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MW Dielectrics with Perovskite-like Structure Based on Sm-containing Systems

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Abstract

The material formation conditions in the systems $BaO–Sm_2O_3–nTiO_2$ *(*$n = 4–5$*) and* $(Ba_{1-x}Ca_x)O–Sm_2O_3–4{\cdot}5TiO_2$ *(where* $x = 0–0{\cdot}1$*), and the electrophysical properties of materials were investigated. It was shown that in samarium-containing specimens there are temperature anomalies of permittivity, which make it possible to control the dielectric characteristics of microwave materials. © 1999 Elsevier Science Limited. All rights reserved*

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1 Introduction

When developing communication systems operating in the UHF band, a need arises for ceramic materials with higher permittivity ($\varepsilon > 80–100$) as a basis for dielectric resonators and substrates. The effective size of these components decreases with increasing ε value in a material. In recent years, complex rare-earth titanates have served as a basis for these materials. In the system $BaO–Ln_2O_3–TiO_2$ the formation of several compounds was reported as follows: $BaLn_2Ti_3O_{10}$ and $BaLn_2Ti_5O_{14}$ (where Ln = Nd),[1] $BaLn_2Ti_2O_8$, $BaLn_2Ti_3O_{10}$ and $BaLn_2Ti_4O_{12}$ (where Ln = La),[2] and the existence of the last one with 1:1:4 ratio of starting oxides was also confirmed for Ln = Nd, Sm.[3] Later on '1:1:4' compound was shown to belong to solid solubility region with general formula $Ba_{6-x}Ln_{8+2x/3}Ti_{18}O_{54}$.[4] In the system $BaO–Ln_2O_3–TiO_2$ the partial substitution of Pb^{2+}, Sr^{2+} for Ba^{2+}, and Bi^{3+} for Nd^{3+} was investigated with a view to improve the temperature coefficient of permittivity (τ_ε).[5,6] However, the nature of variation of τ_ε value and sign remains uncertain.

The aim of this study was to investigate the material formation conditions in the system $BaO–Ln_2O_3–nTiO_2$ (Ln = Sm), the partial substitution of calcium for barium in the system $(Ba_{1-x}Ca_x)O–Sm_2O_3–4.5TiO_2$, and MW dielectric properties of the ceramics sintered.

2 Experimental Procedure

$BaO–Sm_2O_3–nTiO_2$ materials were investigated at n varied from 4 to 5 and $(Ba_{1-x}Ca_x)O–Sm_2O_3–4{\cdot}5TiO_2$ materials at $x = 0$, 0·03, 0·05, 0·08, 0·1.

Extra pure $BaCO_3$, $CaCO_3$, Sm_2O_3 and TiO_2 were used as starting reagents. Phase transformations were studied on hardened specimens using thermogravimetry on a Q-1000 OD-102 device. Hardening was performed by quickly cooling specimens from the calcination temperature to room temperature. The products obtained were identified by powder diffractograms taken on a DRON-3M device using CuKα radiation. The electrophysical characteristics of sintered specimens were measured by the dielectric resonator method at frequencies of about 10 GHz in the temperature range of 20–200°C.

3 Results and Discussion

During the synthesis of $BaO–Sm_2O_3–nTiO_2$ materials, when $n = 4$, barium–samarium tetratitanate is formed, which belongs at the same time to the system $Ba_{6-x}Sm_{8+2x/3}Ti_{18}O_{54}$ at $x = 1{\cdot}5$.

According to the results of a thermal and X-ray phase analysis, $BaCO_3$ decomposes at 800–1000°C, barium and titanium oxides interacting to form barium metatitanate ($BaTiO_3$):

$$BaCO_3 + TiO_2 \rightarrow BaTiO_3 \qquad (1)$$

At 950°C, the barium tetratitanate ($BaTi_4O_9$) phase begins to crystallize:

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$$BaTiO_3 + 3TiO_2 \rightarrow BaTi_4O_9 \qquad (2)$$

At temperatures of over 1000°C, the $Sm_2Ti_2O_7$ phase appears in X-ray diagrams. At the same temperatures, the $Sm_{2/3}TiO_3$ phase ($Sm_2Ti_3O_9$) with perovskite structure appears, whose peaks coincide with those of the $BaTiO_3$ phase.[7] The barium–samarium tetratitanate phase also appears in the X-ray diagrams of specimens calcined at over 1000°C. The presence of the intermediate phase $Sm_{2/3}TiO_3$ ($Sm_2Ti_3O_9$) can be recognized by the character of the intensity variation of the peaks of the intermediate perovskite phases as a function of calcination temperature. Increasing the temperature of calcination of specimens to 1150°C does not lead to the appearance of new phases. Only quantitative changes are observed: the amount of the barium–samarium tetratitanate phase increases, whereas the amount of the intermediate phases decreases. At over 1250°C, the specimens are single-phase ones. On the basis of the data obtained it can be stated that in the temperature range 1000–1350°C barium-samarium tetratitanate is formed as follows:

$$Sm_2O_3 + 2TiO_2 \rightarrow Sm_2Ti_2O_7 \qquad (3)$$

$$3Sm_2Ti_2O_7 + BaTi_4O_9 \rightarrow 9Sm_{2/3}TiO_3 + BaTiO_3 \qquad (4)$$

$$3Sm_{2/3}TiO_3 + BaTiO_3 \rightarrow BaSm_2Ti_4O_{12} \qquad (5)$$

In the system $BaO–Sm_2O_3–nTiO_2$, three compositions corresponding to $n = 4$, 4·5, 5 were studied. The literature contains contradictory data on the phase composition of the $BaO–Sm_2O_3–nTiO_2$ system ($n = 4 - 5$). For instance, the authors of Refs 3 and 8 claim that only the compound $BaSm_2Ti_4O_{12}$ exists, and that the compositions are at $n > 4$ multiphase ones and are a mixture of the phases $BaSm_2Ti_4O_{12}$, $BaTi_4O_9$, $Ba_2Ti_9O_{20}$, and TiO_2. The phase diagram for the system $BaO–Sm_2O_3–nTiO_2$ was examined,[8] and it was confirmed that at $n > 4$ the materials are multiphase ones. At the same time, Ref. 9 states that the individual compound $BaSm_2Ti_5O_{14}$ is formed.

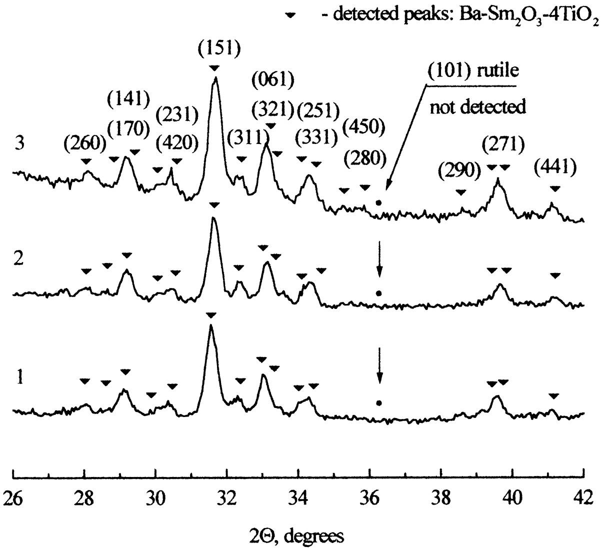

Fig. 1. X-ray diffraction patterns for specimens of the system $BaO–Sm_2O_3–nTiO_2$, calcined at 1350°C. (1) $n = 4$; (2) $n = 4{\cdot}5$; (3) $n = 5$.

The results of a qualitative assessment of the composition of specimens calcined at 1000–1350°C are shown in Fig. 1. The X-ray diagrams of materials exhibit only barium–samarium titanate peaks after calcination at 1350°C (Fig. 1). In the temperature range 1100–1200°C, only the amount of the intermediate barium tetratitanate phase ($BaTi_4O_9$) changes with increasing of *n*. The investigations carried out show that a solid solutions of barium–samarium tetratitanate ($BaSm_2Ti_4O_{12}$) and TiO_2 are probably formed in the $BaO–Sm_2O_3–nTiO_2$ system:

$$BaSm_2Ti_4O_{12} + nTiO_2 \rightarrow BaSm_2Ti_{4+n}O_{12+2n} \qquad (6)$$

To confirm the formation of solid solutions in the system $BaO–Sm_2O_3–nTiO_2$, TiO_2 (rutile) powder was added to single-phase $BaSm_2Ti_4O_{12}$ powder in 1:0.5 and 1:1 molar ratios, mixed thoroughly, and the mixture was calcined at a high temperature. The rutile peaks are clearly seen in the X-ray diagrams of the mixture of $BaSm_2Ti_4O_{12}$ and TiO_2 (rutile) powders before calcination, whereas after calcination only the peaks corresponding to barium–samarium tetratitanate are seen. When *n* is increased from 4 to 5, the lattice parameters change only slightly and are in the following ranges: *a* varies from 12·13 to 12·18 Å, *b* varies from 22·34 to 22·68 Å, and *c* varies from 3·78 to 3·83 Å. The data given indicate that the phases $BaSm_2Ti_4O_{12}$ and TiO_2 interact to form probably solid solutions.

