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The synthesis and microwave dielectric properties of $Sr_xBa_{1-x}Al_2Si_2O_8$ and $Ca_yBa_{1-y}Al_2Si_2O_8$ ceramics

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Abstract

Dense, single-phase $Sr_xBa_{1-x}Al_2Si_2O_8$ ($0 \le x \le 1$) and $Ca_yBa_{1-y}Al_2Si_2O_8$ ($0 \le y \le 0.05$) ceramics were synthesized and then structurally and dielectrically characterized. The substitution of Ba with Ca or Sr promotes the transformation of hexacelsian to monocelsian. The substitution with Ca led to a more-than-two-times-lower $Q \times f$ value at $y = 0.05$, whereas the $Q \times f$ value of the $Sr_{0.05}Ba_{0.95}Al_2Si_2O_8$ ($x = 0.05$) was only 5% lower than the $Q \times f$ value of the $BaAl_2Si_2O_8$, which exhibited $Q \times f$ values of 70,600 and 77,700 GHz when sintered at 1500 °C for 12 and 40 h, respectively. The improvement in the $Q \times f$ value with the prolongation of the heat-treatment time, which can be attributed to an increase in the Al:Si ordering, was also noticed for other $Sr_xBa_{1-x}Al_2Si_2O_8$ solid solutions. In contrast to the dielectric losses, the permittivity ($\varepsilon = 7.3$ and 7.2 at 1 MHz and 10.5 GHz, respectively) did not change significantly with the composition and the sintering conditions.

Keywords: Solid-state reaction of powders; X-ray methods; Dielectric properties; Silicate

1. Introduction

Low-permittivity and low-loss dielectric ceramics have recently become of great importance due to their potential for use as substrate materials in low-temperature co-fired ceramic (LTCC) technology and also as dielectrics for high-frequency applications (>10 GHz) such as satellite communications and automotive equipment.[1] Although $BaAl_2Si_2O_8$ has been used as a constituent in low-permittivity substrate dielectrics,[2] there are only a few studies relating to its dielectric properties.[3,4] In contrast, far more attention was paid to its synthesis and structural modifications.[5–11] There are four known polymorphs of $BaAl_2Si_2O_8$: two occur naturally and two were prepared synthetically. The monoclinic form, named monocelsian (or shortly celsian), with the space group $I2/c$, is far more abundant in nature than the other monoclinic polymorph, paracelsian, with the space group $P2_1/a$, which in contrast to the monocelsian has never been prepared synthetically.[3] The other two crystalline modifications, hexagonal (hexacelsian) and the orthorhombic polymorph, can only be found in synthetic products.[7] Although hexacelsian is thermodynamically stable at temperatures (T) between 1590 °C and its melting point (1760 °C), it can also exist as a metastable phase at 300 °C < T < 1590 °C.[6] Actually, hexacelsian always forms during the solid-state or sol–gel synthesis, and once formed, it sluggishly transforms to the monoclinic form.[8] Around 300 °C hexacelsian undergoes a reversible structural transformation to the orthorhombic form, which is accompanied by a relatively large volume change (~3–4%) that can cause microcracks. This is, in addition to its large thermal expansion coefficient (~6–8 × 10^{-6}/°C), the main reason why the hexacelsian phase is regarded as being undesirable for electrical applications.[4,5] This means that only the monoclinic celsian has attractive properties. It is known that the addition of $SrAl_2Si_2O_8$, $CaAl_2Si_2O_8$, Li_2O, LiF, B_2O_3 and $ZrSiO_3$ accelerates the hexacelsian-to-celsian transformation.[4] In general, the additives would be expected to have a detrimental effect on the dielectric properties of celsian. Talmy et al.,[4] in their study of $Sr_xBa_{1-x}Al_2Si_2O_8$ ceramics, showed that even a small addition of Sr ($x = 0.05$) increased the microwave dielectric losses of celsian by more than 100%.

