

Improved dielectric properties of bismuth-doped LaAlO_3

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Bismuth-doped LaAlO_3 was prepared in the form of solid solution, $\text{La}_{(1-x)}\text{Bi}_x\text{AlO}_3$ ($0 \leq x \leq 0.2$), by solid-state reactions. The materials were characterized by x-ray diffraction and dielectric spectroscopy. With increasing bismuth amount (x), the dielectric constant increases from 31.6 for pure LaAlO_3 to 34.6 for $x=0.2$, while the loss tangent drops from 0.03 to 0.004 ($f=100$ Hz). The frequency dispersion of the dielectric constant is attenuated. The improved dielectric properties in the Bi-doped LaAlO_3 are attributed to the high polarizability of Bi^{3+} ion with a lone electron pair.

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Dielectric materials play an important role in integrated circuit (IC) technology. Currently, the most widely used gate dielectric material for this application is silicon dioxide (SiO_2).^{1,2} However, as the silicon dioxide based transistors continue to be sized down, the leakage in the metal-oxide-semiconductor field-effect transistors will become unacceptably high. Therefore, much attention has recently been given to the development of alternative gate dielectric materials as replacement for SiO_2 ,¹⁻⁵ which has a relatively low dielectric constant ($K \approx 3.9$ at room temperature).³ Ideally, the candidate materials would have a higher dielectric constant, a reduced loss tangent, and a reduced leakage current when compared to currently used materials.¹

Ferroelectric materials are known to exhibit high dielectric constant.⁶ This suggests that they might be good candidates for gate dielectrics. However, their nonlinear dielectric response to applied electric field (i.e., hysteresis)^{7,8} and relatively slow polarization switching⁷ make them unsuitable for such applications.¹

Lanthanum aluminate, LaAlO_3 (LAO), was previously investigated for its ferroelastic properties⁹ and catalytical effects.¹⁰⁻¹² It has also been used as substrates for the growth of high-temperature superconductors.^{10,11,13-15} Recently, LAO has received much attention as a potential high- K gate dielectric (Refs. 4, 16, and 17) because it exhibits a relatively high room-temperature dielectric constant of 20–27 (Refs. 18 and 19) and a good thermal stability up to very high temperatures (>2100 K).⁴ Bismuth-doped LAO was previously studied only as a potential oxide-ion conductor for solid-oxide fuel cells as it was hoped that this material would combine the ionic conductivity of bismuth oxide, Bi_2O_3 , with the thermal stability of LAO.²⁰ In this work, we have studied the effects of the substitution of bismuth for lanthanum on the dielectric properties of LAO, as we expected that the high polarizability of the Bi^{3+} ion due to the lone electron pair would enhance the dielectric properties of LAO.

Bismuth doping was achieved by forming the solid solution between LAO and the nominal compound “ BiAlO_3 ,” i.e., $(1-x)\text{LaAlO}_3-x\text{BiAlO}_3$ or $\text{La}_{(1-x)}\text{Bi}_x\text{AlO}_3$. Samples

with compositions varying from $x=0$ up to $x=0.5$ were prepared by solid-state reactions of Bi_2O_3 (99.975%, Alpha-Aesar), Al_2O_3 (Matheson, Coleman, and Bell), and La_2O_3 (99.9%, Rare Earth Metallic Co.). The oxides were mixed in stoichiometric amounts and ground in an agate mortar in the presence of acetone. The dried mixtures were then pressed into pellets and calcined on a Pt plate. The calcinations took place in air at 1400°C for 3 h. This temperature was chosen based on a previous work showing that it is the minimum temperature for the formation of relatively pure perovskite LAO.¹⁵ After calcining, the samples were reground for 1 h in acetone. The mixtures, with a few drops of polyvinyl alcohol (PVA, ~ 1 wt %) added as a binding agent, were then pressed at ~ 1 ton into pellets of 1 cm in diameter and sintered at 1500°C for 1.5 h on a Pt plate. The circular surfaces of the sintered ceramic samples were polished in preparation for the structural and dielectric characterizations.