During the synthesis of $(Ba_{1-x}Ca_x)O–Sm_2O_3–4{\cdot}5TiO_2$ materials, the partial substitution of barium by calcium does not change the phase transformations which were observed during the synthesis of the system $BaO–Sm_2O_3–nTiO_2$. When x is increased from 0 to 0·1, the lattice parameters change only slightly.

All materials investigated possess in the MW range (10 GHz) a high permittivity ($\varepsilon = 70–80$), a low dielectric loss ($\text{tg}\ \delta = 10^{-3}$) and a high temperature stability of the properties ($\tau_f = -10 \ldots +10$ ppm/°C) (Figs 2 and 3 and Table 1). The presence of a diffuse peak in the plot of permittivity against temperature $\varepsilon(T)$ is a distinctive feature of samarium-containing

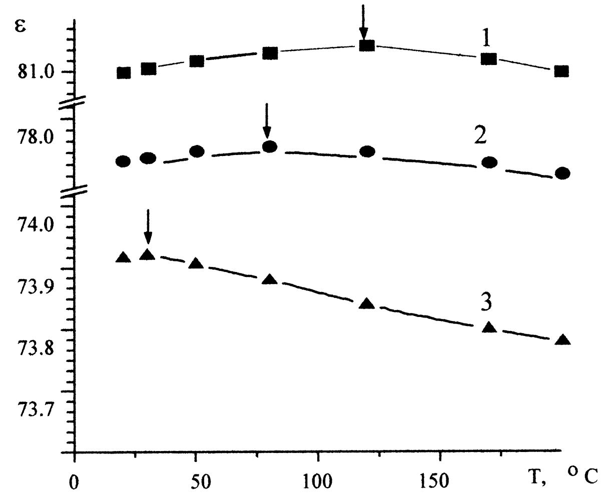

Fig. 2. Permittivity ε as a function of temperature at 10 GHz for BaO–Sm_2O_3–$n$$TiO_2$ materials. (1) $n=4$; (2) $n=4{\cdot}5$; (3) $n=5$.

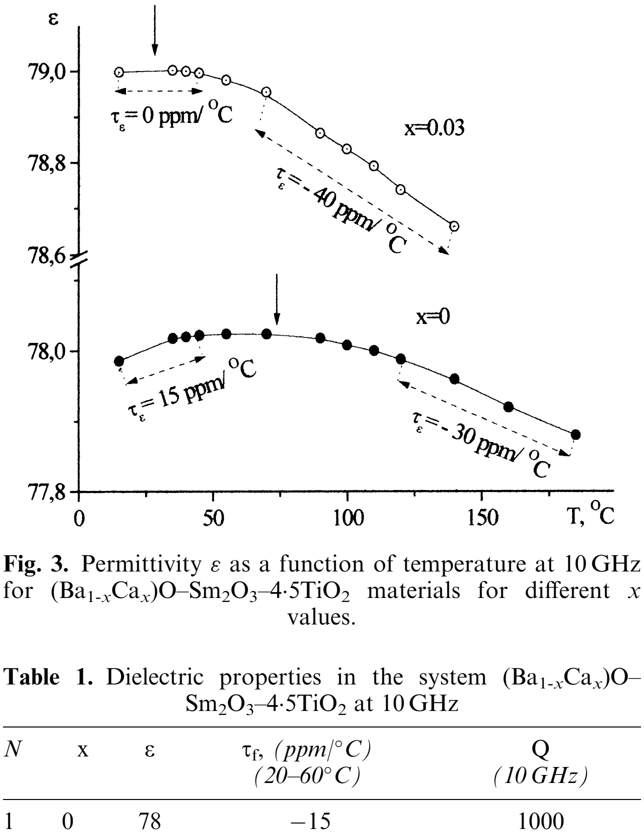

Fig. 3. Permittivity ε as a function of temperature at 10 GHz for $(Ba_{1\text{-}x}Ca_x)O$–Sm_2O_3–4·5TiO_2 materials for different x values.

Table 1. Dielectric properties in the system $(Ba_{1\text{-}x}Ca_x)O$–Sm_2O_3–4·5TiO_2 at 10 GHz