The polymorphism of $SrAl_2Si_2O_8$ is very similar to that of $BaAl_2Si_2O_8$.[3,12,13] For this reason, the terms monocelsian (celsian) and hexacelsian are also often used in the literature to denote the monoclinic and hexagonal varieties of $SrAl_2Si_2O_8$, respectively. The same notation is also used in this article.

The main focus of this work was a systematic study of the dielectric properties of the $Sr_xBa_{1-x}Al_2Si_2O_8$ and $Ca_yBa_{1-y}Al_2Si_2O_8$ ceramics. We will show that the deterio-

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ration of the dielectric properties of $BaAl_2Si_2O_8$ due to the substitution is not so significant as was previously reported.

2. Experimental

$Sr_xBa_{1-x}Al_2Si_2O_8$ and $Ca_yBa_{1-y}Al_2Si_2O_8$ ceramics were synthesized from reagent-grade powders of $SrCO_3$, $BaCO_3$, $CaCO_3$, Al_2O_3 and SiO_2 using the solid-state reaction technique. Stoichiometric mixtures of the corresponding initial compounds were homogenized in acetone and then pre-reacted at 1000–1200 °C for 12 h with an intermediate grinding to enhance the formation of the $Sr_xBa_{1-x}Al_2Si_2O_8$ and $Ca_yBa_{1-y}Al_2Si_2O_8$ compounds. An additional pre-reaction at 1300 °C was performed for $x = 0$ and 1 in order to enhance the hexacelsian-to-monocelsian transformation and the formation of monocelsian, respectively. Prior to sintering the powders were ball-milled in ethanol using yttrium-doped zirconium-oxide (Y–ZrO_2) balls with diameters of 3 and 0.8 mm. The milled powders, with a median particle size of 1 μm, were uniaxially pressed into pellets at approximately 10 MPa and sintered at 1500 °C for 12 or 40 h and then cooled slowly with a controlled cooling rate (0.7 °C/min). The progress of the reaction after each pre-reaction step was monitored by powder X-ray diffraction (Bruker AXS, D4 Endeavor). The X-ray powder-diffraction data were collected from $10° < 2\Theta < 60°$ with a step of 0.04°, a counting time of 4 s, and a variable V12 slit. The DIFFRAC plus TOPAS R program was used to determine the lattice parameters of the $Sr_xBa_{1-x}Al_2Si_2O_8$ ceramics. Microstructural analyses were performed using a scanning electron microscopy (SEM) (JEOL, JXA 840A) coupled with energy-dispersive X-ray spectroscopy (EDX) and appropriate 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 microwave (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 Kajfez and Hwan.[14] 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 20 to 60 °C.

3. Results and discussion

3.1. Synthesis and structural characterization

The presence of phases in the samples with the nominal compositions $Sr_xBa_{1-x}Al_2Si_2O_8$ and $Ca_yBa_{1-y}Al_2Si_2O_8$ were examined using the X-ray powder-diffraction technique after each pre-reaction. Due to the detrimental influence of the Ca substitution on the dielectric properties, the $Ca_yBa_{1-y}Al_2Si_2O_8$ solid solutions were examined only up to $y = 0.05$, whereas the $Sr_xBa_{1-x}Al_2Si_2O_8$ solid solutions were analyzed across the whole concentration range ($0 \le x \le 1$). The diffraction lines that correspond to hexacelsian, started to appear by 1000 °C in the XRD patterns of the compositions with $0 \le x \le 0.75$ and $0 \le y \le 0.05$ (Table 1). At higher temperatures the hexacelsian transformed to monocelsian. The formation of hexacelsian and its transformation to monocelsian were expected, on the basis of the literature data.[3,4] In addition to hexacelsian the formation of phases such as barium silicates ($BaSiO_3$, Ba_2SiO_4), barium aluminium oxide ($BaAl_2O_4$), strontium silicates (Sr_2SiO_4, $SrSiO_3$) and strontium aluminium oxide ($SrAl_2O_4$) were also noticed at 1000 °C. The type and amount of the phases formed strongly depended on the composition (Table 1). At $0 \le x < 0.25$ the prevailing phases were various barium silicates and barium aluminium oxide, whereas at $0.6 \le x \le 1$ the diffraction lines of the strontium silicates and strontium aluminium oxide were significantly less intense than those of the unreacted Al_2O_3 and SiO_2. Only when the pre-reaction temperature was increased to 1100 °C did the strontium silicate start to become the dominate phase in Sr-rich compositions ($0.6 < x \le 1$) (Fig. 1). The $SrSiO_3$ seemed to be, like the Al_2O_3, a very unreactive species, since it was still present after firing at 1200 °C. In contrast, the barium silicates and barium aluminium oxide disappeared by 1100 °C ($0.1 < x < 1$), or at least by 1200 °C ($0 \le x \le 0.1$) (Figs. 1 and 2). The great difference in the reactivity of $BaSiO_3$ and $SrSiO_3$ was one of the reasons why the formation of the $Sr_xBa_{1-x}Al_2Si_2O_8$ solid solutions was nearly completed at 1100 °C for $0.25 \le x \le 0.4$ (Fig. 1), whereas for higher values of x a similar level of celsian formation was not obtained until 1300 °C.

