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Influence of lead titanate seed layer on orientation behaviour and ferroelectric characteristics of sol–gel derived PZT thin films

Jianming Zeng†, Miao Zhang, Lianwei Wang and Chenglu Lin

National Laboratory of Functional Materials for Informatics, Shanghai Institute of Metallurgy, Chinese Academy of Sciences, 865 Changning Road, 200050 Shanghai, People's Republic of China

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Abstract. Lead zirconate titanate ($Pb(Zr_{0.50}Ti_{0.50})O_3$) thin films with a $PbTiO_3$ seed layer were successfully deposited on platinized silicon substrates by a modified sol–gel processing using a new zirconium source. The $PbTiO_3$ seed layer between the platinum bottom electrode and the PZT films could promote formation of perovskite phase and enhance the crystallinity of the PZT films due to the presence of sufficient nucleation sites. It was observed that the use of the $PbTiO_3$ seed layer resulted in a great improvement in the ferroelectric characteristics and much better surface morphology. The phenomenon of the different orientation behaviour in $PbTiO_3$ seeded and unseeded PZT films was mainly discussed. The x-ray diffraction (XRD) and atom force microscopy (AFM) techniques were selected to investigate the microstructure of the prepared PZT thin films. The ferroelectric properties of the prepared PZT thin films were measured using a modified Sawyer–Tower circuit.

1. Introduction

Ferroelectric thin films with the perovskite crystal structure have been studied intensively for their proposed practical applications in various fields [1, 2]. Ferroelectricity is a directional property in which a reversible spontaneous polarization occurs only in the direction of the polar axis. However, most ferroelectric materials consist of randomly oriented domains that are separated by a domain wall from an adjacent region that shows a different polarization direction [3]. The presence of the randomly oriented domain structure results in energy loss and poor electrical properties. Therefore, to fully utilize the excellent anisotropy-dependent properties of ferroelectrics, it is necessary to carefully control the orientation during processing. Materials with preferred orientation exhibit unique and improved properties, compared with those of randomly oriented structure. Iijima and coworkers [4] demonstrated that oriented ferroelectric thin films show higher polarizations, higher electro-optic coefficients, lower coercive fields, lower dielectric constants and lower optical loss than the randomly oriented films.

Lead zirconium titanate ($Pb(Zr_{1-x}Ti_x)O_3$, PZT) thin film [5–11] has been a potential candidate in fabrication of non-volatile memories, microactuators, infrared detectors and electro-optic devices for its excellent properties such as ferroelectricity, piezoelectricity, pyroelectricity and electro-optic phenomena [12, 13]. Recently, the sol–gel process [14, 15], among the various deposition techniques of ferroelectric thin films, has been investigated

† Addressee for correspondence. Fax: +86-21-62513510. E-mail address: jmzeng@kali.com.cn.

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with great emphasis, because of its many advantages for preparing thin films, for example, relatively low processing temperature, simple process, excellent control of stoichiometry and homogeneous film over large areas. The recent progress in the sol–gel technique has made it possible to prepare a homogeneous PZT thin film on silicon-based substrates such as Pt/Ti/SiO_2/Si and Pt/$SrTiO_3$. However, the elevated temperature in the post-heat-treatment processing causes random orientation and interdiffusion in the PZT films. Such random orientation and interdiffusion deteriorates the formation of perovskite and degrades electric properties of the films. Thus, interest in finding solutions to overcome this difficulty has been increasing. Recent research [16–18] has focused on the use of seed layers that promote the formation of oriented thin films and reduce the annealing temperature of the films which results in suppressing interdiffusion between PZT films and substrates.

In the present work, the orientation behaviour and electrical properties of the sol–gel derived $Pb(Zr_{0.5}Ti_{0.5})O_3$ ferroelectric thin films on platinum-coated silicon substrates with and without a $PbTiO_3$ seed layer were investigated. Meanwhile, a modified sol–gel process was developed to form PZT film with solely a perovskite phase directly from the amorphous phase and completely eliminated the formation of an intermediate phase such as the pyrochlore phase.

