APPLIED PHYSICS LETTERS VOLUME 77, NUMBER 11 11 SEPTEMBER 2000

Anomalies in the temperature dependence of the microwave dielectric properties of $Ba_{6-x}Sm_{8+2x/3}Ti_{18}O_{54}$

Anatolii G. Belous and Oleg V. Ovchar
V. I. Vernadskii Institute of General and Inorganic Chemistry, Ukrainian National Academy of Sciences, 32/34 Palladina Avenue, 03680 Kyiv-142, Ukraine

Matjaz Valant[a] and Danilo Suvorov
''Jožef Stefan'' Institute, Jamova 39, 1000 Ljubljana, Slovenia

(Received 27 April 2000; accepted for publication 14 July 2000)

Measurements of the microwave dielectric properties of $Ba_{6-x}Sm_{8+2x/3}Ti_{18}O_{54}$ solid solutions revealed the existence of a broad maximum in the temperature dependence of the permittivity as well as the dielectric loss. Submillimeter-wave frequency measurements confirmed the intrinsic origin of the observed anomaly, which could possibly be ascribed to phase transition with unknown nature in the $Ba_{6-x}Sm_{8+2x/3}Ti_{18}O_{54}$ solid solution. The temperature of the anomaly, which is in the range of 90–120 °C, depends on composition of $Ba_{6-x}Sm_{8+2x/3}Ti_{18}O_{54}$ and decreases with an increase in *x*. © *2000 American Institute of Physics.* [S0003-6951(00)02737-6]

One of the most important trends in wireless technology is the miniaturization of electronic systems. To achieve this, ceramic components such as oscillating or filtering devices must be manufactured from high-permittivity materials. At present, the only commercially available group of high-permittivity microwave materials are ceramics based on the $Ba_{6-x}Ln_{8+2x/3}Ti_{18}O_{54}$ (Ln=La–Gd) solid solutions with permittivities ranging from 75 to 90. This makes them technologically very important and has triggered extensive research into the chemical and physical phenomena associated with these materials.

The crystal structure of $Ba_{6-3x}Ln_{8+2x}Ti_{18}O_{54}$ solid solutions includes elements of the tungsten–bronze structure with channels extending in the short-axis direction.[1,2] Corner-sharing TiO_6 octahedra form a network with three types of channels: pentagonal, rhombic, and triangular. Rare-earth ions occupy the rhombic channels, Ba ions completely fill the pentagonal channels (for $x<2/3$), while the remaining Ba ions share the rhombic channels. The triangular channels are empty. The extension of the homogeneity region decreases with the ionic size of the rare earth and for the Sm analogue is restricted to $0.9<x<2.1$.[3,4]

Decades of investigations of the dielectric properties of $Ba_{6-x}Ln_{8+2x/3}Ti_{18}O_{54}$ solid solutions have revealed their close correlation with the nature of the rare-earth ions. The permittivity is the highest for the La analogue ($\kappa'=93$ for $x=1.5$),[5] and decreases with decreasing polarizability of the rare-earth ions from La to Gd ($\kappa'=76$ for $x=1.5$).[6] The permittivity also varies as a function of composition (x) within each rare-earth's solid-solubility region, where it decreases with increasing rare-earth concentration (increasing x) as a result of a decrease in the total dielectric polarizability.[4] The temperature coefficient of resonance frequency (τ_f) is highly positive for the La analogue but decreases with decreasing size of the rare-earth ions and reaches negative values for Sm, Eu, and Gd analogues. Inside each solid-solubility region, τ_f decreases as x increases. In addition, the dielectric losses vary systematically over the solid-solubility region. Consistently, the quality factor (Q value), which is the inverse of the dielectric loss ($\tan\delta$), is low for low-x values and increases as x increases. Interestingly, the Q value has a maximum at the high-x-end member for the Nd[4] and Pr systems,[7] but in the case of the Sm system, the maximum Q value is reached at approximately $x=1.8$.[3,4] The Eu analogue shows the highest $Q\cdot f$ values (14 000 GHz), and with increasing rare-earth ionic size, the $Q\cdot f$ values decrease and reach values around 2300 GHz for the La analogue. Clearly, the trend is violated by Gd which, although smaller than Eu, exhibits a very low $Q\cdot f$ value of 2050 GHz.[3–7]