In the case of $SrAl_2Si_2O_8$ ($x = 1$) the hexacelsian phase was not observed at 1000 °C or even at 1100 °C. The weak diffraction lines corresponding to the monocelsian phase only started to appear in the XRD patterns of the $SrAl_2Si_2O_8$ sample fired at 1100 °C (Fig. 1). When the temperature was increased to

Table 1
Phases formed during the synthesis of $Sr_xBa_{1-x}Al_2Si_2O_8$ (determined from X-ray powder diffraction spectra)

	$x = 0$	$x = 0.25$	$x = 0.6$	$x = 1$
1000 °C	$BaSiO_3$, Ba_2SiO_4, $BaAl_2O_4$, Al_2O_3, hexacelsian	$BaSiO_3$, Al_2O_3, $BaAl_2O_4$, hexacelsian	Al_2O_3, SiO_2, $SrSiO_3$, Sr_2SiO_4, $SrAl_2O_4$, hexacelsian	Al_2O_3, Sr_2SiO_4, $SrAl_2O_4$, $SrSiO_3$, SiO_2
1100 °C	$BaSiO_3$, Al_2O_3, hexacelsian, $BaAl_2O_4$, $Ba_4Si_6O_{16}$, $BaSi_2O_5$	Hexacelsian, monocelsian, Al_2O_3	Monocelsian, hexacelsian, $SrSiO_3$, Al_2O_3	$SrSiO_3$, Al_2O_3, SiO_2, $SrAl_2O_4$, monocelsian, $SrAl_2SiO_7$
1200 °C	Hexacelsian, monocelsian, Al_2O_3	Monocelsian, Al_2O_3	Monocelsian, $SrSiO_3$, Al_2O_3	Monocelsian, $SrSiO_3$, Al_2O_3
1500 °C	Monocelsian, hexacelsian	Monocelsian	Monocelsian	Monocelsian

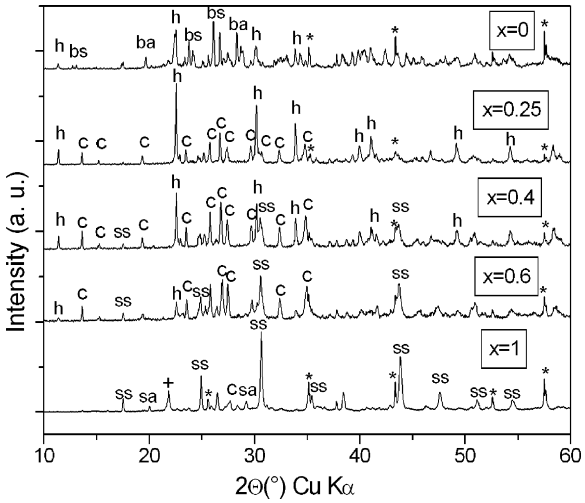

Fig. 1. X-ray powder-diffraction patterns of the samples with the nominal composition $Sr_xBa_{1-x}Al_2Si_2O_8$ at 1100 °C (h: hexacelsian; bs: barium silicate; ba: barium aluminium oxide; c: celsian; ss: strontium silicate; sa: strontium aluminium oxide; *: aluminium oxide; +: silicon oxide).

