Large strain actuation in barium titanate single crystals under stress and electric field

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Abstract: Large strain actuation in barium titanate ($BaTiO_3$) single crystals subjected to combined uniaxial stress and electric field is examined. A maximum strain of about 0.45% is measured under a combined loading of 2.7 MPa compressive stress and ±1.25 MVm^{-1} cyclic electric field. Above 2.7 MPa, the crystal does not cycle fully between the in-plane and out-of-plane polarized states due to large compressive stress, and consequently, a considerable reduction in actuation strain is apparent. The hysteresis evolution of the crystal under combined electromechanical loading reveals incomplete switching characteristics and a considerable disproportion of slope gradients at zero electric field for the measured polarization and strain hysteresis curves. A likely cause for the disproportion of slope gradients is the cooperative operation of multiple 90° switching systems by which "polarization-free" strain changes are induced.

Keywords: $BaTiO_3$, domain switching, electromechanical loading, hysteresis, single crystals.

1 Introduction

Among all ferroelectric materials, single crystal ferroelectrics have received extensive attentions recently due to their ability to provide a high degree of polarization domain alignment with electrical poling, which could in turn give rise to superb piezoelectric characteristics. Various attempts have been carried out to develop large strain actuation in ferroelectric single crystals either via phase transition or via domain switching [1-3]. Park and Shrout [1] introduced a single crystal relaxor ferroelectric PZN-PT (a solid solution of lead zirconate niobate and lead titanate) which possesses an electrostrictive strain up to 1.7% with very little hysteresis. Ren [2] demonstrated that the symmetry conforming property of point defects can give rise to large electrostrains (up to 0.75% at 0.2 MVm^{-1}) in thermally aged barium titanate ($BaTiO_3$) single crystals. Burcsu *et al*. [3] examined the 90°-switching-induced strain of $BaTiO_3$ single crystals under combined electrical and mechanical loadings. Large strain changes in ferroelectric crystals caused by domain switching are typically induced through angles other than 180° [4,5]. It is therefore essential to investigate factors which might influence the "effectiveness" of non-180° switchings. By doing so, the achievable strain by an electromechanical loading could potentially be gauged accurately. In the present study, the switching characteristics of $BaTiO_3$ single crystals are investigated. This is achieved through examining their hystereses in the electric polarization (*P*) vs. electric field (*E*) and strain (e) vs. electric field (*E*) responses. The effect of constant bias stress on the hysteresis behavior is also examined. $BaTiO_3$ single crystals are chosen for this study because they are readily available at a reasonable cost.

2 Experimental procedure

A series of polarization and strain hysteresis measurements under combined uniaxial electrical and mechanical loadings were performed on unpoled (001)-oriented cuboidal $BaTiO_3$ single crystals measuring $5 \times 5 \times 2$ mm^3. The crystals were obtained from MTI Co., CA, USA. Conductive silver paints were used to produce electrodes on the 5×5 mm^2 surfaces. A loading fixture shown in Fig. 1 was developed for the simultaneous application of uniaxial compressive stress and electric field. The loading fixture consisted of brass plates, providing electrical contact to the electrode surfaces of the crystal, and nylon spacers to insulate the crystal from the mechanical load frame. The upper brass plate was connected to ground via a ferroelectric analyzer (Model TF2000, aixACCT, Germany) for charge measurement. The lower brass plate was connected to a high voltage amplifier (Model 20/20C, Trek, USA) which supplied the electrical loading (±1.25 MVm^{-1} at 0.2 Hz; sinusoidal waveform). Mechanical loading (stress up to 4.0 MPa) was applied using a universal test frame (Model HT-9102, Hung-Ta, Taiwan). Miniature strain gauges (Model FBX-04-11-005LE, TML, Japan) were attached onto the 5×2 mm^2 faces of the crystal to measure strain changes in the loading

