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Low loss microwave ferroelectric ceramics for high power tunable devices

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Abstract

In this paper we report the influence of the composition and concentration of Mg-containing additions such as Mg_2TiO_4, MgO and a mixture of Mg_2TiO_4–MgO on ceramics based on a mixture of $BaTiO_3/SrTiO_3$. Phase relations, crystal structure, microstructures, microwave dielectric properties (ε, $\tan\delta$) and DC tunability have been studied over a wide range of frequencies. The temperature dependence of the dielectric properties has been measured as well. Among the compositions synthesized were low loss bulk ferroelectrics with dielectric constants in the range 150–800 and relatively high DC tunabilities (up to 1.49 under a DC electric field of 40 kV/cm). These materials can be used for high power tunable microwave devices.

Keywords: (A) Sintering; (B) Microstructure; Electron microscopy; (C) Dielectric properties; (D) $BaTiO_3$ and titanates; MgO

1. Introduction

Ferroelectric ceramics consisting of (Ba,Sr)TiO_3 (BSTO) solid solutions with various additives of non-ferroelectric microwave dielectric materials with low dielectric constant such as MgO, Al_2O_3, ZrO_2, $MgTiO_3$, $MgAl_2O_4$ etc. can be used as the basis of ceramics for the design of microwave devices controlled by a DC electric field like modulators, filters, phase-shifters and other devices.[1–3] Moreover, there has been recent interest in the use of bulk ferroelectrics as control elements of high-power phase-shifters and switches for linear colliders. Ferroelectric layers can also be used as a control element for high power accelerating structures with dielectric loading.[4,5]

The main requirement for the electrical properties of ceramic materials to be used in such devices is a combination of relatively low dielectric constant ($\varepsilon \leq 600$) and low dielectric losses ($\tan\delta \leq 0.006$) in the microwave frequency range, and electric field tunability $n > 1.1$–1.2 at bias fields ~(20–50) kV/cm. (Here $n = \varepsilon(0)/\varepsilon(E_0)$ where E_0 is the biasing field magnitude.)

The required value of the dielectric constant in the system of BSTO solid solutions with perovskite structure can be achieved by increasing the content of strontium titanate accompanied by the shift of the Curie temperature and/or increasing the bulk concentration of non-ferroelectric additives with low ε in heterogeneous mixture to ≥30%. Meanwhile, according to the data in the available literature the increase in content of strontium titanate or non-ferroelectric additive leads to decrease of both the dielectric constant of the ferroelectrics and the electric field tunability.[6,7]

In this study we have investigated the structure and the electric properties (mainly ε, $\tan\delta$ and n) of the ferroelectric ceramics made of a mixture of previously synthesized $BaTiO_3$ (BTO) and $SrTiO_3$ (STO) depending on the composition and concentration of Mg-containing additives introduced into the initial BTO/STO mixture. We used magnesium orthotitanate Mg_2TiO_4 as the essential additive having a spinel structure, MgO or a mixture of Mg_2TiO_4–MgO. As seen from the constitution diagrams published in Ref. 8, Mg_2TiO_4 is the highest temperature-stable and chemically stable compound among the known magnesium

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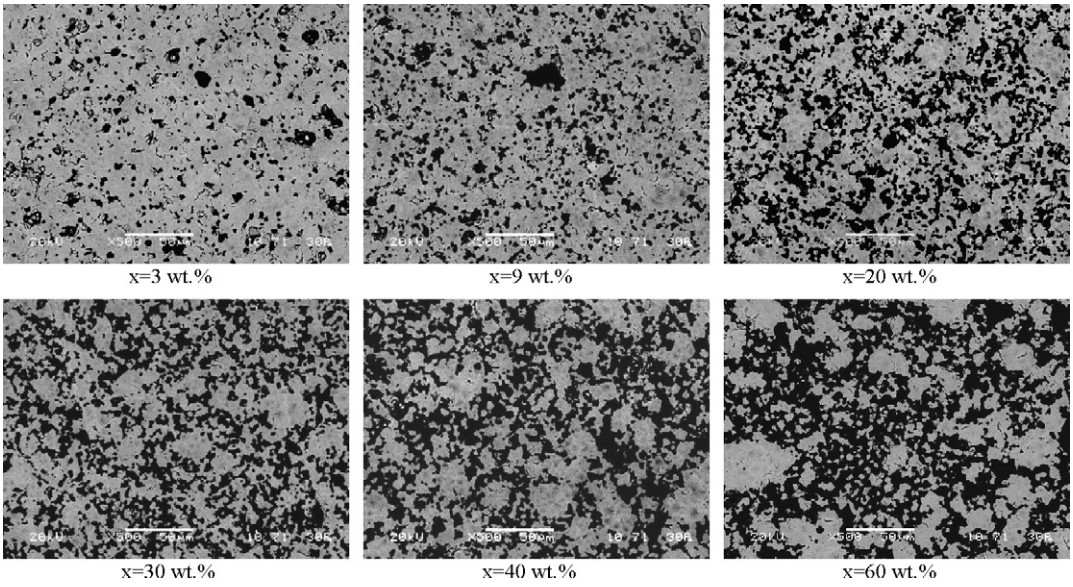