N	x	ε	τf, *(ppm/°C) (20–60°C)*	Q *(10 GHz)*
1	0	78	−15	1000
2	0·03	79	−5	1050
3	0·05	81	+2	1100
4	0·08	82	+15	1000
5	0·1	84	+25	950

materials. Investigation of BaO–Sm_2O_3–$n$$TiO_2$ ($n=4$–5) materials shows that the permittivity–maximum temperature shifts towards lower values (Fig. 2). These results agree with the results of X-ray diffraction analysis and indicate the formation of solid solutions to be possible in this region since in the case of multiphase systems anomalies of the temperature dependence $\varepsilon(T)$ in the MW range would be observed at one temperature. The presence of diffuse peaks in the plot of $\varepsilon(T)$, whose variation as a function of temperature is independent of frequency, was first revealed and attributed to the presence of 'displacive' transitions.[10] The presence of $\varepsilon(T)$ anomalies makes it possible to synthesize materials in the BaO–Sm_2O_3–$n$$TiO_2$ system with controlled temperature stability of electrophysical properties in the MW range through volume temperature compensation mechanism. Volume temperature compensation can be effected by the partial substitution of samarium (samarium-containing materials have negative τ_f) by some other rare-earth elements such as lanthanum or neodymium (lanthanum- and neodymium-containing materials have positive τ_f). Volume temperature compensation in this system can be also affected by the partial substitution of barium by alkaline-earth elements, e.g. strontium.[6] In this study, the possibility of affecting volume temperature compensation by the substitution of barium by calcium was examined.

Investigations showed that insignificant substitutions of barium by calcium in the system $(Ba_{1\text{-}x}Ca_x)O$–Sm_2O_3–4·5TiO_2 (where $x=0$–0·1) lead to a shift of the permittivity maximum towards lower temperatures (Fig. 3). In this case, the lattice parameters and the quantities ε and Q change only slightly, whereas τ_f varies continuously from −15 to +25 ppm/°C (Table 1).

4 Conclusion

The formation conditions of barium–samarium titanate ($BaSm_2Ti_4O_{12}$), which is characterized by the presence of a maximum in the plot of permittivity against temperature [$\varepsilon(T)$] in the MW range, has been studied. It has been shown that in the system $BaSm_2Ti_4O_{12}$–$n$$TiO_2$ ($n=4$–5), there is a shift of the permittivity–maximum temperature towards lower values with increasing amount of TiO_2. These data may indicate the formation of solid solutions in this system to be possible.

It has been found that volume temperature compensation in this system can be affected by the partial substitution of barium by calcium.

References

1. Kolar, D., Gabersek, S., Volvasek, B., Parker, H. S., and Roth, R. S. Synthesis and crystal chemistry of $BaNd_2Ti_3O_{10}$, $BaNd_2Ti_5O_{14}$, and $Nd_4Ti_9O_{20}$. *J. Solid State Chem.*, **38** 1981, 158–164.
2. Razgon, Y. S., Gens, A. M., Varfolomeev, M. B., Korovin, S. S. and Kostomarov, V. S., On complex barium and lanthanum titanates. *Zhurn. Neorg. Khimii*, 1980, **25**(6), 1701–1703.
3. Takahashi, J., Ikegami, T., and Kageyama, K., Occurrence of dielectric 1:1:4 compound in the ternary system

BaO–Ln_2O_3–TiO_2 (Ln = La, Nd, and Sm). *J. Am. Ceram. Soc.*, 1991, **74**, 1868–1879.

4. Varfolomeev, M. B., Mironov, A. S., Kostomarov, V. S., Golubtsova, L. A. and Zolotova, T. A., Synthesis and phase homogeneity regions of $Ba_{6-x}Ln_{8+2x/3}Ti_{18}O_{54}$. *Zhurn. Neorg. Khimii*, 1988, **33**(4), 1070–1071.
5. Wakino, K., Minai, K. and Tamura, H., Microwave characteristics of (Zr, Sn)TiO_4 and BaO–PbO–Nd_2O_3–TiO_2. *J. Am. Ceram. Soc.*, 1984, **67**, 278–282.
6. Nishigaki, S., Kato, H., Yano, S. and Kamimura, R., Microwave dielectric properties of (Ba,Sr)O–Sm_2O_3–TiO_2 ceramics. *Am. Ceram. Soc. Bull.*, 1987, **66**(9), 1405–1410.
7. Sych, A. M., Bilyk, D. I., Klemus, V. G. and Novik, T. V., Lanthanum, praseodymium and neodymium metatitanates. *Zhurn. Neorg. Khimii*, 1976, **21**(12), 3220–3223.
8. Negas, T., Yeager, G., Bell, S. and Amren, R., Chemistry and properties of temperature compensated microwave dielectrics. *NIST Spec. Publ.*, 1991, **804**, 21–37.
9. Polyakov, S. M., Gindin, Y. I., Prohvatilov, V. G. and Shtelmah, S. V., On the composition and structure of barium–lanthanide tetratitanate. *Zhurn. Neorg. Khimii*, 1983, **28**(11), 2973–2974.
10. Butko, V. I., Belous, A. G. and Nenasheva, Y. A., Microwave dielectric properties of barium–llanthanide tetratitanates. *Fizyka Tvyordogo Tela*, 1984, **26**(10), 2951–2956.