Ceramic radiotransparent materials on the basis of BaO-Al_2O_3-SiO_2 and SrO-Al_2O_3-SiO_2 systems

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Abstract
Based on the literature review, the authors made a justified choice of ceramic materials with a low dielectric constant and dielectric loss tangent. The composition and process parameters (burning temperature - 1550 °C, burning duration - 5 hours) of producing of celsian and Sr-anorthite ceramics with low dielectric properties were defined. The phase composition of products of burning was examined. X-ray phase studies of Sr-ceramics after burning were conducted.
Keywords: Ceramic radiotransparent materials, celsian, Sr-anorthite, dielectric constant, reflection coefficient of radio waves

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1. Introduction

Ceramic radiotransparent materials are non-metallic materials which do not substantially alter the amplitude and phase of the electromagnetic wave of radio-frequency range passing through them. Radiotransparency of ceramic materials is provided by low dielectric losses in the range of operating temperatures ($tg\delta = 10^{-2}...10^{-5}$, $\varepsilon<10$) and by low value of reflection coefficient of radio waves (S). Ceramic radiotransparent materials are mainly used for the manufacture of radomes protecting antennas against the environmental influences. Besides the above mentioned requirements radio-ceramic materials must have: a high value of thermal resistance, low coefficient of linear thermal expansion and at the same time should protect the equipment from external influences [1-8].

Nowadays a large number of materials in the world practice are used as radiotransparent silicate materials. Classification of radiotransparent silicate materials is shown in *Fig. 1*.

The main disadvantages of radiotransparent materials based on the vitroceramics and glass materials are their brittleness and the disadvantage of composite materials is their high manufacturing cost.

At the moment ceramic materials based on quartz, high-alumina and mullite ceramics, silicon nitride, boron and others are widely used for the production of radiotransparent materials. *Table 1* shows the most important advantages and disadvantages of the main ceramic radiotransparent materials.

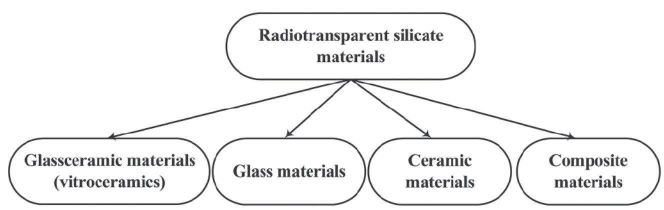

Fig. 1 Classification of radio-silicate materials
1. ábra Rádió-szilikát anyagok csoportosítása

Name of material	Advantages	Disadvantages
Quartz ceramics	High thermal stability, stability of dielectric properties over a wide temperature range	High melting temperature, low mechanical strength, the upper limit of operating temperature is 1000 °C
High-alumina ceramics	High mechanical properties, resistance to corrosion	High temperature of sintering, low resistance to thermal shock – not higher than 200 °C
Ceramics based on silicon nitride	High strength characteristics at high temperatures (1500 °C), good resistance to oxidation and thermal stresses	High sintering temperature, complex technological process of production
Ceramics based on boron nitride	Has the best dielectric properties at temperatures up to 2000 °C	

Table 1 Radiotransparent ceramic materials
1. táblázat Rádiótranszparens kerámia anyagok

2. Experimental

The direction of manufacturing of radiotransparent ceramic materials based on electrical ceramics was chosen on the basis of the literature review. Physical and chemical properties of crystals which form the basis of electrical materials are shown in *Table 2*.

Compound	Dielectric constant, ε	Dielectric loss tangent, 104 tgδ, 1 MHz
Anorthite $SrO\cdot Al_2O_3\cdot 2SiO_2$	6.2–6.8	11–50
Anorthite $CaO\cdot Al_2O_3\cdot 2SiO_2$	6–7	2–3
Wollastonite $CaO\cdot SiO_2$	5	3
Quartz β-SiO2	4.5	3
Clinoenstatite $MgO\cdot SiO_2$	7	3
Corundum α-Al_2O_3	9.9–10.5	1–2
Mullite $3Al_2O_3\cdot 2SiO_2$	7	5–10
Boron nitride BN	4.2	2
Silicon nitride Si_3N_4	8	2.4
Spodumene $Li_2O\cdot Al_2O_3\cdot 2SiO_2$	7.4	70–155
Forsterite $2MgO\cdot SiO_2$	7	1–3
Celsian $BaO\cdot Al_2O_3\cdot 2SiO_2$	6.5–7	1–2
Spinel $MgO\cdot Al_2O_3$	8	3

