

# Polymorphism and dielectric electric properties of Ba- and Sr-containing feldspars

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The polymorphism and dielectric properties of  $\text{Ba}_{1-x}\text{Sr}_x\text{Al}_2\text{Si}_2\text{O}_8$  ( $x = 0.00, 0.01, 0.05, 0.10,$  and  $1.0$ ) feldspars were examined. Strontium additions enhanced the formation of the monoclinic phase, decreasing heat treatment times from three days to 24 hrs. The dielectric constants of all compositions varied between 7 and 8 over a temperature range of  $-175$  to  $200^\circ\text{C}$  and at 1, 10, and 100 kHz. An abrupt change (about 5%) in the dielectric constant of Sr-feldspar occurred at  $-70^\circ\text{C}$ , confirming the existence of the triclinic low temperature polymorph. © 2000 Kluwer Academic Publishers

## 1. Introduction

### 1.1. Summary of structure

The feldspars are the most abundant of all natural minerals and for that reason have been studied extensively even though they are one of the more complex of mineral groups. Structurally the feldspars are composed of a three-dimensional framework of corner-shared silica tetrahedra with each tetravalent silicon ion being surrounded by four divalent oxygen ions and each oxygen ion shared between two silicon ions (or their substitutes). If silicon were the only cation present the structure would be electrically neutral, however, the feldspars contain one or two trivalent aluminum ions substituted for silicon. To balance the charge, either alkali or alkaline earth cations are introduced into the structure. The effective size of the large cation (i.e., Ba) and the aluminum-silicon distribution determines the symmetry of the lattice. The large cations tend to support a more open monoclinic symmetry, whereas smaller cations (i.e., Ca) may allow the structure to collapse to triclinic symmetry facilitated by preferential ordering of the trivalent aluminum ions in the tetrahedral sites. A triclinic form at high temperature would tend to convert to monoclinic due to increases in effective ionic sizes and Al-Si disorder. The key structural feature is the formation of double chains parallel to the  $a$ -axis in a *crankshaft* fashion composed of four-membered rings of tetrahedra corner-shared with adjacent rings [1]. Since the bond lengths of the large cation to oxygen vary, the coordination of these large cations can vary depending on where one selects the coordination sphere [2]. The ideal coordination is seven, although most real materials are actually nine. The feldspars of interest for the present study are  $\text{BaAl}_2\text{Si}_2\text{O}_8$  and  $\text{SrAl}_2\text{Si}_2\text{O}_8$ . According to Newham and Megaw [3], barium is in 10-fold coordination, whereas strontium is believed to be in seven or nine as reported by Chiara *et al.* [4]. Ordering of the Al-Si tetrahedra is normal, however, disorder (generally not com-

plete) is commonly found in samples that are quenched rapidly from high temperature [2].

### 1.2. Polymorphism

Barium feldspar occurs in four polymorphs: two naturally and two synthetically occurring. In 1968 Lin and Foster [5] presented what has been accepted as the correct pressure-temperature relationships. The two naturally occurring forms are both monoclinic. The more abundant naturally occurring stable monoclinic form of  $\text{BaAl}_2\text{Si}_2\text{O}_8$  is called *celsian* (space group  $I2/c$ ) and the less abundant metastable form is called *paracelsian* (space group  $P2_1/a$ ). Since the transition from paracelsian to celsian is irreversible and since paracelsian has never been prepared synthetically, it is believed that paracelsian is truly a metastable form. Early investigators in an attempt to synthesize monoclinic celsian obtained a hexagonal variety [6], what was then called  $\alpha$ -*celsian*. Later studies [7] indicated that this variety, at room temperature, was really a pseudo-hexagonal (actually orthorhombic) variety with a rapidly reversible transition at  $300^\circ\text{C}$ . Müller [8] reported the space groups of these two forms as  $P6_3/mcm$  and  $Immm$  for the high and low temperature forms, respectively. The transition between the monoclinic celsian and the high temperature hexagonal synthetic variety, although reversible, is very sluggish. These facts along with similar XRD patterns for the synthetic varieties have caused some confusion in the early literature. Over the many years of investigation of these materials some disagreement has existed concerning the relationships among these forms and their nomenclature.