The samples for the dielectric property measurements were prepared from reagent-grade $BaCO_3$, Sm_2O_3, and TiO_2. The starting reagents were mixed in the appropriate ratios and homogenized by ball milling. The mixture was dried and prereacted at 1150–1200 °C for 2–3 h to achieve equilibrium. Prereacted samples were powdered, pressed into the pellets and sintered at 1330–1380 °C for 2–3 h. The dielectric constant (ϵ) and dielectric loss ($\tan\delta$) of the materials were measured at ~10 GHz using a modification of the dielectric resonator method on appropriate disk samples, which resided in the isolated waveguide section. The dielectric constant was calculated from the model of the dielectric core with ''magnetic walls.''[8] The dielectric losses of the materials were estimated from the frequency dependence of the transfer constant in the vicinity of the resonant frequency.[9] Submillimeter-wave frequency measurements were carried out using a backward-wave tube by measuring the optical-path length and absorption (α) in a parallel-plate ceramic sample coated with a quarter-wavelength antireflecting coating.[10]

Microwave dielectric property measurements of the dielectric resonators, based on single-phase $Ba_{4.5}Sm_9Ti_{18}O_{54}$ $(x=1.5)$, revealed a broad, diffuse minimum in the temperature dependence of the resonant frequency, occurring at a temperature of ~100 °C. This minimum is related to the existence of a broad maximum in the

---

[a] Electronic mail: matjaz.valant@ijs.si

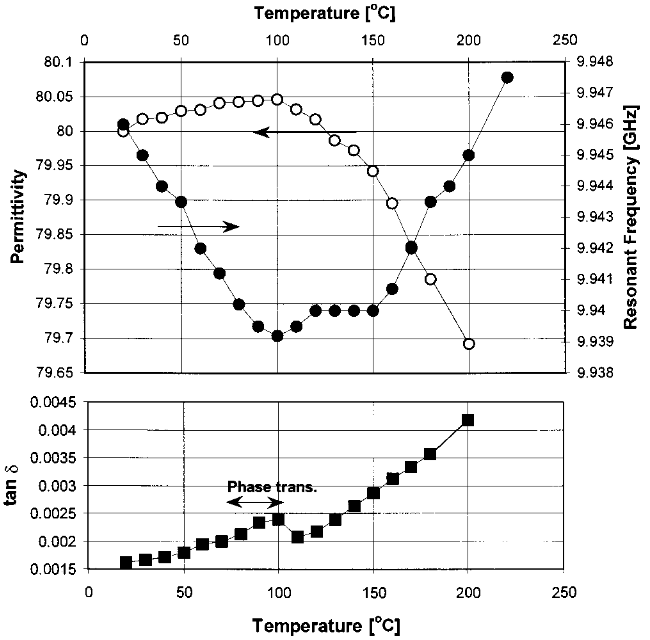

FIG. 1. Temperature dependence of permittivity, resonance frequency, and dielectric losses of the ceramic disk with composition $Ba_{6-x}Sm_{8+2x/3}Ti_{18}O_{54}$ ($x=1.5$).