Fig. 1. Microstructure (SEM) of ceramic samples of the $BaTiO_3/SrTiO_3$ (55/45) + x wt.% Mg_2TiO_4 system.

titanates; moreover, it is within the composition range with a magnesia excess. Magnesium orthotitanate, Mg_2TiO_4, is a linear dielectric with ε of about 14 and the smallest dielectric losses ($\tan\delta = 0.6 \times 10^{-4}$ at a frequency on the order of 10 GHz)[9] among all known compounds of magnesium–titanium. We have therefore studied the influence of this substance on the dielectric properties of ferroelectric compositions of the BSTO type with initial BTO/STO content ratios of 50/50, 55/45 and 60/40.

2. Experimental procedure

High purity MgO and TiO_2 (99.95%) were used as the starting materials for the preparation of the Mg_2TiO_4 additive. After milling in a vibration mill for 3 h the MgO–TiO_2-mixture was calcined in air at 1200 °C for 4 h, then the calcined powder was re-milled by ball milling for 3 h to a grain size ≤ 1 μm. Pre-synthesized $BaTiO_3$ (HPBT-1) and $SrTiO_3$ (HST-1) (Fuji Titanium Industry Co., Japan) with Ba/Ti and Sr/Ti 0.996 mol. ratio and the Mg-containing compositions were mixed in the desired ratios in a vibration mill for 3 h.

Samples of the required geometrical shape and size were prepared by hydraulic pressing; 10% solution of polyvinyl alcohol was taken as a binder. The prepared samples were sintered in air within the temperature range of 1360–1420 °C (3 h) in a chamber electric furnace until zero water absorbance and porosity less than 4% was obtained.

The measurements of the relative dielectric constant, $\tan\delta$, and Q-factor ($1/\tan\delta$) were performed in the 3.5–10 GHz range on disc samples 6 mm in diameter and 0.8–3.0 mm thick by the waveguide dielectric resonator[10] method. The measurements of the dielectric properties were performed using a 1 MHz rf voltage and a constant electric voltage supplied on the 0.5 mm thick Au-metallized disk samples using the measurement described in Ref. 11. Sintered samples were studied on a DRON-3 diffractometer with a Cu-K_α, Ni filter. Further measurements were made using a scanning electron microscope (SEM) JSM-6460LV JEO (Japan) and an EDS-spectrometer for X-ray microanalysis.

3. Results and discussion

Fig. 1 and Table 1 show electron micrographs and X-ray analysis data for the samples of the 55 wt.% $BaTiO_3$–45 wt.% $SrTiO_3$ system, containing 3–60 wt.% Mg_2TiO_4 over 100% of the initial mixture. T_{sin} of the samples equals 1400 °C. Each sample is a mixture of two main crystalline phases. The first phase (clear) is a solid solution BSTO type with the cubic perovskite structure. The cell parameter for this phase (Table 1) is almost the same for all studied compositions in the system. The slight increase of the cell parameter for compositions with a low concentration of the magnesium-containing additive can be connected with the possible partial substitution of Ti^{4+} by Mg^{2+} in the BSTO lattice.[12] The obtained unit cell parameter data (Table 1) for samples of the 55 wt.% $BaTiO_3$–45 wt.% $SrTiO_3$ system containing 3–60 wt.% MgO have not shown any significant difference in

