

# Synthesis and Characterization of Aurivillius Phases in the Bi-Ag-Ti-O System

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New Aurivillius phases in the Bi–Ag–Ti–O system were investigated by means of a solid-state reaction and X-ray diffraction. We found that the oxygen partial pressure has a significant influence on the synthesis of the Aurivillius phases. The mixed-layer Aurivillius phase  $Ag_{0.5}Bi_{8.5}Ti_7O_{27}$  was observed after firing in an O<sub>2</sub> flow, but a single-phase material is difficult to obtain. A single-phase compound of the four-layer Aurivillius phase  $Ag_{0.5}Bi_{4.5}Ti_4O_{15}$  was obtained on firing in an oxygen partial pressure of 10 bar ( $1 \times 10^6$  Pa). The dielectric properties (at 1 MHz) of the  $Ag_{0.5}Bi_{4.5}Ti_4O_{15}$  compound were as follows:  $T_{max} = 687^{\circ}$ C,  $\varepsilon_r = 166$  ( $\sim 20^{\circ}$ C), and tan  $\delta = 0.004$  ( $\sim 20^{\circ}$ C).

## I. Introduction

**R**ECENTLY, a great deal of attention has been given to the Aurivillius phase compounds because of their potential for applications in ferroelectric non-volatile memories (Fe-RAM) and high-temperature piezoelectrics.<sup>1,2</sup> The Aurivillius phases are a family of layered bismuth oxides that have been known for 50 years.<sup>3</sup> The structural formula of these compounds is usually described as  $[Bi_2O_2]^{2+}[A_{n-1}B_nO_{3n+1}]^{2-}$ , which consists of perovskite-like  $(A_{n-1}B_nO_{3n+1})^{2-}$  layers interleaved with  $[Bi_2O_2]^{2+}$  layers along the *c*-axis. The Aurivillius phases also occur as mixed-layer compounds with the general formula  $[Bi_2O_2][A_{n-1}B_nO_{3n+1}][Bi_2O_2][A_{m-1}B_mO_{3m+1}]$ . The structure is made up of an intergrowth of one half of the unit cell of the usual bismuth layer-structured oxides  $Bi_2A_{n-1}B_nO_{3n+3}$  along each *c*-axis.

The restriction placed on the choice of A and B ions in Aurivillius phases is that electrical neutrality must be maintained in the overall composition. Armstrong and Newnham<sup>4</sup> suggested that the instability could be related to the stability of the perovskite layer and the size mismatch between the  $[Bi_2O_2]^{2^-}$ and the perovskite layers. The A site can be occupied by large 12-fold-coordinated cations, such as Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, Sr<sup>2+</sup>,  $Ba^{2+}$ ,  $Pb^{2+}$ ,  $Bi^{3+}$ , or  $Ln^{3+}$ , and the B site by sixfold-coordinated cations, such as  $Fe^{3+}$ ,  $Cr^{3+}$ ,  $Ti^{4+}$ ,  $Nb^{5+}$ ,  $Ta^{5+}$ , or  $W^{6+}$ . Although Ag<sup>+</sup> has a radius similar to Na<sup>+</sup> and Sr<sup>2+</sup>, Subbarao<sup>5</sup> failed to obtain Ag<sub>0.5</sub>Bi<sub>4.5</sub>Ti<sub>4</sub>O<sub>15</sub> and so suggested that the electronic configuration or polarizability also played a role in the stability of the Aurivillius phases. However, in reality, it is the poor thermal stability of Ag<sub>2</sub>O that prevents the synthesis of Ag-based compounds via a conventional solid-state reaction method. To synthesize the perovskite compound  $Ag_{1/2}Bi_{1/2}TiO_3$ , high-temperature, high-pressure techniques were used by Park et al.,<sup>6</sup> and the oxidizing conditions generated by the decomposition of Ag<sub>2</sub>O were used by Inaguma et al.<sup>4</sup>

It is possible that many compounds might exist, but have remained undetected because of their extremely low free energy of formation compared with neighboring compounds and the high nucleation barrier to complex-phase formation compared with that of a simpler structure. Morgan PED<sup>8</sup> suggested that fast or slow firing of molecularly mixed or other unusual precursor mixtures would be helpful in finding these compounds.

