Hydrothermal synthesis of lead-free perovskite $(\text{Bi}_{1/2}\text{K}_{1/2})(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ powders

Makoto ITO, Manabu HAGIWARA[†] and Shinobu FUJIHARA

Department of Applied Chemistry, Faculty of Science and Technology, Keio University,
3–14–1 Hiyoshi, Kohoku-ku, Yokohama 223–8522, Japan

We developed a hydrothermal synthesis method for lead-free perovskite $(\text{Bi}_{1/2}\text{K}_{1/2})(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ (BKZT) powders. Single-phase BKZT powders with various nominal Zr contents as high as $x = 0.10$ were obtained using amorphous hydrous oxide $(\text{Zr}_x\text{Ti}_{1-x})\text{O}_2 \cdot n\text{H}_2\text{O}$ precursors prepared by the hydrolysis of Zr- and Ti-alkoxides, whereas a reaction using a mixture of crystalline TiO_2 and ZrO_2 powders did not provide single-phase BKZT. Elemental analysis revealed that the Zr contents of the obtained BKZT powders were slightly higher than the nominal values. The powders had fine particle sizes smaller than 300 nm and were stable against a high-temperature heat treatment at 1000°C. These observations suggest that the hydrothermally derived powders are suitable for use in fabricating bulk BKZT ceramics via sintering.

©2017 The Ceramic Society of Japan. All rights reserved.

Key-words : $(\text{Bi}_{1/2}\text{K}_{1/2})\text{TiO}_3$, Element substitution, Hydrothermal method, Lead-free piezoelectric ceramics

[Received November 11, 2016; Accepted February 16, 2017]

1. Introduction

The existence of a morphotropic phase boundary (MPB), where a crystal system changes abruptly in response to a change in composition, plays an important role in the development of high-performance piezoelectric ceramics.^{1)–7)} In the case of the well-known lead zirconate titanate $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ (PZT) solid-solution system, the tetragonal distortion originating from PbTiO_3 (PT) decreases with increasing Zr content, and an MPB between the tetragonal and the rhombohedral phases appears at a Zr content of $x \approx 0.48$.^{1),2)} The dielectric permittivity, piezoelectric constant, and electro-mechanical coupling factor of PZT are maximal at this composition.^{1),2)} Because the piezoelectric properties of PZT ceramics can be tailored by adjusting their Zr content x , by doping acceptor/donor ions into their lattice, and by forming ternary solid-solutions with another perovskite, PZT-based piezoelectric ceramics have been used in a wide variety of devices, including actuators, sensors, and ultrasonic transducers.⁸⁾ However, the toxicity of lead has been poses a serious problem, necessitating the development of alternative lead-free piezoelectric materials.

Bismuth-based perovskite compounds, represented by bismuth sodium titanate $(\text{Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_3$ (BNT), are regarded as good candidates for lead-free piezoelectric materials because of the similar electronic configurations of Bi^{3+} and Pb^{2+} ions.⁹⁾ Among these compounds, bismuth potassium titanate $(\text{Bi}_{1/2}\text{K}_{1/2})\text{TiO}_3$ (BKT), a structural analog of BNT, has recently been attracting increasing attention because, like PT, it has a tetragonal symmetry at room temperature.^{10)–15)} Although the ferroelectricity of BKT was first reported over 50 years ago,¹⁶⁾ its basic properties remained unexplored for many years because BKT is difficult to sinter as a consequence of its low melting point ($\sim 1070^\circ\text{C}$) and the high volatility of Bi and K.¹¹⁾ Hiruma et al. prepared dense BKT ceramics via a hot-pressing technique using a Bi_2O_3 additive as a sintering aid.¹⁰⁾ Recently, we developed a process

for fabricating dense BKT ceramics via the normal sintering of hydrothermally derived BKT fine powders.¹⁷⁾ Electrical measurements of these high-quality BKT ceramics revealed that they possess a high depolarization temperature of approximately 300°C and a high piezoelectric constant d_{33} of approximately 100 pC/N,^{10),13),14)} suggesting that BKT-based ceramics are highly promising materials for piezoelectric applications.