X-ray diffraction was performed on a Rigaku R-Axis diffractometer with $\text{Cu } K\alpha$ radiation. The diffraction patterns for $x=0, 0.1$, and 0.2 are shown in Fig. 1, where the peaks are indexed according to the spectrum of LAO in Ref. 15. The samples with $x \leq 0.2$ show a pure perovskite phase, indicating the formation of the $\text{La}_{(1-x)}\text{Bi}_x\text{AlO}_3$ solid solution. The samples with $x > 0.2$, however, contain some excess

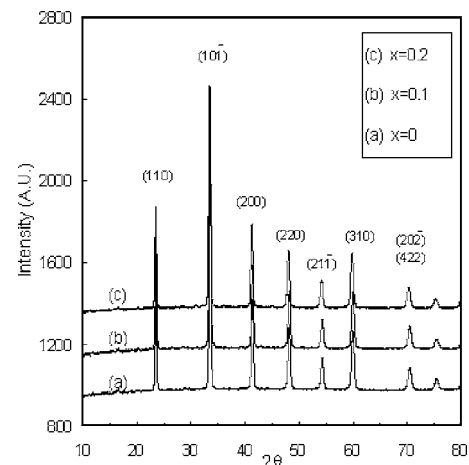


FIG. 1. X-ray diffraction patterns of the $\text{La}_{(1-x)}\text{Bi}_x\text{AlO}_3$ solid solution ceramics.

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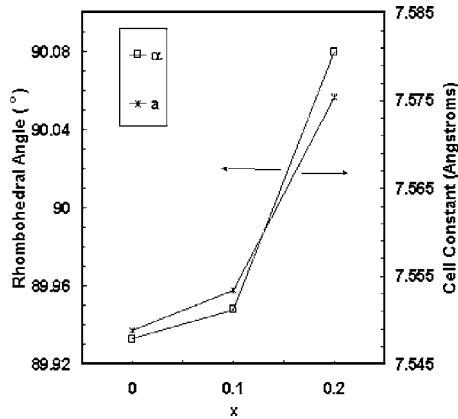


FIG. 2. Variations of the lattice constant (a) and the rhombohedral angle (α) as a function of the different compositions of $\text{La}_{(1-x)}\text{Bi}_x\text{AlO}_3$.

Al_2O_3 , suggesting that the limit of solubility has been reached at $x=0.2$ (the excess Bi_2O_3 has likely evaporated during the synthesis). For this reason, only the results from the samples with $x \leq 0.2$ are reported hereafter.

The structure and lattice parameters of the samples were refined using JADE software.²¹ All the three samples show the rhombohedral symmetry with space group $R\bar{3}c$, i.e., the same as the parent phase LAO.²² Figure 2 shows the variation of the unit cell parameters as a function of the bismuth doping amount. A monotonic increase in both the cell constant (a) and the rhombohedral angle (α) with increasing bismuth amount is observed, indicating a distortion of the LAO structure induced by the Bi doping. The variations of the cell parameters with composition provide an additional evidence for the formation of the $\text{La}_{(1-x)}\text{Bi}_x\text{AlO}_3$ solid solution. Similar variations of lattice parameters were recently observed in the $\text{La}_{(1-x)}\text{Bi}_x\text{CrO}_3$ solid solution, which was attributed to the structural distortion resulting from an increased tilting of oxygen octahedra as a result of bismuth substitution.²³

