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**DEVELOPMENT OF LOW COST  
(Sr,Ca)<sub>3</sub>Al<sub>2</sub>O<sub>6</sub> DIELECTRICS FOR  
Bi<sub>2</sub>Sr<sub>2</sub>CaCu<sub>2</sub>O<sub>8+δ</sub> APPLICATIONS**

**Timothy Haugan, Winnie Wong-Ng, Lawrence P. Cook,  
Richard G. Geyer, Henrietta J. Brown, Lydon  
Swartzendruber, and James Kaduk**



**OCTOBER 2003**

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<b>14. ABSTRACT</b> Aspects of the development of low-cost (Sr,Ca) <sub>3</sub> Al <sub>2</sub> O <sub>6</sub> dielectrics for Bi <sub>2</sub> Sr <sub>2</sub> CaCu <sub>2</sub> O <sub>8+d</sub> superconductor applications were investigated. A tie-line phase equilibrium relationship between Bi <sub>2</sub> Sr <sub>2</sub> CaCu <sub>2</sub> O <sub>8+d</sub> and Sr <sub>2</sub> CaAl <sub>2</sub> O <sub>6</sub> compositions was observed at 860 °C. When the Bi-2212 and (Sr,Ca) <sub>3</sub> Al <sub>2</sub> O <sub>6</sub> solid-solution compositions were changed slightly, the tie-line relationship was not preserved, and a new phase was observed to form with composition ~ BiSr <sub>1.5</sub> Ca <sub>0.5</sub> Al <sub>2</sub> O <sub>x</sub> . Composites of (0 to 24) volume fraction % Sr <sub>2</sub> CaAl <sub>2</sub> O <sub>6</sub> + Bi <sub>2</sub> Sr <sub>2</sub> CaCu <sub>2</sub> O <sub>8+d</sub> equilibrated at 860 °C slightly reduced the T <sub>c</sub> (by 2 K to 4 K) and superconducting volume percentage of the 2212 phase.							
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# Development of Low Cost $(\text{Sr,Ca})_3\text{Al}_2\text{O}_6$ Dielectrics for $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$ Applications

Timothy Haugan, Winnie Wong-Ng, Lawrence P. Cook, Richard G. Geyer, Henrietta J. Brown, Lydon Swartzendruber, and James Kaduk

**Abstract**—Aspects of the development of low-cost  $(\text{Sr,Ca})_3\text{Al}_2\text{O}_6$  dielectrics for  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$  superconductor applications were investigated. A tie-line phase equilibrium relationship between  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$  and  $\text{Sr}_2\text{CaAl}_2\text{O}_6$  compositions was observed at 860 °C. When the Bi-2212 and  $(\text{Sr,Ca})_3\text{Al}_2\text{O}_6$  solid-solution compositions were changed slightly, the tie-line relationship was not preserved, and a new phase was observed to form with composition  $\sim \text{BiSr}_{1.5}\text{Ca}_{0.5}\text{Al}_2\text{O}_x$ . Composites of (0 to 24) volume fraction %  $\text{Sr}_2\text{CaAl}_2\text{O}_6$  +  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$  equilibrated at 860 °C slightly reduced the  $T_c$  (by 2 K to 4 K) and superconducting volume percentage of the 2212 phase. The dielectric properties of (Sr = 1.0 to 2.5) members of solid-solution  $(\text{Sr,Ca})_3\text{Al}_2\text{O}_6$  were measured at 77 K and 297 K in the range of (10 to 11) GHz for cylindrical samples using resonant system methods. The dielectric constant  $\epsilon_r$  varied from 9.7 to 13.2, and the loss tangent  $\tan \delta$  was from  $3 \times 10^{-4}$  to  $8 \times 10^{-4}$ .

**Index Terms**—  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$ , dielectric constant and loss tangent,  $(\text{Sr,Ca})_3\text{Al}_2\text{O}_6$ , tie-line phase equilibrium.