Table 1
Unit cell parameters of the main perovskite phase of BTO/STO = 55/45 + wt.% Mg_2TiO_4 and BTO/STO = 55/45 + wt.% MgO samples (T_{sint} = 1400 °C).

wt.% of additions	Unit cell parameters of perovskite phases (Å)	
	Mg_2TiO_4	MgO
0	3.9513	3.9513
3	3.9538(6)	3.9535(4)
6	3.9536(6)	3.9540(5)
9	3.9541(5)	3.9532(5)
12	3.9538(6)	–
15	3.9545(6)	3.9535(4)
20	3.9548(6)	3.9548(6)
25	3.9548(6)	3.9548(6)
30	3.9545(7)	3.9534(6)
40	3.9546(7)	3.9544(6)
60	3.9550(7)	3.9533(7)

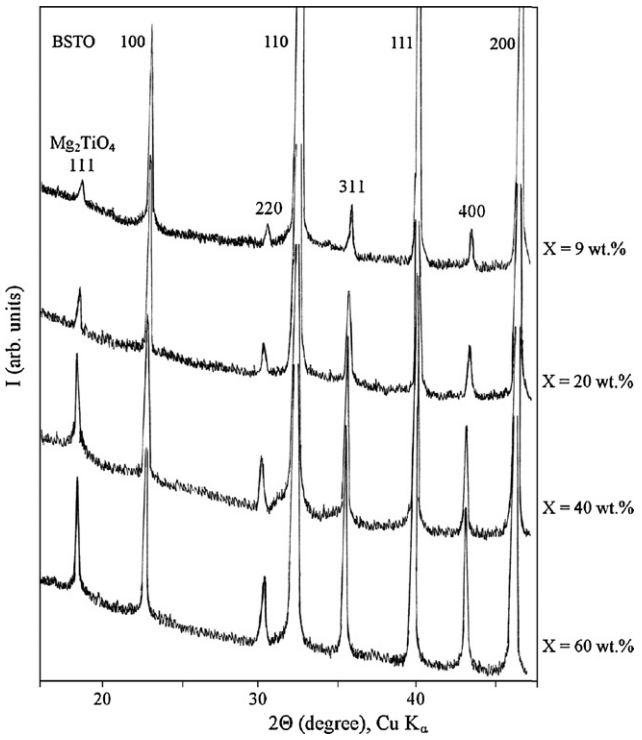


Fig. 2. X-ray patterns of ceramic samples of the $BaTiO_3/SrTiO_3$ (55/45) + x wt.% Mg_2TiO_4 system.

the parameters over the whole concentration range. At the same time in the samples of the investigated systems two additional phases of perovskite with unit cell parameters in the ranges of 3.935–3.941 Å and 3.954–3.966 Å (for the compositions with the Mg_2TiO_4 additive) or in the ranges of 3.929–3.936 Å and 3.956–3.966 Å (for the compositions with the MgO additive) were detected; their total content did not exceed 3–5%.

The second main phase (gray) in Fig. 1 is the spinel structure. Electron micrographs of the samples in the investigated system show that the volume content of the gray phase identified by EDS and X-ray phase analysis (Fig. 1) as the spinel-structured phase Mg_2TiO_4 increases with the increase of the Mg_2TiO_4 content in the initial mixture (Fig. 2).

Fig. 3 shows a comparison of the data on the electrical parameters, namely the dielectric constant, its maximum temperature, tunability by the electric field and tan δ at 10 GHz for the ceramic samples based on the $BaTiO_3/SrTiO_3$ = 55/45 mixture as a function of the additive percentage. The additives, over 100% to the initial mixture, were magnesium orthotitanate (the above-described system, curve 2) or magnesia (curve 1). The data show that magnesia, being added to BTO/STO mixture, leads to a sharper decrease of ε for the composition, which falls to ~200 when adding 60% of magnesia additive. Adding the same amount of Mg_2TiO_4 results in a decrease of ε for the samples to only 400. It is seen that with the increase of magnesia concentration in the composition the temperature of the dielectric constant maximum smoothly shifts towards the range of lower temperatures. The tunability coefficient for such samples displays a tendency to decrease. Such behavior of the investigated parameters correlates well with the data known from the literature.[3,7] However, the use of the magnesium orthotitanate additive instead of magnesia leads to the reverse (relative to curve 1) dependences for the dielectric constant maximum temperature and the tunability coefficient of ferroelectric samples. The increase of magnesium orthotitanate concentration in the composition leads to the increase of the temperature of the dielectric constant maximum together with the increase of the tunability coefficient n by almost a factor of two with the increase of the additive percentage to 60 wt.%. accompanied by some increase of tan δ of the samples.