By analogy with the PZT system, it is expected that the substitution of Zr^{4+} ions for Ti^{4+} ions may further improve the ferroelectric and piezoelectric properties of BKT. Bengagi et al. attempted to fabricate Zr-substituted BKT [i.e., $(\text{Bi}_{1/2}\text{K}_{1/2})(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$, denoted as BKZT hereafter] ceramics via a conventional solid-state reaction and found that the products included two perovskite phases with different Zr/Ti ratios even after extended thermal annealing as long as 100 h.¹⁸⁾ In another study, Liu et al. reported the preparation of single-phase BKZT powders via a solid-state reaction involving a similar long calcination time.¹⁹⁾ However, in their case, a large excess of K_2CO_3 was added to the samples to compensate for the evaporation of K_2O during the prolonged calcination. Such a large excess of K makes adjusting the composition of the final product to the stoichiometric composition difficult and may lead to a degradation of the electrical insulation properties of BKZT ceramics, similar to the effect reported for BKT.¹⁵⁾ In contrast to solid-state reactions, solution processes enable ionic-level mixing of the constituent cations at low temperatures. Thus, we can reasonably expect solution processes to be effective for preparing single-phase BKZT.

Herein, we report a route for synthesizing BKZT powders via a hydrothermal reaction. The single-phase BKZT powders with a particle size less than 300 nm were obtained in the composition range $0.00 \leq x \leq 0.10$. The influence of Zr content on the crystal structure and morphology of the BKZT particles is investigated.

2. Experimental procedure

In this study, we examined two synthesis routes using two different of Zr and Ti sources to obtain single-phase BKZT. In the first procedure, oxide powders of ZrO_2 and TiO_2 were used in

[†] Corresponding author: M. Hagiwara; E-mail: hagiwara@apple.keio.ac.jp

[‡] Preface for this article: DOI <http://doi.org/10.2109/jcersj2.125.P6-1>

accordance with our previously reported method for synthesizing BKT powder.¹⁷⁾ Various molar ratios of ZrO_2 (99.8%, Daiichi Kigenso Kagaku Kogyo Co., Ltd.) and anatase TiO_2 (99.9%, Toho Titanium Co., Ltd.) were weighed out such that the combined amount of these oxides was 15.0 mmol; the powders were subsequently dispersed in 10 mL of deionized water together with 1.95 g (7.50 mmol) of $\text{Bi}(\text{OH})_3$ (99.9%, Kojundo Chemical Laboratory Co., Ltd.). Fifty milliliters of 14.4 mol/L KOH aqueous solution was added, and the resulting mixture was stirred for 10 min in an ultrasonic bath at room temperature. The resulting white-yellow suspension was placed into a Teflon-lined autoclave that was subsequently heated to 160°C, immediately cooled to 110°C, and then maintained at 110°C for 6 h under stirring at 400 rpm. After the hydrothermal reaction, the autoclave was allowed to naturally cool to room temperature. The product powders were first collected by filtration, ultrasonically treated in 120 mL of ethanol for 30 min to remove the residual KOH, and then collected again by centrifugation (10000 rpm for 10 min). The final products were dried at 60°C overnight.

In the other procedure, alkoxides of Zr and Ti were used as starting materials. Various molar ratios of zirconium propoxide ($\text{Zr}[\text{OCH}_2\text{CH}_2\text{CH}_3]_4$, 70 wt.% 1-propanol solution, Sigma-Aldrich) and titanium isopropoxide ($\text{Ti}[\text{OCH}_2(\text{CH}_3)_2]_4$, 97.0%, Sigma-Aldrich) with a total amount of 15.0 mmol were dissolved together in 5 mL of ethanol and mixed well; the resulting solution was added dropwise to 20 mL of deionized water to form a white suspension of amorphous hydrous oxide $(\text{Zr}_x\text{Ti}_{1-x})\text{O}_2 \cdot n\text{H}_2\text{O}$. The $(\text{Zr}_x\text{Ti}_{1-x})\text{O}_2 \cdot n\text{H}_2\text{O}$ suspension was added with 39.0 g (0.72 mol) of KOH and 20 mL of deionized water. Then 1.95 g (7.50 mmol) of $\text{Bi}(\text{OH})_3$ dispersed in 10 mL of deionized water was added to the mixture in an ultrasonic bath, and the resulting mixture was further stirred for 10 min at room temperature to achieve the complete dissolution of KOH. The mixture was then separated into an aqueous lower layer dispersing the powders and an alcoholic clear upper layer due to the salting-out effect. After the upper layer was removed, deionized water was added to adjust the total volume to approximately 60 mL. The suspension was hydrothermally treated, and the product was collected in the same manner described for the first sample.