## I. INTRODUCTION

$\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$  (Bi-2212) superconductors with  $T_c \leq 95$  K are candidates for bulk and thin film applications such as power filters, microwave devices, and long length wires [1]. Bi-2212 conductors have achieved high  $J_c$ s ( $> 10^5$  A/cm<sup>2</sup> at 5 K and  $> 2 \times 10^4$  A/cm<sup>2</sup> at 77 K) when processed by lower cost methods such as thick film coating on Ag [2] or Ni [3]. For many superconducting applications, the development and

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use of low-cost dielectric materials with minimal chemical reaction would be desired to improve processing and reduce costs. For long length conductor applications, the use of lower-cost materials is a critical factor in determining their viability.

In the literature, there are limited studies available on the chemical compatibility of dielectric materials with Bi-2212. Many of the common dielectric materials, such as  $\text{MgO}$ ,  $\text{Al}_2\text{O}_3$ , and  $\text{Zr(Y)O}_2$  are known to react with Bi-2212 [4].

A possible class of low-cost materials to consider for dielectrics are Bi-Sr-Ca-Cu-Al oxides.  $\text{Al}_2\text{O}_3$  or Al-based oxides are well-characterized dielectric materials for high-temperature-superconductor (HTS) applications [5], [6] and Al is easily available at very low cost. The use of Bi-Sr-Ca-Cu-Al-O phases would provide a lower cost alternative than Bi-Sr-Ca-Cu-O phases. However the crystalline phases in  $\text{BiO}_{1.5}\text{-SrO-CaO-CuO-AlO}_{1.5}$  multi-dimensional equilibrium phase space are not completely known, as even the ternary phase diagrams for  $\text{BiO}_{1.5}\text{-SrO-AlO}_{1.5}$  and  $\text{BiO}_{1.5}\text{-CaO-AlO}_{1.5}$  have not been studied, and there are no quaternary Bi-Sr-Ca-Cu-Al-O phases listed in the ICDD powder diffraction pattern database [7] thus far. The Gibbs phase rule predicts that, in general, Bi-2212 will coexist in (stable) chemical equilibrium with various combinations of four other phases in  $\text{BiO}_{1.5}\text{-SrO-CaO-CuO-AlO}_{1.5}$  phase space. These phases and combinations, and the nature of the tie-line distributions connecting Bi-2212 to other phases, are not completely known yet.

The reaction of  $\text{Al}_2\text{O}_3$  with Bi-2212 type compositions has been observed in thick film tapes on Ag [8]-[10], in bulk compounds and subsolidus reactions [4], [11]-[13], for fiber or single crystal growth [14], [15] and for thick film growth on  $\text{Al}_2\text{O}_3$  [16]. The formation of  $(\text{Sr,Ca})_3\text{Al}_2\text{O}_6$  (and other Bi-Sr-Ca-Cu-Al-O phases) has been observed in reactions of films and bulk composites [4], [8]-[13], [16].

This paper presents additional evidence of the chemical stability of  $(\text{Sr,Ca})_3\text{Al}_2\text{O}_6$  with Bi-2212, and measures the dielectric properties of  $(\text{Sr,Ca})_3\text{Al}_2\text{O}_6$  at 297 K and at operational temperature for some devices (77 K).

## II. EXPERIMENTAL

Precursor powders of Bi-Sr-Ca-Cu-Al-O were prepared by the solid-state method, using high purity ( $> 99.95\%$ ) powders of  $\text{Bi}_2\text{O}_3$ ,  $\text{SrCO}_3$ ,  $\text{CaCO}_3$ ,  $\text{CuO}$ , and ( $\sim 0.3 \mu\text{m}$ )  $\text{Al}_2\text{O}_3$  as reactants. Solid-state powders were mixed and ground with agate mortar and pestle, calcined by heating from 650 °C to  $T_{\text{calcine}}$  at 25 °C/h, and subsequent annealing at higher