The polymorphism of  $\text{SrAl}_2\text{Si}_2\text{O}_8$  has been reported to be very similar to that of  $\text{BaAl}_2\text{Si}_2\text{O}_8$ . Three variations have been reported by Bruno and Gazzoni [9]. These include a naturally occurring monoclinic form similar to paracelsian that is called *slawsonite* ( $P2_1/a$ ), a synthetic monoclinic form ( $I2/c$ ) similar to celsian,

TABLE I Crystallographic data for BaAl<sub>2</sub>Si<sub>2</sub>O<sub>8</sub>

Polymorph	$\alpha$ -Hexacelsian		$\beta$ -Hexacelsian	Paracelsian
	Celsian [3]	[8]	[6]	[14]
$a(\text{\AA})$	8.627(2)	5.3	5.25	9.02(9)
$b$	13.045(3)	9.2	—	9.50(9)
$c$	14.408(4)	15.6	7.84	8.47(9)
$\beta$	115°13'(3)	—	—	90(0.5)°
Space Group	I2/c	Immm	P6 <sub>3</sub> /mcm	P2 <sub>1</sub> /a

TABLE II Crystallographic data for SrAl<sub>2</sub>Si<sub>2</sub>O<sub>8</sub>

Polymorph	Sr-feldspar	$\alpha$ -Hexacelsian	$\beta$ -Hexacelsian	Slawsonite
	[10]	[10]	[10]	[15]
$a(\text{\AA})$	8.3923(7)	—	5.1931(15)	8.888(2)
$b$	12.9708(8)	—	—	9.344(2)
$c$	14.2681(12)	—	7.5963(23)	8.326(3)
$\beta$	115.451(5)°	—	—	90.33°(2)
Space Group	I2/c	Immm	P6/mmm	P2 <sub>1</sub> /a

and a second synthetic form (P6/mmm) similar to hexacelsian. Slawsonite when heated transforms into the monoclinic form at 500°C, which is then stable to its melting point of 1650°C. Only quenching from the melt could form the hexagonal variety. Topel-Schadt *et al.* [10] and Bahat [11] reported a fourth form similar to the low temperature  $\alpha$ -hexacelsian with orthorhombic symmetry (Immm) that transforms to the high temperature hexagonal form at about 600°C. According to Bahat the hexagonal form has no field of stability. Topel-Schadt *et al.* also reported a second hexagonal variety with space group P6<sub>3</sub>/mcm. The ordering of the Al-Si tetrahedra determines which hexagonal variety forms. A monoclinic-to-triclinic transition has been reported to occur at room temperature and 32 kbar by McGuinn and Redfern [12]. A hexagonal form made from a mixture of Sr-sulfate and halloysite was reported earlier by Sorrell [13].

Due to the conflicting results published in the literature and the diversity of publications where these results are reported, the crystallographic data of these various polymorphs are summarized in Tables I and II as an aid to the reader.

### 1.3. Applications

Although BaAl<sub>2</sub>Si<sub>2</sub>O<sub>8</sub> has been studied for over 100 years, the first reported applications were in 1936 by Singer [16] for use in aluminum melting furnaces and salt-glaze stoneware kilns. These refractory materials were called *barium anorthite* and were prepared from BaCO<sub>3</sub> and clay. Some thought was given to the development of hexacelsian as a refractory by Yoshiki and Matsumoto [6] after it was found as a reaction product between alumino-silicate refractories and barium crown glasses. Its high melting point (>1700°C) was a prime factor in this idea. Although this may have been a reasonable concept, it was never developed as a refractory presumably due to the complexity of its polymorphism that was not very well understood at that time. More recent interest lies in the use of celsian as the

matrix material in fiber-reinforced composites for use in applications that require low electromagnetic wave absorption (e.g., radomes) [17]. The current study was undertaken to evaluate celsian as a substrate for electrical applications.

