

# Ferroelectric Phase Transitions and Electroconducting Properties of Ceramic BIMEVOX Solid Solutions (Me = La, Zr)

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Ceramic solid solutions  $Bi_4(V_{1-x}Zr_x)_2O_{11-z}$  (I),  $(Bi_{1-y}La_y)_4V_2O_{11-z}$  (II) and  $(Bi_{1-y}La_y)_4(V_{0.96}Zr_{0.05})_2O_{11-z}$  (III) with x < 0.30, y < 0.20, were prepared by the solid state reaction method and were investigated by means of various experimental techniques. The low temperature ferroelectric  $\alpha$ -phase exists in the solid solutions with  $x, y \le 0.05$ . The phase transition to paraelectric  $\beta$ -phase was revealed in these compositions by the dielectric spectroscopy, SHG and DTA/DSC methods. Dielectric permittivity measurements confirmed an effect of the domain walls "pinning" due to the presence of oxygen vacancies inherent to the bismuth vanadate based structures. Switching of ferroelectric domains by an external electric field was observed in Piezoresponse Force Microscopy experiments.

**Keywords** Ferroelectric phase transition; ionic conductivity; BIMEVOX; domain switching

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### Introduction

Ceramic solid solutions on the base of bismuth vanadate  $Bi_4V_2O_{11-y}$  attract a significant interest due to extremely high ionic conductivity revealed in the tetragonal  $\gamma$ -phase,  $\sigma \sim 0.02$  S/cm at T < 900 K. Various modification of cation composition were studied aimed to stabilize the so called BIMEVOX phases that possess tetragonal structure at room temperature [1–9].

Bismuth vanadate  $Bi_4V_2O_{11-y}$  was first synthesized as a member of the Aurivillius family  $(Bi_2O_2)^{2+}(A_{n-1}B_nO_{3n+1})^{2-}$  with n = 1 [10]. This compound consists of alternating layers of  $(B_2O_2)_n^{n2+}$  and  $(VO_{3.5-y} \varphi_{0.5+y})_n^{n2-}$ , with  $Bi^{3+}$  cations being in square pyramidal coordination and  $V^{5+}$  cations being in octahedral coordination with oxygen. With increasing

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temperature a series of phase transitions from the monoclinic  $\alpha$ - to the orthorhombic  $\beta$ near 700 K and then to the tetragonal  $\gamma$ -phase near 850 K was observed [9, 11–13].

The tetragonal  $\gamma$ -phase can be stabilized at room temperature via substitution of V<sup>5+</sup> and/or Bi<sup>3+</sup> by various cations in BIMEVOX solid solutions. Incorporation of vacancies in the vanadate layer may stimulate a decrease in coordination numbers of vanadium cations from 6 to 4 or 5 that influences the stability limits and properties of the BIMEVOX polymorph modifications [5].

Structure of the low-temperature  $\alpha$ -phase has been identified as monoclinic one, though true unit cell is commensurate modulated and consists of alternating vanadium-oxygen tetrahedra and oxygen-deficient octahedra along the modulation  $c_{\rm m}$  axis. The modulation depends on oxygen vacancies ordering and valence modulations of both vanadium and bismuth cations [14].

The transition from the monoclinic  $\alpha$ -phase to the orthorhombic  $\beta$ -phase near  $\sim$ 700 K was ascertained as a ferroelectric-paralectric one [15–19]. The presence of the lone pair of electrons Bi 6s<sup>2</sup> is regarded as a main reason of structural distortion within the vanadium polyhedra and leads to ferroelectric properties in the parent bismuth vanadate [5].

Though ferroelectric phases exist in various BIMEVOX compositions and influence their electroconducting properties there is scarce information on their features.

In this work, ceramic solid solutions  $Bi_4(V_{1-x}Zr_x)_2O_{11-z}$  (I),  $(Bi_{1-y}La_y)_4V_2O_{11-z}$  (II) and  $(Bi_{1-y}La_y)_4(V_{0.96}Zr_{0.05})_2O_{11-z}$  (III) with x < 0.30, y < 0.20 were prepared by the solid state reaction method. Ferroelectric phase transitions in compositions from  $\alpha$ -phase domain were studied by the X-ray diffraction, DTA/DSC, Dielectric Spectroscopy, Atomic and Piezo- Force Microscopy (AFM and PFM, respectively) methods.