2. Experimental procedure

An enhanced sol–gel route for the preparation of PZT thin films and $PbTiO_3$ seed layer is shown in figure 1. Lead acetate trihydrate, $Pb(CH_3COO)_2$; zirconium oxynitrate dihydrate, $ZrO(NO_3)_2 \cdot 2H_2O$; and tetrabutyl titanate, $Ti(C_4H_9O)_4$ were used as starting materials to prepare the spin-coating solutions of $Pb(Zr_{0.5}Ti_{0.5})O_3$ and $PbTiO_3$. The selection of zirconium oxynitrate dihydrate instead of the widely used zirconium alkoxide was aimed at obtaining the moisture-resistant precursor solution and, as expected, resulted in a simple process. The lead acetate trihydrate and zirconium oxynitrate dihydrate were dried by distillation in 2-methoxyethanol at ambient atmosphere, and then cooled to room temperature, before the addition of the $Ti(C_4H_9O)_4$–methoxyethanol solution. During solution preparation, 5 mol% extra $Pb(CH_3COO)_2$ was added. This excess of lead was used to compensate for lead loss during the post annealing process. The Pb–Zr–Ti and Pb–Ti complex solutions were fully mixed, respectively, at room temperature. The solution was diluted with 2-methoxyethanol to form a suitable concentration of the precursor solution. Finally, a suitable volume of additive was added to the solution in order to improve the drying behaviour. The whole sol–gel preparation process of PZT thin films was performed in an ambient atmosphere.

The $PbTiO_3$ seed layers were prepared on bare Pt/Ti/SiO_2/Si wafers by a spin-coating process. These bare (111) platinum-coated silicon substrates were prepared by sputtering $\sim$20 nm of titanium onto oxidized ($\sim$600 nm SiO_2) silicon substrates and then sputtering $\sim$150 nm of platinum. After the $PbTiO_3$ seed layers were baked at 300 °C for 30 min in each spin-on process, and then crystallized with a annealing process at 600 °C for 90 min. As shown in figure 1, the coating solution of PZT films was deposited on to bare Pt/Ti/SiO_2/Si substrates and the $PbTiO_3$ seed layer coated Pt/Ti/SiO_2/Si substrates by spin-coating process at 3000 r.p.m. for 30 s. After each spin coating process, samples were baked directly at 500 °C for 20 min. Because the perovskite phase was expected to form directly from the amorphous phase, the pyrochlore phase formation was eliminated completely when the rapid pyrolysis of PZT gel films was achieved at a relatively high baking temperature. Multiple coatings were performed to obtain the desired film thickness. These PZT films were subsequently converted to crystalline $Pb(Zr_{0.5}Ti_{0.5})O_3$ ferroelectric thin films by post-annealing between 600 °C and 700 °C in an ambient atmosphere.

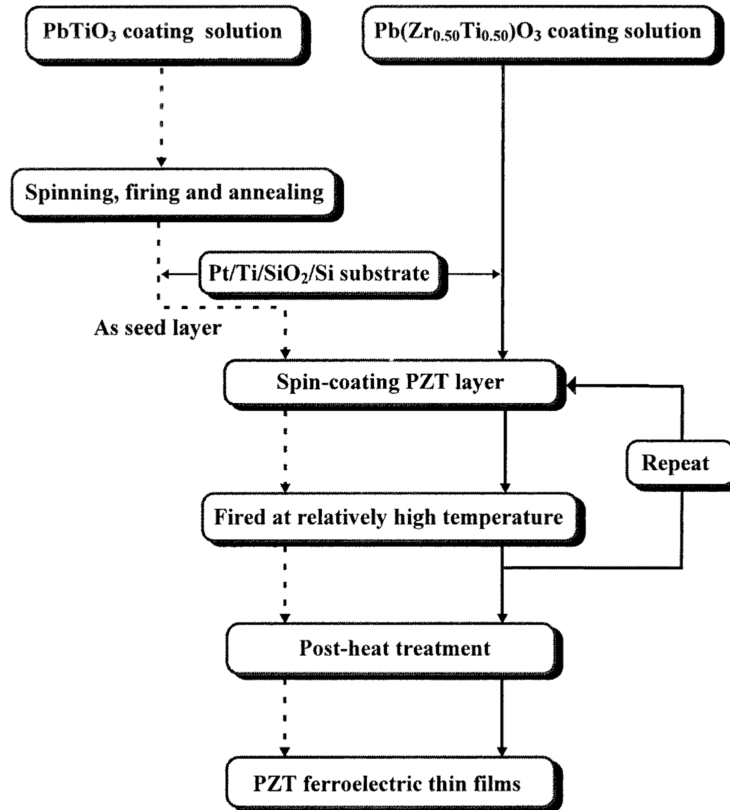

Figure 1. The flow chart of a processing route for the PZT thin films and $PbTiO_3$ seed layer.

