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Preparation of $SrBi_2Ta_2O_9$ thin films with a single alkoxide sol–gel precursor

Yongtae Kim,[a] Hee K. Chae,*[a] Kyu S. Lee[b] and Wan I. Lee*[b]

[a]*Department of Chemistry, Hankuk University of Foreign Studies, Yongin 449-791, Korea*
[b]*Department of Chemistry and Center for Chemical Dynamics, Inha University, Inchon 402-751, Korea*

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For the first time, a single alkoxide sol–gel precursor solution for the ferroelectric strontium bismuth tantalate ($SrBi_2Ta_2O_9$, SBT) was synthesized and utilized for the fabrication of its thin films. The precursor was prepared from a 2-methoxyethanol solution of $Sr(OCH_2CH_2OCH_3)_2$, $Bi(OCH_2CH_2OCH_3)_3$, and $Ta(OCH_2CH_2OCH_3)_5$. ^1H and ^{13}C NMR spectra of the precursor in benzene show only one set of alkoxy groups, indicating the same chemical environment in solution. This observation suggests that it is a single sol–gel precursor, which is ideal for the sol–gel processing of SBT thin films. The SBT films derived from this precursor present outstanding ferroelectric properties and surface morphology.

The sol–gel process is a versatile method for producing ceramics and glasses with a variety of applications which include electronic, magnetic, optic and optoelectronic materials, as well as hard and protective coatings.[1,2] In recent years this technique has been extended to the fabrication of thin films of $SrBi_2Ta_2O_9$ (SBT), which has been attracting profound interest as a fatigue-free ferroelectric material.[3] A variety of fabrication methods, such as magnetron sputtering,[4] metal-organic chemical vapor deposition (MOCVD),[5] pulsed laser deposition (PLD),[6] sol–gel process,[7] *etc.*, have been applied for the Bi-based ferroelectric thin films including SBT. Among them, the sol–gel process is considered to be the most successful method in terms of composition control. However, the control of stoichiometry in the film has still been a knotty problem because of the relatively high volatility of bismuth components. Conventionally, mixed metal esters including 2-ethylhexanoate have been used for this sol–gel process,[3,7] but they are not regarded as suitable precursors to obtain high quality SBT films. Recently, some papers have reported sol–gel processed SBT thin films derived from mixed alkoxide solutions prepared by mixing the individual metal alkoxides, but none of them have prepared any single alkoxide precursors.[8,9] In the fabrication of multicomponent metal oxide films, precise control of stoichiometry, crystallographic phase and grain structure in the film is crucial and these properties could be tuned from the molecular level homogeneity, which is likely achieved from a single metal-organic precursor that evolves directly to a mixed-metal oxide, reproducibly. Prior to this study, however, little information was available regarding the preparation and characterization of single precursors for the $Sr(OR)_2$–$Bi(OR)_3$–$Ta(OR)_5$ system.

Here, we demonstrate a synthesized single alkoxide sol–gel precursor for the fabrication of SBT thin films. It has been found that only the stoichiometric amount of the Bi precursor, differently from other sol–gel solution systems, is necessary for the formation of a ferroelectric SBT phase. SBT thin films with this precursor present outstanding ferroelectric properties and the surface morphology of the film is considerably improved compared with that of films from conventional 2-ethylhexanoate sol–gel solution.

The sol–gel precursor solution was prepared as follows. Bismuth 2-methoxyethoxide, $Bi(OCH_2CH_2OCH_3)_3$, was obtained by modifying the literature method from the reaction between $BiCl_3$ and $Na(OCH_2CH_2OCH_3)$ in tetrahydrofuran. The bismuth complex, $Bi(OCH_2CH_2OCH_3)_3$, was recrystallized in benzene–hexane. Yield was 78% based on Bi. The ^1H and ^{13}C NMR spectra of the complex in benzene-d_6 show only one set of peaks for 2-methoxyethoxide.[10] Tantalum 2-methoxyethoxide, $Ta(OCH_2CH_2OCH_3)_5$, was synthesized quantitatively by the reaction of alcohol exchange from $Ta(OCH_2CH_3)_5$ in $HOCH_2CH_2OCH_3$, and characterized by NMR spectroscopy.[11] Yellow powders of strontium 2-methoxyethoxide, $Sr(OCH_2CH_2OCH_3)_2$, were also obtained quantitatively from the direct reaction of Sr chips with $HOCH_2CH_2OCH_3$.[12] We observed that a homogeneous 2-methoxyethanol solution containing $Sr(OCH_2CH_2OCH_3)_2$, $Bi(OCH_2CH_2OCH_3)_3$, and $Ta(OCH_2CH_2OCH_3)_5$ in a 1:2:2 ratio could be prepared by refluxing the mixtures for 2 hours. The solvent was removed *in vacuo* to give a colorless syrup-like complex. The complex $[SrBi_2Ta_2(OCH_2CH_2OCH_3)_{18}]$ was characterized by ^1H and ^{13}C NMR spectroscopy which shows three peaks at 4.65, 3.52 and 3.38 ppm and 76.00, 68.54 and 58.84 ppm, respectively, indicating that only one set of 2-methoxyethoxide exists in solution (see Fig. 1).[13] The peaks are quite different from those of the starting materials. This is evidence for the formation of a single alkoxide precursor. The