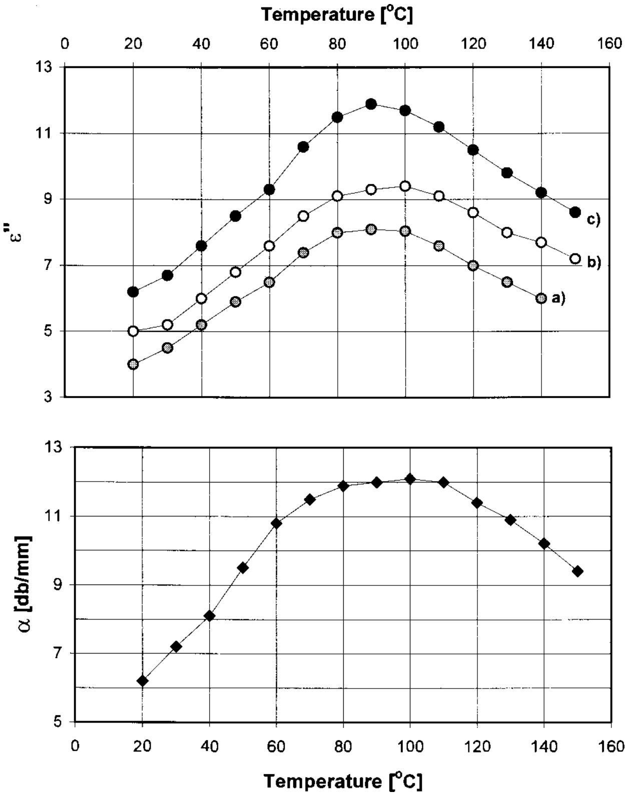

FIG. 2. Temperature dependence of absorption factor (α) measured at 134 GHz and imaginary dielectric constant (ϵ'') measured at 96.7 GHz (a), 134 GHz (b), and 180 GHz (c) of the sample with composition $Ba_{6-x}Sm_{8+2x/3}Ti_{18}O_{54}$ ($x=1.5$).

temperature dependence of the permittivity and dielectric losses (Fig. 1). Previous studies of the same system have never reported such a phenomenon, but rather assumed a linear dependence.[4,11–13] The only study indicating an anomaly in the temperature dependence of permittivity is the study of Butko *et al.*,[14] where they observe a minimum in the temperature dependence of the resonant frequency. A similar behavior of the temperature dependence of the resonant frequency was described by Nishigaki *et al.*[15] for the 0.15 $(Ba_{0.95}Sr_{0.15})O\cdot 0.15Sm_2O_3\cdot 0.7TiO_2$ system, which is no longer thought to belong to the $Ba_{6-x}Sm_{8+2x/3}Ti_{18}O_{54}$ homogeneity region.

Because of the very faint and diffuse nature of the observed anomalies, additional measurements were performed at submillimeter-wave frequencies to eliminate any possibility of their appearance being related to the extrinsic properties of the ceramic sample. The temperature dependence of the absorption factor (α) and dielectric losses (ϵ''), which were measured in the frequency range from 96.7 to 180 GHz, again exhibited a similar anomaly at approximately the same temperature as in the microwave frequency region (Fig. 2). This confirms the assumption of the unknown phase transition, which for the Sm analogue with $x=1.5$ occurs at ~100 °C.

By analogy with the ferroelectric and antiferroelectric solid solutions, it is expected that the temperature of the permittivity maximum will be sensitive to the composition on the $Ba_{6-x}Sm_{8+2x/3}Ti_{18}O_{54}$ solid solution. Indeed, detailed microwave measurements of the samples with composition $x=1.0$, 1.5, and 2.0, showed that by increasing x the temperature of the permittivity maximum decreases from ~120 to ~100 °C and, finally, to ~90 °C (Fig. 3; for $x=1.5$, see Fig. 1). Accordingly, the maximum in the dielectric losses that appears correlated to the permittivity maximum, shifts within the same temperature interval.

The existence of the observed anomaly can also explain the decrease in Q value observed for the compositions with $x>1.8$, which within the family of $Ba_{6-x}Ln_{8+2x/3}Ti_{18}O_{54}$ solid solutions occurs only for the Sm analogue.[3,4] Since, with an increase in x, the temperature region where the dielectric loss maximum is observed approaches room tem-