1200 °C the monocelsian phase started to prevail, although there was still a non-negligible amount of $SrSiO_3$ and Al_2O_3 present, which disappeared at 1400 °C. These results did not agree completely with the observations of Kobayashi and Inagaki,[13] and Sung and Kim,[12] who observed the formation of the hexagonal phase of $SrAl_2Si_2O_8$ at 900–1000 °C and its transformation to monocelsian at 1100 °C. This difference most probably arose from the different starting materials and an alternative synthesis route. In both previous studies of $SrAl_2Si_2O_8$[12,13] it was found that additives (B_2O_3,[12] TiO_2[12] and an excess of SrO[13]) accelerate the hexacelsian-to-monocelsian transformation. Similarly, it is known that additives also promote the hexacelsian-to-monocelsian transformation of $BaAl_2Si_2O_8$.[4–7] The effect of the Ca and Sr substitutions for Ba in the $Sr_xBa_{1-x}Al_2Si_2O_8$ and $Ca_yBa_{1-y}Al_2Si_2O_8$ solid solutions on the rate of the hexacelsian-to-celsian transformation at 1200 °C is illustrated

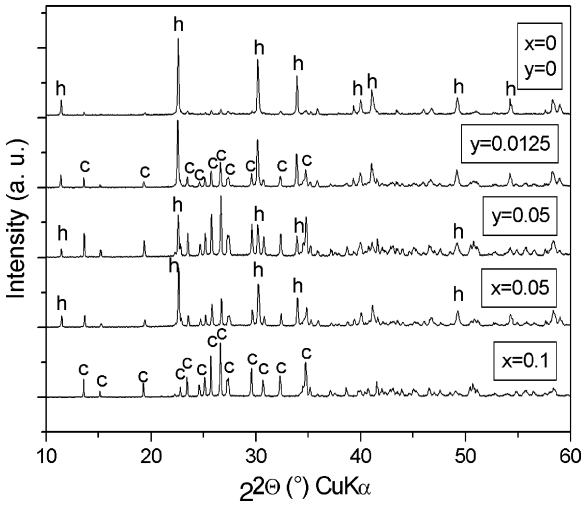

Fig. 2. X-ray powder-diffraction patterns of the samples with the nominal compositions $Sr_xBa_{1-x}Al_2Si_2O_8$ and $Ca_yBa_{1-y}Al_2Si_2O_8$ at 1200 °C (h: hexacelsian; c: celsian).

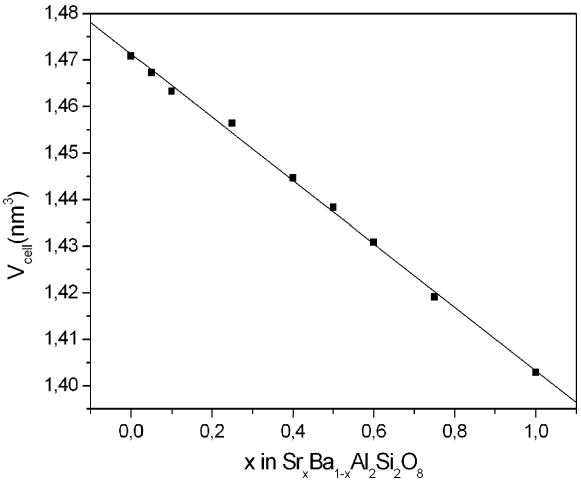

Fig. 3. Unit-cell volume of the $Sr_xBa_{1-x}Al_2Si_2O_8$ solid solutions as a function of composition.