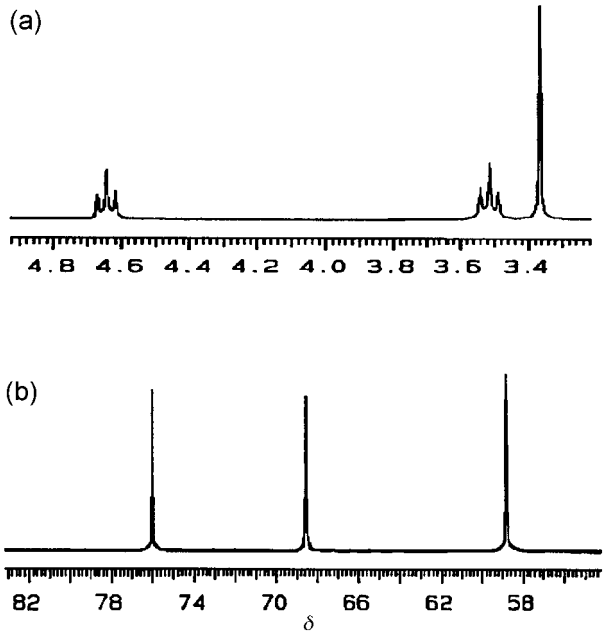

Fig. 1 NMR spectra of complex isolated from SBT precursor solution in benzene-d_6. (a) ^1H NMR; (b) ^{13}C NMR.

complex contains strontium, bismuth and tantalum in a 1:2:2 ratio as determined by elemental analysis and the complex does not undergo dissociation in alcohol solution. Mass spectrometry data obtained so far indicate that the complex does not exist in the monomeric form, but as a dimer. Hence, the synthesized solution could be an ideal sol–gel precursor for the fabrication of SBT thin films.

The precursor solutions used for the SBT films contain the stoichiometric amount of Bi (that is, the molar ratio of Sr:Bi:Ta is 1.0:2.0:2.0) and the concentration was adjusted to 0.10 M. The solution is stable for more than one month and the aging effect is negligible. Spin-coated films at 2500 rpm were baked at 120 °C and subsequently at 320 °C to remove organic solvents. The spin coating and baking cycles were repeated three times to obtain a film of final thickness about 250 nm. The baked samples were then heat-treated at 800 °C for 1 h in oxygen atmosphere to produce a ferroelectric phase. The substrates used for the SBT deposition were $Pt/Ti/SiO_2/Si$. On the Si(100) substrate with 300 nm of SiO_2 deposited, a 20 nm layer of Ti and a 240 nm layer of Pt were sputter-deposited, respectively.

The glancing angle mode XRD patterns in Fig. 2 indicate that the SBT films consist of a pure ferroelectric phase. The field emission SEM image of a fabricated SBT thin film shown in Fig. 3 indicates that the surfaces of prepared thin films are considerably homogeneous, grains are very dense and there seemed to be no secondary structures between the grains.

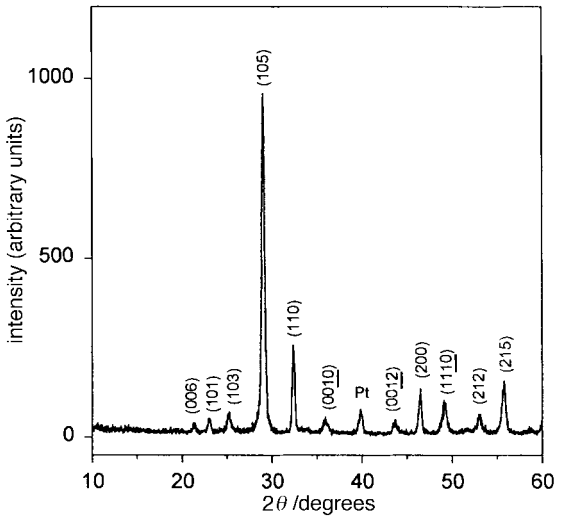

Fig. 2 XRD patterns of the SBT thin films (glancing angle: 3°).