## 2. Experimental

Compositions were prepared by mixing dry reagent-grade BaCO<sub>3</sub>, SrCO<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub>, and calcined silicic acid. The starting materials were thoroughly mixed with acetone, dried, and heat treated to 900°C for 12 hrs in platinum crucibles. The samples were then remixed with acetone, dried, and pressed into 12-mm pellets and heat treated to 1200°C/12 hrs. This process was repeated with a subsequent heat treatment at 1500°C/72 hrs. All samples were remixed and repressed prior to further thermal treatment. Routine phase identification was determined by a Siemens X-ray diffractometer using nickel-filtered Cu K $\alpha$  radiation and a scanning rate of 1° 2 $\theta$ /min. The expansion of the two pure feldspars was thermally characterized by a Harrop Laboratories dilatometer at a heating rate of 2°C/min. on a 2 inch long sample. The dielectric properties were determined on sintered one gram pellets that had been polished and electroded with a thin film of gold and silver paint. The dielectric constant and dissipation factor were determined at 1, 10, and 100 kHz using an HP 4194/A instrument cooled from 200°C to -175°C at a rate of 2°C/min.

## 3. Result and discussion

### 3.1. Polymorphism

The main emphasis of the current work was to examine the dielectric properties of celsian, since it had been reported to have a low dielectric constant. However, for practical applications the polymorphism had to be understood and appropriate processing had to be developed. As expected the initial attempts at preparing Ba-celsian yielded the hexagonal form. Studies were undertaken to determine the heat treatment necessary to form the monoclinic phase. The conversion from the hexagonal to the monoclinic form took several days, confirming the sluggishness of this reaction reported in the literature. Not wanting to add mineralizers that would affect the electrical properties, it was decided to investigate the incorporation of strontium. As reported by Bansal *et al.* [18] and Talmy *et al.* [19] additions of strontium act to enhance the formation of the monoclinic Celsian solid solution phases due to increased lattice distortions. Thus the compositions listed in Table II were prepared and investigated. All samples were prepared by solid state reaction unlike many studies reported in the literature where the compositions were first melted and then recrystallized. This was done predominately due to the high temperature required for melting—above 1750°C.

The calcined materials were heat treated at temperatures ranging from 1400 to 1650°C for times ranging from several hours to several days. It was found that the Ba only compositions could be converted from

the hexagonal to the monoclinic form and back to the hexagonal form with heat treatments of 48 hrs when treated at temperatures about 50°C on either side of the inversion temperature of 1590°C. Lower temperatures required progressively longer times for formation of the monoclinic phase. The Sr only composition had formed the monoclinic phase after the preliminary heat treatments and thus further processing was unnecessary. The hexagonal form of the Sr only phase was never encountered, presumably due to the solid state reaction method used in this study versus the melting and recrystallization used by others. The metastable hexagonal phase forms first upon crystallization of a glass at temperatures less than 1000°C as reported by Bansal *et al.* [18]. Thus the existence of the Sr hexagonal phase with its inversion to the Sr orthorhombic phase was not confirmed. The only pure Sr phase encountered was the monoclinic form. Mixtures of Ba and Sr were found to form a complete series of single phase crystalline solutions with monoclinic symmetry. Reaction times required for formation of the monoclinic phase were decreased to 24 hrs for the compositions near the pure Ba composition. Although these times are a major improvement over the several days for the pure Ba compositions, they are not unreasonable. Shorter times gave mixtures of the monoclinic and hexagonal phases.

The thermal expansion coefficient (TEC) for the Ba-feldspar was  $2.52 \times 10^{-10}/^\circ\text{C}$  (40–1000°C). Both the polymorphism and the expansion coefficient indicated that the monoclinic phase was the most desirable for practical applications. The TEC of the Sr only phase was very similar to that of the Ba only phase, being slightly higher at  $2.68 \times 10^{-10}/^\circ\text{C}$  (40–1000°C). Thus no major variations of the TEC for the crystalline solutions were expected and none were found.

