

Dielectric Behavior and Cofiring with Silver of Monoclinic BiSbO₄ Ceramic

Di Zhou, Hong Wang[†], Xi Yao, and Li-Xia Pang

Electronic Materials Research Laboratory, Key Laboratory of the Ministry of Education, Xi'an Jiaotong University, Xi'an 710049, China

Pure monoclinic phase of BiSbO₄ ceramic was synthesized using the solid-state reaction method. BiSbO₄ ceramics can be well sintered between 960° and 1080°C. The dielectric constant of BiSbO₄ ceramic was about 20.1 and dielectric loss was about $0.055\text{--}2.5 \times 10^{-4}$ at 1 MHz. With the measured frequencies increasing from 100 to 900 kHz, the temperature coefficients of permittivity decreased from +224.1 to +95.9 ppm/°C. At the microwave range, the best microwave dielectric properties were obtained in the ceramic sintered at 1080°C/2 h with a permittivity of 19.3, a Q_f value of about 70 000 GHz, and a temperature coefficient of resonant frequency of -62 ppm/°C. Cofiring between BiSbO₄ ceramic and 20 wt% Ag was also investigated, and it was found that after cofiring at 900°C for 5 h only very little unknown phase containing a little amount of Ag was formed and most Ag was scattered in grain boundaries.

I. Introduction

RECENTLY, the rapid growth of communication devices using microwave frequencies, such as portable phones and car telephones, has required the miniaturization of microwave components such as band pass filters and local oscillators. The application of multilayer microwave devices will satisfy this requirement. By applying low-temperature cofired ceramics (LTCC) technology, components can be integrated in monolithic, highly reliable LTCC modules that consist of several layers of ceramic substrates with integrated components (inductors, capacitors, resonators), which are interconnected by three-dimensional strip-line circuitry.¹ In the fabrication of multilayer microwave devices, low-firing microwave dielectric materials with high dielectric constant ϵ_r , low dielectric loss, and near-zero temperature coefficient of resonant frequency TCF/τ_f are needed to cofire with low loss and low-melting-point conductors such as Ag (melting point = 961°C) or Cu (1064°C).

Bismuth-based dielectric ceramics are well known as low-fired materials and have been investigated for application as multilayer capacitors.^{2,3} The microwave dielectric properties of Bi₂O₃–Nb₂O₅ systems were first studied by Kagata *et al.* in 1992.⁴ Their results showed that BiNbO₄ ceramics with CuO or V₂O₅ additions had a Q_f value of about 16 000 GHz, an ϵ_r value of 43, and a TCF value of 38 ppm/°C. Later, a number of researchers performed several of studies on the modification of BiNbO₄ ceramics with low-melting oxides addition, such as V₂O₅, CuO, B₂O₃, etc.,^{5–8} or equivalent ionic substitution for A-site Bi^{9–11} and B-site Nb.^{12–14} Ta⁵⁺ and Sb⁵⁺ have the most similar ionic radii and chemical characteristic to Nb⁵⁺. Wang *et*

al.^{14,15} used Ta⁵⁺ and Sb⁵⁺ to substitute for Nb⁵⁺ in BiNbO₄, and a pure orthorhombic phase of BiNb_{1-x}(TaSb)_xO₄ could be obtained for $0 \leq x \leq 0.4$. But they did not study the microwave dielectric behavior of pure BiSbO₄ ceramic. In fact as early as in the 1960s, X-ray diffraction (XRD) analysis of the group ABO₄ compounds (A = Bi³⁺ or Sb³⁺, and B = Nb⁵⁺, Ta⁵⁺, Sb⁵⁺, or Bi⁵⁺) showed that all the compounds were isostructural, although various modifications are possible, in which BiSbO₄ showed monoclinic structure.^{16–20} A single crystal of BiSbO₄ was synthesized by Popolitov *et al.*²⁰ and they regarded BiSbO₄ as an antiferroelectric in the temperature range of 20°–550°C. BiSbO₄ has also been reported in detail as a novel p-block metal oxide, possessing a visible light response for the photocatalytic degradation of methylene blue by Lin *et al.*²¹ Considering various applications, it is necessary and meaningful to clarify the dielectric behavior of monoclinic BiSbO₄ ceramics, especially in wide frequency and temperature ranges.