Various techniques, including atomic force microscopy (AFM) and x-ray diffraction (XRD), were performed to investigate the surface morphology, crystallization characteristics and orientation behaviour of the PZT films. For the measurement of ferroelectric properties of the prepared PZT thin films, top electrodes of platinum with 0.3 mm diameter were prepared on the PZT films through a shadow mask by the ultra-high vacuum (UHV) evaporation technique. Ferroelectric hysteresis loops were measured at room temperature using a modified Sawyer–Tower circuit at 100 Hz.

3. Results and discussion

X-ray diffraction patterns showed that the $PbTiO_3$ seed layer with a perovskite crystal structure was prepared after a heat treatment at 600 °C for 90 min by a conventional thermal annealing (CTA) process, as shown in figure 2. The fully (100)-textured structure was observed in the $PbTiO_3$ films, and there was no evidence of any other orientations and phases in the films. This result indicated that high quality $PbTiO_3$ seed layers were prepared prior to the deposition of PZT ferroelectric thin films. The appearance of full a-axis orientation in the $PbTiO_3$ films is probably due to an inherent self-orientation tendency in which the plane has the lowest surface energy. In the case of perovskite phase of $PbTiO_3$, (100) is considered to be the lowest surface energy plane [19], that is, the slowest growing plane.

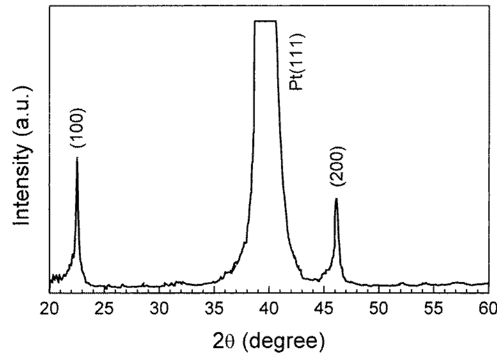

Figure 2. X-ray diffraction patterns of $PbTiO_3$ seed layer deposited on $Pt/Ti/SiO_2/Si$ substrate.

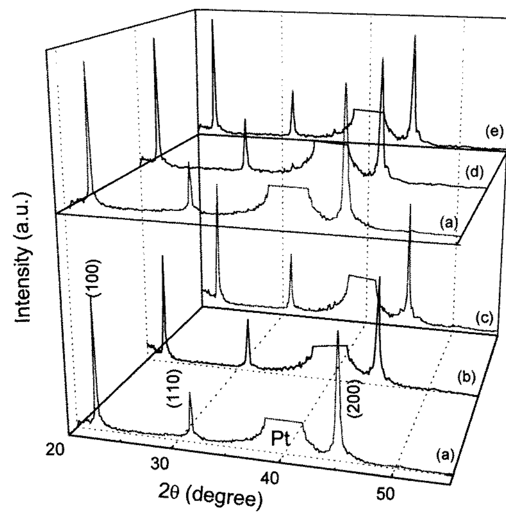

Figure 3. The x-ray diffraction patterns of PZT/PT samples (*a*) as grown; (*b*), (*c*) annealed at 600 and 700 °C for 2 min by an RTA process, respectively; (*d*), (*e*) annealed at 600 and 700 °C for 2 h by a CTA process, respectively.

Figure 3 shows the x-ray diffraction patterns of the PZT films deposited on $PbTiO_3$ seeded $Pt/Ti/SiO_2/Si$ substrates under different post-annealing conditions. The as-grown PZT/PT samples (PZT/PT denotes PZT films which were deposited on $PbTiO_3$ seeded $Pt/Ti/SiO_2/Si$ substrates) just fired at 500 °C had a pure perovskite phase with (100)-preferred orientation. The oxygen-deficient metastable pyrochlore phase was not observed in our films. The PZT/PT samples post-annealed at higher temperature (600–700 °C) by an RTA (rapid thermal annealing) or CTA process had also a (100)-preferred orientation and pure perovskite phase with better crystallinity. This shows that the perovskite PZT/PT samples have been successfully grown directly from the amorphous phase and could completely eliminate the formation of the intermediate phase in the sol–gel processing. The x-ray diffraction patterns of the PZT films prepared on bare $Pt/Ti/SiO_2/Si$ substrates (PZT/Pt samples) are shown in figure 4. It exhibited much poorer crystallinity though it also had single perovskite phase in both as-grown and annealed PZT films. The most critical process in the thin film growth is the nucleation