direction. A thin coat of epoxy resin was applied to the exposed surface of the strain gauges to afford extra insulation against electrical breakdown. The entire loading fixture was supported in a silicon oil bath to prevent breakdown arcing, and all tests were carried out at temperatures in the range of 20-25°C.
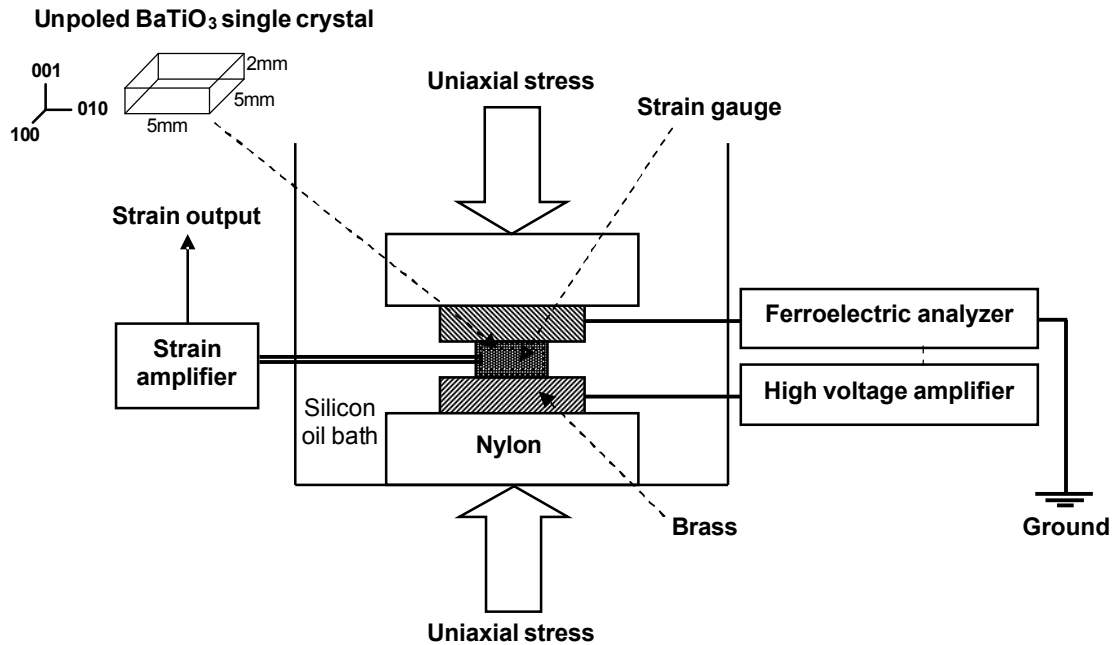

FIG. 1. Schematic of the combined uniaxial electromechanical loading apparatus.

3 Measurements and discussion

3.1 Hysteresis behaviors

Figures 2a and 2b show the stable P-E and e-E hysteresis curves for the $5 \times 5 \times 2$ mm^3 unpoled (001)-oriented BaTiO$_3$ single crystal measured at various compressive stresses ranging from 0 to 4.0 MPa. The applied cyclic electric field has a frequency of 0.2 Hz and an amplitude of ±1.25 MVm^{-1}. At zero compressive stress, the crystal exhibits a remanent polarization (P_r) of 21.0 µCcm^{-2}, a coercive field (E_c) of 0.35 MVm^{-1}, and a total electrostrain ($e_{33,total}$) of about 0.14% in the 33-direction. It is evident from Fig. 2b that with increasing compressive stress, $e_{33,total}$ increases significantly and eventually reaches a maximum value of 0.45% at 2.7 MPa. As the compressive stress increases to levels higher than 2.7 MPa, $e_{33,total}$ is quickly reduced and the classic butterfly-shaped strain hysteresis becomes squashed and broadened. This hysteresis behavior suggests that at stresses higher than 2.7 MPa, polarization switching is happened over a wider range of electric field and high strain actuation is harder to achieve even with an applied electric field much higher than the coercive field. A similar trend to $e_{33,total}$ is also observed for the apparent piezoelectric coefficient (d_{33}), obtained from the slope gradient of the strain hysteresis curve at zero electric field. A maximum apparent d_{33} value of 6700 pCN^{-1} is measured at 2.7 MPa of compressive stress. Further increase of stress leads to a gradual decrease in the apparent d_{33}.