temperatures (up to  $T_{\max}$ ), with intermediate grinding. Powders were annealed until phase equilibrium was reached at  $T_{\max}$  (~ 3 - 4 times), as determined by X-ray diffraction (XRD). Powders were annealed in air with different  $T_{\text{calcine}}$  and  $T_{\max}$  temperatures: for Bi-Sr-Ca-Cu-O  $T_{\text{calcine}} = 830$  °C and  $T_{\max} = 860$  °C, for Bi-Sr-Ca-Cu-Al-O  $T_{\text{calcine}} = 800$  °C and  $T_{\max} = 850$  °C, and for  $(\text{Sr,Ca})_3\text{Al}_2\text{O}_6$   $T_{\text{calcine}} = 1225$  °C and  $T_{\max} = 1275$  °C to 1325 °C. Powders were reacted in pellet form (~ 1 cm diameter, ~ 0.5 g to ~ 1.0 g batches), formed by lightly pressing (~  $10 \times 10^6$  Pa) in molds. Pellets were reacted on sacrificial powder in contact with polycrystalline MgO supports. The slow-heat calcination reaction (25 °C/h) was used to reduce intermediate melting reactions of sacrificial powders (in particular containing  $\text{Bi}_2\text{O}_3$ ) with MgO supports, and reduce formation of intermediate compounds [17].

Composites of solid-solution Bi-2212 and  $(\text{Sr,Ca})_3\text{Al}_2\text{O}_6$  (0 to 24 volume fraction % addition) were prepared by reacting fully sintered Bi-Sr-Ca-Cu-O powders with nanophase  $\text{Al}_2\text{O}_3$ . Nanophase  $\text{Al}_2\text{O}_3$  powder (10 nm to 20 nm, 99.98%, gamma-alpha, density  $\cong 3.965$  g/cm<sup>3</sup>) powder was purchased commercially [18].

X-ray diffraction data was obtained with a Philips\* diffractometer with 12 mm optics, incident Soller slits, a theta compensating slit with graphite monochromator, and automated with the use of Radix Databox interfaces. Two-theta peak positions were externally calibrated using SRM 660,  $\text{LaB}_6$  [19] as a reference. Data was collected using  $\text{Cu K}\alpha$  radiation with a  $2\theta$  step-size of 0.03° and a 1.8 s count time.

Superconducting properties of powders were measured using a SQUID magnetometer (Quantum Design, MPMS/MPMS<sup>2</sup>). Zero-field-cooled (ZFC) and field-cooled (Meissner FC) measurements were measured using heating and cooling cycles from 5 K to 125 K [20]. The superconducting volume percentages were calculated using  $\chi(\%) = 4\pi\chi_v/(1-D*4\pi\chi_v)$ , where  $\chi_v = M/H_{\text{appl}}$  is the measured magnetic susceptibility [emu/cm<sup>3</sup>\*Oe], and  $D = 0.33333$  is the demagnetization factor assuming a spherical particle distribution [20]. The volume percentages were normalized for values achieved with phase pure 2212 powders. The applied magnetic field was  $H_{\text{appl}} = 10$  Oe -  $H_{\text{rem}}$ , where  $H_{\text{rem}}$  is the remnant field of the magnet after resetting to zero measured to  $\pm 0.1$  Oe accuracy.

Densities of crystalline phases used to calculate volumes were  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta} = 6.60$  g/cm<sup>3</sup> [17], [21] and  $\text{Bi}_{2.1}\text{Sr}_{1.66}\text{Ca}_{1.24}\text{Cu}_2\text{O}_{8+\delta} = 6.63$  g/cm<sup>3</sup> [22]. The density of  $\text{Sr}_3\text{Ca}_x\text{Al}_2\text{O}_6$  was calculated for different Ca content ( $x = 0$  to 3) using a polynomial equation fit of Rietveld XRD refinements of powder samples prepared with Ca = 1.0 to 2.0, and ICDD files for Ca = 0 and 3 [7];  $\rho = 4.0894 - 0.179x - 0.084364x^2$  for x Ca content. The densities for  $(\text{Sr,Ca})_3\text{Al}_2\text{O}_6$  using the polynomial fit are in close agreement (< 0.2 %) with values by Walz [23]. The Ca content of  $(\text{Sr,Ca})_3\text{Al}_2\text{O}_6$  in composites was determined using a linear equation fit of multiple measurements of the  $2\theta$  shift of the highest intensity XRD peak of  $(\text{Sr,Ca})_3\text{Al}_2\text{O}_6$  bulk powders with Ca  $\geq 1.0$ .