In the present study, we tried to synthesize Aurivillius phases in the Bi–Ag–Ti–O system with the nominal compositions Ag<sub>0.5</sub>Bi<sub>8.5</sub>Ti<sub>7</sub>O<sub>27</sub>, Ag<sub>0.5</sub>Bi<sub>4.5</sub>Ti<sub>4</sub>O<sub>15</sub>, and AgBi<sub>5</sub>Ti<sub>5</sub>O<sub>18</sub>, where n = 3.5, 4, and 5 corresponds to [Bi<sub>2</sub>O<sub>2</sub>][A<sub>n-1</sub>B<sub>n</sub>O<sub>3n+1</sub>] and n = 3.5 corresponds to the intergrowth of 3+4. The syntheses took place in an O<sub>2</sub> flow and in 10 bar of O<sub>2</sub> (1 × 10<sup>6</sup> Pa). The solid-state reaction method was used to prepare all the compositions. The dielectric and ferroelectric properties of single-phase Ag<sub>0.5</sub>Bi<sub>4.5</sub>Ti<sub>4</sub>O<sub>15</sub> were also investigated.

### **II. Experimental Procedure**

The starting materials used in this study were  $Bi_2O_3$  (99.975%),  $Ag_2O$  (>99%), and  $TiO_2$  (anatase, 99.9%). The  $TiO_2$  powders were dried at 600°C. The powders, in nominal compositions, were homogenized in ethanol by ball milling with 3-mm yttria-stabilized zirconia balls. The powders were placed in alumina crucibles in a tube furnace, fired in an oxygen flow at 10°C/min to 900°C for 12 h. Two more firings in an oxygen flow were also performed on the above reaction product with the nominal composition  $Ag_{0.5}$ .  $Bi_{8.5}Ti_7O_{27}$ . One was heating at 10°C/min to 600°C, followed by 0.1°C/min to 900°C for 12 h. Each time the samples were taken out of the furnace, they were reground and re-milled. The powders were also fired under an oxygen partial pressure ( $P_{O_2}$ ) of 10 bar (10<sup>6</sup> Pa) at 1000°C for 6 h (heating rate 5°C/min). The single-phase  $Ag_{0.5}Bi_{4.5}Ti_4O_{15}$  was sintered at 1000°C for 3 h in 10 bar of O<sub>2</sub>.

The constituent phases were assessed using powder X-ray diffraction (XRD) studies (Bruker AXS D4 Endeavor diffractometer with CuKa radiation, Bruker AXS, Karlsruhe, Germany). The unit-cell parameters were determined using Crysfire and Topas R software. The bulk density of the sintered samples was evaluated by measuring the dimensions and the weight. The dielectric properties were measured with an impedance analyzer (Model HP 4284A LF, Hewlett-Packard, Palo Alto, CA). For the dielectric and ferroelectric property measurements, some silver paste was fired on the samples at 750°C for 10 min. Thermal analyses (DSC) were performed with a Netzsch STA 449C thermal analysis system (Netzsch, Selb, Germany) in an atmosphere of air. The DSC was carried out from room temperature to  $820^{\circ}$ C at a heating rate of  $2^{\circ}$ C/min. The ferroelectric properties were examined with a hysteresis meter (Radiant Technologies, Precision LC, Albuquerque, NM).

## III. Results and Discussion

The nominal compositions of  $Ag_{0.5}Bi_{8.5}Ti_7O_{27}$ ,  $Ag_{0.5}Bi_{4.5}Ti_4O_{15}$ , and  $AgBi_5Ti_5O_{18}$  were heated in an oxygen flow at 10°C/min to 900°C and soaked for 12 h. The XRD analysis of the reaction mixtures revealed the presence of multiple phases

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**Fig. 1.** X-ray diffraction results of the A–C nominal compositions fired at 900°C in an O<sub>2</sub> flow: (a) in the 2 $\theta$  range 10°–60°; (b) in the 2 $\theta$  ranges 15°–19° and 29°–31°. (A, Ag<sub>0.5</sub>Bi<sub>8.5</sub>Ti<sub>7</sub>O<sub>27</sub>; B, Ag<sub>0.5</sub>Bi<sub>4.5</sub>Ti<sub>4</sub>O<sub>15</sub>; C, AgBi<sub>5</sub>Ti<sub>5</sub>O<sub>18</sub>.)

(shown in Fig. 1 and Table I). An Aurivillius phase,  $Bi_4Ti_3O_{12}$  (PDF 72-1019), and a pyrochlore phase,  $Bi_2Ti_2O_7$  (PDF 89-4732), were observed in all the compounds. Because the strongest peak of the Ag phase overlapped with the peak of the  $Bi_4Ti_3O_{12}$  phase, it was difficult to be certain from the XRD results whether Ag is present or not. The existence of Ag was expected in all the compounds because of the dark color of the samples. Additional lines in the 2 $\theta$  ranges  $16.8^{\circ}-17^{\circ}$ ,  $30.3^{\circ}-30.4^{\circ}$ , and  $39^{\circ}-39.3^{\circ}$  were found in all the compounds. Because the additional lines may be associated with the Na<sub>0.5</sub> $Bi_{8.5}Ti_7O_{27}$  phase (PDF 32-1044), the new phase was assumed to be Ag<sub>0.5</sub> $Bi_{8.5}Ti_7O_{27}$ .

The amounts of  $Ag_{0.5}Bi_{8.5}Ti_7O_{27}$  phase can be estimated from the strongest peak of each phase using the following equation:

% Ag<sub>0.5</sub>Bi<sub>8.5</sub>Ti<sub>7</sub>O<sub>27</sub> = 100×
$$I_{118(Ag_{0.5}Bi_{8.5}Ti_7O_{27})}/$$
  
[ $I_{118(Ag_{0.5}Bi_{8.5}Ti_7O_{27})}+I_{117(Bi_4Ti_3O_{12})}$   
+ $I_{222(Bi,Ti_2O_7)}$ ]

A similar equation is frequently used for calculating the amounts of pyrochlore phase during the fabrication of

Pb(Mg<sub>1/3</sub>Nb<sub>2/3</sub>)O<sub>3</sub>.<sup>9</sup> To increase the amount of the Ag<sub>0.5</sub>Bi<sub>8.5</sub>-Ti<sub>7</sub>O<sub>27</sub> phase, the above reaction product with the nominal composition Ag<sub>0.5</sub>Bi<sub>8.5</sub>Ti<sub>7</sub>O<sub>27</sub> was heated at 10°C/min to 600°C, followed by 0.1°C/min to 900°C, and soaked for 6 h, the so-called slow-heating method.<sup>8</sup> The amount of Ag<sub>0.5</sub>Bi<sub>8.5</sub>Ti<sub>7</sub>O<sub>27</sub> increased from 20% to 75% and the pyrochlore phase disappeared, as shown in Fig. 2. Next, after the slow-heating method, the reaction product was heated at 10°C/min to 900°C and soaked for 12 h. The amount of Ag<sub>0.5</sub>Bi<sub>8.5</sub>Ti<sub>7</sub>O<sub>27</sub> increased from 75% to 85%.

It is well-known that the presence of a pyrochlore phase is always unfavorable for the synthesis of a perovskite phase such as  $Pb(Mg_{1/3}Nb_{2/3})O_3$ .<sup>9</sup> It was initially thought that firing a mixture of  $Bi_4Ti_3O_{12}$ ,  $TiO_2$ , and  $Ag_2O$  corresponding to the nominal composition of  $Ag_{0.5}Bi_{8.5}Ti_7O_{27}$  might aid the formation of the  $Ag_{0.5}Bi_{8.5}Ti_7O_{27}$  phase. Disappointingly, however, only traces of the  $Ag_{0.5}Bi_{8.5}Ti_7O_{27}$  phase were observed. Using the above slow-heating method for the corresponding reaction product, the amount of  $Ag_{0.5}Bi_{8.5}Ti_7O_{27}$  phase could be increased from 5% to 45%.

It is possible that the poor thermal stability of Ag<sub>2</sub>O may prevent the synthesis of Ag-based compounds such as Ag<sub>0.5-</sub>  $Bi_{0.5}TiO_3$  via a conventional solid-state reaction method.<sup>6,7</sup> To reduce the influence of the poor thermal stability of the Ag<sub>2</sub>O compound, an oxygen partial pressure of 10 bar was used during the formation of the present compounds. The XRD results of three nominal compositions fired at 1000°C for 6 h in 10 bar of  $O_2$  are shown in Fig. 3. For the nominal composition  $Ag_{0.5}Bi_{4.5}$ - $Ti_4O_{15}$ , all the reflection lines can be matched to the  $SrBi_4Ti_4O_{15}$ phase (PDF 43-0973). In Ag<sub>0.5</sub>Bi<sub>4.5</sub>Ti<sub>4</sub>O<sub>15</sub>, no silver metal was obtained after the calcinations and sintering, and the powders or pellets remained yellow. For the nominal composition Ag<sub>0.5-</sub>  $Bi_{8.5}Ti_7O_{27}$ , the single phase that we expected was not obtained. The dominant phases were the two Aurivillius compounds: Bi<sub>4</sub>Ti<sub>3</sub>O<sub>12</sub> and Ag<sub>0.5</sub>Bi<sub>4.5</sub>Ti<sub>4</sub>O<sub>15</sub>; we observed only the shoulders of some peaks related to Ag<sub>0.5</sub>Bi<sub>8.5</sub>Ti<sub>7</sub>O<sub>27</sub>, as shown in Fig. 3. For the nominal composition AgBi<sub>5</sub>Ti<sub>5</sub>O<sub>18</sub>, which is on the line between Ag<sub>0.5</sub>Bi<sub>4.5</sub>Ti<sub>4</sub>O<sub>15</sub> and Ag<sub>0.5</sub>Bi<sub>0.5</sub>TiO<sub>3</sub>, the following three phases were detected: Ag<sub>0.5</sub>Bi<sub>4.5</sub>Ti<sub>4</sub>O<sub>15</sub>, Bi<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub>, and silver metal.