The corresponding P-E hystereses shown in Fig. 2a also display stress-dependent characteristics. At zero or low stress levels ($\leq$ 1.7 MPa), a P_r of about 21.0 µCcm^{-2} is measured, which is lower than the theoretical spontaneous polarization value of 26.0 µCcm^{-2} for BaTiO$_3$ [4,6]. This is most likely to be caused by the incomplete switching of polarization during the loading cycle. In other words, the unpoled $5 \times 5 \times 2$ mm^3 BaTiO$_3$ single crystal tested in the present study is unable to produce one single polarization domain at 1.25 MVm^{-1}. This inability is also evident from the relatively large measured E_c value (0.35 MVm^{-1}), and from the considerable deviation of the P-E hysteresis from the classic boxy rectangular shape typically expected for single crystal ferroelectrics. It is evident from Fig.

2a that as the compressive stress is increased above 1.7 MPa, the corners of the *P-E* hysteresis become rounded, both the saturation polarization (P_{sat}) and P_r start to decrease, and switching is completed over a wider range of electric field. The measured P_r value at 4.0 MPa is approximately 15% smaller than the P_r value at zero stress.
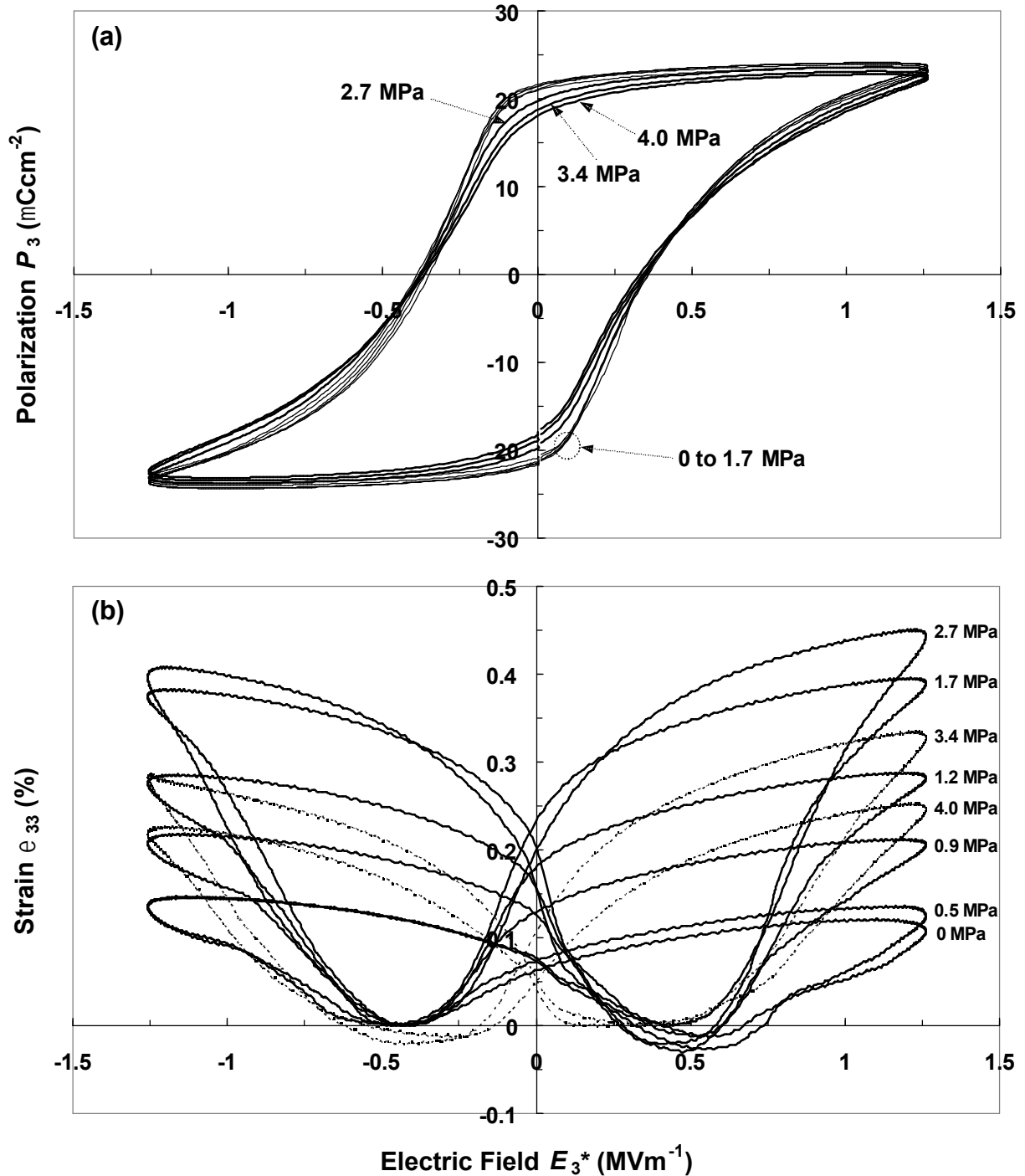