in Fig. 2. In the spectrum of $BaAl_2Si_2O_8$ at 1200 °C a hardly noticeable amount of monocelsian can be observed (Fig. 2, curve at $x = 0$, $y = 0$). Even a small substitution of Ba with Ca caused a considerable increase in the monocelsian content at 1200 °C (Fig. 2, curve at $y = 0.0125$), while the complete transformation occurred at 1300 °C. With a further increase in y the amount of monocelsian at 1200 °C increased at the expense of a diminishing amount of hexacelsian phase (Fig. 2, curve $y = 0.05$). If the effectiveness of the Ca and Sr substitution on the rate of the hexacelsian-to-celsian transformation are compared, we find that at the same level of substitution the Ca is more effective than the Sr (Fig. 2, curves at $x = 0.05$ and $y = 0.05$). However, the complete transformation of hexacelsian to monocelsian in $Sr_xBa_{1-x}Al_2Si_2O_8$ was already obtained at $x = 0.1$ and 1200 °C. In contrast, $BaAl_2Si_2O_8$ did not transform entirely to monocelsian, even at 1500 °C.

The formation of $Sr_xBa_{1-x}Al_2Si_2O_8$ solid solutions across the whole concentration range $0 \leq x \leq 1$ was confirmed by XRD and microstructural analyses. The unit-cell volume decreased linearly from $BaAl_2Si_2O_8$ to $SrAl_2Si_2O_8$, obeying Vegard's rule (Fig. 3). The SEM micrographs revealed a dense, single-phase microstructure for all compositions (Fig. 4).

3.2. Dielectric characterization

In order that the measured dielectric properties represented, as near as possible, the intrinsic properties of the material the powders were sintered to dense ceramics with typical porosity, as shown in Fig. 4. The measurements of the permittivity at 1 MHz and in the MW frequency region revealed that the permittivity did not change significantly with composition, although Ba^{2+}, Sr^{2+} and Ca^{2+} differ in terms of their dielectric polarizability. The permittivity also showed almost no significant frequency dispersion from 1 MHz ($\varepsilon = 7.3 \pm 0.1$) to 11 GHz ($\varepsilon = 7.2 \pm 0.1$). The dielectric losses at 1 MHz were low for all compositions ($\tan\delta < 10^{-4}$). The effect of substitution on the dielectric losses was noticed only in MW frequency range. In the case of a substitution with Ca the $Q \times f$ values decreased

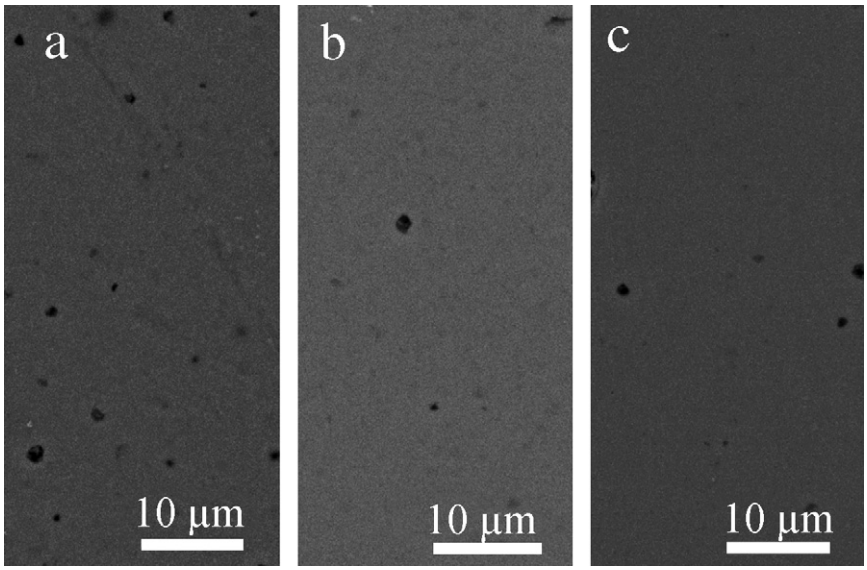

Fig. 4. Scanning electron micrograph of $BaAl_2Si_2O_8$ (a), $Sr_{0.5}Ba_{0.5}Al_2Si_2O_8$ (b) and $Ca_{0.025}Ba_{0.975}Al_2Si_2O_8$ (c) sintered at 1500 °C.

