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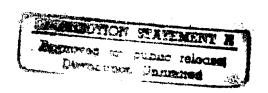
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Navy Case No. 71,959

CERAMIC MATERIAL

BACKGROUND OF THE INVENTION

This invention relates to ceramics and more particularly to aluminosilicate ceramics.

Future classes of advanced tactical missiles will require new ceramic materials for radomes to meet the stringent requirements arising from greater speeds (up to Mach 8) and longer flight times. The critical need is to develop ceramic materials stable up to at least 1400°C with low and thermally stable dielectric constant (ɛ) and loss tangent, low coefficient of thermal expansion (CTE), and high thermal shock and rain erosion resistance. Presently used slip cast fused silica (SCFS) has excellent dielectric and thermal properties for radomes, but the relatively low strength and rain erosion resistance of this material limit its future application. For this reason, research conducted on radome materials is directed both toward improvement of the mechanical properties of SCFS and development of new candidate ceramics.

SUMMARY OF THE INVENTION

Accordingly, an object of this invention is to provide a ceramic material which has a thermally stable, low dielectric constant.

Another object of this invention is to provide a new ceramic material with a dielectric constant that only slightly changes with increasing temperature.

A further object of this invention is to provide a ceramic material which maintains its chemical composition and crystalline modification even at high temperatures.

Yet another object of this invention is to provide a ceramic material that is transparent to electromagnetic waves and has stable dielectric properties at high temperatures.

A still a further object of this invention is to provide a ceramic material suitable for high temperature dielectric applications such as missile radomes.

It is also an object of this invention to provide a ceramic material suitable for substrates for electronic components.

These and other objects of this invention are accomplished by providing:

a material which is ceramics based on monoclinic BaO•Al₂O₃•2SiO₂; or ceramics based on monoclinic SrO•Al₂O₃•2SiO₂; or ceramics based on monoclinic, solid solution of from more than zero to less than 100 mole percent of SrO•Al₂O₃•2SiO₂ with BaO•Al₂O₃•2SiO₂ being the remainder, and a method of making this ceramic material.

This material can be used in radomes.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a phase diagram for the SrO•Al₂O₃•2SiO₂/BaO•Al₂O₃•2SiO₂ system where the materials were prepared directly from oxides and salts as raw materials.

FIG. 2 is a phase diagram for the SrO•Al₂O₃•2SiO₂/BaO•Al₂O₃•2SiO₂ system where the materials were

prepared from previously synthesized monoclinic SrO•Al₂O₃•2SiO₂ and monoclinic BaO•Al₂O₃•2SiO₂ powders;

FIG. 3 is a graph showing the dependency of the relative density on composition and firing temperature for ceramics based on the BaO•Al₂O₃•2SiO₂/SrO•Al₂O₃•2SiO₂ system;

FIG. 4 is a graph showing the dependency of bending strength on composition and firing temperature for ceramics based on BaO•Al₂O₃•2SiO₂/SrO•Al₂O₃•2SiO₂, system; and

FIG. 5 is a graph showing the changes in dielectric constant with temperature for ceramics based on monoclinic $SrO^{\bullet}Al_2O_3^{\bullet}2SiO_2$, monoclinic $BaO^{\bullet}Al_2O_3^{\bullet}2SiO_2$, and a 25 mole percent $SrO^{\bullet}Al_2O_3^{\bullet}2SiO_2/75$ mole percent $BaO^{\bullet}Al_2O_3^{\bullet}2SiO_2$ monoclinic solid solution.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

The ceramic materials of this invention are prepared from fine powders of pure monoclinic BaO•Al₂O₃•2SiO₂ and pure monoclinic SrO•Al₂O₃•2SiO₂. The powders preferably have a surface area of from about 3 to about 6 m²/g and more preferably from 4 to 5.5 m²/g. The ceramic materials produced include pure monoclinic BaO•Al₂O₃•2SiO₂, pure monoclinic SrO•Al₂O₃•2SiO₂, and monoclinic BaO•Al₂O₃•2SiO₂/SrO•Al₂O₃•2SiO₂ solid solutions prepared from intimate mixtures of the pure monoclinic BaO•Al₂O₃•2SiO₂ and pure monoclinic SrO•Al₂O₃•2SiO₂ powders in the desired proportions.