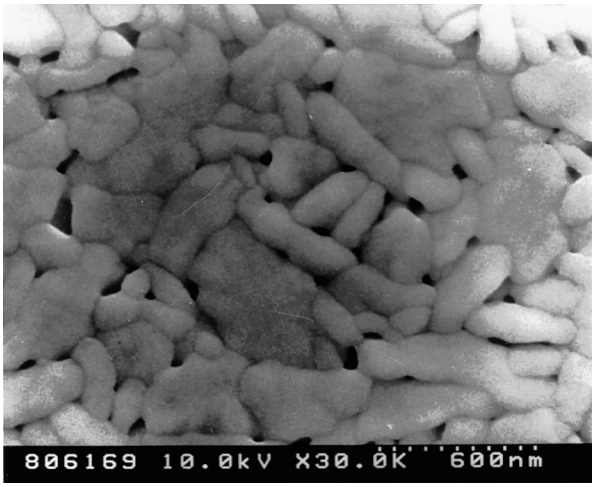

Fig. 3 Field emission SEM image of SBT thin films (film thickness: *ca.* 250 nm).

Fig. 4 shows the hysteresis loop of the Pt/SBT/Pt capacitor. Excellent ferroelectric properties were obtained for a 250 nm thick SBT film. Remanent polarization (P_r) is 9 μC cm^{-2} and the coercive field (E_c) is 33 kV cm^{-1} (or 0.8 V). In addition, its leakage current density (10^{-6}–10^{-7} A cm^{-2}) is very low.

It has been reported that a pyrochlore phase can be incorporated under Bi-deficient conditions and 20–30% more of the Bi component is necessary for the sol–gel solution in order to compensate for the loss of Bi during the heat-treatment. Moreover, several reports indicate that Bi-rich conditions induce better crystallinity in the SBT film and a higher value of remanent polarization as a result.[14,15] In this work, however, we have found a different result, that is, extra Bi is not necessary for the formation of a pure ferroelectric phase, which is directly ascribed to the intrinsic role of the single 2-methoxyethoxide precursor. It is deduced that Bi loss is minimized during the heat-treatment, since the three metals are chemically bonded together. The thermal decomposition behaviour of the prepared single alkoxide sol–gel precursor was analyzed by TGA and DSC. The precursor was dried at 150 °C and then slowly heated in air with a ramp of 5 °C min^{-1}. The weight change and heat exchange as a function of temperature were monitored, and are shown in Fig. 5. The dried single

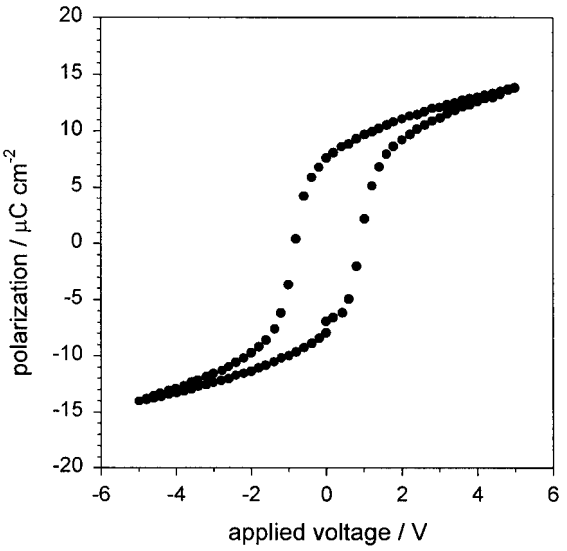

Fig. 4 Hysteresis loop obtained for SBT thin films derived from single alkoxide solution.