Phase determination of the powder samples was performed by X-ray diffraction (XRD) using an X-ray diffractometer (D8-02, Bruker AXS) equipped with a $\text{CuK}\alpha$ radiation source. The morphology and microstructure of the samples were observed by a field-emission scanning electron microscopy (FE-SEM; JSM-7600F, JEOL). The composition of the samples was measured using an X-ray fluorescence (XRF) spectrometer (XGT-2700, Horiba). For the XRF measurements, we used another BKT powder synthesized by solid-state reaction¹⁵⁾ as a reference sample.

3. Results and discussion

Figure 1 shows the XRD patterns for the powders synthesized using TiO_2 and ZrO_2 oxide powders with compositions $x = 0.00$ (i.e., without ZrO_2) and 0.10. All the peaks observed in the diffraction pattern for $x = 0.00$ can be indexed to the tetragonal perovskite structure of BKT, consistent with our previous report.¹⁷⁾ However, the pattern of the sample with $x = 0.10$ shows an additional peak attributed to ZrO_2 . The position of the perovskite (111) peak is identical for both of the samples despite the large difference between the ionic radii of Zr^{4+} and Ti^{4+} (60.5 and 72 pm, respectively, for 6-fold coordination²⁰⁾). The identical peak position indicates that the hydrothermal reaction using ZrO_2 and TiO_2 provides not single-phase BKZT but a mixture of BKT and unreacted ZrO_2 .

Fig. 1. (a) XRD patterns of the products prepared from crystalline TiO_2 and ZrO_2 powders, with nominal compositions of $x = 0.00$ and 0.10, and (b) magnified images of these profiles around the (111) diffraction peak.

Fig. 2. (a) XRD patterns of the products prepared from amorphous hydrous oxides $(\text{Zr}_x\text{Ti}_{1-x})\text{O}_2 \cdot n\text{H}_2\text{O}$ precursors with nominal compositions $x = 0.00, 0.02, 0.04, 0.06, 0.08, 0.10$, and 0.15; and (b) magnified images of these profiles around the (111) diffraction peak.

In the hydrothermal synthesis of pure BKT using TiO_2 , TiO_2 partially dissolves as $\text{Ti}(\text{OH})_4^0$ and reacts with dissolved species of $\text{Bi}(\text{OH})_4^-$ and K^+ to form BKT.¹⁷⁾ This reaction likely occurs immediately after the partial dissolution of TiO_2 because of the high concentrations of $\text{Bi}(\text{OH})_4^-$ and K^+ . In the present system, which includes both ZrO_2 and TiO_2 , ZrO_2 should be also partially dissolved into the solution during the hydrothermal treatment because its solubility under highly alkaline conditions is greater than that of anatase TiO_2 (10^{-5} mol/L for ZrO_2 ²¹⁾ and 10^{-7} mol/L for anatase TiO_2 ¹⁷⁾ at pH 14 and 25°C). Nevertheless, the formation of BKZT was not observed in this study, likely because the nucleation of BKT around TiO_2 was much faster than the diffusion of dissolved ions of Ti and Zr into the bulk of the solution. Zr ions consequently remained unreacted and subsequently reprecipitated as ZrO_2 during cooling to provide the mixture of BKT and ZrO_2 . A possible way to facilitate the mixing of Zr and Ti ions is to increase the reaction temperature. However, a reaction at higher temperatures would lead to the formation of a fibrous secondary phase with a Ti-rich composition.¹⁷⁾ For this reason, obtaining single-phase BKZT powders via the hydrothermal reaction using ZrO_2 and TiO_2 powders as Zr and Ti sources is difficult.