Table 2 Electrical properties of the crystals which form the basis of radiotransparent ceramics
2. táblázat Rádiótranszparens kerámiák alapjául szolgáló kristályok elektromos jellemzői

Table 2 shows that all crystalline phases have low value of dielectric constant and dielectric loss tangent. Celsian ($BaO\cdot Al_2O_3\cdot 2SiO_2$) and Sr-anorthite ($SrO\cdot Al_2O_3\cdot 2SiO_2$) ceramics were selected for further investigation of the possibility of establishing of radiotransparent ceramic materials for missile radomes. These two ceramic materials are promising because of their almost constant values of the dielectric constant and dielectric loss tangent at high temperatures and high frequencies (35 GHz) (*Fig. 2*).

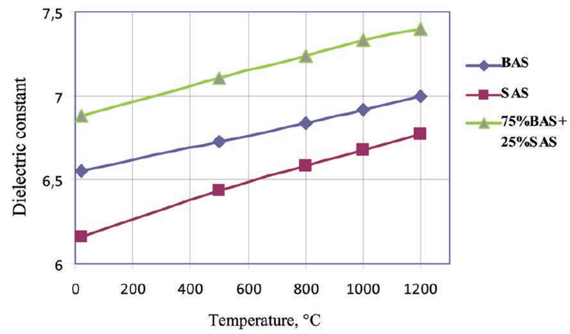

Fig. 2 Temperature dependence of dielectric constant of ceramics (data are derived from [4])
2. ábra Kerámiák dielektromos állandójának hőmérséklet függése (az adatok [4] alapján)

The crystalline phase of celsian and Sr-anorthite of monoclinic modification (symmetry), which in comparison with the hexagonal one has a higher melting point, low thermal expansion coefficient, low dielectric constant and dielectric loss tangent in a wide temperature and frequency range, is used for creation of radiotransparent ceramic materials.

The selection of compositions and the synthesis temperature of celsian and Sr-anorthite ceramics were carried out by the diagrams of relevant three-component systems (*Fig. 3*). Composition of mixtures used for the synthesis of radiotransparent materials meet stoichiometric ratio of forming oxides composed of celsian and Sr-anorthite.