FIG. 2. Measured (a) polarization vs. electric field and (b) strain vs. electric field hysteresis curves for unpoled (001)-oriented BaTiO$_3$ single crystal at various constant compressive stresses.

As mentioned in Section 1, large strain changes in ferroelectric crystals caused by domain switching are typically induced through angles other than 180° [4,5]. At zero compressive stress, the BaTiO$_3$

single crystal cycles between the two out-of-plane polarized states (i.e., 180° domains perpendicular to the top and bottom electrodes) by going rapidly through the in-plane polarized state (i.e., a domain parallel to the electrodes) "sandwiched" in between the two out-of-plane states. Therefore, there is little strain detected at zero compressive stress, and hence the relatively flat e-E hysteresis curve. As the compressive stress is increased, the loading path begins to go through the in-plane 90° polarized state at a slower rate. This is because that the 90° domain state is enhanced through the means of ferroelastic switching (i.e., stress-activated switching). Consequently, the actuation strain rises due to the development of 90° switching. The amount of actuation strain continues to increase with increasing stress and reaches its peak value at 2.7 MPa. Above this stress level, the domains do not cycle fully between the in-plane and out-of-plane polarized states due to large compressive stress. At this point, the crystal experiences a large physical constraint and therefore a considerable reduction in actuation strain is apparent; e.g., at 4.0 MPa, $e_{33,total}$ decreases to about 0.25% only. At large compressive stresses, the incomplete (partial) polarization switching to the out-of-plane polarized states also causes a decrease in both P_{sat} and P_r, as clearly shown in Fig. 2a.