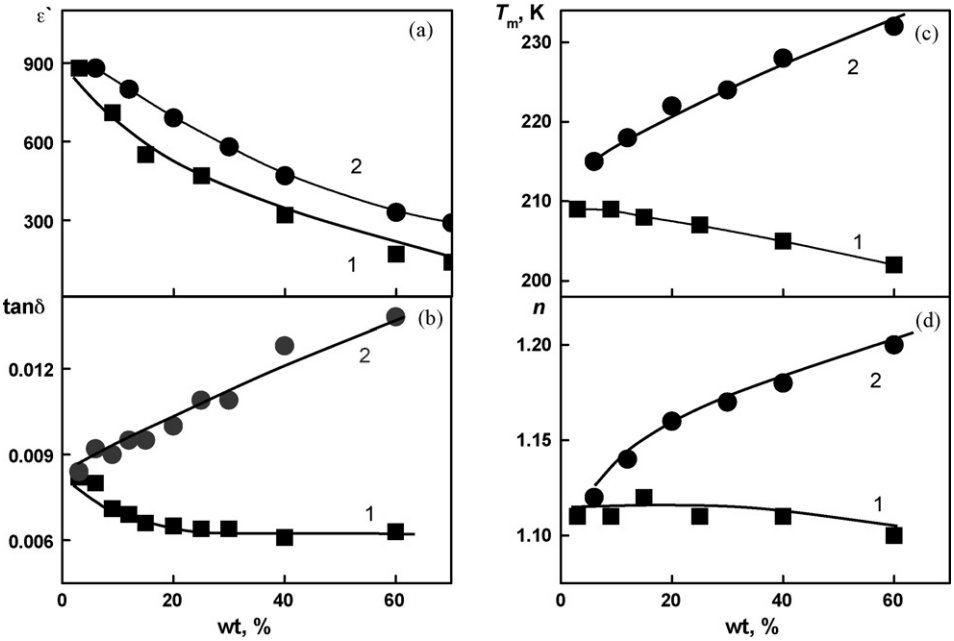
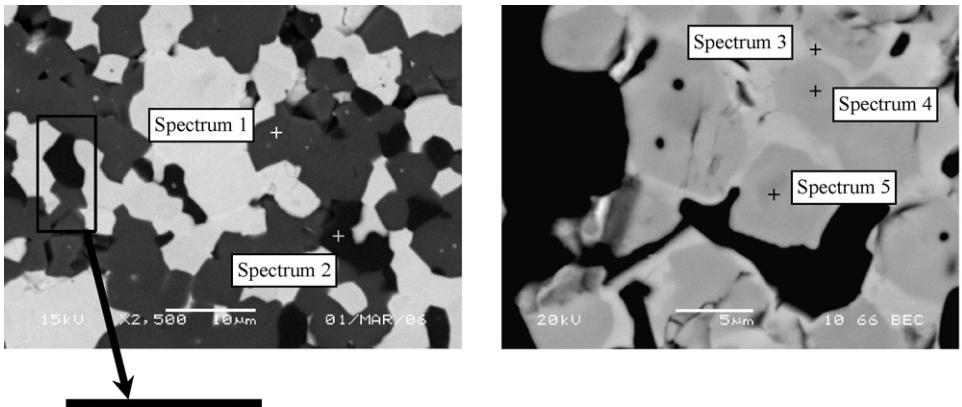
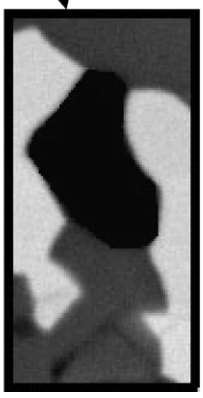


Fig. 3. Dependence permittivity ε' (a), tan δ at f = 10 GHz (b), temperature of maximum permittivity T_m (c) and tunability n (d) for the samples BTO/STO (55/45) from wt.% MgO (1) and Mg_2TiO_4 (2).