In this work, pure monoclinic BiSbO₄ ceramic was synthesized using the solid-state reaction method. Phase structure and microstructure of pure BiSbO₄ ceramic and BiSbO₄ ceramic cofired with 20 wt% Ag were studied. Dielectric behavior of BiSbO₄ ceramic at a frequency range of 100 Hz–1 MHz and a microwave range of about 7 GHz was first reported. Dielectric behavior at frequencies ranging from 100 to 900 kHz as a function of measuring temperature (-180° to $+150^\circ\text{C}$) was also reported and discussed.

II. Experimental Procedure

Proportionate amounts of reagent-grade starting materials of Bi₂O₃ (>99%, Cheng Du of China, Shu Du Chemical, Cheng Du, China) and Sb₂O₃ (>99%, Xi'an of China, State Chemical, Xi'an, China) were prepared according to the composition of BiSbO₄. Powders were mixed and milled for 4.5 h using a planetary mill (Nanjing Machine Factory, Nanjing, China) by setting the running speed at 150 rpm with the zirconia balls (2 mm in diameter) as milling media. To have a thorough oxidation of Sb₂O₃ to Sb₂O₅, the mixed oxides were calcined at 600° and 800°C for 4 h, respectively. After being crushed and remilled for 5 h using ZrO₂ balls and deionized water, powders were pressed into pellets and cylinders (8 mm in diameter and 4 mm in height) in a steel die under a monoaxial pressure of 20 kN/cm² with PVA binder addition. Samples were sintered between 930° and 1080°C for 2 h. Some powders of BiSbO₄ phase were mixed with 20 wt% Ag and remilled for 4 h. Then, powders were pressed into pellets and calcined at 900°C for 5 h to investigate the reaction between BiSbO₄ and Ag. The crystalline structures of samples were investigated using XRD with CuK α radiation (Rigaku D/MAX-2400 X-ray diffractometry, Tokyo, Japan). Microstructure of the surface of BiSbO₄ ceramics was observed by scanning electron microscopy (SEM) (JSM-6360LV, JEOL, Tokyo, Japan). The precipitated phases in ceramics were observed using backscattered electron imaging (BEI) and energy-dispersive X-ray spectrometer (EDS) analysis. The di-

N. Wang—contributing editor

Manuscript No. 23857. Received October 12, 2007; approved December 7, 2007.

This work was supported by the National 973-project of China (2002CB613302), National 863-project of China (2006AA03Z0429) and NCET-05-0840.

[†]Author to whom correspondence should be addressed. e-mail: hwang@mail.xjtu.edu.cn

electric properties of ceramic as a function of frequency (100 Hz–1 MHz) and temperature (-180° to $+150^{\circ}\text{C}$) were carried out with a precision LCR meter (HP, 4284, Santa Rosa, CA) in conjunction with a self-made temperature chamber. The temperature coefficient of permittivity α_e was calculated by the following formula:

$$\alpha_e = \frac{\epsilon_{125} - \epsilon_{25}}{\epsilon_{25} \times (125 - 25)} \quad (1)$$

where ϵ_{25} and ϵ_{125} are permittivities measured at 25° and 125°C , respectively. Dielectric behaviors at microwave frequency were measured by the TE_{018} -shielded cavity method with a network analyzer (8720ES, Agilent, Palo Alto, CA) and a temperature chamber (DELTA 9023, Delta Design, Poway, CA). τ_f was calculated by the following formula:

$$\tau_f(\text{TCF}) = \frac{f_{85} - f_{25}}{f_{25} \times (85 - 25)} \quad (2)$$

where f_{85} and f_{25} are the TE_{018} resonant frequencies at 85° and 25°C , respectively.

III. Results and Discussions

Powder XRD patterns of BiSbO_4 ceramics sintered at different temperatures and the sample cofired with 20 wt% Ag at 900°C for 5 h are shown in Fig. 1. A pure monoclinic phase of BiSbO_4 was revealed in ceramics sintered at 990° and 1080°C for 2 h and diffraction lines of monoclinic BiSbO_4 were also indexed. The chemical compatibility between BiSbO_4 and Ag was very important if BiSbO_4 would be considered for application in microwave LTCC technology. From the XRD patterns result, it is clear that more than two phases could be revealed for BiSbO_4 ceramics cofired with 20 wt% Ag at 900°C for 5 h. Most of the patterns are a combination of two sets of diffraction lines, one of which corresponds to monoclinic BiSbO_4 and the other one corresponds to pure Ag. Diffraction peaks of other unknown phases are very weak and were difficult to identify. This result indicates that BiSbO_4 ceramics are not likely to react with Ag seriously and might be a good candidate for LTCC technology.