For dielectric characterization, the polished ceramic samples were sputtered with gold electrodes and gold wires were attached using colloidal silver paste. The dielectric spectroscopic measurements were performed in the frequency range of 100 Hz–100 kHz using a Solartron SI-1260 impedance/gain phase analyzer combined with a SI-1296 dielectric interface. The temperature was varied from -100 to 300 °C by means of a Delta 9023 heating/cooling chamber. The variations of the real part of dielectric permittivity and the loss tangent measured at 100 Hz at room temperature as a function of composition are shown in Fig. 3. The dielectric constant (ϵ') for the LAO ($x=0$) sample is found to be 31.6, which is already higher than the literature values of 22–27 (Refs. 18 and 19) estimated from the capacitance-voltage (C - V) curves of the LAO thin films (with some discrepancy among them).¹⁸ The higher dielectric constant measured in pure LAO suggests a high quality of the ceramic samples prepared. With increasing Bi doping amount, an increase in the room temperature dielectric constant is observed: it increases from 31.6 in LAO to 34.6 in $\text{La}_{0.8}\text{Bi}_{0.2}\text{AlO}_3$. While the dielectric constant of the samples is increased by about 10%, the loss tangent shows a more dramatic decrease: it drops almost an order of magnitude,

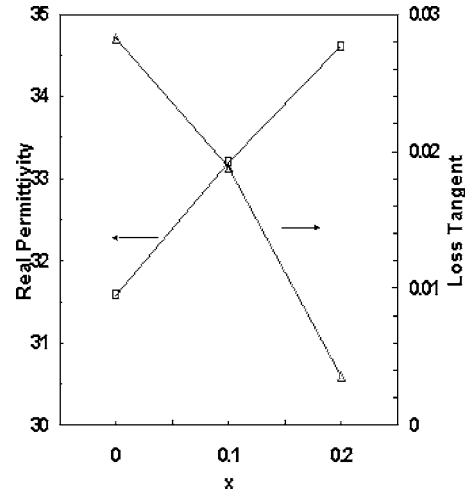


FIG. 3. Dielectric properties of the $\text{La}_{(1-x)}\text{Bi}_x\text{AlO}_3$ solid solution ceramics as a function of composition measured at 25 °C and 100 Hz.

i.e., from 0.03 in $x=0$ to 0.004 in $x=0.2$. The frequency dependence of the room temperature dielectric constant of the samples is shown in Fig. 4. It can be seen that the dielectric constant of the $x=0.1$ and $x=0.2$ samples shows a smaller frequency dispersion than that of pure LAO sample.

The improved dielectric properties in the $\text{La}_{(1-x)}\text{Bi}_x\text{AlO}_3$ solid solution are believed to arise from the substitution of the highly polarizable Bi^{3+} ion with the $6s^2$ lone electron pair for the La^{3+} ion. This explanation is supported by our recent work on Bi-doped lanthanum chromate, $\text{La}_{(1-x)}\text{Bi}_x\text{CrO}_3$ in which the substitution of Bi^{3+} for La^{3+} induces hysteresis loops of ferroelectric appearance, with the remnant polarization increasing as the Bi^{3+} amount increases up to $x=0.30$.²³

In summary, the substitution of Bi^{3+} for La^{3+} in LAO is found to increase the dielectric constant, decrease the loss tangent, and reduce the frequency dispersion of the dielectric constant in the solid solution of $\text{La}_{1-x}\text{Bi}_x\text{AlO}_3$, thus improving the dielectric properties of LAO. The decrease in the loss

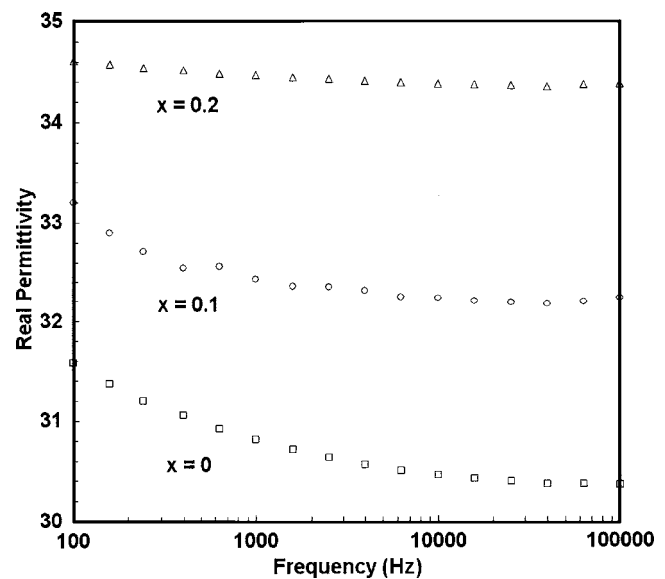


FIG. 4. Frequency dependences of the room-temperature dielectric constant for various compositions of the $\text{La}_{(1-x)}\text{Bi}_x\text{AlO}_3$ solid solution.