3.2 Multiple 90° switching systems

An important discovery is made after carefully examining the hysteresis data shown in Fig. 2 – a significant disproportion of slope gradients at zero electric field for the measured polarization and strain hysteresis curves is apparent, especially at high compressive stresses. Here, the phrase "disproportion of slope gradients" means that the two quantities defined by the rate of change of polarization with respect to electric field and the rate of change of strain with respect to electric field do not remain in a constant ratio. The discovered disproportion characteristic would imply a "decoupling" between switching strain and switching polarization within the BaTiO$_3$ single crystals. This seems to be in contradiction to the common understanding of ferroelectrics that switching-induced strain is accompanied by changes in polarization [4,5]. Although adopting a totally different loading setup, the hystereses measured by Burcsu et al. [3] also display a severe disproportion of slope gradients at zero electric field; see Fig. 3 for Burcsu et al's hysteresis measurements at stresses of 1.07 and 1.78 MPa.
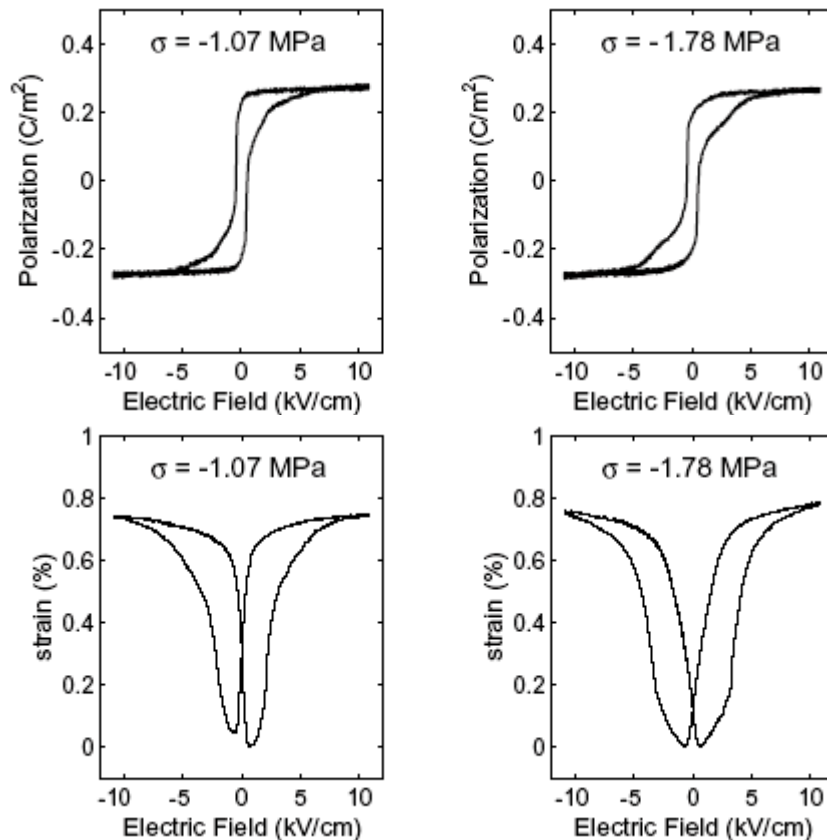
FIG. 3. Burcsu *et al*'s hysteresis measurements at compressive stresses of 1.07 and 1.78 MPa [3].

Theoretically, the maximum possible variations in polarization and strain through 90° switching for the BaTiO$_3$ single crystal, allowed by crystallography, are P_s = 26.0 µCcm^{-2} and e_{max} = 0.011, respectively [6-8]. The percentages of polarization and strain changes from maximum to zero electric field at selected stress levels for the BaTiO$_3$ crystal tested in the present study and Burcsu *et al*'s BaTiO$_3$ crystal [3] are calculated and listed in Table 1. Stress-activated 90° switching typically gives rise to a change in both strain and polarization. However, Figs. 2 and 3 and Table 1 suggest that at high stresses, a sizeable change in strain during electric field unloading is accompanied by a relatively small change in polarization. To exhibit such a behavior, multiple 90° switching systems must exist and operate together in the crystal in such a way that "polarization-free" strain changes are produced. Theoretically this is possible if one considers that a 90° switching of an out-of-plane 180° domain wall into an in-plane 180° domain wall produces no change in polarization. The polarization hystereses shown in Fig. 2a do not have the classic boxy rectangular shape typically expected for BaTiO$_3$ single crystals. Furthermore, they exhibit high coercivity and lower saturation level than the theoretical value. These are strong indications that the single crystal used in the present study possesses hardening and depolarization characteristics and that switching is incomplete at maximum electric field, possibly leaving some domains with 180° relative orientation. Such an arrangement of domains, if it exists at maximum electric field, would be the prerequisite for subsequent multiple stress-assisted 90° switches during electric field unloading where the overall change in polarization is near zero.

TABLE 1. Polarization and strain changes (in percentages) from maximum to zero electric field at selected stress levels for the BaTiO$_3$ single crystal tested in the present study and Burcsu *et al*'s BaTiO$_3$ single crystal [3].