Spectrum	Mg	Ti	Sr	Ba	O	Total
Spectrum 1	29.66	27.47	1.39	2.99	38.49	100.00
Spectrum 2	59.89	0.19	0.26	0.06	39.60	100.00
Spectrum 3	0.19	22.57	16.33	38.09	22.82	100.00
Spectrum 4	0.14	22.62	21.85	32.23	23.16	100.00
Spectrum 5	0.25	23.36	27.91	24.64	23.84	100.00

Fig. 4. SEM images and EDS data for ceramic sample BTO/STO (60/40) + 25 wt.% Mg_2TiO_4 + 20 wt.% MgO (T_{sin} = 1380 °C).

Studying the influence on the structure of the ceramics of the complex Mg-containing MgO–Mg_2TiO_4 additive to the BTO/STO compositions with varying the BTO/STO ratio showed that magnesia phase exists in the phase composition of the samples together with the previously described phases. X-ray studies showed that the lattice parameter for the main perovskite-type phase of BSTO changes very slowly depending on the amount of the additives and their percentage within the investigated concentration range.

X-ray data confirm the electron microscopy microstructure data. Fig. 4 displays micrographs for the 60 wt.% $BaTiO_3$–40 wt.% $SrTiO_3$ with 20 wt.% MgO and 25 wt.% Mg_2TiO_4 (over 100%) additives. Each studied sample includes three main phases: clear phase—BSTO type, gray phase—Mg_2TiO_4 and dark phase—MgO. However, as seen from the given photos, the MgO phase links the Mg_2TiO_4 phase crystal grains lengthening the crystalline aggregates consisting of Mg-containing non-ferroelectric crystalline phases and therefore promoting the formation of a so-called frame or grid, the cells of which are filled with BSTO type ferroelectric. This effect is significant especially for the compositions with high concentrations of Mg-containing additives.

Sintering of the BTO/STO mixture with the composite additive consisting of the mixture of MgO and Mg_2TiO_4 is accompanied (similarly to the samples described above) by the formation of perovskite impurity phases with increased and decreased lattice parameters compared to the parameter of the perovskite main phase, the volume content of which does not exceed 3–5%. Distribution of these phases in the heterogeneous ferroelectric structure is clearly seen in Fig. 4. The clear phase with the increased content of Ba is situated on the main phase crystal boundaries, while the phase with the decreased content

Table 2
Dielectric properties of compositions of BTO/STO + Mg_2TiO_4 + MgO system.

No.	Compositions BTO/STO + (wt.% Mg_2TiO_4 + wt.% MgO)	ε	tan δ (f = 1 MHz)	tan δ (f = 10 GHz)	n (20 kV/cm)	n (40 kV/cm)
1	50/50 + (5 + 20)(BSM1)	520	0.00010	0.004	1.071	1.114
2	50/50 + (20 + 65)	152	0.00011	0.004	1.080	1.122
3	50/50 + (20 + 45)	241	0.00011	0.006	1.093	1.154
4	55/45 + (50 + 25).	210	0.00019	0.006	1.116	1.193
5	55/45 + (75 + 25).	190	0.00016	0.009	1.145	1.293
6	55/45 + (5 + 9)	796	0.00022	0.009	1.107	1.167
7	55/45 + (5 + 20)(BSM3)	560	0.00015	0.006	1.130	1.274
8	60/40 + (5 + 20)(BSM4)	604	0.00020	0.009	1.162	1.384
9	60/40 + (25 + 20)	420	0.00030	0.011	1.224	1.486
10	60/40 + (20 + 40)	278	0.00024	0.012	1.115	1.413

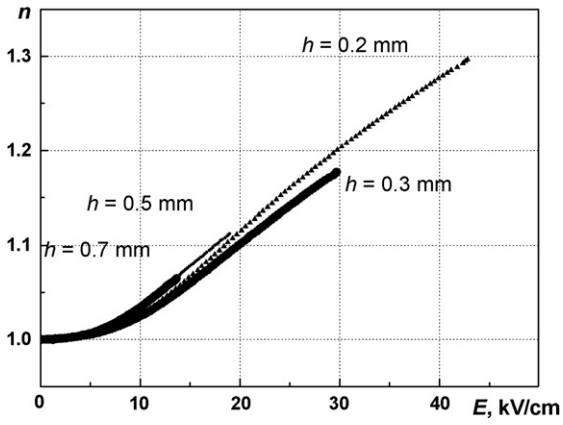


Fig. 5. Dependence tunability (n) of ceramic samples BSM3 from E.

of Ba (darker) can be seen inside the crystals of the main solid solution BSTO phase. The EDS data (see Fig. 4) confirm the obtained results.