Figure 2 shows the XRD patterns for the powders with the nominal composition of $0.00 \leq x \leq 0.15$ synthesized via the hydrothermal reactions using amorphous $(\text{Zr}_x\text{Ti}_{1-x})\text{O}_2 \cdot n\text{H}_2\text{O}$ prepared from the Ti and Zr alkoxides. The patterns of sample

Fig. 3. Relationship between the nominal and measured Zr contents of the BKZT powders prepared from amorphous hydrous oxides $(\text{Zr}_x\text{Ti}_{1-x})\text{O}_2 \cdot n\text{H}_2\text{O}$ precursors. The error bar represents the standard deviation of results measured at five different points in each sample.

without Zr ($x = 0.00$) shows diffraction peaks attributed only to the tetragonal perovskite phase, similar to the pattern of the BKT prepared using TiO_2 . All the peaks observed for the samples with the composition x up to 0.10 can also be indexed to the tetragonal perovskite phase. The position of the perovskite (111) peak in the patterns of the samples of $0.00 \leq x \leq 0.10$ clearly shifted toward lower angles with increasing Zr content, indicating the partial substitution of the larger Zr^{4+} ions for the smaller Ti^{4+} ions in the perovskite lattice. This result indicates that homogeneous mixing of Zr and Ti before the hydrothermal treatment is critically important for obtaining single-phase BKZT powders. We also found that all of the as-synthesized BKZT powders exhibited a substantial tetragonal lattice distortion, as indicated by the tetragonality c/a of approximately 1.05, which is much larger than that reported for BKT synthesized via solid-state reaction. This greater tetragonal distortion of the BKZT powders is attributed to their large concentration of lattice hydroxyl groups, which are believed to align along the c axis.²²⁾ The crystal structure after these hydroxyl groups were eliminated by a heat treatment are presented later in this paper. In contrast to the patterns of samples with low Zr contents, the patterns of the sample with $x = 0.15$ shows additional peaks from Bi_2O_3 and ZrO_2 . This is because the high Zr concentration in the $(\text{Zr}_x\text{Ti}_{1-x})\text{O}_2 \cdot n\text{H}_2\text{O}$ precursor leads to the crystallization of ZrO_2 prior to the formation of the perovskite phase during the hydrothermal treatment. After the crystalline ZrO_2 is formed, it is not involved in the formation reaction of the perovskite, as previously discussed. During cooling after the hydrothermal treatment, the residual Bi source precipitates as the crystalline Bi_2O_3 phase, resulting in the formation of the mixture of the perovskite, ZrO_2 and Bi_2O_3 as the final product.

The chemical composition and the morphology of the samples prepared from $(\text{Zr}_x\text{Ti}_{1-x})\text{O}_2 \cdot n\text{H}_2\text{O}$ ($0.00 \leq x \leq 0.10$) were examined by XRF and FE-SEM, respectively. The variation of the measured Zr content is plotted against the nominal Zr content x in Fig. 3. The measured Zr content increases linearly with increasing x , demonstrating the substitution of Zr^{4+} for Ti^{4+} . In addition, the measured Zr content is larger than the nominal content for all of the investigated x values, although the reason for this phenomenon is unclear at this time. The FE-SEM images of these samples are shown in Fig. 4. The sample without Zr substitution ($x = 0.00$) is composed of small particles with a diameter of approximately 100 nm and with a rounded cubic shape. This particle size is slightly smaller than that of the BKT particles prepared by the

Fig. 4. FE-SEM images of the BKZT powders prepared from amorphous hydrous oxides $(\text{Zr}_x\text{Ti}_{1-x})\text{O}_2 \cdot n\text{H}_2\text{O}$ precursors with various nominal compositions x ; (a) 0.00, (b) 0.02, (c) 0.04, (d) 0.06, (e) 0.08, and (f) 0.10.

hydrothermal reaction using TiO_2 powder as the Ti source (~ 150 nm).¹⁷⁾ With increasing Zr content, the size of the particles tends to increase and their cubic shape becomes evident. Consequently, relatively large 300-nm cubic particles with well-defined crystal facets are observed in the samples with $x = 0.08$ and 0.10. The observed composition dependence of the particle size and morphology of the BKZT powders is attributed to the change in the degree of supersaturation under the hydrothermal conditions. In general, crystal nucleation from the solution is much faster than crystal growth under a high-supersaturation condition, yielding small particles; by contrast, the crystal growth becomes predominant under a low-supersaturation condition. In the present case, the high reactivity of $\text{TiO}_2 \cdot n\text{H}_2\text{O}$ ($x = 0.00$) compared to that of the crystalline TiO_2 leads to its rapid dissolution and to a sudden increase of the degree of supersaturation of the perovskite phase, resulting in the formation of small BKT particles. The reactivity of $(\text{Zr}_x\text{Ti}_{1-x})\text{O}_2 \cdot n\text{H}_2\text{O}$ might decrease upon the incorporation of Zr ions, leading to the decrease in the degree of supersaturation and to the enhanced crystal growth. As a result, larger cubic particles are obtained for the BKZT samples with high Zr contents.