# **Experimental Procedure**

Ceramic solid solutions  $Bi_4(V_{1-x}Zr_x)_2O_{11-z}$  (I),  $(Bi_{1-y}La_y)_4V_2O_{11-z}$  (II) and  $(Bi_{1-y}La_y)_4(V_{0.96}Zr_{0.05})_2O_{11-z}$  (III) with x < 0.30, y < 0.20, were prepared by the solid state reaction method. Preliminary dried at 873–1103 K (2 h) oxides  $Bi_2O_3$  (99.9%),  $V_2O_5$  (99.99%),  $La_2O_3(99.9\%)$  and  $ZrO_2$  (99.99%) were used as starting materials. The stoichiometric mixtures of oxides were calcined at 723–973 K (~15 h), regrinded, pressed into pellets, sintered at 1073–1093 K (~10 h) and slowly cooled to room temperature.

Phase content and parameters of the unit cell of the obtained solid solutions were determined by the X-ray diffraction method (DRON-3M,  $Cu_{k\alpha}$ -radiation).

Phase transitions were studied by the Differential Thermal Analysis (DTA) (MOM Q-1500D) and Differential Scanning Calorimetry (DSC) (SDT Q-600) methods in the range of 300–1100 K with heating rate 10 deg/min, and by the dielectric spectroscopy (Agilent 4284 A LCR meter) in the temperature range from 300 to 1000 K, at probing voltage with amplitude 1 V and frequencies from 100 Hz to 1 MHz. Electrical contacts to the small faces of the samples were deposited by firing a Pt-containing paste at 1170 K.

Microstructure of the samples was controlled by the Atomic Force Microscopy (AFM) (multi-microscope SMM-2000).

The samples were checked for non-centrosymmetricity by the Second Harmonic Generation (SHG) method using a Nd:YAG laser with wavelength,  $\lambda_{\omega} = 1.064 \ \mu \text{m}$ .

Domain structures of the ceramics were studied by Piezoresponse Force Microscopy (PFM). A detailed description of this method can be found elsewhere [20]. Briefly, it is based on the detection of local surface deformations induced by the converse piezoelectric effect. The sign of the deformation depends on the mutual orientation of the probing field

and the local polarization, while its amplitude is a function of the local polarization value. In such a way domains with different orientation of the polarization can be distinguished as regions of different contrast on the PFM images. Prior to the PFM measurements the investigated faces of the ceramic samples were polished to optical quality. On the opposite side a silver electrode was deposited.

#### **Results and Discussion**

According to the X-ray data, perovskite solid solutions are formed in compositions I-III (Fig. 1). In the BIZRVOX system I single phase solid solutions exist in the concentration range  $0.0 \le x \le 0.15$  [21, 22]. The presence of Bi<sub>8</sub>V<sub>2</sub>O<sub>17</sub> and ZrO<sub>2</sub> impurity phases has been revealed in the samples with x > 0.20. At room temperature BIZRVOX solid solutions with  $x \le 0.05$  are in the monoclinic  $\alpha$ -phase, while for the compositions with  $0.10 \le x \le 0.30$  the orthorhombic  $\beta$ -phase was identified. In the BILAVOX system II and in the system III single phase solid solutions exist at x < 0.08, and small peaks of admixture phases were observed in X-ray diffraction patterns of the samples with  $x \ge 0.08$ .

With x increasing, the transformation from monoclinic  $\alpha$ -phase to orthorhombic  $\beta$ phase was revealed in all the systems studied. At room temperature, a and c unit cell parameters increase, while b parameter slightly decreases with x increasing (Fig. 2). The unit cell volume increases in the solubility regions in all solid solutions in accordance with the larger ionic radius of the dopant Zr<sup>4+</sup> and La<sup>3+</sup> cations. These results agree well with those published earlier for BIZRVOX and BILAVOX compositions [2, 3, 5, 7, 23].

Ceramic samples have rather fine microstructure with average size of grains  $< 10 \,\mu$ m.