Specifically excluded from this invention are the hexagonal crystalline form of $BaO \cdot Al_2O_3 \cdot 2SiO_2$ and the hexagonal crystalline form of $SrO \cdot Al_2O_3 \cdot 2SiO_2$. Hexagonal $BaO \cdot Al_2O_3 \cdot 2SiO_2$ transforms

reversibly into low temperature orthorhombic crystalline form at 300°C. This transformation is accompanied by significant volume changes which can weaken or damage the ceramic structures. Because of this fact, hexagonal BaO•Al₂O₃•2SiO₂ is of no practical use as a ceramic material for high temperature, especially, thermal cycling applications.

FIG. 1 is a phase diagram for the SrO*Al₂O₃*2SiO₂/BaO*Al₂O₃*2SiO₂ system where the materials are prepared directly from oxides and salts (BaCO₃, Al₂O₃, SiO₂, and SrCO₃ powders). The hexagonal form of the SrO*Al₂O₃*2SiO₂/BaO*Al₂O₃*2SiO₂ is difficult to avoid in the preferred ranges of composition when this method is used. In contrast, FIG. 2 is a phase diagram for the \$rO*Al₂O₃*2SiO₂/BaO*Al₂O₃*2SiO₂ system where the materials are prepared from fine powders of monoclinic BaO*Al₂O₃*2SiO₂ and monoclinic SrO*Al₂O₃*2SiO₂. As can be seen, the hexagonal form of the SrO*Al₂O₃*2SiO₂/BaO*Al₂O₃*2SiO₂ solid solutions is easily avoided using this method.

The ceramics based on solid solutions containing from more than zero to less than 100 mole percent of monoclinic $SrO^{\bullet}Al_2O_3^{\bullet}2SiO_2$ with the remainder being monoclinic $BaO^{\bullet}Al_2O_3^{\bullet}2SiO_2$ are more sinterable, are denser, and have greater bending strength than do the ceramic materials formed from either monoclinic $SrO^{\bullet}Al_2O_3^{\bullet}2SiO_2$ powder or monoclinic $BaO^{\bullet}Al_2O_3^{\bullet}2SiO_2$ powder alone when fired at optimum temperatures (see FIG. 3 and FIG. 4). Within that broad range, narrower, preferred ranges are selected to emphasize certain desirable

properties. Ceramic based on monoclinic solid solutions having from 15 to 35 and preferably from 20 to 30 mole percent of monoclinic $Sr0^{\bullet}Al_2O_3^{\bullet}2SiO_2$ with the remainder being monoclinic $Ba0^{\bullet}Al_2O_3^{\bullet}2SiO_2$ have the greatest bending strength when fired at optimum temperature for producing the densest material (see FIG. 4).

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The most preferred solid solution compositions are those which are most useful for radomes. These compositions fall in the range of preferably from more than zero to 15, and more preferably from 5 to 10 mole percent of monoclinic SrO•Al₂O₃•2SiO₂ with the remainder being monoclinic BaO•Al₂O₃•2SiO₂. Ceramics based on monoclinic solid solutions of $BaO-Al_2O_3-2SiO_2$ and $SrO-Al_2O_3-2SiO_2$ in these ranges of composition have higher density and bending strength than monoclinic BaO•Al₂O₃•2SiO₂ alone (see FIG. 3 and FIG. 4). Moreover these solid solutions are stable in the monoclinic crystalline form at temperatures above 1590°C whereas pure BaO•Al2O3•2SiO2 is not. For example, at 1600°C pure BaO•Al₂O₃•2SiO₂ transforms from the monoclinic to the hexagonal crystal form. In contrast, a solid solution containing 10 mole percent monoclinic SrO•Al203•2SiO2 and 90 mole percent monoclinic BaO•Al₂O₃•2SiO₂ is stable in the monoclinic form at 1700°C. This means that the material may be used for radomes operating at higher temperatures. FIG. 5 and Table 1 show that the dielectric constant of a ceramic based on monoclinic BaO•Al2O3•2SiO2 changes less significantly with increasing temperature than does a ceramic based on monoclinic

SrO•Al₂O₃•2SiO₂, and ceramics based on solid solutions of these two falling proportionally in between.

When these materials are to be used in the manufacture of radomes, care must be taken not to introduce impurities. Thus natural materials such as kaolin or clay or technical grade purity chemicals containing significant amounts of impurities should not be used. Moreover, additives such as B₂O₃, LiF, Cr₂O₃ CaF₂, ZrSiO₃, etc., which promote the formation of monoclinic BaO•Al₂O₃•2SiO₂, must also be avoided. Impurities can distort the electromagnetic signals passing through the radome.

The monoclinic BaO*Al2O3*2SiO2 ceramic materials, monoclinic SrO•Al₂O₃•2SiO₂ ceramic materials, and the monoclinic BaO•Al₂O₃•S2iO₂/SrO•Al₂O₃•2SiO₂ solid solution ceramic materials are made from high purity monoclinic BaO•Al2O3•2SiO2 and high purity monoclinic SrO*Al2O3*2SiO2 fine powders. The monoclinic Ba@•Al2O3•2SiO2 starting material can be prepared without seed crystals according to example 1. This monoclinic BaO•Al2O3•2SiO2 is then used as seed crystals in the much easier process of example 2 to produced more monoclinic BaO•Al2O3•2SiO2. The monoclinic BaO•Al₂O₃•2SiO₂ produced in example 2 can be used as seed crystals for further batches. The monoclinic SrO•Al2O3•2SiO2 can be produced according to the process of example 3. The monoclinic BaO•Al2O3•S2iO2 and the monoclinic SrO•Al₂O₃•2SiO₂ are each ground into very fine powders. powders will preferably have a surface area of from 3 to 6 m²/g and more preferably of from 4 to $5.5 \text{ m}^2/\text{g}$.

To prepare a ceramic based on monoclinic solid solution of a given composition, the appropriate amounts of monoclinic BaO•Al₂O₃•2SiO₂ and monoclinic SrO•Al₂O₃•2SiO₂ powders are intimately mixed (see example 4). Of course, the monoclinic BaO•Al₂O₃•2SiO₂ powder or the monoclinic SrO•Al₂O₃•2SiO₂ powder can each be used alone to produce either monoclinic BaO•Al₂O₃•2SiO₂ ceramics or monoclinic SrO•Al₂O₃•2SiO₂ ceramics.

Next the monoclinic BaO•Al₂O₃•2SiO₂ powder, or monoclinic SrO•Al₂O₃•2SiO₂ powder, or mixture of monoclinic BaO•Al₂O₃•2SiO₂ and SrO•Al₂O₃•2SiO₂ powders are formed into a green body. This is done by conventional methods such as cold pressing, cold isostatic pressing, extrusion, injection molding, or slip casting, etc. In addition to radomes of various shapes, other structures such as component substrates may be formed.

The green bodies are then fired at a temperature of preferably from about 1550°C to less than 1590°C and more preferably from 1550°C to 1580°C. Referring to FIGS. 3 and 4 it can be seen that relative density and bending strength increase with increasing temperature. Note however that overfiring (1650°C) results in a substantial reduction in these properties. Therefore, care is taken to keep the firing temperature below 1590°C.

The general nature of the invention having been set forth, the following examples are presented as specific illustrations thereof. It will be understood that the invention is not limited to these specific examples but is susceptible to

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various modifications that will be recognized by one of brdinary skill in the art.

EXAMPLE 1

Preparation of monoclinic $BaO^{\bullet}Al_2O_3^{\bullet}2SiO_2$ without seed crystals

A uniform, stoichiometric, raw powder mixture of BaCO3, $\mathrm{Al_2O_3}$, and $\mathrm{SiO_2}$ gel was prepared by the sequential addition of BaCO3 powder and tetraethylorthosilicate (Silbond 40 from Stauffer Chemical Co.) in ethanol to a NH $_4$ OH-stabilized Al $_2$ O $_3$ (0.3 micron) suspension (pH ll). Ammonia served as a catalyst for the hydrolysis of the tetraethylorthosilicate. The mixture was continuously stirred until the hydrolysis was completed and then vacuum dried at 65-70°C. The resulting powdered mixture was uniform and did not contain any agglomerates. The powder was pressed into pellets at 100 MPa and then fired at 1500°C for about 150 hours. The product was monoclinic BaO•Al2O3•2SiO2. It was ground to a particle size less than 60 microns for use as seeds in example 2.