sharply with y in $Ca_yBa_{1-y}Al_2Si_2O_8$ (Fig. 5). Because of this the $Ca_yBa_{1-y}Al_2Si_2O_8$ solid solutions were synthesized and examined only up to $y = 0.05$.

The dependence of the dielectric losses on the composition for the $Sr_xBa_{1-x}Al_2Si_2O_8$ solid solutions in the MW frequency region was rather unexpected (Fig. 5). At first, the $Q \times f$ values decreased linearly with substitution up to $x = 0.4$. However, this decrease in the $Q \times f$ values was considerably smaller than that observed by Talmy et al.,[4] who reported four-times-higher dielectric losses for the $Sr_{0.25}Ba_{0.75}Al_2Si_2O_8$ ($x = 0.25$) ceramics compared to the $BaAl_2Si_2O_8$ ceramics. The $Q \times f$ values of 43,750 GHz (at 35 GHz), determined from $\tan\delta$ ($\tan\delta = 0.0008$ at 35 GHz), for the $BaAl_2Si_2O_8$ ceramics prepared by Talmy et al.[4] are considerably lower than the results ($Q \times f = 70{,}600$ GHz at 10.5 GHz (12 h) and $Q \times f = 77{,}700$ GHz at 10.5 GHz (40 h)) obtained in this study. Since the permittivities determined by Talmy et al. (6.16–7.04) were also lower than those in this study (7.2–7.3), we can deduce that this difference partly results from the different densities of the sintered samples. The higher degree of Al:Si order, which was obtained by a longer heat-treatment time (12, 40 h) and a slow cooling rate (0.7 °C/min), is also a possible reason for the higher $Q \times f$ values of the $Sr_xBa_{1-x}Al_2Si_2O_8$ solid solutions in this study. In Talmy's study the sintering time was only 5 h.[4]

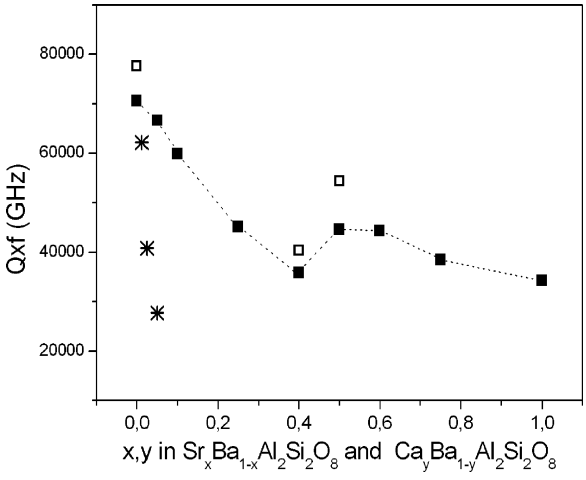

Fig. 5. $Q \times f$ values vs. composition for $Sr_xBa_{1-x}Al_2Si_2O_8$ (■, □) and $Ca_yBa_{1-y}Al_2Si_2O_8$ (✱) sintered at 1500 °C for 12 h (■, ✱) and 40 h (□) determined at 10.5 GHz.

When x was increased from $x = 0.4$ to 0.5 we noticed an unexpected increase in the $Q \times f$ values, which with further substitution began to decrease slightly (Fig. 5). Since the dielectric losses are closely related to the short-range (SRO) and long-range (LRO) orders, extensive studies of the ordering are needed for an explanation of this unusual phenomenon. The measurements of the dielectric properties also revealed a decrease of τ_f with substitution in the $Sr_xBa_{1-x}Al_2Si_2O_8$ material from $\tau_f = -22$ ppm/°C ($x = 0$) to $\tau_f = -30$ ppm/°C ($x = 1$).