Ferroelectric nature of the  $\alpha \leftrightarrow \beta$  phase transition in BIMEVOX compositions with ME = Ga, Fe, Zr, La, was confirmed by the SHG measurements [21, 22]. A relatively low intensity of the second harmonic signal,  $q = I_{2w}/I_{2w}(SiO_2) < 0.3$ , measured in those compositions is due to an intensive red to brown coloration of the samples. A bending on the  $I_{2w}/I_{2w}(SiO_2)(x)$  curves marks the cross-over from non-centrosymmetric to centrosymmetric compositions. A ferroelectric-type phase transition is revealed at ~540 K on the



**Figure 1.** X-Ray diffraction pattern of the sample  $(Bi_{1-y}La_y)_4(V_{0.96}Zr_{0.05})_2O_{11-y}$ . In insert: diffraction peaks at 2  $\theta$  = 45–49 degrees for compositions with y = 0 (solid lines); 0.02 (dash lines); 0.06 (dot lines).



**Figure 2.** Concentration dependences of the unit cell parameters *a*, *b*, *c*, and *V* versus *y* for solid solutions  $(Bi_{1-y}La_y)_4(V_{0.96}Zr_{0.05})_2O_{11-y}$ . Dash line at y = 0.11 marks the transformation to tetragonal structure.

temperature dependence of the SHG signal intensity in the bismuth vanadate samples with x, y = 0 [15, 21, 22]. On concentration dependences of the SHG signal three concentration regions are distinguished that correspond to the stability regions of  $\alpha$ ,  $\beta$  and  $\gamma$  polymorph modifications.

The DTA/DSC data are in agreement with the results obtained by the SHG method (Fig. 3). The DTA/DSC results confirmed the presence of the 1st order (rather sluggish) $\alpha \leftrightarrow \beta$  and  $\beta \leftrightarrow \gamma$  phase transitions at heating-cooling cycles. In the parent Bi<sub>4</sub>V<sub>2</sub>O<sub>11</sub> compound,



**Figure 3.** DTA data for solid solutions  $(Bi_{1-y}La_y)_4V_2O_{11-z}$  (1–3) and  $Bi_4(V_{1-x}Zr_x)_2O_{11-z}$  (4) at heating and cooling with y = 0 (1); 0.02 (2), 0.04 (3), x = 0.05 (4).

the 1st order phase transitions are clearly seen, though they are getting broader in other compositions. The phase transitions  $\alpha \leftrightarrow \beta$  take place only in the samples with  $x, y \leq 0.05$ . Temperature of the  $\beta \leftrightarrow \gamma$  phase transition decreases with x increasing in the range of x > 0.10. This phase transition is characterized with smaller temperature hysteresis in comparison to that measured for the  $\alpha \leftrightarrow \beta$  transition.

The concentration dependence of the infrared absorption indicated variations in electronic part of the conductivity, namely its decreasing at low x values while further restoration in compositions with x > 0.08 in the system II [24]. This may be explained by changes in relative content of vanadium polyhedra with different oxygen coordination, which were proved to exist in the parent compound.

The values of the total conductivity are low at room temperature and are limited to the range of  $10^{-7}$  ÷  $10^{-9}$  S/cm, while at higher temperatures they reach high values  $\sim 0.1$  S/cm at 800 K. In the total conductivity versus reciprocal temperature curves anomalies corresponding to both  $\alpha \leftrightarrow \beta$  and  $\beta \leftrightarrow \gamma$  phase transitions were also observed.

Peaks corresponding to the ferroelectric  $\Leftrightarrow$  paraelectric phase transitions were observed in temperature dependences of dielectric permittivity  $\varepsilon(T)$  and dielectric losses  $\tan\delta(T)$  in I-III ceramics with  $x \le 0.05$  (Fig. 4). These peaks are more pronounced at cooling than at heating. This effect is intimately related to the presence of oxygen vacancies in the structure and to the possibility of their ordering in the temperature domain of the  $\alpha$ -phase stabilization. "Pinned" at domain walls oxygen vacancies may prevent the domain walls motion [25–27].

It should be noted that the oxygen ionic motion may cause strong relaxation effects that were revealed for ceramic compositions BIMEVOX from the  $\beta$ -phase range [24]. Such effects are often observed in other ferroelectric and in ionic conducting ceramics [26–28].

