19000 GHz) could be obtained only after an extended heat treatment at 1500°C, the albite attained Qxf=11200 GHz when sintered at 1025°C. A τ_f close to zero is another advantage of albite over anorthite, which brings albite close to the LTCC requirements. The higher Qxf values of the slow-cooled albite and anorthite samples compared to the fast-cooled samples, indicate the importance of slow cooling when it comes to the ordering of plagioclase feldspars.

References

1. Dai, S. X., Huang, R. F. & Wilcox, D. L., Use of Titanates to achieve a temperature-stable low-temperature cofired ceramic dielectric for wireless applications. J. Am. Ceram. Soc., 2002, **85,** 828-832.

2. Lo, C. L., Duh, J.G., Chiou, B.S. & Lee, W. H., Low temperature sintering and microwave dielectric properties of anorthite-based glass–ceramics. J. Am. Ceram. Soc., 2002, **85**, 2230-2235.

3. Kroll, H. & Ribbe, P. H., Determinative diagrams for Al, Si order in plagioclases. Am. Mineral., 1980, **65,** 449-457.

4. Carpenter, M. A., Mechanisms and kinetics of Al-Si ordering in anorthite: I. Incommensurate structure and domain coarsening. Am. Mineral., 1991, **76**, 1110-1119.

5. Phillips, B. L., Kirkpatrick, R. J. & Carpenter, M. A., Investigation of short-range Al, Si order in synthetic anorthite by ^{29}Si MAS NMR spectroscopy. Am Mineral., 1992, **77,** 484-494.

6. Vinograd , V. L. & Putnis, A., A two-dimensional spin model of Al/Si order in feldspars visualization of short-range and long-range order. Eur. J. Mineral., 2001, **13**, 273-288.

7. Myers, E. R., Heine, V. & Dove, M. T., Thermodynamics of Al/Al avoidance in the ordering of Al/Si tetrahedral framework structures. Phys. Chem. Minerals, 1998, **25**, 457-464.

8. Meneghinello, E., Alberti, A. & Cruciani, G., Order-disorder process in the tetrahedral sites of albite. Am. Mineral., 1999, **84**, 1144-1151.

9. Gordillo, M. C. & Herrero, C. P., Monte Carlo simulation of Al, Si ordering in albite. J. Phys. Chem., 1996, 100, 9098-9103

10. Kajfez, D. & Hwan, E.J. , Q-factor measurement with network analyzer. IEEE T Microw. Theory., 1984, **32**, 666-670.

Figure captions

Figure 1 : XRD patterns of the sample with stoichiometry of albite, heat treated at different temperatures (**x**→$Na_2Si_2O_5$, +→nepheline, o→SiO_2, *→Al_2O_3)

Figure 2 : XRD patterns of the sample with stoichiometry of anorthite, heat treated at different temperatures (o→SiO2, *→Al_2O_3, w→wollastonite, g→gehlenite)

Figure 3: The Qxf as a function of the sintering temperature for fast (-♦-) and slow (-◊-) cooled albite samples and for fast (-✯-) and slow (-🕴-) cooled anorthite samples. The samples were sintered for 15 hours at the indicated temperatures.

Figure 4. SEM micrographs of albite (a) and anorthite (b) sintered at 1050°C and 1400°C, respectively.

.

Figure1:

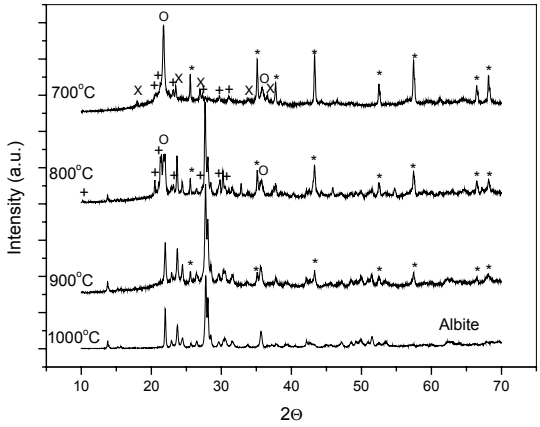

Figure 2:

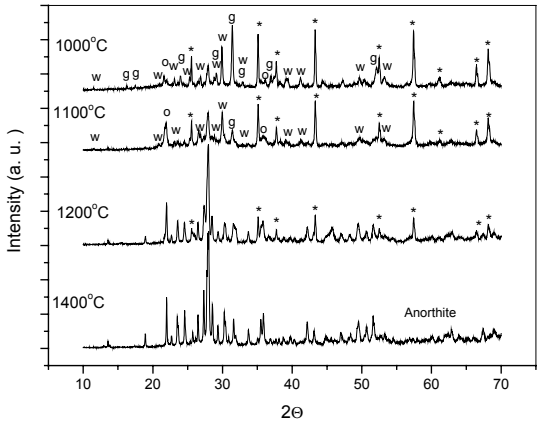

Figure 3:

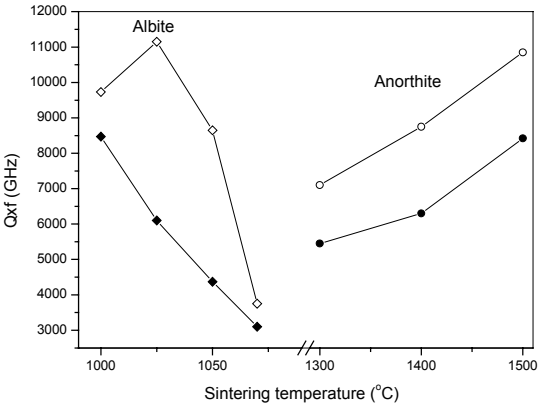

Figure 4: