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Dynamic behaviour of domains during poling by acoustic emission measurements in La-modified $PbTiO_3$ ferroelectric ceramics

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In order to study the dynamic behaviour of domains during poling, the acoustic emission (AE) characteristics of two La-modified $PbTiO_3$ ferroelectric ceramics in which 90° and 180° domains were respectively dominant have been investigated. One sample was a 15 mol % La-doped ceramic with a high tetragonality ratio ($c/a = 1.021$) and the other was a 24 mol % La-doped ceramic where the tetragonality ratio was close to unity ($c/a = 1.007$). The acoustic emission behaviour of the former sample consisted of both burst as well as continuous emission, with the latter sample mainly showing continuous emission. Energy distributions made it possible to distinguish between the AE signals resulting from 90° and 180° domain switching. From the observed results, it was confirmed that most of the AE occurred due to 90° domain switching. By introducing an alternative switching behaviour for the 90° domains, the behaviour of the AE generation during poling could be explained.

1. Introduction

Ferroelectric ceramics consist of a large number of domains which are formed in order to reduce both the elastic strain and depolarization field produced when the cubic paraelectric phase transforms into the non-cubic ferroelectric phase [1, 2]. Ferroelectric domains with tetragonal symmetry can in general be grouped into two categories: 90° domains and 180° domains [1]. Under a d.c. electric field, they are switched favourably towards the field direction, which is called "poling". The poling process is essential to create piezoelectric and pyroelectric properties in ferroelectric ceramics. Because the domain structure configuration has a direct influence on the macroscopic properties of ferroelectric ceramics, numerous efforts [2–12] have been made to investigate the dynamic behaviour of domains under an electric field.

Several techniques have been applied to the study of domain dynamics and they include X-ray diffraction (XRD) [5–7], strain gauge [8] and acoustic emission (AE) [9–13]. The XRD and strain gauge techniques can only be utilized to observe macroscopically the amount of 90° domain switching by measuring the change of X-ray diffraction peaks or strain, respectively. Only a few investigations using the AE technique on ferroelectric materials have been reported on both single and poly-crystalline ceramics such as $BaTiO_3$ [9], $Pb_5Ge_3O_{11}$ [10], $PbTiO_3$ [11], and modified lead zirconium titanate (PZT) [12–14]. These studies revealed that the AE is generated by domain switching, the paraelectric-to-ferroelectric phase transition, and finally microcracking. Unfortunately, no progress in the understanding of the characteristics of AE created by domain switching has been achieved to date. The application of the AE technique to other areas, i.e., the AE from brittle or ductile materials during tensile loading, [15], has confirmed that AE is a very useful tool in the interpretation of cracking behaviour or dislocation dynamics. Therefore, it is thought that the AE technique could offer an insight into the fundamental process of domain dynamics in ferroelectric materials.

It is the intention of this study to investigate the dynamic behaviour of domains by measuring AE from tetragonal ferroelectric ceramics during poling. For this study, two kinds of La-modified $PbTiO_3$ ceramics in which 90° and 180° domains are dominant were prepared. The first sample was 15 mol % La-doped $PbTiO_3$ with a high tetragonality ratio ($c/a = 1.021$) and the other was 24 mol % La-doped $PbTiO_3$ where the tetragonality ratio was close to unity ($c/a = 1.007$). The AE spectra and energy distributions were investigated in detail. The microstructures of the two samples were characterized by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The quantitative information on the amount of domain switching was obtained by the XRD method. The dynamic behaviours of the 90° and 180° domains are discussed in terms of the observed results.

2. Experimental procedure

2.1. Sample preparation

Compositions of $Pb_{1-x}La_xTiO_3 + 0.01MnO_2$ with $x = 0.15$ and 0.24 (abbreviated hereafter as PLTM15 and PLTM24) were prepared from high-purity oxide

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powders, PbO, La_2O_3, TiO_2 and MnO_2. The oxide powders were mixed in a ball mill for 24 h and calcined at 900 °C for 3 h. The calcined powders were ground with 1 wt % poly(vinyl alcohol) used as a binder in a ball mill for 20 h and dried in an oven. Samples were pressed into a 19 mm disks and were then sintered at 1250 °C for 3 h. The samples were then polished to 0.45 mm and were electroded on both sides by gold sputtering.