EXAMPLE 2

Preparation of monoclinic BaO•Al2O3•2SiO2 using monoclinic beeds

Into a uniform, stoichiometric, raw powder mixture of $BaCO_3$, Al_2O_3 (0.3 microns), and SiO_2 gel prepare as described in example 1, was added the monoclinic BaO•Al2O3•2SiO2 seed crystals

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(less than 60 microns in size) prepared in example 1. Batches containing 1, 3, 5, and 10 percent by weight of the monoclinic BaO•Al₂O₃•2SiO₂ seed crystals were prepared and then fired at 1250-1500°C for 5 hours. The addition of monoclinic seeds highly intensified the formation of monoclinic BaO•Al2O3•2SiO2. Even the presence of 1 percent seeds significantly promoted the phase transformation from hexagonal to monoclinic BaO•Al₂O₃•2SiO₂ at 1250°C. Total phase transformation was accomplished by the addition of at least 5 percent by weight of the monoclinic BaO•Al₂O₃•2SiO₂ seed crystals. This was demonstrated by the batches containing 5 and 10 percent by weight of the seed crystals. Note that the completely transformed, 100 percent monoclinic BaO•Al₂O₃•2SiO₂ product can be ground to particles less than 60 microns in size and used as seed crystals for subsequent batches. In other words, the arduous process of example 1 is needed only to prepare an initial batch of monoclinic BaO•Al2O32•SiO2.

EXAMPLE 3

Preparation of monoclinic $SrO^{\bullet}Al_2O_3^{\bullet}2SiO_2$

A uniform, stoichiometric, raw powder mixture of ${\rm SrCO}_3$, ${\rm Al}_2{\rm O}_3$, and ${\rm SiO}_2$ gel was prepared by the sequential addition of ${\rm SrCO}_3$ powder and tetraethylorthosilicate (Silbond 40 from Stauffer Chemical Co.) in ethanol to a ${\rm NH}_4{\rm OH}\text{-stabilized Al}_2{\rm O}_3$ (0.3 micron) suspension (pH 11). Ammonia served as a catalyst for the hydrolysis of the tetraethylorthosilicate. The mixture

was continuously stirred until the hydrolysis was completed and then was vacuum dried at 65-70°C. The resulting dry raw powders were uniform and did not contain any agglomerates. The raw powder mixture was pressed into pellets at 100 MPa and then fired at 1050-1400°C for 5 hours. X-ray diffractograms showed that the reaction was practically completed at 1300°C and the product consisted only of monoclinic SrO*Al₂O₃*2SiO₂.

EXAMPLE 4

Previously synthesized monoclinic $BaO \cdot Al_2O_3 \cdot 2SiO_2$ (BAS) and monoclinic $SrO \cdot Al_2O_3 \cdot 2SiO_2$ (SAS) were used as starting powders for the preparation of ceramics in the BAS-SAS system. The powders were ground in an attritor using ZrO_2 grinding media to surface area up to $5m^2/g$. Specimens having the following compositions were prepared:

9		mole	percent
		BAS	SAS
10		100	0
11		98	2
12			
13		90	10
14		75	25
15	,	50	50
i	ä ,	25	75
16	بغ	10	90
17		5	95
18			
19		2	98
		0	100

All specimens were pressed at 100 MPa. Specimens of each of the compositions were fired at 1500°C, 1550°C, 1600°C and 1650°C with a holding time of 5 hours at each of those temperatures.

The dependence of relative density on composition and firing temperature is shown in FIG. 3. The specimens based on pure BAS were completely densified (open porosity close to zero) at 1600°C, and those based on pure SAS at 1550°C. The

addition of SAS to BAS sharply enhanced densification at 1500°-1550°C and only slightly at 1600°C. The addition of BAS to SAS in amounts up to 10 mole percent promotes densification at 1500°C. Materials containing up to 25 mole percent BAS had the best sinterability in the system and were completely densified at 1550°C. The decrease in density for specimens sintered at 1650°C is due to overfiring. Pure BAS fired at 1650°C consisted of only the hexagonal modification. The addition of 2 mole percent SAS significantly inhibited the hexagonal-to-monoclinic transformation, and 5 mole percent SAS practically stabilized the monoclinic form. Stabilization of the monoclinic modification of BAS with the addition of SAS decreases the sensitivity of BAS to sintering temperatures close to 1600°C and increases the service temperature.

The microstructure of ceramics in the system was studied by SEM of polished specimens thermally etched at 1450°C for 2 hours. All the specimens had fine grained structure with maximum grain size of about 5 microns.

Bending strength was measured in 3-point bending (2.54 mm span) using 4 x 4 x 40 mm bars. The bending strength of specimens of intermediate compositions fired at optimum sintering temperature was higher than that of the end members (FIG. 4). The highest strength of about 130 MPa was shown by specimens containing 75 mole percent BAS and 25 mole percent SAS (75BAS/25SAS), compared to about 80 and 100 MPa for SAS and BAS, respectively. The drop in strength for specimens fired at 1650°C is due to overfiring.

Thermal expansion was measured with a differential dilatometer at temperatures up to $1500\,^{\circ}$ C using dense 25 mm long specimens and a sapphire reference. The coefficient of thermal expansion (CTE) of BAS was $4.56 \times 10^{-6}/\text{degree}$ and of SAS was $4.92 \times 10^{-6}/\text{degree}$, in the $100-1500\,^{\circ}$ C range, with linear dependence on temperature.

The dielectric properties of BAS, SAS, and 75BAS/25SAS ceramics were measured up to 1200°C at 35 GHz. The dielectric data are summarized in Table 1 and FIG. 5. The loss tangent for the samples was very low despite noticeable levels of ZrO₂ impurities (up to 0.85% ZrO₂ from grinding media). At 1200°C, the loss tangent of BAS is 40 x 10⁻⁴ and SAS is 50 x 10⁻⁴, which for all practical applications is negligible. The 75BAS/25SAS specimen showed approximately 2 to 3 times higher loss tangent in the whole temperature range.

The relative increase in dielectric constant with temperature is smallest for BAS and largest for SAS ceramics despite the fact that the room temperature value for SAS is smallest. The results for the 75BAS/25SAS material fall between the end members according to its relative composition ratio.

DIELECTRIC PROPERTIES OF CERAMICS IN THE SYSTEM

BaO•Al₂O₃•2SiO₂ - SrO•Al₂O₃•2SiO₂

AT 35 GHz AS A FUNCTION OF TEMPERATURE

MATERIAL	TEMPERATURE	DIELECTRIC	THERMAL	DIELECTRIC
	(0°)	CONSTANT	CHANGES OF	ross
		ယ	æ	tan 8
	RT	6.55	ı	8 X 10-4
	200	6.73	2.8	i
BaO•Al ₂ O ₃ •2SiO ₂	800	6.84	ታ.	ı
	1000	6.92	5.7	25 X 10 ⁻⁴
	1200	7.00	6.8	40 X 10-4
	RT	7.04	ı	17 X 10 ⁻⁴
95BaO•Al ₂ O ₃ •2SiO ₂	200	7.25	3.0	19 X 10-4
5SrO.Al ₂ O ₃ .2SiO ₂	800	7.37	4.7	29 X 10-4
	1000	7.46	5.9	42 X 10 ⁻⁴
	1200	7.54	7.1	60 X 10-4
	RT	6.88	1	25 X 10 ⁻⁴
75BaO•Al2O3•2SiO2	200	7.11	3,3	1
25SrO*A1 ₂ O ₃ *2SiO ₂	800	7.24	5.2	1
	1000	7.33	6.5	43 X 10-4
	1200	7.40	7.6	65 X 10 ⁻⁴
	RT	6.16	1	11 X 10-4
	500	6.44	4.6	ı
$\mathrm{SrO}\bullet\mathrm{Al}_2\mathrm{O}_3\bullet\mathrm{2SiO}_2$	800	6.58	8.9	ı
	1000	6.68	8.4	30 X 10-4
	000	1	(

Obviously numerous modifications and variations of the present invention are possible in light of the above teachings. It is therefore to be understood that

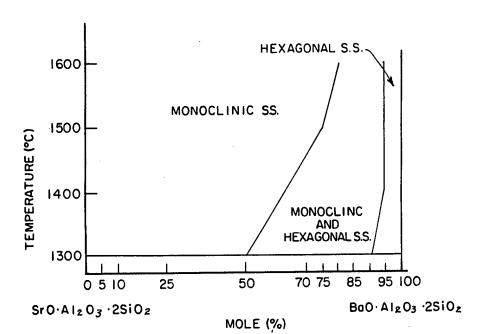
the invention may be practiced otherwise than as specifically described herein.

Navy Case No. 71,959

CERAMIC MATERIAL

ABSTRACT OF THE DISCLOSURE

A ceramic material which is (1) ceramics based on monoclinic BaO•Al₂O₃•2SiO₂; (2) ceramics based on monoclinic SrO•Al₂O₃•2SiO₂; or (3) ceramics based on monoclinic solid solution of BaO•Al₂O₃•2SiO₂ and SrO•Al₂O₃•2SiO₂.



STARTING MATERIAL: OXIDES AND SALTS

FIG. 1

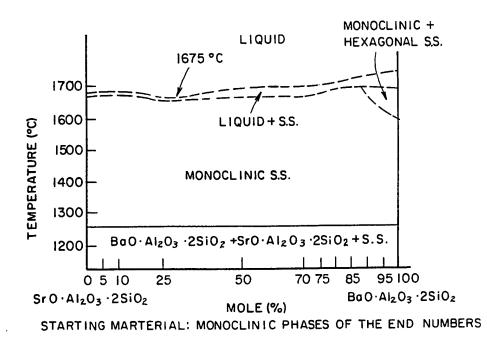


FIG. 2



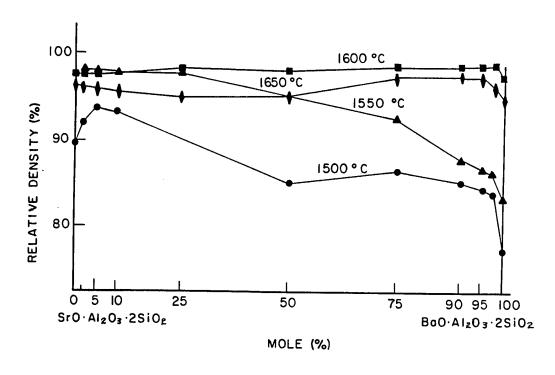


FIG. 3

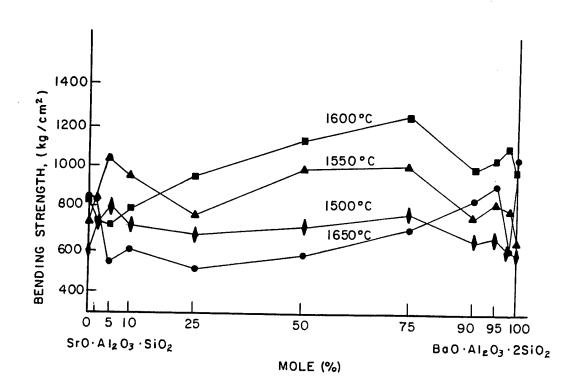


FIG. 4

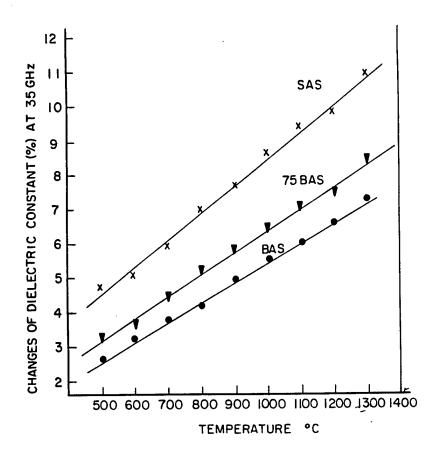


FIG. 5