The phase constituents of the nominal compositions fired under different conditions are shown in Table I. In the present study, there was no evidence for the existence of AgBi<sub>5</sub>Ti<sub>5</sub>O<sub>18</sub>  $(n = 5 \text{ in } [\text{Bi}_2\text{O}_2][\text{A}_{n-1}\text{B}_n\text{O}_{3n+1}])$ . An attempt to synthesize Na-Bi<sub>5</sub>Ti<sub>5</sub>O<sub>18</sub> and KBi<sub>5</sub>Ti<sub>5</sub>O<sub>18</sub> by Subbarao<sup>5</sup> and Uchida and Kiku-chi<sup>10</sup> was also unsuccessful. The maximum value of *n* in the Aurivillius phase is supposed to be 4 when the A site is occupied by a monovalent ion and a Bi ion. The existence of the mixedlayer Aurivillius phase Ag<sub>0.5</sub>Bi<sub>8.5</sub>Ti<sub>7</sub>O<sub>27</sub> was confirmed by the XRD results when the nominal compositions were fired in an oxygen flow. It was difficult to obtain the single-phase mixedlayer structure of  $Ag_{0.5}Bi_{8.5}Ti_7O_{27}$  because of the presence of the simpler three-layer structure of Bi<sub>4</sub>Ti<sub>3</sub>O<sub>12</sub>. It is believed that a small concentration of Ag can be incorporated into the Bi<sub>4-</sub>  $Ti_3O_{12}$  phase, and the  $Bi_4Ti_3O_{12}$  phase with dissolved Ag has a composition close to Ag<sub>0.5</sub>Bi<sub>8.5</sub>Ti<sub>7</sub>O<sub>27</sub>. A slow heating rate or a prolonged dwelling time should be used to enhance the formation of the Ag<sub>0.5</sub>Bi<sub>8.5</sub>Ti<sub>7</sub>O<sub>27</sub> phase because of the higher free energy of formation of  $Ag_{0.5}Bi_{8.5}Ti_7O_{27}$  compared with that of  $Bi_4Ti_3O_{12}$ . The structure of the  $Ag_{0.5}Bi_{8.5}Ti_7O_{27}$  phase was refined in the orthorhombic space group I2 cm, suggested by Boullay *et al.*,<sup>11</sup> Z = 1, and the lattice parameters are a = 5.451(1)Å, b = 5.419(1) Å, and c = 36.751(8) Å.

Table I. Starting Nominal Compositions of Aurivillius Phases and Phases Detected by XRD

Nominal composition	Fired in O <sub>2</sub> flow (at 900°C for 12 h)	Fired in $10^6$ Pa O <sub>2</sub> (at 1000°C for 6 h)
$\begin{array}{l} Ag_{0.5}Bi_{8.5}Ti_7O_{27} \\ Ag_{0.5}Bi_{4.5}Ti_4O_{15} \\ AgBi_5Ti_5O_{18} \end{array}$	$\begin{array}{l} Bi_4Ti_3O_{12} + Bi_{8.5}Ag_{0.5}Ti_7O_{27} + Bi_2Ti_2O_7 + Ag\\ Bi_4Ti_3O_{12} + Bi_2Ti_2O_7 + Ag_{0.5}Bi_{8.5}Ti_7O_{27} + Ag\\ Bi_4Ti_3O_{12} + Ag_{0.5}Bi_{8.5}Ti_7O_{27} + Bi_2Ti_2O_7 + Ag\end{array}$	$\begin{array}{c} Bi_4Ti_3O_{12} + Ag_{0.5}Bi_{4.5}Ti_4O_{15} + Ag_{0.5}Bi_{8.5}Ti_7O_{27} \\ Ag_{0.5}Bi_{4.5}Ti_4O_{15} \\ Bi_2Ti_2O_7 + Ag_{0.5}Bi_{4.5}Ti_4O_{15} + Ag \end{array}$

XRD, X-ray diffraction.