Figure 5 shows both topography and piezoresponse images of the bismuth vanadate ceramics (x = 0, y = 0). In some grains a regular domain pattern is observed. Here bright and dark stripes correspond to domains with the normal component of the



**Figure 4.** Dielectric permittivity versus temperature curves for ceramic solid solutions  $(Bi_{1-y}La_y)_4V_2O_{11-z}(a, b)$  and  $Bi_4(V_{1-x}Zr_x)_2O_{11-z}(c)$ . a)y = 0, f = 1 kHz, 1 –heating, 1'–cooling; f = 10 kHz, 2 –heating, 2'–cooling; b)y = 0.04. f = 1 kHz, 1 –heating, 1'–cooling; f = 10 kHz, 2 –heating, 2'–cooling; c)x = 0.05, f = 10 kHz, first cycle 1–heating, 1'–cooling; second cycle 2–heating, 2'–cooling.

polarization oriented up and down relative to the sample surface, respectively. The boundaries between domains are straight and parallel. Therefore we can suppose that the observed pattern corresponds to ferroelastic domain structure. In this case the domain boundaries have to be parallel to certain crystallographic directions [29], while for pure ferroelectric



**Figure 5.** The topography (*a*) and piezoresponse images (*b*) of the  $Bi_4V_2O_{11-z}$  ceramics. (See Color Plate I)



**Figure 6.** The topography (*a*) and initial piezoresponse (*b*) images of  $\text{Bi}_4 V_{1.9} \text{Zr}_{0.1} O_{11-z}$  ceramics. The piezoreponse images after the area  $10 \times 10 \ \mu\text{m}^2$  was scanned under dc bias +50 V (*c*), and -50 V (*d*). (See Color Plate II)

(180-degree) domains their orientation is arbitrary in general. The local piezoresponse value inside individual domains is rather weak, which indicates a small value of spontaneous polarization in an agreement with data published for thin films ( $P_s = 4.6 \cdot 10^{-2} \mu \text{C/cm}^2$  [30] and  $P_s = 2.2 \cdot \mu \text{C/cm}^2$  [31]). This is also a reason why a large fraction of the surface shows a negligible piezoresponse (an intermediate contrast). Due to small value of polarization and hence small value of piezoelectric coefficients, the PFM contrast is seen only in grains with a favorable crystallographic orientation, were the longitudinal piezoresponse is maximal.

A similar domain pattern was observed also in Zr-doped bismuth vanadate ceramics I with x = 0.05 (Fig. 6b). After a selected area (approximately the dashed square in the Fig. 6b) was scanned under an applied dc bias voltage above certain threshold value, the piezoresponse contrast inside this area became unipolar (Fig. 6c). Hereafter it could be reversed by application of the opposite dc bias (Fig. 6d). All these observations confirm that this compound is in the ferroelectric state at room temperature. However, the maximal value of the piezoresponse is approximately two times smaller in comparison to the pure bismuth vanadate, which points out decreasing of the spontaneous polarization in the Zr-doped compositions.

## Conclusions

The formation of single phase solid solutions  $Bi_4(V_{1-x}Zr_x)_2O_{11-z}$  (I),  $(Bi_{1-y}La_y)_4V_2O_{11-z}$  (II) and  $(Bi_{1-y}La_y)_4(V_{0.96}Zr_{0.05})_2O_{11-z}$  (III) with x < 0.30, y < 0.20 has been revealed. The stabilization of the monoclinic  $\alpha$ -phase has been proved for  $x \le 0.05$ . The formation of orthorhombic  $\beta$ -phase and tetragonal  $\gamma$  -phase has been observed in solid solutions with higher dopants content. Ferroelectric phase transitions were observed in the  $\alpha$ -domain samples using the DTA/DSC, laser second harmonic generation (SHG) method and

dielectric spectroscopy. A decrease of the ferroelectric  $\alpha - \beta$  phase transition temperature was observed while the increase in the thermal hysteresis interval of the transition was revealed. The oxygen vacancy "pinning" on the ferroelectric domain walls was proposed to be responsible for the dielectric properties features in the  $\alpha \leftrightarrow \beta$  phase transitions observed. Switching of ferroelectric domains by an external electric field was observed in PFM experiments and their ferroelastic origin is proposed.

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## References

- I. Abrahams, J. C. Boivin, and Nowogrocki G. G. Mairesse, BIMEVOX series. A new family of high performances oxide ion conductors. *Solid State Ionics*. 40/41, 934–937 (1990).
- J. Yan and M. Greenblatt, Ionic conductivities of Bi<sub>4</sub>V<sub>2-x</sub>M<sub>x</sub>O<sub>11-x/2</sub> (M = Ti, Zr, Sn, Pb) solid solutions. *Solid State Ionics*. 81, 225–233 (1995).
- O. Joubert, M. Ganne, R. N. Vannier, and G. Mairesse, Solid phase synthesis and characterization of new BIMEVOX series: Bi<sub>4</sub>V<sub>2-x</sub>M<sub>x</sub>O<sub>11-x</sub> (M = Cr<sup>III</sup>, Fe<sup>III</sup>). *Solid State Ionics*. 82, 199–207 (1996).
- I. Abrahams, A. J. Bush, F. Krok, G. E. Hawkes, K. D. Sales, P. Thornton, and W. Bogusz, Effects of preparation parameters on oxygen stoichiometery in BiVO. *J. Mater. Chem.* 8, 1213–1217 (1998).
- I. Abrahams and F. Krok, Defect chemistry of the BIMEVOXes. J. Mater. Chem. 12, 3351–3162 (2002).
- I. Abrahams and F. Krok, A model for the mechanism of low temperature ionic conduction in divalent-substituted BIMEVOXes. *Solid State Ionics*. 157, 139–145 (2003).
- W. Wrobel, I. Abrahams, F. Krok, A. Kozanecka, S. C. M. Chan, W. Bogusz, and J. R. Dygas, Phase transitions in the BIZRVOX system. *Solid State Ionics*. **176**, 1731–1737 (2005).
- F. Krok, I. Abrahams, W. Wrobel, A. Kozanecka-Szmigiel, and J. R. Dygas, Oxide-ion conductors for fuel cells. *Mater. Sci.-Poland.* 24, 13–22 (2006).
- S. P. Simner, D. Suarez-Sandoral, J. D. Mackenzie, and B. Dunn, Synthesis, Densification and Conductivity Characteristics of BICUVOX oxygen-ion-conducting Ceramics. *J. Am. Ceram. Soc.* 80, 2563–2568 (1997).
- A. A. Bush and Y. U. N. Venevtsev, Crystals of the new phase Bi<sub>4</sub>V<sub>2</sub>O<sub>11</sub> in the system Bi<sub>2</sub>O<sub>3</sub>-V<sub>2</sub>O<sub>5</sub>. *Russian Journal of Inorganic Chem.* **31**, 769–771 (1986).
- G. Mairesse, P. Roussel, R. N. Vannier, M. Anne, C. Pirano, and G. I. Nowogrocki, Crystal structure determination of α-, β- and γ-phase polymorphs. Part I: γ and β-Bi<sub>4</sub>V<sub>2</sub>O<sub>11</sub>. *Solid State Sciences.* 5, 851–859 (2003).
- G. Mairesse, P. Roussel, R. N. Vannier, M. Anne, and G. Nowogrocki, Crystal structure determination of α-, β- and γ-phase polymorphs. Part II: crystal structure of α-BiVO. Solid State Sciences. 5, 861–869 (2003).
- R. N. Vannier, E. Pernot, M. Anne, O. Isnard, G. Nowogrocki, and G. Mairesse, Bi<sub>4</sub>V<sub>2</sub>O<sub>11</sub> polymorh crystal structures related to their electrical properties. *Solid State Ionics*. **157**, 147–153 (2003).
- 14. O. Joubert, A. Jouanneaux, and M. Ganne, Crystal structure of low-temperature form of bismuth vanadium oxide determined by Rietveld refinement of x-ray and neutron diffraction data  $\alpha$ -Bi<sub>4</sub>V<sub>2</sub>O<sub>11</sub>. *Materials Research Bulletin*. **29**, 175–184 (1994).
- À. À. Bush, S. Yu. Stefanovich, and Yu. V. Titov, Preparation and properties of crystals in the system Bi<sub>2</sub>O<sub>3</sub>-V<sub>2</sub>O<sub>5</sub>. *Russian Journal of Inorganic Chem.* 41, 1568–1574 (1996).

- V. G. Osipyan, L. M. Savchenko, V. L. Elbakyan, and P. B. Avakyan, Bismuth vanadate ferroelectrics with layered structure. *Russ. Bull. Acad. Sci. Ser. Inorg. Mater.* 23, 523–525 (1987).
- V. N. Borisov, V. M. Pashkov, Y. U. M. Poplavko, P. B. Avakian, and V. G. Osipian, Dielectric spectra of Bi<sub>4</sub>V<sub>2</sub>O<sub>11</sub>. *Izv.Akad. Nauk SSSR, Ser. Fiz.* 54, 1221–1224 (1990).
- S. K. Ramasesha, A. K. Singh, and K. B. R. Varma, Effect of Pressure on dielectric and ferroelectric propweries of bismuth vanadate. *Mater. Chem. and Phys.* 48, 136–139 (1997).
- K. Shantha and K. B. R. Varma, Frequency dependence of the dielectric properties of ferroelectric Bi<sub>2</sub>VO<sub>5.5</sub>. Solid State Ionics. 99, 225–231 (1997).
- A. L. Kholkin, I. K. Bdikin, D. A. Kiselev, V. V. Shvartsman, and S. H. Kim, Nanoscale characterization of polycrystalline ferroelectric materials for piezoelectric applications. *J. Electroceram.* 19, 81–94 (2007).
- V. V. Murasheva, E. A. Fortalnova, E. D. Politova, M. G. Safronenko, and S. Yu, Stefanovich SYU and N.U. Venskovskii NU: Phase Transitions in the BIMEVOX Solid Solutions with Me = Ga, Zr. *Materials Science Forum*. 587–588, 114–117 (2008).
- E. A. Fortalnova, V. V. Murasheva, M. G. Safronenko, N. U. Venskovskii, S. Y. U. Stefanovich, and E. D. Politova, Investigation of ferroelectric phase transitions in solid solutions on the base of vismuth vanadate. *Bull. Russ.Acad. Sci. Phys.* 72, 1094–1097 (2008).
- A. A. Yaremchenko, V. V. Kharton, E. N. Naumovich, and V. V. Samokhval, Oxygen ionic and electronic conductivity of La-doped BIMEVOX. *Solid State Ionics*. 111, 227–236 (1998).
- E. D. Politova, E. A. Fortalnova, G. M. Kaleva, A. V. Mosunov, L. I. Andronova, S. A. Andropova, M. G. Safronenko, and N. U. Venskovskii, Ferroelectric phase transitions in ionic conductors on the base of bismuth vanadate. *Russian J. Solid State Phys.* 2008; in press.
- M. Valleja, M. T. Dove, and E. K. H. Salje, Trapping of oxygen vacancies on twin walls of CaTiO3: a computer simulation study. J. Phys.: Condens Matter. 15, 2301–2307 (2003).
- C. Wang, Q. F. Fang, Y. Shi, and Z. G. Zhu, Internal friction study of oxygen vacancies and domain walls in Pb(Zr,Ti)O<sub>3</sub> ceramics. *Mater. Res. Bull.* 36, 2657–2665 (2001).
- Y. Y. Yao, C. H. Song, P. Bao, D. Su, X. M. Lu, and J. S. Zhu, Doping effect on the dielectric property in bismuth titanate. J. Applied Physics. 95, 3126–3130 (2004).
- A. V. Mosunov, N. U. Venskovskii, and G. M. Kaleva, Dielectric properties of oxygen ionconductive (La,Sr)(Ga,Mg)O<sub>3-v</sub> ceramics. *Ferroelectrics*. 299, 149–152 (2004).
- J. Fousek and V. Janovec, The orientation of domain walls in twinned ferroelectric crystals. J. Appl. Phys. 40, 135–142 (1969).
- K. V. R. Prasad, K. B. R. Varma, A. R. Raju, K. M. Satyalakshmi, R. M. Mallya, and M. S. Hegde, Growth and ferroelectric properties of Bi<sub>2</sub>VO<sub>5.5</sub> thin-films with metallic LaNiO<sub>3</sub> electrodes. *Appl. Phys. Lett.* 63, 1898–1900 (1993).
- M. Joseph, H. Y. Lee, H. Tabata, and T. Kawai, Ferroelectric behaviour of epitaxial Bi<sub>2</sub>VO<sub>5.5</sub> thin films on Si(100) formed by pulsed-laser deposition. *J. Appl. Phys.* 88, 1193–1195 (2000).