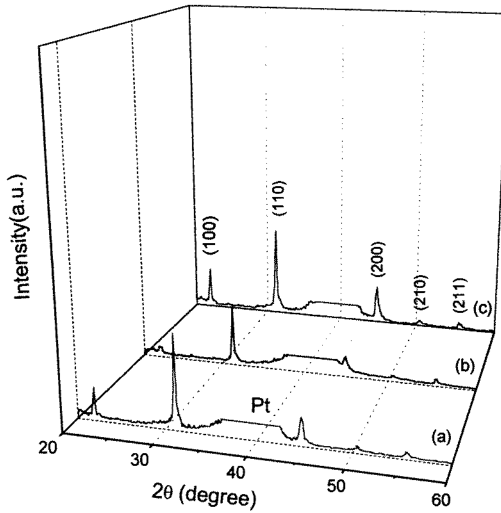

Figure 4. X-ray diffraction patterns of PZT/Pt samples (*a*) as grown; (*b*), (*c*) annealed at 600 and 700 °C for 2 min by an RTA process, respectively.

Table 1. The degree of preferred orientation in the PZT/Pt and PZT/PT samples.

Samples	$f(100)$	$f(200)$	$f(110)$
PZT/Pt (a)[a]	19.7%	16.4%	55.4%
PZT/Pt (b)	10.1%	19.7%	57.0%
PZT/Pt (c)	22.7%	20.7%	49.7%
PZT/PT (a)[b]	40.3%	39.9%	19.8%
PZT/PT (b)	40.9%	39.2%	19.9%
PZT/PT (c)	45.5%	36.9%	17.6%

[a] PZT/Pt (a), (b), (c) are shown in figures 4(a), (b), (c), respectively.
[b] PZT/PT (a), (b), (c) are shown in figures 3(a), (b), (c), respectively.

control at the interface between the film and the substrate. The difference of crystallinity in the PZT films with and without $PbTiO_3$ seed layer could be explained by the kinetics of the crystallization of the perovskite phase [16]. The $PbTiO_3$ seed layer was crystallized into high quality perovskite phase before the deposition of PZT films which offered sufficient nucleation sites at the interface. Therefore, it was considered that the $PbTiO_3$ seed layer could enhance the crystallinity of PZT films and promote the formation of perovskite phase.

The most interesting result, from an applications viewpoint, is the preferential orientation of the sol–gel-derived PZT films. The as-grown and post-annealed PZT/PT thin films exhibited a strongly (100)-preferred orientation, shown in figure 3, whereas a slightly (110)-preferred orientation was observed in the PZT/Pt thin films, appearing in figure 4. If the degree of (hkl) orientation, $f(hkl)$, is represented using the definition proposed by Lotgerling [20], as follows:

$$f(hkl) = \frac{I(hkl)}{\sum I(hkl)}$$

where $I(hkl)$ represents the x-ray diffraction intensity of the (hkl) reflection. The degree of (100) and (110) orientation for the PZT films deposited on the substrates with and without $PbTiO_3$ seed layer is presented in table 1. Note that (110) is the most intense reflection for the polycrystalline PZT/Pt samples. The reason for this preferential orientation is not

completely understood at this time. In contrast, when PZT films were deposited on $PbTiO_3$-seeded $Pt/Ti/SiO_2/Si$ substrates (PZT/PT samples), well crystallized PZT films with very strong {100} reflection formed, as shown in figure 3 and table 1. The reason for the (100) preferred orientation in the PZT/PT samples is attributed to the (100)-oriented-particle-$PbTiO_3$-seeded layer which provides energetically favourable nucleation sites and decreases the nucleation energy, thus promoting the formation of similarly oriented crystallites with (100)-oriented $PbTiO_3$ seed layer in the PZT thin films. These differences in orientation behaviour may be also related to the difference in thermal expansion properties of PZT films and the $PbTiO_3$ seed layer. The coefficient of thermal expansion for PZT above its Curie temperature is $\sim 7.0 \times 10^{-6}$ K^{-1}, while the coefficient for lead titanate is $\sim 5.5 \times 10^{-6}$ K^{-1} between 400 and 700 °C [21, 22]. Thus, a crystallized PZT film is in tension during cooling if the seed layer has a lower thermal expansion coefficient. The stress at the Curie temperature will force the *c*-axis into the plane of the film, that is, *a*-axis-oriented films will be obtained. Some researchers also stated that the type of stress created in the film by the thermal expansion differences determined what preferred orientation was obtained [23].