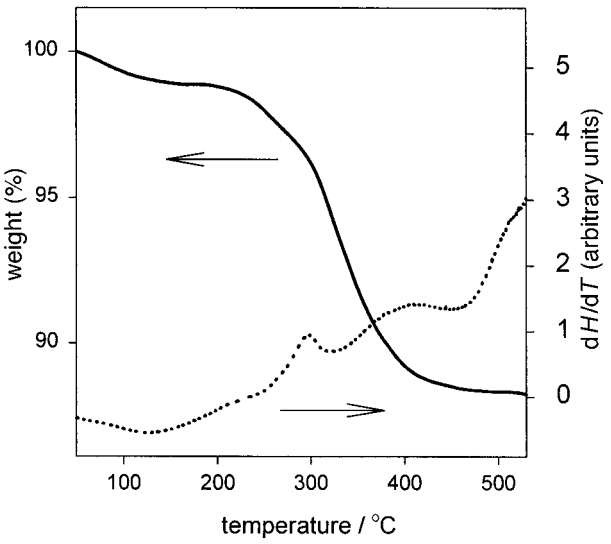

Fig. 5 TGA and DSC curves for the dried single alkoxide sol–gel precursor.

alkoxide precursor was decomposed slowly and monotonously with no abrupt heat release. This is another important factor in retarding the loss of Bi component and in improving grain structure.

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Notes and references

1 C. D. Chandler, C. Roger and M. J. Hampden-Smith, *Chem. Rev.*, 1993, **93**, 1205.
2 R. C. Mehrotra, A. Singh and S. Sogiani, *Chem. Rev.*, 1994, **94**, 1643.
3 C. A. Araujo, J. D. Cuchiaro, L. D. McMillan, M. C. Scott and J. F. Scott, *Nature*, 1995, **374**, 627.
4 H.-M. Tsai, P. Lin and T.-Y. Tseng, *Appl. Phys. Lett.*, 1998, **72**, 1787.
5 T. Li, Y. Zhu, S. B. Desu, C.-H. Peng and M. Nagata, *Appl. Phys. Lett.*, 1996, **68**, 616.
6 H. Tabata, H. Tanaka and T. Kawai, *Jpn. J. Appl. Phys.*, 1995, **34**, 5146.
7 K. Amanuma, T. Hase and Y. Miyasaka, *Appl. Phys. Lett.*, 1995, **66**, 221.
8 I. Koiwa, T. Kanehara, J. Mita, T. Iwabuchi, T. Osaka, S. Ono and M. Maeda, *Jpn. J. Appl. Phys.*, 1996, **35**, 4946.
9 T. Hayashi, T. Hara and H. Takahashi, *Jpn. J. Appl. Phys.*, 1997, **36**, 5900.
10 IR (Nujol mull, cm^{-1}): 1235 w, 1197 w, 1126 w, 1061 w, 1019 w, 964 w, 894 w, 834 w, 559 w. ^{1}H NMR (C_6D_6): δ 4.98 (t, 6 H, CH_2, J_{H-H}=4.5 Hz), 3.53 (t, 6 H, CH_2, J_{H-H}=4.6 Hz), 3.25 (s, 9 H, CH_3). ^{13}C NMR (C_6D_6): δ 77.75 (s, CH_2), 62.45 (s, CH_2), 58.17 (s, CH_3).
11 ^{1}H NMR (C_6D_6): δ 4.78 (br, 10 H, CH_2), 3.61 (br, 10 H, CH_2), 3.27 (s, 15 H, CH_3). ^{13}C NMR (C_6D_6): δ 75.61 (s, CH_2), 71.18 (s, CH_2), 58.47 (s, CH_3).
12 ^{1}H NMR (C_6D_6): δ 4.27 (br, 4 H, CH_2), 3.63 (br, 4 H, CH_2), 3.39 (s, 6 H, CH_3). ^{13}C NMR (C_6D_6): δ 79.19 (s, CH_2), 63.08 (s, CH_2), 58.66 (s, CH_3).
13 Anal calc. for $C_{54}H_{126}O_{36}SrBi_2Ta_2$: C, 29.23; H, 5.72; Sr, 3.95; Bi, 18.84; Ta, 16.30. Found: C, 28.95; H, 5.75; Sr, 3.71; Bi, 17.93; Ta, 15.45%. ^{1}H NMR (C_6D_6): δ 4.65 (t, 36 H, CH_2), 3.52 (t, 36 H, CH_2), 3.38 (s, 54 H, CH_3). ^{13}C NMR (C_6D_6): δ 76.00 (s, CH_2), 68.54 (s, CH_2), 58.84 (s, CH_3).
14 T.-C. Chen, T. Li, X, Zhang and S. B. Desu, *J. Mater. Res.*, 1997, **12**, 1569.
15 I. Koiwa, Y. Okada, J. Mita, A. Hashimoto and Y. Sawada, *Jpn. J. Appl. Phys.*, 1997, **36**, 5904.

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