Figure 2 presents the microstructure photos of BiSbO_4 ceramics sintered at different temperatures, and the BEI and EDS results of BiSbO_4 ceramics cofired with 20 wt% Ag at 900°C for 5 h. Homogeneously fine microstructures with almost no pores

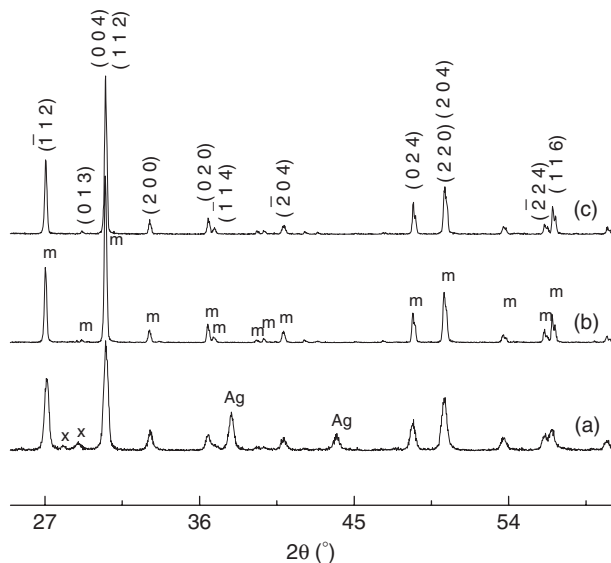


Fig. 1. Powder X-ray diffraction patterns of BiSbO_4 sintered at 990° (b) and 1080°C for 2 h (c), and cofired with 20 wt% Ag at 900°C for 2 h (a) (m, monoclinic phase of BiSbO_4 ; Ag, cubic silver phase; x, unknown phase).

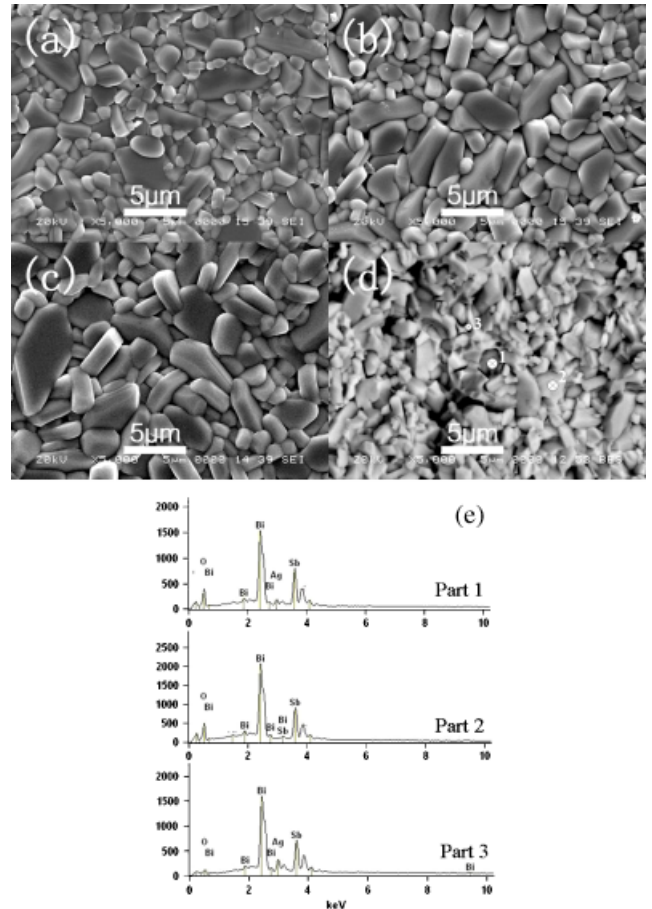


Fig. 2. Scanning electron microscopy photos of BiSbO_4 ceramics sintered at 960° (a), 990° (b), 1050°C for 2 h (c), backscattered electron imaging of fracture surface for BiSbO_4 with 20 wt% Ag ceramics (d), and energy-dispersive X-ray spectrometer result (e) of fracture surface of BiSbO_4 with 20 wt% Ag shown in (d).

are revealed in BiSbO_4 ceramics sintered at 960° , 990° , and 1050°C for 2 h, as shown in Figs. 2(a)–(c). Average grain size increased from about 1–2 μm to 2–5 μm as sintering temperature increased from 960° to 1050°C , and there was no obvious abnormal grain growth. A BEI photo of BiSbO_4 ceramic cofired with 20 wt% Ag at 900°C for 5 h is shown in Fig. 2(d) and the corresponding EDS analysis is shown in Fig. 2(e). Considering the small grain size ($< 2 \mu\text{m}$) and experimental precision, BEI and EDS analysis just gave some qualitative and assistant conclusions, which should be in agreement with XRD analysis. Most homogeneous grains marked with no. 2 had a light color and were proved to be BiSbO_4 phase from EDS analysis. Only very few inhomogeneous grains marked with no. 1 and some matter lying between grain boundaries marked with no. 3 with dark color were observed. From EDS analysis, it was found that no. 1 grain contained only a little Ag and more of bismuth and antimony elements. Considering that there were very few abnormal grains like no. 1, it might be the unknown phase indicated in the XRD patterns as shown in Fig. 1(a). Most Ag might be homogeneously scattered in grain boundaries but their sizes were too small to be observed clearly under the present BEI and EDS precision. Combined with the XRD results, it should be concluded that BiSbO_4 phase was not likely to react with Ag. Further detailed study should be carried out, such as penetration between interfaces of BiSbO_4 ceramics and Ag electrode etc., if BiSbO_4 ceramics are to be applied in LTCC technology in future.

Figure 3 shows the dielectric constant and dielectric loss of BiSbO_4 ceramic as a function of frequency (100 Hz–1 MHz). As frequency increased from 100 Hz to 1 MHz, the dielectric constant decreased from 21.5 to about 20.1. Meanwhile, dielectric

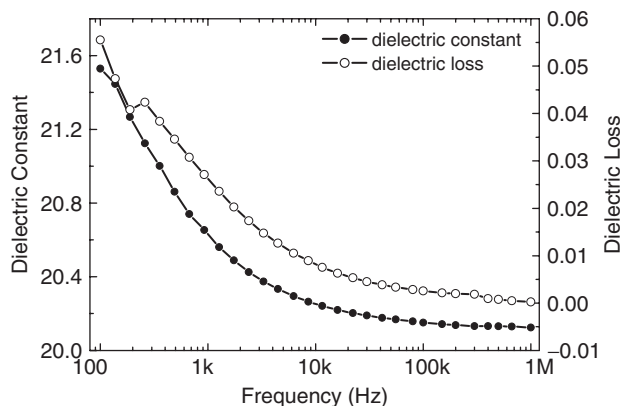


Fig. 3. Dielectric constant and dielectric loss of BiSbO₄ ceramics as a function of frequency (100 Hz–1 MHz).

loss decreased from 0.055 to 2.5×10^{-4} . The decrease of permittivity and dielectric loss could be generally explained due to the decreasing responses of polarizations. As with the frequency increasing, low frequency responded polarizations gradually could not catch the change frequency of the electric field thus their contributions to permittivity and losses became weakened. Figure 4 shows the dielectric properties of BiSbO₄ ceramics as a function of temperature between -180° and 150°C . With an increase in the measuring temperature, the dielectric constant of BiSbO₄ ceramics increased linearly from about 23.8 at -180°C to about 25.1 at 150°C at 100 kHz. At all frequencies between 100 and 900 kHz, the change trends were similar to each other. Dielectric constant decreased as frequency increased. Dielectric loss was maintained at about 0.005 below 80°C and then increased sharply as temperature increased further. The α_e between $+25^\circ$ and $+125^\circ\text{C}$ was $+224.1$, $+216.4$, $+196.3$, $+142.8$, $+95.9$ ppm/ $^\circ\text{C}$ respectively at the frequency range of 100–900 kHz.

The microwave dielectric behavior of BiSbO₄ ceramics as a function of sintering temperature is illustrated in Fig. 5. As sintering temperature increased from 930° to 990°C , the permittivity increased from 16.1 to 19.3 accompanied by the elimination and shrinkage of pores, and reached the saturated value. The Q_f value also increased with an increase in the sintering temperature because of the good densification of ceramics and growth of grains, which decreased dielectric losses caused by boundaries. The TCF of BiSbO₄ ceramics was not influenced remarkably by sintering temperature and remained about -62 ppm/ $^\circ\text{C}$. The best microwave dielectric properties were obtained in samples sintered at 1080°C for 2 h with a permittivity of 19.3, a Q_f value of about 70 000 GHz, and a TCF of -62 ppm/ $^\circ\text{C}$.