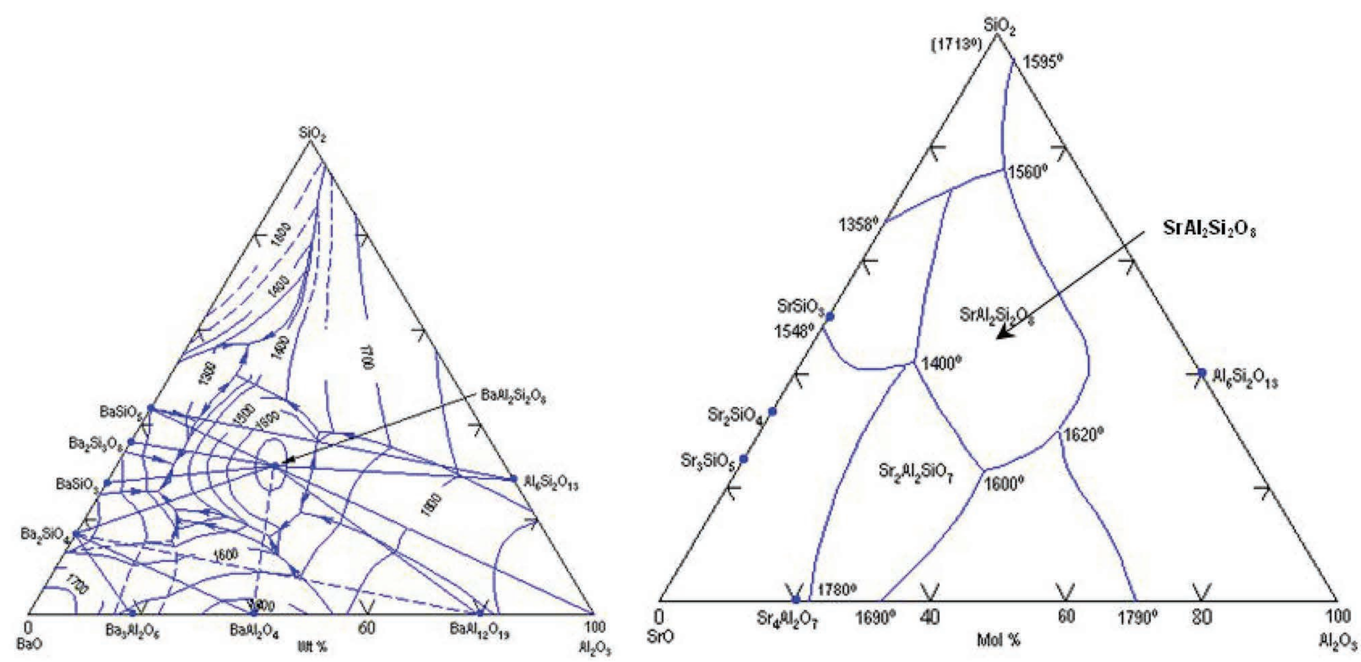

Fig. 3 Three-component systems $BaO-Al_2O_3-SiO_2$ and $SrO-Al_2O_3-SiO_2$ (Three-component systems are obtained from the Phase Equilibria Diagrams database, The American Ceramic Society Publishing House)
Fig. 3 3. ábra Háromfázisú rendszerek $BaO-Al_2O_3-SiO_2$ és $SrO-Al_2O_3-SiO_2$ (a háromfázisú rendszerek forrása: Phase Equilibria Diagrams database, The American Ceramic Society Publishing House)

The main objective of research was to obtain the minimum value of dielectric constant, dielectric loss tangent and water absorption and maximum value of the strength in compression of Sr-anorthite and celsian ceramics.

The following raw materials were used during the research to produce celsian and Sr- anorthite tailor-made ceramics: barium carbonate, strontium carbonate, quartz sand from Vishnevetske field, aluminium earth. Composition of mixtures used for the synthesis of radiotransparent materials meet stoichiometric ratio of forming oxides composed of celsian and Sr-anorthite (*Table 3*).

Compositions code	Oxide content, wt. %						
	SrO	BaO	SiO_2	Al_2O_3	MgO	CaO	Fe_2O_3
SAS	31.73	–	36.8	31.37	0.01	0.08	0.01
BAS	–	40.75	31.93	27.23	0.01	0.07	0.01
SAS+BAS	14.74	21.82	34.2	29.15	0.01	0.07	0.01

Table 3 Chemical composition of test samples
3. táblázat Vizsgálati minták kémiai összetétele

The preparation of the ceramic samples was carried out by the following technology. Raw components were mixed in a porcelain mill to give a residue on sieve 4-6% 10,000 holes/cm^2 for preparation of the powder mixture. Pressing of samples was carried out at a pressure of 20 MPa. Pressed samples were dried in the drying oven to the residual moisture content of 2%. Firing was performed in Naberterm electric furnace, the duration of heat treatment at a firing temperature of 1550 °C was 5 hours.

The following properties were studied for the obtained materials: water absorption, bending strength, packed density, dielectric constant and the reflection ratio coefficient of radio waves was calculated. Properties of the investigated ceramics are shown in *Table 4*.

Properties	Compositions code, wt. %		
	SAS	BAS	SAS+BAS
Water absorption, %	1.59	0.64	2.54
Bending strength, MPa	398.8	490.2	564.2
Packed density, kg/m^3	2.64	2.83	2.70
Dielectric constant	6.8	9.7	9.2
Reflection coefficient of radio waves (S)	0.198	0.263	0.253

Table 4 Properties of ceramics radiotransparency
4. táblázat Rádiótranszparens kerámiák tulajdonságai

3. Methods

Water absorption and packed density were determined by means of hydrostatic weighting of water-presaturated test samples. Vacuum method was used to saturate the samples. The compressive strength was determined using a press GMS-50 (with a maximum load of 500 kN). Phase changes in ceramic masses during firing, were studied using X-ray diffraction analysis. X-ray diffractograms were taken with diffractometer DRON-3M with Cu Kα radiation and nickel filter at constant conditions of its perfomance. X-ray diffractograms transcript was done using ASTM (USA) catalog. The coefficient of