tangent of the material is especially interesting because, due to the faster and faster switching times required, a gate dielectric material for use in the dynamic random access memory devices must have a loss tangent of less than 0.005,¹ and the $\text{La}_{1-x}\text{Bi}_x\text{AlO}_3$ solid solution with $x=0.2$ can meet this requirement since it exhibits a loss tangent below that level. Thus, bismuth doping significantly improves the dielectric properties of LAO, making it very promising as a high- K gate dielectric material for applications in microelectronics. To make such applications possible, it is necessary to prepare and characterize the thin films of Bi-LaAlO₃; such a work is being pursued.

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¹A. M. Stoneham, J. L. Gavartin, and A. L. Shluger, *J. Phys.: Condens. Matter* **17**, S2027 (2005).

²A. Wallace, *Appl. Surf. Sci.* **231-232**, 543 (2004).

³R. Wallace and G. Wilk, *Semicond. Int.* **24**, 227 (2001).

⁴L. Yan, H. B. Lu, G. T. Tan, F. Chen, Y. L. Zhou, G. Z. Yang, W. Liu, and Z. H. Chen, *Appl. Phys. A: Mater. Sci. Process.* **77**, 721 (2003).

⁵H. Treichel, C. Hood, C. Porter, and Y. Okuyama, *Solid State Technol.* **48**, 28 (2005).

⁶G. Haertling, *J. Am. Ceram. Soc.* **82**, 797 (1999).

⁷D. Damjanovic, *Rep. Prog. Phys.* **61**, 1267 (1998).

⁸Z.-G. Ye, *Key Eng. Mater.* **155-156**, 81 (1998).

⁹R. Harrison, S. Redfern, and E. Salje, *Phys. Rev. B* **69**, 144101 (2004).

¹⁰M. Chroma, J. Pinkas, I. Pakutinskiene, A. Beganskiene, and A. Kareiva, *Ceram. Int.* **31**, 1123 (2005).

¹¹P. Peshev and V. Slavova, *Mater. Res. Bull.* **29**, 255 (1994).

¹²M. Kakihana and T. Okubo, *J. Alloys Compd.* **266**, 129 (1998).

¹³R. Elsebrock, C. Makovicka, P. Meuffels, and R. Waser, *J. Electroceram.* **10**, 193 (2003).

¹⁴A. K. Adak and P. Pramanik, *Mater. Lett.* **30**, 269 (1997).

¹⁵G. Y. Sung, K. Y. Kang, and S. Park, *J. Am. Ceram. Soc.* **74**, 437 (1991).

¹⁶P. Delugas, V. Fiorentini, and A. Filippetti, *Phys. Rev. B* **71**, 134302 (2005).

¹⁷X. B. Lu, Z. G. Liu, X. Zhang, R. Huang, H. W. Zhou, X. P. Wang, and B. Y. Nguyen, *J. Phys. D* **36**, 3047 (2003).

¹⁸B. E. Park and H. Ishiwara, *Appl. Phys. Lett.* **82**, 1197 (2003).

¹⁹X. B. Lu *et al.*, *Appl. Phys. Lett.* **85**, 3543 (2004).

²⁰I. Bloom, M. Hash, J. Zebrowski, K. Myles, and M. Krumpelt, *Solid State Ionics* **53-56**, 739 (1992).

²¹JADE XRD analysis software from Materials Data Inc., <http://www.materialsdata.com/>

²²J. Zhao, N. Ross, and R. Angel, *J. Phys.: Condens. Matter* **16**, 8763 (2004).

²³J. I. L. Chen, M. M. Kumar, and Z.-G. Ye, *J. Solid State Chem.* **177**, 1501 (2004).