Even a slight deviation in chemical composition of BKT from its stoichiometric formula is known to cause the formation of K-rich or Bi-rich secondary phases during high-temperature heat treatment or sintering.^{11),15),17)} The lattice hydroxyl groups in the hydrothermal BKT particle have also been shown to be removed by heat treatment at temperatures greater than 800°C, leading to a drastic change of the lattice parameters.²²⁾ Thus, to investigate the impact of a heat treatment on the phase purity and the crystal structure of the BKZT powders synthesized from $(\text{Zr}_x\text{Ti}_{1-x})\text{O}_2 \cdot n\text{H}_2\text{O}$ ($0.00 \leq x \leq 0.10$), samples were heated at 1000°C for 1 h. No significant change in the particle size and morphology was observed for all of the samples after the heat treatment. The XRD profiles of the heat-treated BKZT powders are shown in Figs. 5(a) and 5(b). No secondary phase appeared in any of the sample after the heat treatment, indicating that these samples have almost stoichiometric compositions [i.e., $\text{Bi}:\text{K}:(\text{Ti} + \text{Zr}) = 1:1:2$]. If a heat-treated sample includes two perovskite phases with different Zr/Ti ratios as reported for the solid-state synthesis, a strong split of the (111) peak in its XRD pattern should be observed.¹⁸⁾ However, none of the (111) peaks for the various compositions are split. Moreover, with increasing Zr content, these peaks obviously shift toward lower angles, as observed in the case of the as-synthesized samples; accordingly, the unit-cell volume monotonically increases, as shown in Fig. 5(c). These observations confirm that the chemical homogeneity of Zr^{4+} and

Fig. 5. (a) XRD patterns of the heat-treated BKZT powders with the nominal compositions $x = 0.00, 0.02, 0.04, 0.06, 0.08$, and 0.10 ; (b) magnified images of these profiles around the (111) diffraction peak; and (c) the unit-cell volume as a function of the measured Zr content.

Ti^{4+} ions was maintained during the heat treatment. We also found that the tetragonal lattice distortion was drastically decreased by the heat treatment because of the elimination of the lattice hydroxyl groups. No obvious splitting of ($h00$) and ($00l$) peaks due to tetragonal symmetry is observed, not even in the sample with $x = 0.00$ (BKT), which should exhibit a large c/a of 1.02. The lack of obvious tetragonal distortion is due to the size effect on the crystal lattice, where c/a of perovskite ferroelectrics such as BaTiO_3 , PT, and BKT decreases in submicron-sized small particles or grains.^{13,23–26} Thus, to reveal the intrinsic effect of Zr substitution on the lattice parameters and the crystal system of BKZT, ceramic samples composed of large grains are required. We are currently attempting to prepare coarse-grained BKZT ceramics by sintering the hydrothermal BKZT powders synthesized in this study.

4. Conclusions

Single-phase BKZT powders ($0.00 \leq x \leq 0.10$) were successfully obtained by a hydrothermal reaction method. The source of Zr and Ti used in the hydrothermal reaction was found to be critically important for obtaining single-phase BKZT. The reaction using amorphous hydrous oxide $(\text{Zr}_x\text{Ti}_{1-x})\text{O}_2 \cdot n\text{H}_2\text{O}$ provided the single-phase BKZT, whereas that using the mixture of ZrO_2 and TiO_2 powders resulted in the formation of a mixture of BKT and ZrO_2 . The BKZT powders obtained by this method had

a small particle size less than 300 nm and good phase stability against the high-temperature heat treatment. To investigate the effect of Zr substitution on the crystal structure and piezoelectric properties, we are currently developing a method to sinter BKZT powders into dense ceramics.