### 3.2. Electrical properties

The room temperature dielectric constants and dissipation factors determined at 1, 10, and 100 kHz are listed in Tables III and IV. These measurements are the average of three samples for each of the compositions. The

TABLE III Room temperature dielectric constants

COMPOSITION	1 kHz	10 kHz	100 kHz
BaAl <sub>2</sub> Si <sub>2</sub> O <sub>8</sub>	7.91 ± 0.03	7.79 ± 0.03	7.77 ± 0.03
Ba <sub>0.99</sub> Sr <sub>0.01</sub> Al <sub>2</sub> Si <sub>2</sub> O <sub>8</sub>	7.33 ± 0.17	7.21 ± 0.15	7.20 ± 0.15
Ba <sub>0.95</sub> Sr <sub>0.05</sub> Al <sub>2</sub> Si <sub>2</sub> O <sub>8</sub>	7.04 ± 0.05	7.08 ± 0.15	7.02 ± 0.08
Ba <sub>0.90</sub> Sr <sub>0.10</sub> Al <sub>2</sub> Si <sub>2</sub> O <sub>8</sub>	7.23 ± 0.06	7.11 ± 0.05	7.09 ± 0.05
SrAl <sub>2</sub> Si <sub>2</sub> O <sub>8</sub>	7.50 ± 0.43	7.41 ± 0.44	7.39 ± 0.42

TABLE IV Room temperature dissipation factors

COMPOSITION	1 kHz ( $\times 10^{-2}$ )	10 kHz ( $\times 10^{-2}$ )	100 kHz ( $\times 10^{-2}$ )
BaAl <sub>2</sub> Si <sub>2</sub> O <sub>8</sub>	3.36 ± 0.24	0.35 ± 0.01	0.18 ± 0.01
Ba <sub>0.99</sub> Sr <sub>0.01</sub> Al <sub>2</sub> Si <sub>2</sub> O <sub>8</sub>	3.79 ± 0.15	0.37 ± 0.05	0.19 ± 0.02
Ba <sub>0.95</sub> Sr <sub>0.05</sub> Al <sub>2</sub> Si <sub>2</sub> O <sub>8</sub>	4.31 ± 0.92	2.23 ± 0.70	0.69 ± 0.31
Ba <sub>0.90</sub> Sr <sub>0.10</sub> Al <sub>2</sub> Si <sub>2</sub> O <sub>8</sub>	3.76 ± 0.13	0.03 ± 0.03	0.18 ± 0.02
SrAl <sub>2</sub> Si <sub>2</sub> O <sub>8</sub>	3.31 ± 0.52	0.27 ± 0.02	0.15 ± 0.01

dielectric constant was approximately 7 to 8, which is desirable for substrate materials. Since the dielectric constant is a measure of the ease of forming electric dipoles, one would expect a structure that is more loosely bound and one that has more irregular polyhedra to have a higher dielectric constant. Since the Al-Si network of the pure Ba- and Sr-feldspars is very similar any structural differences should be due mostly to differences in the Ba and Sr polyhedra. The Ba polyhedra in Ba-feldspar have been reported to be more regular than the Sr polyhedra in Sr-feldspar [4]. In addition the coordination of the Ba polyhedra is greater than the Sr polyhedra (10 vs 7 or 9), meaning a slightly weaker bonding. Bonding within the Al-Si network is strong and will not easily orient with an applied electric field. In addition the heavy Ba and Sr ions restrict polarization since they are difficult to move. The higher coordination and weaker bonding would lead one to expect the Ba-feldspar to have a higher dielectric constant than the Sr-feldspar, although the more regular polyhedra of barium would lead one to expect the opposite. Since the Ba-feldspar has the higher dielectric constant it appears that the weaker bonding is more important than regularity of the polyhedra. These values are slightly higher than those reported by Talmy *et al.* [19] most likely due to being determined at a higher frequency (35 GHz) than the current study (1–100 kHz). The values of dielectric constant obtained for the solid solutions were all lower than either pure end member. Although one would expect them to be lower than the pure Ba-feldspar, the reason they are lower than the Sr-feldspar is not clear. Using the above structural reasoning, the lower dielectric constants for the solid solutions may indicate that their polyhedra are even more strongly bonded than the pure Sr-feldspar. Consistent with the data of Talmy *et al.* [19] the three intermediate solid solutions all had higher dissipation factors even though Talmy's were determined at a higher frequency where the polarization mechanisms are different. However the dielectric constants reported by Talmy *et al.* were higher for the solid solutions, opposite to that found in the present study.