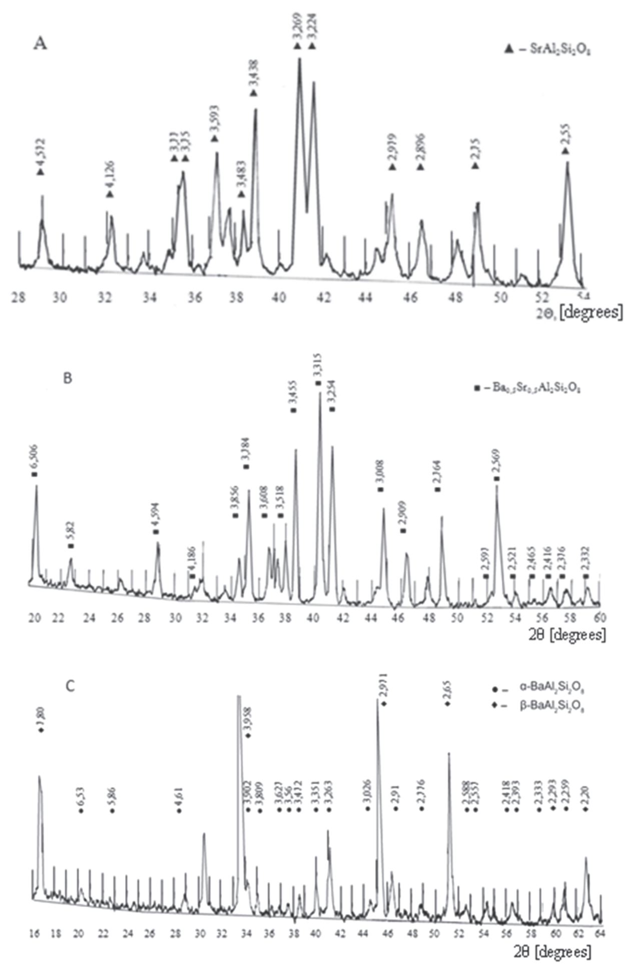

Fig. 4 X-ray diffraction pattern of synthesized ceramics
4. ábra A szintetikus kerámiák röntgendiffraktogramjai

reflection (S) was calculated on the basis of the fundamental Maxwell equations at specified harmonic law of variation of the incoming plane wave of super high frequency electromagnetic field. Dielectric constant (ε) was determined using a three-electrode cell and a digital automatic AC bridge for measuring the capacitance (immittance meter E7-14).

4. Results and discussion

Analysis of the received data indicates the possibility of obtaining materials with the desired electrophysical properties based on Sr-ceramics and celsian ceramics. Sr-ceramics, which has the lowest value of dielectric constant, is characterized by the optimal properties in terms of radio transparency.

With the help of X-ray phase analysis, the completeness of the reaction of the BAS, SAS and SAS + BAS formation has been investigated and the phase composition of the products obtained by heat treatment of the samples has been defined. The Barcode radiograph of synthesis products is shown in *Fig. 4*. It can be seen that the formation process of Sr-anorthite was completely finished, as evidenced by the presence of the respective spikes (*Fig. 4.a*). Continuous solid solutions of celsian and strontium anorthite were identified in the composition of the calcined products of BAS + SAS ceramics (*Fig. 4.b*). Monoclinic celsian β-$BaO{\cdot}Al_2O_3{\cdot}SiO_2$ and hexagonal celsian α-$BaO{\cdot}Al_2O_3{\cdot}SiO_2$ were identified in the composition of the calcined products of BAS ceramics (*Fig. 4.c*). It is known that $BaO{\cdot}Al_2O_3{\cdot}2SiO_2$ of monoclinic modification (syngonies), which compared to hexagonal one has a high melting point, low thermal expansion coefficient, low values of the dielectric constant and dielectric loss tangent in a wide temperature and frequency range is used for the manufacturing of radio-ceramic materials. Therefore, in our view it is necessary to increase the firing time or add mineralizing impurities for more complete transition of β-celsian → α-celsian in the composition of BAS.

5. Conclusions

Conducted research demonstrated the prospects of further study of the $SrO\text{-}Al_2O_3\text{-}SiO_2$ system for the development of ceramic materials with low dielectric constant and dielectric loss tangent and high strength characteristics. Further investigation aimed at lowering the temperature and duration of Sr-ceramics firing.

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Rádiótranszparens kerámia anyagok $BaO\text{-}Al_2O_3\text{-}SiO_2$ és $SrO\text{-}Al_2O_3\text{-}SiO_2$ rendszerek alapján

Irodalmi adatok alapján a szerzők kiválasztottak kerámiákat, amelyek dielektromos állandója és dielektromos veszteség tangense kicsi. Megvizsgálták (5 órás, 1500 °C szinterelési hőmérsékleten) az összetételi jellemzőket bárium földpát és stroncium anortit alapanyagok felhasználásával. A fázisösszetételt röntgendiffrakcióval határozták meg a kerámiákon. Az eredmények igazolják a vizsgált kerámiák rádiótranszparens jellemzőit és nagy szilárdságát.

Kulcsszavak: kerámia rádiótranszparens anyagok, bárium földpát, stroncium anortit, dielektromos állandó, rádióhullám visszaverődési együttható