Dielectric properties of  $(\text{Sr,Ca})_3\text{Al}_2\text{O}_6$  were measured at 297 K and 77 K using the specimen as a cylindrical dielectric resonator situated between the endplates of a copper cavity [24], [25]. Cylindrical rod specimens (~ 8 mm diameter and height) were prepared by calcining pellets for ~ 1000 h to achieve high density: 88% (Sr = 2.5), 90% (Sr = 2.0, 1.5) and 94% (Sr = 1.0) of theoretical density. After densification, the cylindrical rods were uniform and free of defects. The ends of the cylinders were leveled and optically polished for measurements. The average diameter and height of the cylinders were measured to an accuracy of  $\pm 0.00005$  cm (relative uncertainty < 0.015 %). Dielectric constant and loss tangent measurements were corrected to theoretical density using the Bruggeman effective medium theory formulation for a two-phase composite [26], and assuming the same difference between observed and theoretical density at 77 K as that at 297 K.

Temperatures used for processing were measured at reaction sites with S-type thermocouples calibrated with gold melting (standard uncertainty ~ 2°C).

\*Certain commercial equipment is identified in order to adequately specify the experimental procedure; recommendation or endorsement by the National Institute of Standards and Technology is not therein implied.

### III. RESULTS

#### A. Subsolidus Chemical Reactions

Fig. 1 shows XRD patterns of  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_x + \text{Sr}_2\text{CaAl}_2\text{O}_6$  composites, after high-temperature annealing at 860 °C for > 500 h. The XRD patterns in Fig. 1 did not change significantly with additional annealing, indicating that chemical equilibrium has been reached. The peaks for  $\text{Sr}_2\text{CaAl}_2\text{O}_6$  are clearly seen in Fig. 1 for increasing volume % addition (6 % to 24 %). With no changes in XRD, Figure 1 indicates that a tie-line relationship exists between  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$  and  $\text{Sr}_2\text{CaAl}_2\text{O}_6$  phase compositions in multi-dimensional  $\text{Bi}_{1.5}\text{O-SrO-CaO-CuO-Al}_{1.5}\text{O}$  equilibrium phase space.

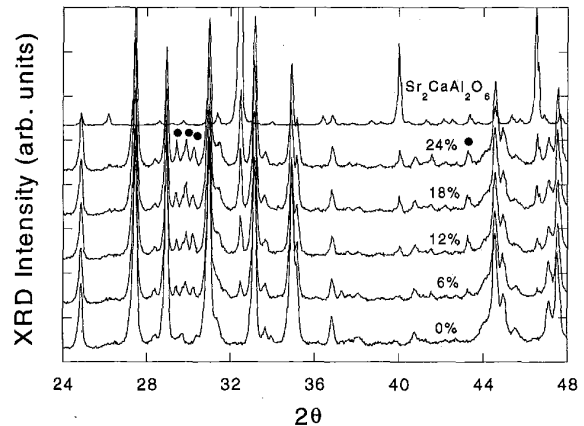


Fig. 1. XRD patterns of phase-pure  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$  (0%), Bi-2212 + N volume %  $\text{Sr}_2\text{CaAl}_2\text{O}_6$  composites sintered at 860 °C, and  $\text{Sr}_2\text{CaAl}_2\text{O}_6$ ; • is  $\text{Bi}_2(\text{Sr,Ca})_{3.9}\text{O}_y$  phase (Cu-free).