Figs 1 and 2 show the variation of the dielectric constant with temperature. It can be seen that very little temperature effect was present and a slight increase was noted with increasing frequency. The most interesting

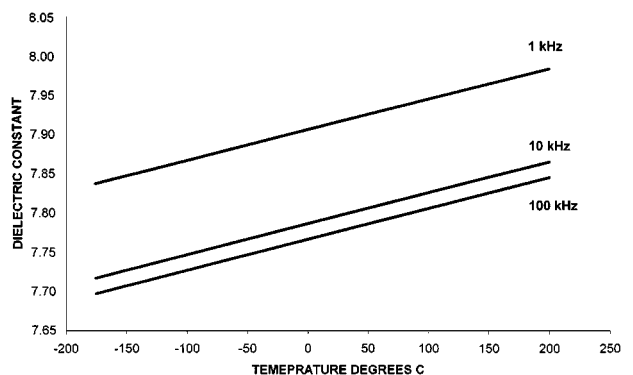


Figure 1 Variation of dielectric constant with temperature at 1, 10, and 100 kHz of BaAl<sub>2</sub>Si<sub>2</sub>O<sub>8</sub>.

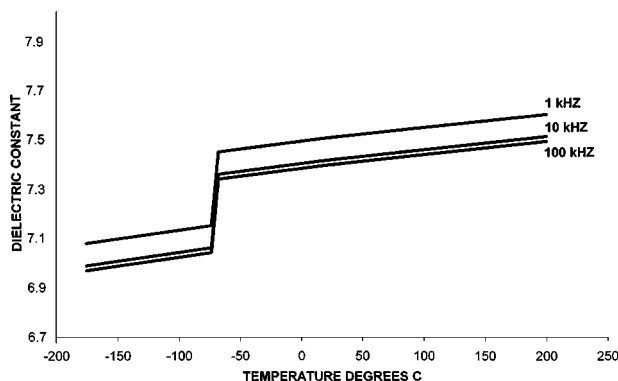


Figure 2 Variation of dielectric constant with temperature at 1, 10, and 100 kHz of  $\text{SrAl}_2\text{Si}_2\text{O}_8$ .

temperature effect was present in the Sr only phase (see Fig. 2). In this composition the dielectric constant exhibited an abrupt change at about  $-70^\circ\text{C}$ . This change was present in all samples tested and at all three frequencies. It is believed that this change was due to the transformation between the monoclinic and triclinic forms of Sr feldspar. This is consistent with the formation of the triclinic phase reported by McGuinn and Redfern [12] at room temperature and 32 kBar. It is well known that temperature and pressure have opposite effects on transformation temperatures. Thus the increase in pressure of 32 kBar and the decrease in temperature of about  $90^\circ\text{C}$  have the same effect on the structure. With increasing temperature the dielectric constant increased abruptly by about 5% at the transition. This transition did not show up in any of the other compositions. A lower dielectric constant for the low temperature form is consistent with the low temperature triclinic form being more tightly bonded than the high temperature monoclinic form. Although a trend of decreasing dielectric constant with increasing strontium content was not readily apparent, and realizing that the composition containing 5% Sr had a slightly higher porosity than the others (thus yielding a lower dielectric constant), it is believed that the minimum in dielectric constant may occur at higher strontium contents than examined in this study.

#### 4. Conclusions

Barium feldspar with its low dielectric constant is an excellent candidate as a substrate material for electrical applications. However, small additions of a second cation, like Sr, are required to enhance the formation of the monoclinic phase. Also the incorporation of Sr acts to slightly lower the dielectric constant, even below that of the pure Sr phase. It is believed that the minimum in dielectric constant may occur at a com-

position containing more strontium than was examined in this study. The monoclinic phase must be obtained to eliminate any problems associated with polymorphic transitions. The relatively low thermal expansion makes these materials desirable material for those applications where expansion may be a problem. The abrupt change in the dielectric constant on cooling to  $-70^\circ\text{C}$  for the monoclinic Sr-feldspar is believed to confirm the presence of a triclinic phase reported earlier by McGuinn and Redfern.

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