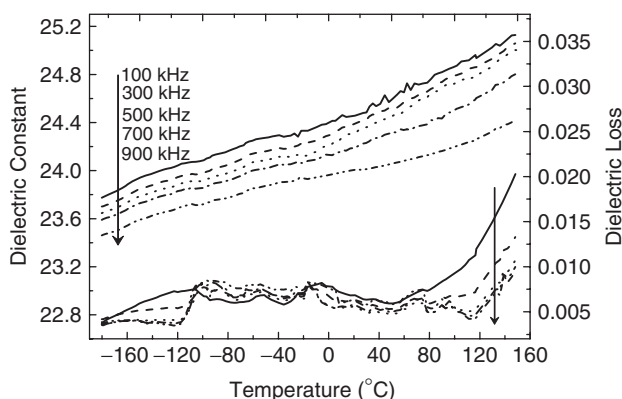


Fig. 4. Dielectric constant and dielectric loss of BiSbO₄ ceramics as a function of temperature (-180° to 150°C) at frequency range 100–900 kHz.

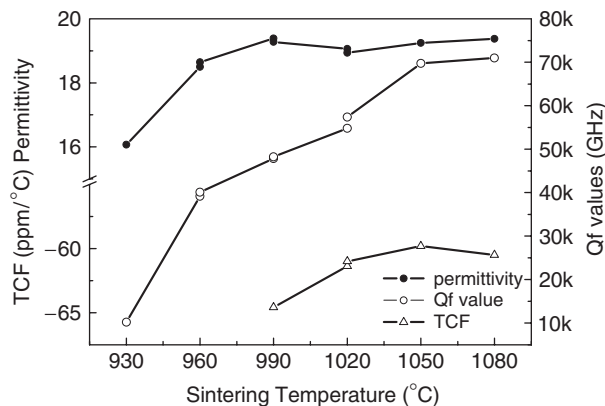


Fig. 5. Microwave permittivity, Q_f values, and temperature coefficients of resonant frequency (TCF) of BiSbO₄ ceramics as a function of sintering temperature.

IV. Conclusions

Pure monoclinic BiSbO₄ ceramics were synthesized using the solid-state reaction method in this paper. BiSbO₄ ceramics could be well sintered above 960°C . Dielectric constant was about 20.1 and dielectric loss was about 0.055 – 2.5×10^{-4} at 1 MHz. As measuring frequencies increased from 100 to 900 kHz, the temperature coefficients of permittivity decreased from $+224.1$ to $+95.9$ ppm/ $^\circ\text{C}$. The best microwave dielectric properties were obtained in ceramic sintered at 1080°C for 2 h with a permittivity of 19.3, a Q_f value of about 70 000 GHz, and a TCF of -62 ppm/ $^\circ\text{C}$. It was found that after cofiring with 20 wt% Ag at 900°C for 5 h only very little unknown phase consisting of a little Ag was formed, and most Ag was scattered in the grain boundaries. BiSbO₄'s chemical compatibility with Ag needs further study and it might be a good candidate for LTCC use.