2.2. Poling and AE measurements

The poling conditions including the applied electric field and temperature were chosen so that each sample was sufficiently poled. At the same applied electric field of 4 kV mm^{-1}, the PLTM15 sample (T_c = 210 °C) was poled at 105 °C and the PLTM24 sample (T_c = 80 °C) at 40 °C. The c/a ratio values were determined to be 1.012 at 105 °C for PLTM15 and 1.004 at 40 °C for PLTM24.

AE measurements on the ferroelectric ceramics under poling conditions were performed using the experimental set-up schematically represented in Fig. 1. A high d.c. field was applied to the ferroelectric ceramics held in a silicon oil bath and the resulting AE was monitored, using an AET 5500 system (Hartford Steam Boiler Inspection Technologies, CA, USA). The AE spectra was detected by a AE sensor with a resonant frequency of 175 kHz via a glass rod and filtered by a band pass filter with a range of 0.125 –1 MHz. The overall gain was 70 dB and the threshold voltage was chosen as 0.1 V.

2.3. Characterization

In order to observe the microstructures before and after poling by using SEM, the samples were polished with SiC abrasive papers and Al_2O_3 abrasive powders and etched with a HNO_3 and HF solution for about 10 s. The changes in the (200) and (002) peaks with poling time were measured by using an X-ray diffractometer with the following operating conditions: CuK_α radiation, tube voltage 40 kV, tube current 40 mA, and scanning speed 1° mm^{-1}. The observation of domain structure was achieved using TEM. For the TEM observations, specimens were prepared by polishing, mechanical dimple grinding and ion milling with an argon ion gun at 5 kV.

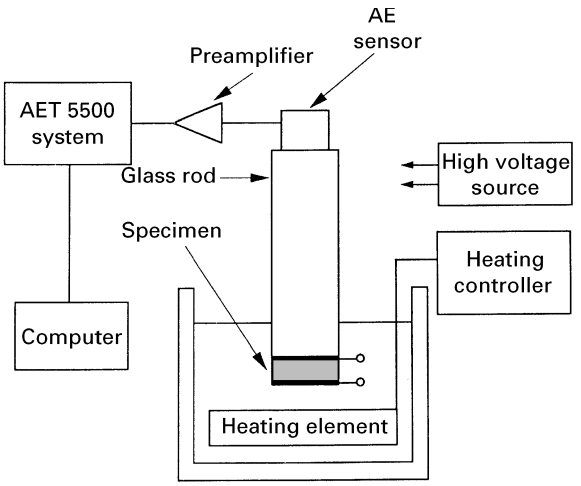

Figure 1 A schematic representation of the experimental set-up for the AE measurements.

3. Results and discussion

Two typical AE spectra for the PLTM15 and PLTM24 samples, under poling at an electric field of 4 kV mm^{-1} are shown in Fig. 2(a and b). The AE spectra for the two samples show two regions with different emission forms. One region is marked "A" and appears in the form of continuous emission and the other is marked "B" and shows an overlapped form of continuous and burst emissions. There are also some differences between the two AE spectra. Most noticably, the sample with the high c/a ratio PLTM15 displays a greater amount of AE generation than sample PLTM24 which has a lower c/a ratio. Furthermore, the former sample clearly shows frequent burst emissions. It seems that the AE spectrum of this sample is similar to the AE generation behaviour due to cracking in brittle materials under loading [15]. On the other hand, the AE spectrum of the latter sample shows mainly continuous emission, and thus it is similar to the AE generation behaviour observed during plastic deformation of ductile materials under loading [15].

In order to investigate the characteristics of the observed AE, the energy distributions in the regions "A" and "B" of the two samples have been analysed and are shown in Fig. 3(a and b). In this study, the AE energy is calculated as a function of both peak amplitude and duration time: energy = peak amplitude + 10 log(duration time), where the peak amplitude is in dB above 0.1 mV at the preamplifier output, duration time in seconds, and the energy in dB [17]. One interesting feature of these plots is that all of the energy distributions can be classified into two features. One feature is a narrow distribution peak in the small energy region around 40 dB. The other is a broad