BaTiO$_3$ crystal	Compressive stress S_{33}^{*} (MPa)	$\dfrac{\left\| P_3^{E=0} - P_3^{E_{max}} \right\|}{P_s} \times 100\%$	$\dfrac{\left\| \text{e}_{33}^{E=0} - \text{e}_{33}^{E_{max}} \right\|}{\text{e}_{max}} \times 100\%$
Present study	2.7	16.04	25.54
	1.7	10.27	15.28
Burcsu *et al*.	1.78	24.23	61.10
	1.07	8.92	43.16

A simple calculation is conducted to verify the above argument. Let C_1 and C_2 denote, respectively, the volume fraction of out-of-plane domains oriented in a direction identical to the applied electric field and in a direction parallel but opposite to the applied electric field. The volume fraction of in-plane domains is therefore equal to $(1 - C_1 - C_2)$. In terms of C_1 and C_2, the polarization and actuation strain in the loading direction are $\langle P_3 \rangle = P_s(C_1 - C_2)$ and $\langle \text{e}_{33} \rangle = \text{e}_{max}(1 - C_1 - C_2)$, respectively, where $\langle \cdots \rangle$ denotes the volume average. At 2.7 MPa and maximum electric field, the crystal tested in the present study exhibits a polarization value of 23.5 µCcm^{-2} (see Fig. 2a) which is about 90% of the theoretical maximum value. At this stage of loading, if only out-of-plane 180° domains exist in the crystal, the relationships between C_1 and C_2 can be stated as $C_1 + C_2 = 1$ and $C_1 - C_2 = 0.9$. Hence, $C_1 = 0.95$ and $C_2 = 0.05$ can be derived. Assume that 0.05 out of 0.95 C_1-domains and all C_2-domains switch 90° cooperatively to form in-plane 180° domains when the applied electric field decreases from maximum to zero at constant compressive stress; it can then be worked out that the 90° switching of this "cooperative pair" gives rise to zero change in P_3, while a change of magnitude

$e_{max} \times 10\%$ is produced in e_{33}. The above-described calculation indicates a 10% difference in the magnitude of change between polarization and strain during electric field unloading at 2.7 MPa when polarization-free straining is in operation. This estimation is in good agreement with the experimental data which show a 9.5% difference (see Table 1).

4 Conclusions

Strain actuation in BaTiO$_3$ single crystals subjected to combined uniaxial stress and electric field is examined. The enhancement of 90° domain switching by additional compressive stress (i.e., stress-activated ferroelastic switching) results to larger strains. A maximum strain of about 0.45% is measured under a combined loading of 2.7 MPa compressive stress and ±1.25 MVm^{-1} cyclic electric field. The BaTiO$_3$ single crystal used in the present study possesses hardening and depolarization characteristics. Consequently, the observed disproportion of slope gradients at zero electric field for the measured polarization and strain hysteresis curves is likely due to the operation of multiple 90° switching systems. Further investigations based on *in-situ* domain observations throughout the entire electromechanical loading sequence should reveal clearer details.

Acknowledgements

References

[1] S. E. Park and T. R. Shrout, J. Appl. Phys. **82**, 1804 (1997).

[2] X. B. Ren, Nat. Mater. **3**, 91 (2004).

[3] E. Burcsu, G. Ravichandran, and K. Bhattacharya, J. Mech. Phys. Solids **52**, 823 (2004).

[4] F. Jona and G. Shirane, *Ferroelectric Crystals* (Pergamon, New York, 1962).

[5] J. E. Huber, Curr. Opin. Solid State Mater. Sci. **9**, 100 (2005).

[6] S. Wada, S. Suzuki, T. Noma, T. Suzuki, M. Osada, M. Kakihana, S. E. Park, L. E. Cross, and T. R. Shrout, Jpn. J. Appl. Phys., Part 1 **38**, 5505 (1999).

[7] Y. C. Shu and K. Bhattacharya, Philos. Mag. B **81**, 2021 (2001).

[8] D. Liu and J. Y. Li, Appl. Phys. Lett. **83**, 1193 (2003).