References

- B. Geller, B. Thaler, A. Fathy, M. J. Liberatore, H. D. Chen, G. Ayers, V. Pendrick, and Y. Narayan, "LTCC-M: An Enabling Technology for High Performance Multilayer RF Systems," *Microwave J.*, **42** [7] 6–8 (1999).
- H. C. Ling, M. F. Yan, and W. W. Rhodes, "High Dielectric Constant and Small Temperature Coefficient Bismuth-Based Dielectric Compositions," *J. Mater. Res.*, **5**, 1752–62 (1990).
- D. H. Liu, Y. Liu, S. Q. Huang, and X. Yao, "Phase Structure and Dielectric Properties of Bi₂O₃–ZnO–Nb₂O₅-Based Dielectric Ceramics," *J. Am. Ceram. Soc.*, **76**, 2129–32 (1993).
- H. Kagata, T. Inoue, J. Kato, and I. Kameyama, "Low-Fire Bismuth-Based Dielectric Ceramics for Microwave Use," *Jpn. J. Appl. Phys.*, **31**, 3152–5 (1992).
- D. Zhou, H. Wang, and X. Yao, "Microwave Dielectric Properties and Co-Firing of BiNbO₄ Ceramics with CuO Substitution," *Mater. Chem. Phys.*, **104**, 397–402 (2007).
- Ch. F. Yang, "Improvement of Quality Value and Shift of τ_f Value of BiNbO₄ Ceramics with Addition of CuO–V₂O₅ Mixtures," *Jpn. J. Appl. Phys.*, **38**, 6797–800 (1999).
- Ch. L. Huang, M. H. Weng, and G. M. Shan, "Effect of V₂O₅ and CuO Additives on Sintering Behavior and Microwave Dielectric Properties of BiNbO₄ Ceramics," *J. Mater. Sci.*, **35**, 5443–7 (2000).
- W. Ch. Tzou, Ch. F. Yang, Y. Ch. Chen, and P. Sh. Cheng, "Improvements in the Sintering and Microwave Properties of BiNbO₄ Microwave Ceramics by V₂O₅ Addition," *J. Eur. Ceram. Soc.*, **20**, 991–6 (2000).
- W. Choi and K. Y. Kim, "Effects of Nd₂O₃ on the Microwave Dielectric Properties of BiNbO₄ Ceramics," *J. Mater. Res.*, **13** [10] 2945–9 (1998).
- Ch. L. Huang, M. H. Weng, and Ch. Ch. Wu, "Microwave Dielectric Properties and the Microstructures of La₂O₃-Modified BiNbO₄ Ceramics," *Jpn. J. Appl. Phys.*, **39**, 3506–10 (2000).
- W. Ch. Tzou, Ch. F. Yang, Y. Ch. Chen, and P. Sh. Cheng, "Microwave Dielectric Characteristics of (Bi_{1-x}Sm_x)NbO₄ Ceramics," *Ceram. Int.*, **28**, 105–10 (2002).
- Ch. L. Huang and M. H. Weng, "Microwave Dielectric Properties and the Microstructures of Bi(Nb, Ta)O₄ Ceramics," *Jpn. J. Appl. Phys.*, **38**, 5949–52 (1999).
- D. Zhou, H. Wang, X. Yao, and L. X. Pang, "Microwave Dielectric Properties and Co-firing of BiNbO₄ Ceramics with CuO–WO₃ Substitution," *Mater. Sci. Eng. B*, **142**, 106–11 (2007).

¹⁴N. Wang, M. Y. Zhao, and Zh. W. Yin, "The Sintering Behavior and Microwave Dielectric Properties of Bi(Nb, Sb)O₄ Ceramics," *Ceram. Int.*, **30**, 1017–22 (2004).

¹⁵N. Wang, M. Y. Zhao, and Zh. W. Yin, "Effects of Ta₂O₅ on Microwave Dielectric Properties of BiNbO₄ Ceramics," *Mater. Sci. Eng. B*, **99**, 238–42 (2003).

¹⁶R. S. Roth and J. L. Waring, "Synthesis and Stability of Bismutotantalite, Stibiotantalite and Chemically Similar ABO₄ Compounds," *Am. Mineral.*, **48**, 1348–56 (1963).

¹⁷C. Keller, "Über ternäre Oxide des Niobs und Tantals vom Typ ABO₄," *Z. Anorg. Allg. Chem.*, **318**, 89–106 (1962).

¹⁸A. C. Skapski and D. Rogers, "The Structure of SbNbO₄, α -Sb₂O₄, and SbTaO₄," *Chem. Commun.*, **23**, 611–3 (1965).

¹⁹E. T. Keve and A. S. Skapski, "The Structure of Triclinic BiNbO₄ and BiTaO₄," *Chem. Commun.*, **6**, 281–3 (1967).

²⁰V. I. Popolitov, A. N. Lobachev, and V. F. Peskin, "Antiferroelectrics, Ferroelectrics and Pyroelectrics of a Stibiotantalite Structure," *Ferroelectrics*, **40**, 9–16 (1982).

²¹X. P. Lin, F. Q. Huang, W. D. Wang, and K. L. Zhang, "A Novel Photocatalyst BiSbO₄ for Degradation of Methylene Blue," *Appl. Catal. A: Gen.*, **307**, 257–62 (2006). □