The average Ca content of the  $(\text{Sr,Ca})_3\text{Al}_2\text{O}_6$  phase in the composites in Fig. 1 was  $\text{Ca} = 1.01 \pm 0.01$ , exactly similar to the Ca content of the  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_x$  phase composition.

In contrast to Fig. 1, the reaction of solid-solution Bi-2212 with  $(\text{Sr,Ca})_3\text{Al}_2\text{O}_6$  when the Bi-Sr-Ca ratios were varied slightly did not result in a pure tie-line relationship. When  $\text{Bi}_{2.1}\text{Sr}_{1.66}\text{Ca}_{1.24}\text{Cu}_2\text{O}_x$  (solid-solution Bi-2212 [22]) was sintered with 12 volume % of  $\text{Sr}_{1.71}\text{Ca}_{1.29}\text{Al}_2\text{O}_6$  (via reaction of Bi-Sr-Ca-Cu-O with nanosize  $\text{Al}_2\text{O}_3$ ), new XRD peaks appeared in the pattern, as shown in Fig. 2. The new XRD peaks in Fig. 2 corresponded closely to XRD peaks for  $\text{BiSr}_{1.5}\text{Ca}_{0.5}\text{Al}_2\text{O}_x$  composition, a new phase whose exact composition, lattice parameters, and solid-solution range have not been accurately determined yet [12]. Fig. 2 indicates a small amount of  $\sim \text{Sr}_{1.6}\text{Ca}_{1.4}\text{Al}_2\text{O}_6$  was also observed in the composite, which suggests the composition lies within a multiphase region in  $\text{BiO}_{1.5}\text{-SrO-CaO-CuO-AlO}_{1.5}$  phase space.

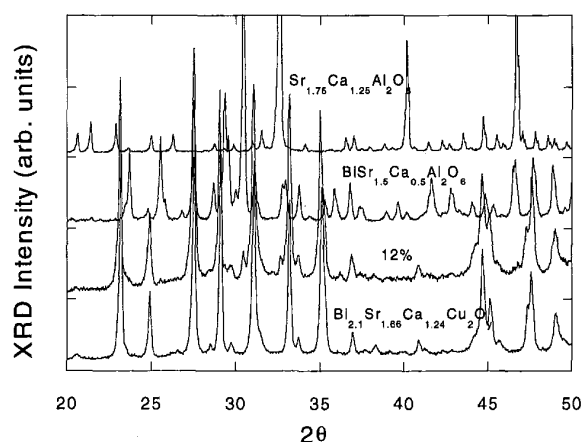


Fig. 2. XRD patterns of phase pure  $\text{Bi}_{2.1}\text{Sr}_{1.66}\text{Ca}_{1.24}\text{Cu}_2\text{O}_x$  (0%), a composite of  $\text{Bi}_{2.1}\text{Sr}_{1.66}\text{Ca}_{1.24}\text{Cu}_2\text{O}_x + \sim \text{BiSr}_{1.5}\text{Ca}_{0.5}\text{Al}_2\text{O}_x + \sim \text{Sr}_{1.6}\text{Ca}_{1.4}\text{Al}_2\text{O}_6 +$  unknown phases ( $\sim 12\%$  Al-type phases) sintered at  $860^\circ\text{C}$ , and reference patterns of Al-type phases.

### B. Superconducting Properties of Bi-2212 + $\text{Sr}_2\text{CaAl}_2\text{O}_6$ Composites

The superconducting properties of Bi-2212 +  $\text{Sr}_2\text{CaAl}_2\text{O}_6$  composites equilibrated at  $860^\circ\text{C}$  are given in Table I, for different volume percent addition of  $\text{Sr}_2\text{CaAl}_2\text{O}_6$ . The Meissner and ZFC volume fractions of superconducting material reduced to 75% to 70%, similar to results by Kazin [12]. The reduction observed, however was not a function of the volume percentage of  $\text{Sr}_2\text{CaAl}_2\text{O}_6$  added. Some reduction of superconductive volume fractions was expected in the composites, as the reaction route used (sintering of Bi-Sr-Ca-Cu-O with nanosize  $\text{Al}_2\text{O}_3$ ) produced a large amount of Cu-free phase as seen in Fig. 1. The Cu-free phase is most normally observed during processing of  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$  composition powders [27], and can only be eliminated (as shown in Fig. 1) by precise control of the heating temperatures and times during calcination and sintering.