Acknowledgement This work was supported by a Grant-in-Aid for Young Scientists (B) (No.16K18241) from the Japan Society for the Promotion of Science (JSPS).

References

- 1) B. Jaffe, W. R. Cook and H. Jaffe, "Piezoelectric Ceramics", Academic, London (1971) pp. 135–183.
- 2) B. Jaffe, *J. Appl. Phys.*, **25**, 809–810 (1954).
- 3) T. Takenaka, K. Maruyama and K. Sakata, *Jpn. J. Appl. Phys.*, **30**, 2236–2239 (1991).
- 4) R. E. Eitel, C. A. Randall, T. R. Shrout, P. W. Rehrig, W. Hackenberger and S.-E. Park, *Jpn. J. Appl. Phys.*, **40**, 5999–6002 (2001).
- 5) Y. Saito, H. Takao, T. Tani, T. Nonoyama, K. Takatori, T. Homma, T. Nagaya and M. Nakamura, *Nature*, **432**, 84–87 (2004).
- 6) W. Liu and X. Ren, *Phys. Rev. Lett.*, **103**, 257602 (2009).
- 7) D. Damjanovic, *Appl. Phys. Lett.*, **97**, 062906 (2010).
- 8) G. H. Haertling, *J. Am. Ceram. Soc.*, **82**, 797–818 (1999).
- 9) J. Rödel, W. Jo, K. T. P. Seifert, E. M. Anton, T. Granzow and D. Damjanovic, *J. Am. Ceram. Soc.*, **92**, 1153–1177 (2009).
- 10) Y. Hiruma, R. Aoyagi, H. Nagata and T. Takenaka, *Jpn. J. Appl. Phys.*, **44**, 5040–5044 (2005).
- 11) J. König, M. Spreitzer, B. Jančar, D. Suvorov, Z. Samardžija and A. Popović, *J. Eur. Ceram. Soc.*, **29**, 1695–1701 (2009).
- 12) M. Otoničar, S. D. Škapin, B. Jančar, R. Ubič and D. Suvorov, *J. Am. Ceram. Soc.*, **93**, 4168–4173 (2010).
- 13) M. Hagiwara and S. Fujihara, *Appl. Phys. Lett.*, **107**, 012903 (2015).
- 14) M. Hagiwara and S. Fujihara, *Jpn. J. Appl. Phys.*, **54**, 10ND10 (2015).
- 15) J. König and D. Suvorov, *J. Eur. Ceram. Soc.*, **35**, 2791–2799 (2015).
- 16) C. F. Bührer, *J. Chem. Phys.*, **36**, 798–803 (1962).
- 17) M. Hagiwara and S. Fujihara, *J. Mater. Sci.*, **50**, 5970–5977 (2015).
- 18) M. Bengagi, F. Morini, M. E. Maaoui and P. Marchet, *Phys. Status Solidi*, **209**, 2063–2072 (2012).
- 19) S. Liu, P. E. R. Blanchard, Z. Zhang, B. J. Kennedy and C. D. Ling, *Dalton Trans.*, **44**, 10681–10688 (2015).
- 20) R. D. Shannon, *Acta Crystallogr., Sect. A: Cryst. Phys., Diff., Theor. Gen. Crystallogr.*, **32**, 751–767 (1976).
- 21) R. P. Denkewicz, K. S. TenHuisen and J. H. Adair, *J. Mater. Res.*, **5**, 2698–2705 (1990).
- 22) M. Hagiwara, M. Ito and S. Fujihara, *J. Asian Ceram. Sci.*, **5**, 31–35 (2017).
- 23) M. Frey and D. Payne, *Phys. Rev. B*, **54**, 3158–3168 (1996).
- 24) Z. Zhao, V. Buscaglia, M. Viviani, M. T. Buscaglia, L. Mitoseriu, A. Testino, M. Nygren, M. Johnsson and P. Nanni, *Phys. Rev. B*, **70**, 024107 (2004).
- 25) W. L. Zhong, B. Jiang, P. L. Zhang, J. M. Ma, H. M. Cheng and Z. H. Yang, *J. Phys.: Condens. Matter*, **5**, 2619–2624 (1993).
- 26) Y. Hiruma, H. Nagata and T. Takenaka, *Jpn. J. Appl. Phys.*, **46**, 1081–1084 (2007).