Figure 5 shows the surface morphology of the PZT/PT samples annealed at 700 °C for 2 min in an ambient atmosphere by the atomic force microscopy (AFM) technique. The square plate-like growth in the films is clearly observed in the 3D image. The roughness of the PZT/PT films is about 1.1 nm with a maximum roughness of 12.8 nm. It is much smoother than that of PZT/Pt samples. These results revealed that the nano-scale uniform surfaces were obtained in PZT/PT samples, and confirmed that the $PbTiO_3$ seed layer was also useful to improve the surface morphology of the films.

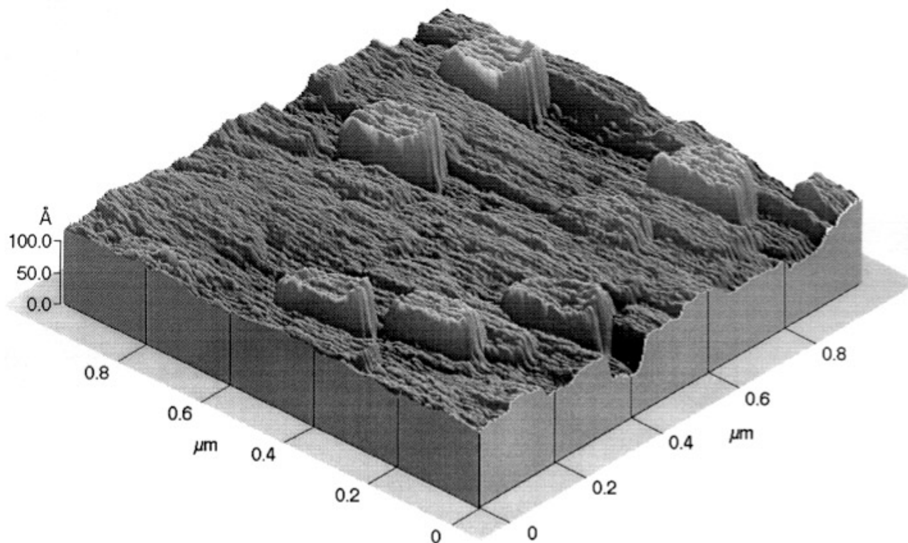

Figure 5. Atomic force microscopy 3D image of the surface morphology for PZT/PT sample with an RTA process at 700 °C for 2 min.

Ferroelectric hysteresis loops for the PZT films deposited on the seeded and unseeded platinum-coated silicon substrates are presented in figure 6. For the PZT films that were grown on the unseeded substrates, a poor polarization–electric field behaviour was observed, as shown in figure 6(*b*). The remanent polarization and coercive field were 1.10 μC cm^{-2} and 55.1 kV cm^{-1}, respectively. In the case of PZT films which were deposited on seeded

substrates, the remnant polarization was significantly improved, at 3.67 μC cm^{-2}, in which the coercive field was 54.5 kV cm^{-1} obtained from the P–E hysteresis loop of PZT/PT samples (figure 6(*a*)).

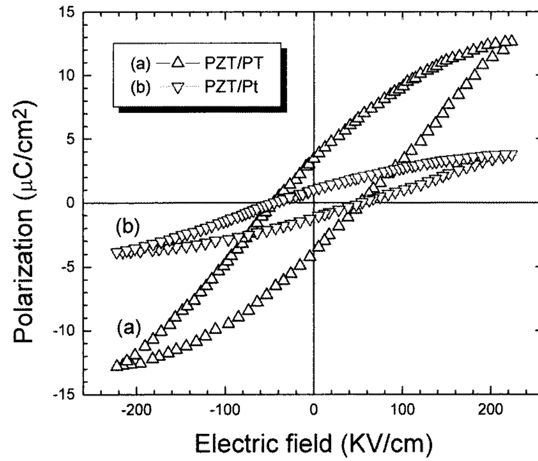

Figure 6. The P–E hysteresis loops for the PZT/PT and PZT/Pt samples with an RTA process at 700 °C for 2 min.