The superconducting transition temperatures ( $T_c$ ) in Table I for Bi-2212 +  $\text{Sr}_2\text{CaAl}_2\text{O}_6$  composites reduced to (78 – 80) K from 82 K. The slight reduction of  $T_c$  could result from substitution of Al for Cu in Bi-2212 ( $< 0.1$  concentration per formula unit) [14], or from Bi-2212 composition variations resulting from the presence of Cu-free or other impurity phases. Other studies have shown no reduction of  $T_c$  with Al addition [13], so it's unknown whether the decrease in  $T_c$  in Table I is from Al substitution on the Cu site, or slight changes in Bi-Sr-Ca-Cu-O composition by varying processing conditions.

TABLE I  
SUPERCONDUCTING PROPERTIES OF  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_x + \text{Sr}_2\text{CaAl}_2\text{O}_6$   
COMPOSITE POWDERS

$\text{Sr}_2\text{CaAl}_2\text{O}_6$ Volume Percent (%)	Meissner FC Volume Fraction* ( $\pm 1\%$ )	ZFC Volume Fraction* ( $\pm 1\%$ )	$T_c$ ( $\pm 0.5^\circ\text{K}$ )
0	100	100	82
6	74	71	78
12	73	69	78
18	75	72	78
24	74	72	80

\*Measured for Bi-Sr-Ca-Cu-O volume.

### C. Dielectric Properties of $(\text{Sr,Ca})_3\text{Al}_2\text{O}_6$

It is essential to determine the dielectric properties for device performance and modeling. Table II gives the dielectric properties of ( $\text{Sr} = 1.0$  to  $2.5$ ) solid-solution members of  $(\text{Sr,Ca})_3\text{Al}_2\text{O}_6$ . The  $\text{Sr} = 1.0$  to  $2.0$  compositions in Table II were phase pure materials after extended annealing and pellet densification. The XRD patterns of the  $\text{Sr} = 1.0$  to  $2.0$  powders could be fitted by the Rietveld method using a cubic crystal system with space group Pa3 (#205), which was also used to fit the XRD patterns of  $\text{Sr} = 0$  and  $3$  members (JCPDS cards #24-1187 and #38-1429 [7]). The XRD pattern of the  $\text{Sr} = 2.5$  member, however, has not been accurately fitted by the Rietveld method thus far. The XRD pattern contains extra peaks, which indicates a crystal structure with lower symmetry, or a mixture of phases in the sample. Additional annealing at higher temperatures ( $1400^\circ\text{C} - 1450^\circ\text{C}$ ) did not change the pattern appreciably.

The dielectric constant  $\epsilon_r$  for  $(\text{Sr,Ca})_3\text{Al}_2\text{O}_6$  in Table II decreases from  $\sim 12$  to  $10$  with increasing replacement of Sr for Ca. The Clausius-Mossotti relationship predicts  $\epsilon_r$  should increase with increasing Sr content, as the ionization polarizability of Sr is greater than Ca [28], [29]. However, the unit cell size increases with increasing Sr content [26 and herein], which has an opposing effect [28], [29]. The dielectric constant at  $77\text{ K}$  increased slightly for all compositions, compared to values measured at  $297\text{ K}$ . The slight change is similar to previous results for  $\text{Al}_2\text{O}_3$ ,  $\text{LaAlO}_3$ , and  $\text{NdGaO}_3$ , however is in large contrast to results for  $\text{SrTiO}_3$  (which increased significantly) [24]. The dielectric loss tangent  $\tan \delta$  has low values at  $77\text{ K}$  ( $3 \times 10^{-4}$  to  $6 \times 10^{-4}$ ), comparable to results for  $\text{LaAlO}_3$  or  $\text{MgO}$ , and an order of magnitude lower than  $\text{SrTiO}_3$  and  $\text{NdGaO}_3$  [24].