**Fig. 2.** X-ray diffraction results of the nominal composition  $Ag_{0.5}Bi_{8.5}Ti_7O_{27}$  in the 2 $\theta$  ranges  $15^\circ$ – $19^\circ$  and  $29^\circ$ – $31^\circ$ . (a, firing at  $10^\circ$ C/min to 900°C for 12 h; b,  $10^\circ$ C/min to 600°C, followed by  $0.1^\circ$ C/min to 900°C and soaked for 6 h).

When fired under a pressure of oxygen, single-phase Ag<sub>0.5</sub>-Bi<sub>4.5</sub>Ti<sub>4</sub>O<sub>15</sub> (n = 4) could be obtained. The structure of the Ag<sub>0.5</sub>Bi<sub>4.5</sub>Ti<sub>4</sub>O<sub>15</sub> phase was refined in the orthorhombic space group<sup>12</sup> A2<sub>1</sub>am, Z = 2, and the cell parameters are a = 5.4586(4)Å, b = 5.4293(7) Å, and c = 40.758(3) Å ( $R_{wp} = 0.1634$ ) (Fig. 4(b)). We also heated the single-phase Ag<sub>0.5</sub>Bi<sub>4.5</sub>Ti<sub>4</sub>O<sub>15</sub>



**Fig. 3.** X-ray diffraction results of the A–C nominal compositions fired at  $P_{O2}$  with  $10^7$  Pa: (a) in the 2 $\theta$  range  $10-60^\circ$ ; (b) in the  $2\theta$  ranges  $15^\circ-19^\circ$  and  $29^\circ-31^\circ$ . (A,  $Ag_{0.5}Bi_{8.5}Ti_7O_{27}$ ; B,  $Ag_{0.5}Bi_{4.5}Ti_4O_{15}$ ; C,  $AgBi_5Ti_5O_{18}$ .)



**Fig. 4.** (a) X-ray diffraction results of  $Ag_{0.5}Bi_{4.5}Ti_4O_{15}$  (A, single phase; B, reheating single phase in an O<sub>2</sub> flow at 900°C for 6 h); (b) Rietveld refinement results of  $Ag_{0.5}Bi_{4.5}Ti_4O_{15}$ . (The upper graph shows the fit between the experimental and calculated patterns, while the lower graph shows the difference between these two patterns.)

in flowing oxygen at 900°C for 6 h. The dominant phase was still  $Ag_{0.5}Bi_{4.5}Ti_4O_{15}$ , but the reflection of  $Ag_{0.5}Bi_{8.5}Ti_7O_{27}$  appears at the shoulder of some peaks, and the pyrochlore phase is observed, as shown in Fig. 4(a). We concluded that  $Ag_{0.5}Bi_{4.5}Ti_4O_{15}$  is not stable when fired in flowing oxygen.

Dense ceramics (>94% of the theoretical density) were obtained when sintering  $Ag_{0.5}Bi_{4.5}Ti_4O_{15}$  at 1000°C for 3 h in pressurized O<sub>2</sub>. After sintering, the ceramic shows the same yellow color as the powders after calcinations. A dielectric constant,  $\varepsilon_r$ , of 166 and a dielectric loss, tan $\delta$ , of 0.004 were obtained at 1 MHz at room temperature. From room temperature to 300°C, the dielectric constant was found to be almost temperature independent, as shown in Fig. 5. A sharp peak was found at 687°C, which coincides with the minimum of the dielectric loss. No significant difference was found for the value of  $T_{\text{max}}$ , whether the temperature-dependence measurement was



Fig. 5. Temperature dependence of the dielectric properties of the Ag<sub>0.5</sub>Bi<sub>4.5</sub>Ti<sub>4</sub>O<sub>15</sub> ceramic. (The inset shows DSC analysis results;  $T_{\text{max}}$ , the temperature of  $\varepsilon_{\text{max}}$ ).