4. Conclusion

Sol–gel-derived PZT thin films with a dense, uniform surface morphology were successfully prepared, by inserting a $PbTiO_3$ seed layer between the platinum bottom electrode and the PZT films in order to promote formation of a preferentially oriented perovskite phase and enhance the crystallinity of the PZT films by offering ample nucleation sites and decreasing the nucleation energy. Pure perovskite PZT thin films with strongly (100)-preferred orientation deposited on $PbTiO_3$-seeded substrates were obtained, whereas a slightly (110)-preferred orientation was observed in the unseeded PZT films. The difference of orientation behaviour was attributed to two reasons: (1) the (100)-oriented $PbTiO_3$ seed layer could offer ample nucleation sites and decrease the nucleation energy; (2) the stress caused by thermal expansion mismatch existing between PZT films and $PbTiO_3$ seed layer during cooling through the Curie temperature. The improved remnant polarization and the coercive field of the PZT thin films, prepared on $PbTiO_3$-seeded substrates, were 3.67 μC cm^{-2} and 54.5 kV cm^{-1}, respectively, compared to those of 1.10 μC cm^{-2} and 55.1 kV cm^{-1} for unseeded PZT thin films. The results in the present study revealed that use of a $PbTiO_3$ seed layer in the preparation of PZT thin films by the sol–gel process could control the orientation behaviour in the PZT thin films, and is helpful in improving the microstructure and ferroelectric properties of the PZT thin films.

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References

[1] Swartz S L and Wood V E 1992 *Condens. Matter News* **1** 4
[2] Scott J F and Paz de Araujo C A 1989 *Science* **246** 1440
[3] Xu X H 1990 *Ferroelectric Materials and Their Applications* (New York: Wiley)
[4] Iijima K, Tomita Y, Takayama R and Veda I 1986 *J. Appl. Phys.* **60** 361
[5] Takashi Y and Yamaguchi K 1990 *J. Mater. Sci.* **25** 3950
[6] Selvaraj V, Brooks K, Prasadarao A U, Komarneni S, Roy R and Cross L E 1993 *J. Am. Ceram. Soc.* **76** 1441
[7] Tohge N, Takahashi S and Minami T 1991 *J. Am. Ceram. Soc.* **74** 67
[8] Hwang K S, Manade T, Yamaguchi I and Mizuta S 1997 *Japan. J. Appl. Phys.* **36** 5221
[9] Ontalus V, Cobianu C, Vasiliu F and Parlog C 1996 *J. Mater. Sci.* **31** 3639
[10] Kurchania R and Milne S J 1998 *J. Mater. Sci.* **33** 659
[11] Chang L H and Anderson W A 1997 *Thin Solid Films* **303** 94
[12] Sheppard B P 1992 *Am. Ceram. Soc. Bull.* **71** 81
[13] Haertling G H 1991 *J. Vac. Sci. Technol.* **9** 414
[14] Lakeman C D E and Payne D A 1982 *J. Am. Ceram. Soc.* **75** 3091
[15] Kim S H, Kim C E and Oh Y J 1995 *J. Mater. Sci.* **30** 5643
[16] Al-Shareef H N, Takayama R and Veda I 1995 *J. Appl. Phys.* **77** 2146
[17] Lee C, Kawano S, Itoh T and Suga T 1996 *J. Mater. Sci.* **31** 4559
[18] Kim S H, Kim C E and Oh Y J 1997 *Thin Solid Films* **305** 321
[19] Tani T, Xu Z and Payne D 1993 *Ferroelectric Thin Films III, Mater. Res. Soc. Symp. Proc.* vol 310, ed E R Myers *et al* (Pittsburgh, PA: Materials Research Society) p 269
[20] Lotgerling F K 1959 *J. Inorg. Nucl. Chem.* **9** 113
[21] Shirane G, Suzuki K and Takeda A 1952 *J. Phys. Soc. Japan* **7** 12
[22] Touloukian Y (ed) 1997 *Thermal Expansion Non-Metallic Solids (Thermal Physical Properties of Matter, TPRC Data Series13)* (New York: IFI–Plenum)
[23] Tossell D, Obhi J and Shorrocks N 1992 *Proc. 8th IEEE Int. Symp. on Applications of Ferroelectrics* ed M Lin (Piscataway, NJ: IEEE) p 11