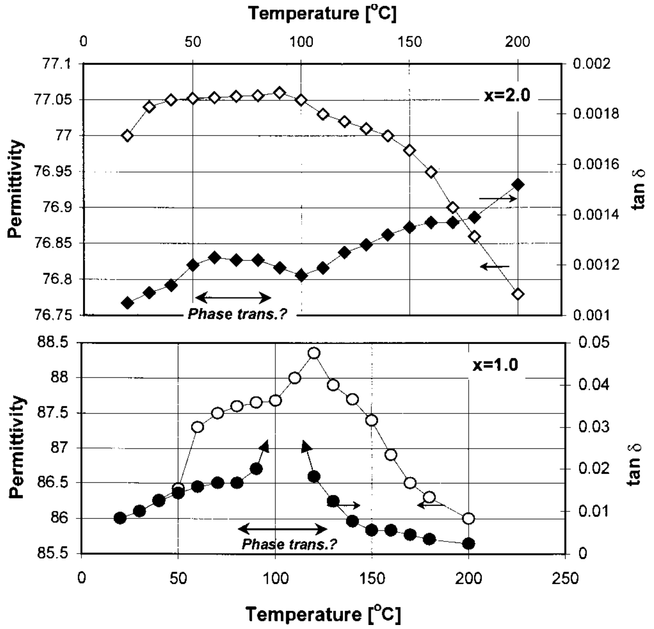

FIG. 3. Temperature dependence of permittivity and dielectric losses of the ceramic disk with composition $Ba_{6-x}Sm_{8+2x/3}Ti_{18}O_{54}$ and $x=1.0$ and 2.0 measured at ~10 GHz (for $x=1.5$, see Fig. 1). Dielectric losses at $T=100$ and 110 °C are for the $x=1.0$ sample, too high to be measured by the dielectric resonator method.

perature, the decrease in the Q values of high-x compositions might be related to the proximity of the structural relaxation.

Summarizing the results of the dielectric measurements, it can be concluded that the anomaly in the dielectric properties in the $Ba_{6-x}Sm_{8+2x/3}Ti_{18}O_{54}$ solid solution does occur. The temperature of this anomaly is within the range 90–120 °C, but strongly depends on x. The anomaly is characterized by a broad maximum in the temperature dependence of permittivity and the corresponding maximum in the dielectric losses. Findings related to the behavior of dielectric losses in the transition region show that for the development of low-loss dielectrics for microwave applications based on the $Ba_{6-x}Sm_{8+2x/3}Ti_{18}O_{54}$ solid solution, the proximity of the temperature of the anomaly must be avoided.

[1] R. G. Matveeva, M. B. Varfolomeev, and L. S. Il'yuhchenko, Russ. J. Inorg. Chem. **29**, 17 (1984).

[2] C. J. Rawn, D. P. Birnie, M. A. Bruck, J. H. Enemark, and R. S. Roth, J. Mater. Res. **13**, 187 (1998).

[3] H. Ohsato, T. Ohhashi, S. Nishigaki, T. Okuda, K. Sumia, and S. Suzuki, Jpn. J. Appl. Phys., Part 1 **32**, 4323 (1993).

[4] T. Negas and P. K. Davies, Ceram. Trans. **53**, 179 (1995).

[5] C. Hoffmann and R. Waser, Ferroelectrics **201**, 127 (1997).

[6] M. Valant, D. Suvorov, and D. Kolar, Jpn. J. Appl. Phys., Part 1 **35**, 144 (1996).

[7] K. Fukuda, R. Kitoh, and I. Awai, J. Mater. Res. **10**, 312 (1995).

[8] A. A. Bokrinskaya and M. E. Ilchenko, Izv. Vyssh. Uchebn. Zaved. Radioelektron. **14**, 151 (1971).

[9] I. M. Buzin and I. M. Angelov, Prib. Tekh. Eksp. **4**, 114 (1974).

[10] V. V. Meriakri and E. F. Ushatkin, Prib. Tekh. Eksp. **2**, 143 (1973).

[11] P. Laffez, G. Desgardin, and B. Raveau, J. Mater. Sci. **27**, 5229 (1992).

[12] H. Ohsato, H. Kato, M. Mizuta, S. Nishigaki, and T. Okuda, Jpn. J. Appl. Phys., Part 1 **34**, 5413 (1995).

[13] H. Seemoolanadhan, M. T. Sebastain, and P. Mohanan, Br. Ceram. Trans. **95**, 79 (1996).

[14] V. I. Butkov, A. G. Belous, Y. A. Nanasheva, Y. M. Poplavko, and E. F. Ushatkin, Sov. Phys. Solid State **26**, 1783 (1984), translated from Fiz. Tvrd. Tela **26**, 2951 (1984).

[15] S. Nishigaki, H. Kato, S. Yano, and R. Kamimura, Am. Ceram. Soc. Bull. **66**, 1405 (1987).