In principle, the molar ratio Al:Si = 2:2 in $Sr_xBa_{1-x}Al_2Si_2O_8$ enables complete ordering of the Al and Si. However, this Al:Si ordering cannot be examined by XRD due to the small differences in the X-ray scattering efficiencies of Al and Si. Transmission electron microscopy (TEM) is, in this respect, a more useful technique for the study of LRO, whereas SRO should be studied by techniques that are sensitive to the local structure. Al:Si ordering in $CaAl_2Si_2O_8$ is known to be a sluggish process.[15] The fact that Al:Si ordering in $SrAl_2Si_2O_8$ is a slower process than in $CaAl_2Si_2O_8$ makes a study of the ordering in $Sr_xBa_{1-x}Al_2Si_2O_8$ even more difficult.[16] Since the $Q \times f$ values increased after a prolongation of the heat-treatment time from 12 to 40 h (Fig. 5), the samples heat treated for 12 h most probably did not attain the equilibrium state of Al:Si ordering. The increase in the $Q \times f$ values when x increased from 0.4 to 0.5 was even more pronounced for the samples with a prolonged heat treatment (40 h) (Fig. 5). Ba^{2+} and Sr^{2+} have the same charge, they differ only in size. For this reason the explanation for this increase in $Q \times f$ values is most probably not the ordering of the Ba:Sr, although their molar ratio is 1:1 at $x = 0.5$; most likely it is that the Ba:Sr ratio some-

how influences the Al:Si ordering. However, this must be proved by a detailed study of the dielectric properties in relation to the SRO and LRO of the variously heat-treated $Sr_xBa_{1-x}Al_2Si_2O_8$ solid solutions.

4. Conclusions

The substitution of Ba with Ca or Sr in $Sr_xBa_{1-x}Al_2Si_2O_8$ and $Ca_yBa_{1-y}Al_2Si_2O_8$ solid solutions promoted the hexacelsian-to-monocelsian transformation. Although the substitution with Ca was more efficient in the hexacelsian-to-monocelsian transformation than a substitution with Sr, it caused a greater increase in the dielectric losses, even for low values of y. While the permittivity at 1 MHz and 11 GHz was 7.3 and 7.2, respectively, regardless of the composition and the heat-treatment time (12, 40 h), the heat-treatment conditions and the composition influenced the microwave dielectric losses to a greater extent. Like with $BaAl_2Si_2O_8$, where the $Q \times f$ values increased from 70,600 to 77,700 GHz, when sintered for 12 and 40 h, respectively, the other $Sr_xBa_{1-x}Al_2Si_2O_8$ solid solutions also showed an increase in the $Q \times f$ values with a prolongation of the heat-treatment time. The higher $Q \times f$ values of the $Sr_xBa_{1-x}Al_2Si_2O_8$ solid solutions with the prolonged heat treatment most probably reflected a higher degree of Al:Si ordering. The $Q \times f$ values of the $Ca_yBa_{1-y}Al_2Si_2O_8$ decreased sharply with substitution, leading to a more-than-two-times lower $Q \times f$ value at $y = 0.05$, whereas the deterioration of the $Q \times f$ value of the $Sr_xBa_{1-x}Al_2Si_2O_8$ solid solutions was only 5% for the same level of substitution ($x = 0.05$). The $Q \times f$ values of the $Sr_xBa_{1-x}Al_2Si_2O_8$ solid solutions linearly decreased with x up to $x = 0.4$. At $x = 0.5$ a sudden increase in the $Q \times f$ values was observed. With further substitution ($0.5 < x \leq 1$) the $Q \times f$ values slightly decreased once again. The deviation from the linear decrease of the $Q \times f$ values at $x = 0.5$, which was even more pronounced after a prolonged heat treatment, can be attributed to the influence of the Ba:Sr ratio on the Al:Si ordering.

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