TABLE II  
DIELECTRIC PROPERTIES OF  $(\text{Sr,Ca})_3\text{Al}_2\text{O}_6$

Material	T (K)	Frequency (GHz)	$\epsilon_r$ ( $\pm 0.2\%$ )	$\tan \delta$ ( $\pm 2 \times 10^{-5}$ )
$\text{SrCa}_2\text{Al}_2\text{O}_6$	297	10.540	12.245 (13.29)	$4.29 \times 10^{-4}$ ( $4.3 \times 10^{-4}$ )
$\text{Sr}_{1.5}\text{Ca}_{1.5}\text{Al}_2\text{O}_6$	297	11.126	10.92 (12.58)	$3.83 \times 10^{-4}$ ( $3.9 \times 10^{-4}$ )
$\text{Sr}_2\text{CaAl}_2\text{O}_6$	297	11.362	10.31 (11.97)	$3.10 \times 10^{-4}$ ( $3.2 \times 10^{-4}$ )
$\text{Sr}_{2.5}\text{Ca}_{0.5}\text{Al}_2\text{O}_6$	297	11.567	9.73 (11.50)	$8.11 \times 10^{-4}$ ( $8.3 \times 10^{-4}$ )
$\text{SrCa}_2\text{Al}_2\text{O}_6$	77	10.167	13.2 (14.33)	$5.62 \times 10^{-4}$ ( $5.7 \times 10^{-4}$ )
$\text{Sr}_{1.5}\text{Ca}_{1.5}\text{Al}_2\text{O}_6$	77	10.761	11.7 (13.49)	$5.86 \times 10^{-4}$ ( $6.0 \times 10^{-4}$ )
$\text{Sr}_2\text{CaAl}_2\text{O}_6$	77	11.191	10.65 (12.37)	$3.18 \times 10^{-4}$ ( $3.2 \times 10^{-4}$ )
$\text{Sr}_{2.5}\text{Ca}_{0.5}\text{Al}_2\text{O}_6$	77	11.451	9.94 (11.76)	$5.85 \times 10^{-4}$ ( $6.0 \times 10^{-4}$ )

\*Data corrected for pellet densification is given in brackets.

### CONCLUSIONS

A tie-line phase equilibrium relationship between  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$  and  $\text{Sr}_2\text{CaAl}_2\text{O}_6$  compositions was observed at 860 °C in multi-dimensional  $\text{BiO}_{1.5}\text{-SrO-CaO-CuO-AlO}_{1.5}$  phase space. When the Bi-2212 and  $(\text{Sr,Ca})_3\text{Al}_2\text{O}_6$  solid-solution compositions were changed slightly to  $\text{Bi}_{2.1}\text{Sr}_{1.66}\text{Ca}_{1.24}\text{Cu}_2\text{O}_x$  and  $\text{Sr}_{1.71}\text{Ca}_{1.29}\text{Al}_2\text{O}_6$ , the tie-line relationship was not preserved, and a new phase was observed to form with composition  $\sim \text{BiSr}_{1.5}\text{Ca}_{0.5}\text{Al}_2\text{O}_x$ . Composites of (0 to 24) volume fraction %  $\text{Sr}_2\text{CaAl}_2\text{O}_6$  + Bi-2212 equilibrated at 860 °C slightly reduced the  $T_c$  by (2 to 4) K and superconducting volume fractions (to 70 % to 75 %) of the 2212 phase. Dielectric properties of (Sr = 1.0 to 2.5) members of  $(\text{Sr,Ca})_3\text{Al}_2\text{O}_6$  were measured at 77 K and 297 K.

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