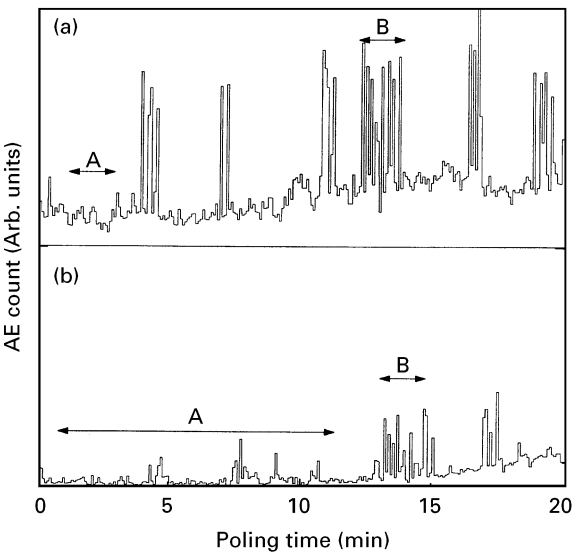

Figure 2 Electrically induced AE generation patterns of the samples (a) $Pb_{0.85}La_{0.15}TiO_3 + 0.01\ MnO_2$ with $c/a = 1.012$ and (b) $Pb_{0.76}La_{0.24}TiO_3 + 0.01\ MnO_2$ with $c/a = 1.004$.

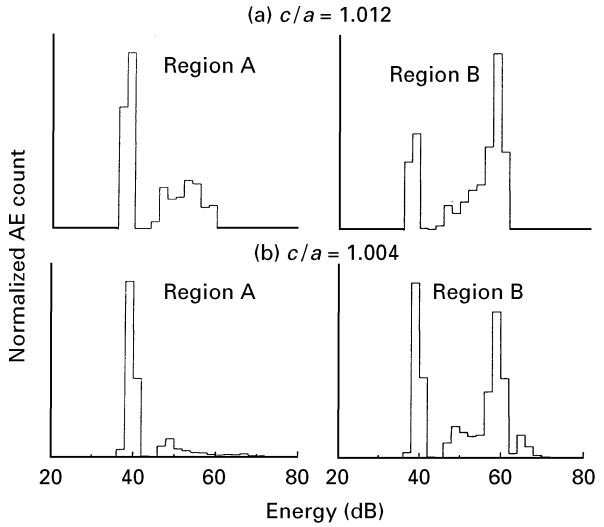

Figure 3 Energy distributions in the regions 'A' and 'B' of the AE generation patterns (Fig. 2) of the samples with different tetragonality ratios: (a) $c/a = 1.012$ and (b) $c/a = 1.004$.

distribution peak in the large energy region in the range of 50–65 dB.

Another observation from Fig. 3 is the difference in the energy distribution between the regions "A" and "B" of the two samples. The region "A" shows that a large part of the AE generation is concentrated in the small energy group. This trend is more evident in the case of the low c/a ratio. In contrast, the region "B" shows that most of the AE is concentrated in the large energy group. It is known that the observed AE energy is the parameter most influenced by the type and nature of the AE source [13, 16]. Consequently, the finding described above suggests that the AE in this study is generated from two kinds of sources.

For ferroelectric ceramics under poling, it should be noted that there are two kinds of AE sources, i.e., microcracking and domain switching [12]. The microstructure before and after poling is first examined to determine whether or not electrically induced microcracking takes place. Microcracks in ceramics are divided into intergranular and transgranular microcracks. Chung *et al.* [18] have reported that electrically induced microcracks in lead zirconate titanate (PZT) and barium titanate (BT) were not intergranular but transgranular in nature. In fact, the absence of intergranular microcracks was confirmed by the SEM observation of the two samples before chemical etching.

A detailed examination for the occurrence of transgranular microcracks was performed on the PLTM15 and PLTM24 samples after chemical etching and the results are shown in Fig. 4(a–d). Transgranular microcracks are visible near grain boundaries in both poled and unpoled cases, but quantitative changes in the microcracking was rarely observed. Therefore, it is presumed that most of the observed microcracks result from the cubic to tetragonal phase transition that occurs during cooling after the sintering [14].