**Fig. 6.** P-E hysteresis loops of Ag<sub>0.5</sub>Bi<sub>4.5</sub>Ti<sub>4</sub>O<sub>15</sub> ceramic with increasing electric field (at 100 Hz).

performed at a heating rate of 5° or 2°C/min. Usually,  $T_{\text{max}}$  can be approximated as  $T_{\text{C}}$ . The DSC results shown in the inset graph of Fig. 5 suggest that the phase transition at the  $T_{\text{C}}$  of Ag<sub>0.5</sub>Bi<sub>4.5</sub>Ti<sub>4</sub>O<sub>15</sub> is not of the first order, but of the second order. For bismuth layer-structured ferroelectrics, the  $T_{\text{C}}$  is strongly influenced by the  $r_i$  of the A-site cations, and bismuth layerstructured ferroelectrics with smaller A-site cations tend to show a higher  $T_{\text{C}}$ . The  $r_i$  of Ag<sup>+</sup> is larger than that of Na<sup>+</sup>, but the  $T_{\text{C}}$ (687°C) of the Ag<sub>0.5</sub>Bi<sub>4.5</sub>Ti<sub>4</sub>O<sub>15</sub> is higher than that (662°C in Ahn *et al.*<sup>13</sup> and 655°C in Ben Jannet *et al.*<sup>14</sup>) of the Na<sub>0.5</sub>Bi<sub>4.5</sub>Ti<sub>4</sub>O<sub>15</sub>. Ti<sub>4</sub>O<sub>15</sub>. The large electronegativity of the Ag<sup>+</sup> (1.93) may play a role in the influence on the Curie temperature (the electronegativity of Na<sup>+</sup> is 0.93). The  $T_{\text{C}}$  of both the Ag<sub>0.5</sub>Bi<sub>4.5</sub>Ti<sub>4</sub>O<sub>15</sub> and the Na<sub>0.5</sub>Bi<sub>4.5</sub>Ti<sub>4</sub>O<sub>15</sub> is higher than that of the SrBi<sub>4.5</sub>Ti<sub>4</sub>O<sub>15</sub> (520°C)<sup>15</sup> and lower than that of the CaBi<sub>4</sub>Ti<sub>4</sub>O<sub>15</sub> (820°C).<sup>16</sup>

The *P*–*E* hysteresis loops of the Ag<sub>0.5</sub>Bi<sub>4.5</sub>Ti<sub>4</sub>O<sub>15</sub> ceramic are shown in Fig. 6. The distorted loops indicate a lossy nonlinear capacitor behavior. Because both the polar orthorhombic structure and the sharp peak from the dielectric constant measurement suggest a ferroelectric phase at room temperature in Ag<sub>0.5</sub>Bi<sub>4.5</sub>Ti<sub>4</sub>O<sub>15</sub>, we believe that the loops are the result of both the weak ferroelectric properties and the leakage current. The leakage–current density measured at 10 kV/cm was  $8 \times 10^{-7}$  A/cm<sup>2</sup>. When the soaking time was increased, a larger  $P_r$  and a round curve were obtained because of the leakage current.

#### IV. Conclusions

The nominal compositions of Aurivillius phases (Ag<sub>0.5</sub>Bi<sub>8.5</sub>. Ti<sub>7</sub>O<sub>27</sub>, Ag<sub>0.5</sub>Bi<sub>4.5</sub>Ti<sub>4</sub>O<sub>15</sub>, and AgBi<sub>5</sub>Ti<sub>5</sub>O<sub>18</sub>) in the Bi–Ag–Ti–O system were investigated by means of a solid-state reaction and XRD. The mixed-layer Aurivillius phase Ag<sub>0.5</sub>Bi<sub>8.5</sub>Ti<sub>7</sub>O<sub>27</sub> was found after firing in an O<sub>2</sub> flow. A slow heating rate and a prolonged dwelling time can increase the amount of the Ag<sub>0.5</sub>Bi<sub>8.5</sub>. Ti<sub>7</sub>O<sub>27</sub> phase. On firing in an oxygen partial pressure of 10 bar (1 × 10<sup>6</sup> Pa), a single-phase compound of the four-layer Aurivillius phase Ag<sub>0.5</sub>Bi<sub>4.5</sub>Ti<sub>4</sub>O<sub>15</sub> was obtained. There was no evidence for the existence of AgBi<sub>5</sub>Ti<sub>5</sub>O<sub>18</sub>. The dielectric properties (at 1 MHz) of the Ag<sub>0.5</sub>Bi<sub>4.5</sub>Ti<sub>4</sub>O<sub>15</sub> phase were as follows:  $T_{max} = 687^{\circ}$ C,  $\varepsilon_r = 166$  (~20°C), and tan $\delta = 0.004$  (~20°C).

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