Preparation and dielectric properties of $Sr_5LnSn_3Nb_7O_{30}$ (Ln = Nd, La) ceramics

H. ZHANG, L. FANG*
State Key Laboratory of Advanced Technology for Materials Synthesis and Processing, Wuhan University of Technology, Wuhan 430070, People's Republic of China; Institute of Inorganic Chemistry, RWTH Aachen University, Aachen 52056, Germany
E-mail: fangliang001@263.net

T. H. HUANG, R. Z. YUAN
State Key Laboratory of Advanced Technology for Materials Synthesis and Processing, Wuhan University of Technology, Wuhan 430070, People's Republic of China

R. DRONSKOWSKI
Institute of Inorganic Chemistry, RWTH Aachen University, Aachen 52056, Germany

Electronic materials with high dielectric constants, high Q-values and good stability of temperature coefficient of resonant frequency and low dielectric loss have been extensively studied because of their applications in discrete and multilayer (MLC) capacitors, microwave telecommunication applications, and low loss substrates for microwave integrated circuits [1–4]. The high dielectric constant materials are also very important in advanced microelectronic technologies such as dynamic random access memories (DRAM) [5]. So far, many dielectric materials have been studied such as BaO-TiO_2, BaO-Nd_2O_3-TiO_2. However, these materials ($\varepsilon < 100$) are not sufficient for miniaturization of microelectronic devices. Hence, the development of new materials with dielectric constant in excess of 100 has become very important. Sebastian *et al.* proposed some promising compounds with tungsten bronze (TB) structure under the formula $Ba_3(RE)_3Ti_5Nb_5O_{30}$ (RE = La, Y, Sm, Nd) for their high dielectric constants of above 130 [6, 7]. Chen and Fang *et al.* also reported the presence of dielectric materials with filled TB structure with high dielectric constant and low dielectric loss in the BaO-Ln_2O_3-TiO_2-Ta_2O_5 and BaO-Ln_2O_3-ZnO-Ta_2O_5 system (Ln = La, Sm, Nd) [8–12]. However, very little data are available on the dielectric properties of materials with the TB structure in the SrO-Ln_2O_3-SnO_2-Nb_2O_5/Ta_2O_5 system. This paper presents the preparation, characterization, and dielectric properties of two ceramics in this system, namely $Sr_5NdSn_3Nb_7O_{30}$ and $Sr_5LaSn_3Nb_7O_{30}$ ceramics, for the first time.

High purity powders of $SrCO_3$ (>99.9%), Ln_2O_3(Ln = Nd or La) (>99.9%), SnO_2 (>99.95%), and Nb_2O_5 (>99.9%) were weighed to $Sr_5LnSn_3Nb_7O_{30}$ (Ln = Nd or La) stoichiometry, respectively. The compounds with Ln as Nd and La will be referred to as SNSN and SLSN, respectively, in the remaining part of the text. The powders were ground in agate mortar to obtain homogeneous mixture and calcined at 1360 °C for 48 hrs. The calcined powders were reground into very fine powders and pressed into disks of 11 mm diameter and about 2–4 mm thickness using a cold isostatic pressing with a pressure of 200 MPa. The pellets were sintered in air at 1410 °C for 4 hrs and cooled naturally to room temperature. The densities of the compacts were measured by the Archimedes method. Phase identification and microstructure characterization were performed using a Rigaku D/MAX-RB Powder X-ray diffraction (XRD) using Cu K_α radiation ($\lambda = 0.154\ 06$ nm) and a JSM-5610LV SEM. Silver paste was applied to the circular faces, then dried at 600 °C for 20 min and cooled naturally to room temperature.

The temperature-dependent dielectric measurements were made using an HP4284A LCR meter equipped with a thermostat from room temperature (30 °C) to 400 °C at 1, 10, 100 kHz and 1 MHz. The temperature coefficients of the dielectric constants (τ_ε) were calculated using the data in the temperature range of 30 to 400 °C at 1 MHz. The capacitance and the loss factor were determined at room temperature in the range 1 kHz to 1 MHz.

The SNSN and SLSN compositions sintered into dense ceramics without the use of any additive, and they exhibit bulk densities of 5.393 gcm^{-3} (94.7%) and 5.384 gcm^{-3} (95.3%) respectively. The XRD patterns obtained using Cu K_α radiation are shown in Fig. 1a and b. These compositions were found to exhibit a single phase tetragonal TB structure in agreement with JCPDS file No. 34-409 of $Sr_3TiNb_4O_{15}$. The unit cell parameters of those ceramics refined by the least squares method are as follows: $a = 12.4674(4)$ Å; $c = 3.9013(2)$ Å for SLSN; and $a = 12.4521(3)$Å; $c = 3.8906(1)$ Å for SNSN. The replacement of La with relatively smaller cation Nd leads to the smaller unit cell parameters of SNSN being smaller than that of SLSN.

Figs 2 and 3 show the SEM photographs of the fracture surfaces of the SLSN and SNSN ceramics. These ceramics have good sinterability with a low porosity.

*Author to whom all correspondence should be addressed.

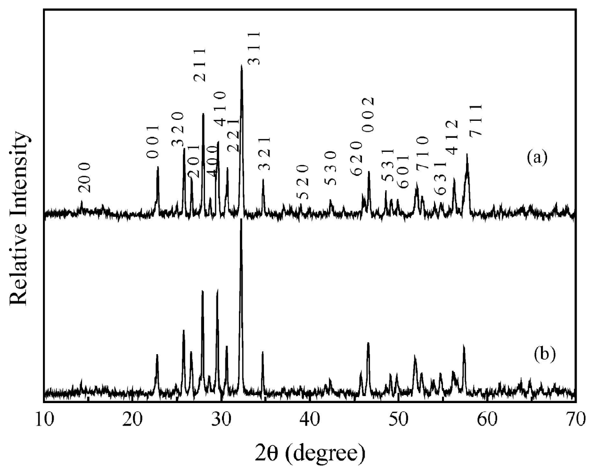

Figure 1 XRD patterns of (a) SNSN and (b) SLSN.

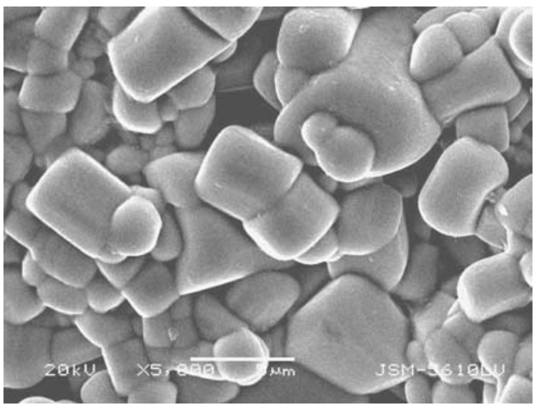

Figure 2 SEM micrographs of SLSN ceramic.

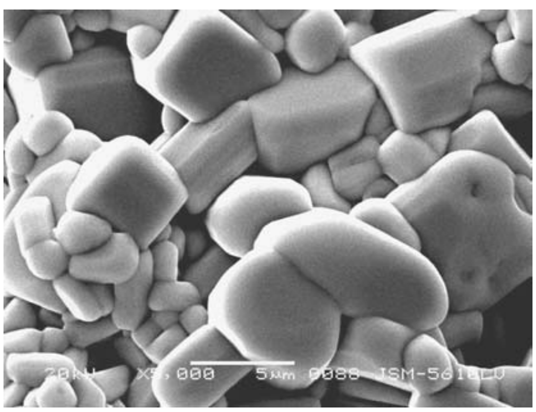

Figure 3 SEM micrographs of SNSN ceramic.

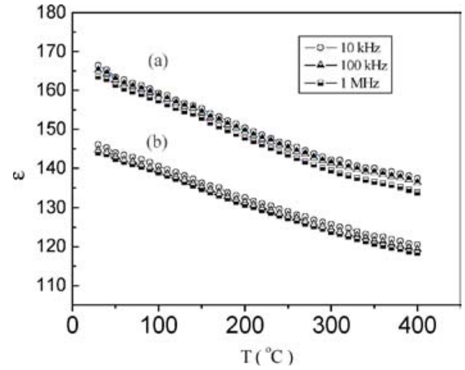

Figure 4 Temperature dependence of dielectric constants of (a) SLSN and (b) SNSN ceramics.

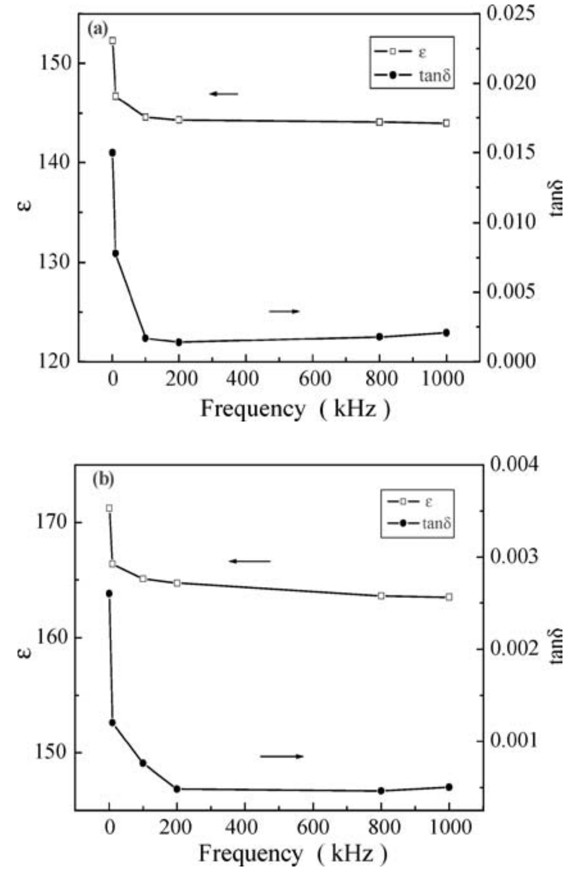

Figure 5 Frequency dependence of dielectric constant and dielectric loss of (a) SNSN and (b) SLSN ceramics.

The microstructure indicates a monophase constitution with packed grains in the size range of 2–7 μm for SLSN and SNSN.

The temperature dependencies of the dielectric constants at 10, 100 kHz, and 1 MHz frequencies for both compounds are shown in Fig. 4. As the temperature increases from 30 to 400 °C, the relative dielectric constants ε of the SNSN and SLSN ceramics gradually decrease, and no dielectric peak for the ferroelectric/ paraelectric phase transition is observed such that the Curie point is below room temperature; obviously, SNSN and SLSN belong to the paraelectric phase of the TTB structure. The temperature coefficients of the dielectric constants (τ_ε) at 1 MHz are –487 ppm °C^{-1} for SNSN and −497 ppm °C^{-1} for SLSN, which is much smaller compared with those of the TB compounds in the BaO-Ln_2O_3-TiO_3-Nb_2O_5/Ta_2O_5 system such as $Ba_5NdTi_3Ta_7O_{30}$ (−2500 ppm°C^{-1} at 10 kHz) [9].

Fig. 5 demonstrates the room temperature dielectric characteristics of the SNSN and SLSN ceramics. The dielectric constants and the dielectric losses of SNSN and SLSN ceramics vary gradually with the frequency. The dielectric constant of the SNSN ceramic decreases from 152 to 144 upon increase of frequency from 1 kHz to 1 MHz due to the reduction of active polarization mechanism. The dielectric loss sharply lowers from 0.015 to 0.0014 with increasing frequency from 1 to

100 kHz, then slightly increases to 0.0021 at 1 MHz. Similarly, the dielectric constant of the SLSN ceramic decreases from 171 to 163 with increase of frequency, while the dielectric loss sharply lowers from 0.0026 to 0.0048 upon increase of frequency from 1 to 200 kHz, then slightly increases to 0.0054 at 1 MHz.

Two $Sr_5LnSn_3Nb_7O_{30}$ (Ln = Nd, La) ceramics in the $SrO\text{-}Ln_2O_3\text{-}SnO_2\text{-}Nb_2O_5$ quaternary system were prepared and characterized. Both are paraelectric phases and adopt filled tetragonal TB structures at room temperature. At 1 MHz the two ceramics exhibit high dielectric constants of 144 and 163 together with low dielectric losses of 0.0021 and 0.0054, respectively. Further, the temperature coefficients of the dielectric constants (τ_ε) are significantly reduced compared to those of the TB compounds in the $BaO\text{-}Ln_2O_3\text{-}TiO_3\text{-}Ta_2O_5$ system. These materials have potential application in temperature-compensating capacitors. Considering the microwave application, the key issue of the two ceramics was to lower the dielectric loss further and to obtain near zero temperature coefficient of the dielectric constant.

Acknowledgments

This work was financially supported by Natural Science Foundation of China (NSFC No. 50002007) and the Major Program of MOE of China (No. 0201). Hui Zhang is thankful to DAAD for a scholarship.

References

1. D. LIU, Y. LI, S. Q. HUANG and X. YAO, *J. Amer. Ceram. Soc.* **76** (1993) 2129.
2. T. M. HERBERT, "Ceramic Dielectrics and Capacitors" (Gordon & Breach Science Publishers, New York, 1985) p. 188.
3. R. UBIC, I. M. REANEY and W. E. LEE, *Intern. Mater. Rev.* **43** (1998) 205.
4. M. T. SEBASTIAN, *J. Mater. Sci.: Mater. Electron* **10** (1999) 475.
5. G. L. ROBERTS, R. J. CAVA and W. F. PECK, *J. Amer. Ceram. Soc.* **58** (1997) 526.
6. R. P. RAO, S. K. GHOSH and P. KOSHY, *J. Mater. Sci.: Mater. Electron* **12** (2001) 729.
7. P. KOSHY, L. P. KUMARI and M. T. SEBASTIAN, *ibid.* **9** (1998) 43.
8. X. M. CHEN and J. S. YANG, *J. Eur. Ceram. Soc.* **19** (1999) 139.
9. X. M. CHEN, Y. H. SUN and X. H. ZHENG, *ibid.* **23** (2003) 1571.
10. L. FANG, H. ZHANG, J. B. YAN and W. M. YANG, *Acta Phys.-Chim. Sin.* **19** (2003) 82.
11. L. FANG, H. ZHANG, J. F. YANG, R. Z. YUAN and H. X. LIU. *J. Mater. Sci.: Mater. Electron.* **15** (2004) 327.
12. *Idem.*, *Mater. Res. Bull.* **39** (2004) 1903.

Received 23 October 2003
and accepted 29 March 2004