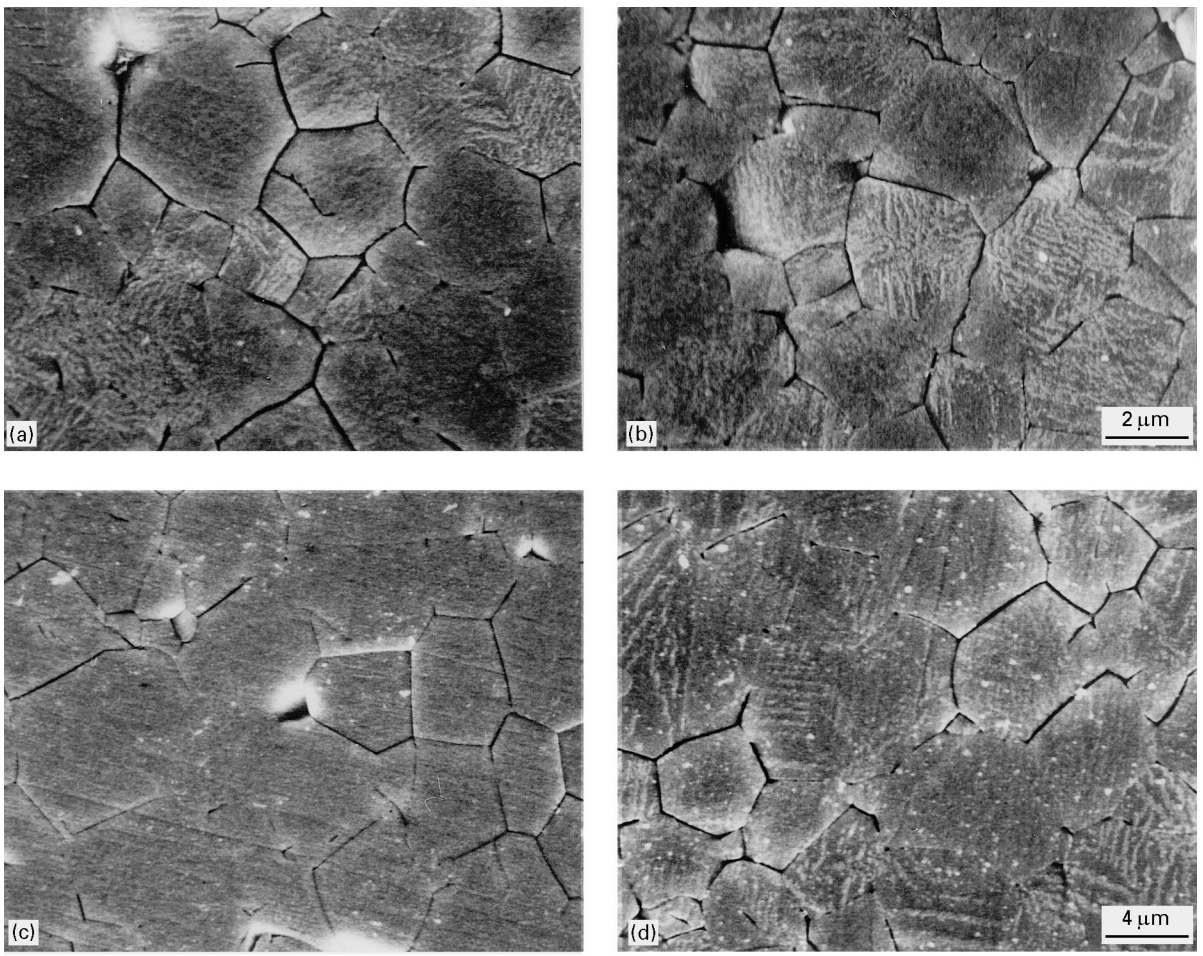

Figure 4 SEM micrographs showing the change of the microcracking (a) before and (b) after poling for the sample with $c/a = 1.012$ and (c) before and (d) after poling for the sample with $c/a = 1.004$.

Initial reports [18–20] have pointed out that electrically induced microcracks can occur in ferroelectric ceramics when the grain size was at least larger than 10 μm. As is shown in Fig. 4(a–d), the average grain size of the PLTM15 and PLTM24 samples is about 3 and 6 μm, respectively. Therefore, it is possible to say that the AE generation in Fig. 2(a and b) is not caused by microcracking, but instead the main AE source can be regarded as domain switching.

The two points that the AE generates from domain switching and, as explained in Fig. 3, it has two kinds of sources, suggest that the switching behaviour of the domains during poling takes place with two different mechanisms, probably corresponding to 90° and 180° domain switching. It is well known that 180° domain switching easily occurs, but only a part of 90° domain switching, which is dependent on the poling field, can take place due to mechanical strain effects [7, 8]. This behaviour indicates that the low energy AE around 40 dB is related to 180° domain switching and the high energy AE between 50–65 dB is related to 90° domain switching.