The electric properties of the ceramic samples of BTO/STO + 50/50, 55/45 and 60/40 with different composition and concentration of complex additive in the initial composition are given in Table 2. The analysis of the results shows that the increase of the complex additive (mixture of magnesia and magnesium orthotitanate) content introduced into the heterogeneous mixture is accompanied with a certain decrease in the dielectric constant of the samples. At the same time, the value of its tunability by the electric field within the given composition range increases together with the increase of the concentration of Mg_2TiO_4 .The higher the concentration of this compound in the composition of Mg-containing additive, the more prominent the tunability increase.

Tunability of polished samples 0.2, 0.3, 0.5, and 0.7 mm thick of the BSM3 composition (see Table 2) showed that starting from $E \sim 5$ kV/cm n increases proportionally to the electric force and reaches the value of ~1.27 at $E = 40$ kV/cm (Fig. 5), tan δ of this sample equals 0.006 at 10 GHz, or Qf, = 1600–1800 GHz.

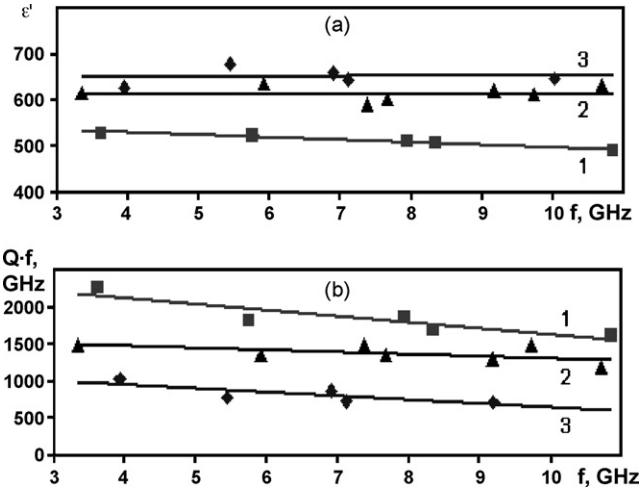


Fig. 6. Frequency dependence of ε' (a) and Qf (b) for ceramic samples: 1—BSM1; 2—BSM3; 3—BSM4.

Fig. 6 shows the results of the studies of Qf of the samples based on $BaTiO_3/SrTiO_3$ = 50/50, 55/45, 60/40 ratios that include the complex additive of the previously described magnesium compounds denoted as BSM1, BSM3 and BSM4 (see Table 2). The data show that at 20 °C the value of ε is within 500–600 for all the compositions. The samples BSM4 have a higher dielectric loss level compared to the other compositions. The frequency dependence of ε and Qf shows that the Qf value weakly changes with frequency within the range studied.

4. Conclusions

The bulk ferroelectric composite ceramics based on mixtures of powders of $BaTiO_3/SrTiO_3$ in the ratios 50/50, 55/45, 60/40 with Mg-contained additions such as Mg_2TiO_4, MgO and mixtures of Mg_2TiO_4–MgO in a wide range of compositions were fabricated and characterized. Phase relation, crystal structure, microstructures and dielectric properties of composite ferroelectrics were investigated. It was shown that the increase of concentration of Mg_2TiO_4 in compositions $BaTiO_3/SrTiO_3$–Mg_2TiO_4 and $BaTiO_3/SrTiO_3$–Mg_2TiO_4 + MgO leads to a decrease of the dielectric constant of the mixture and the increase of its tunability by a DC field. Based on mixtures of barium titanates and strontium titanates with Mg-containing additives Mg_2TiO_4 + MgO, low loss ferroelectric materials were synthesized, with parameters ε = 150–800, $n \sim 1.12$–1.49 with $E = 40$ kV/cm. These materials have potential uses in microwave tunable devices for high-power particle accelerators.

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