From the results described so far, the observed AE spectra can be related to the domain switching behaviour. With reference to Fig. 3(a and b), most of the AE in region "A" showing only continuous emission occurs due to 180° domain switching. In particular, this trend appears to be more evident in the PLTM15 sample with a low c/a ratio. On the other hand, we conclude that the burst emission behaviour which appears in region "B" is mainly due to 90° domain switching.

The quantitative information on the domain switching during poling was evaluated by measuring the value of N^{90° [5] which indicates the percentage of 90° domain switching. The values of N^{90° are calculated from the intensity ratio of the (002) and (200) peaks before and after poling. Fig. 5 shows the variation of N^{90° with poling time for the two samples. It seems that the switching behaviours of 90° domains in the two samples are similar to each other. The two samples show a gradual increase of N^{90° with time in the early stage of poling and saturation above approximately 10 min. However the PLTM15 sample with the high c/a ratio has a larger amount of 90° domain switching compared with the PLTM24 sample with a low c/a ratio. This fact is consistent with the difference in the amount of high energy AE resulting from 90° domain switching between the two samples. In other words, the amount of high energy AE in the case of the high c/a ratio is larger than that amount in the case of the low c/a ratio.

An important difference between the behaviour of AE generation and 90° domain switching with poling time is that, even though the amount of 90° domain switching, as determined by XRD measurements, is saturated above 10 min, the AE generation constantly occurs during the poling. According to the model reported by Iwasaki and Izumi [10], the domains have characteristic threshold field levels to switch their polarization directions. Based on this model, behaviour of the AE generation and domain switching can be described as follows. In the early stage of the application of the electric field, 180° and 90° domains with low threshold voltage levels will rapidly switch towards the field direction with or without detectable AE generation, which is affected by the limit of detection sensitivity. Further application of the electric field causes 90° domains with a higher threshold field level than the poling field to overcome geometrical constraints and reverse their polarization directions. These events contribute to the generation and detection of the high energy AE which then appears in the form of burst emission. This behaviour of the 90° domains will induce a large elastic stress field and make neighbouring domains return to their original directions [10]. Therefore, it can be interpreted that the continuous AE results from the switching of 90° domains towards the field directions or their original directions and the switching of the 180° domains interacting with the 90° domain switching. The difference between the behaviour of AE generation and 90° domain switching with poling time can be explained by this alternative switching behaviour of the 90° domains.

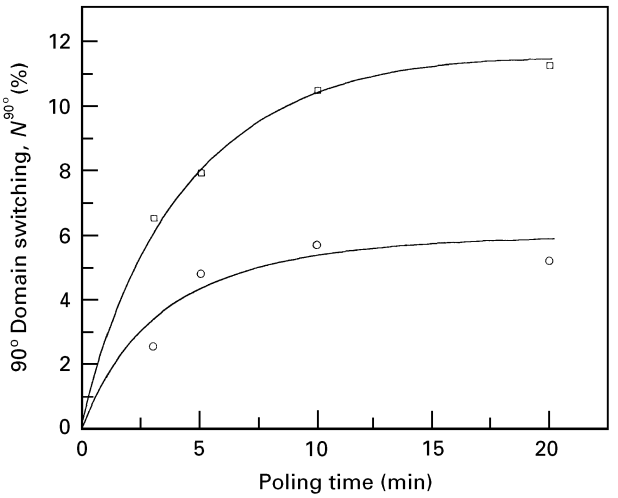

Figure 5 The variation of the value of N^{90° with poling time for the samples with tetragonality ratios of (□) 1.012 and (○) 1.004.

Fig. 6(a) shows a bright-field image obtained from the PLTM15 sample after poling, which shows a typical 90° domain configuration observed in ferroelectric ceramics [3, 21]. This should be compared with the domain structure shown in the PLTM24 sample, which is seen in Fig. 6(b). In the case of PLTM15 which has a low c/a ratio, there is no lamellar structure indicating the presence of 90° domains, however a slight difference in contrast is seen in the grains. This may be due to the presence of 180° domains [3, 21]. King and Goo [21]have also observed that in compositions where the c/a ratio is close to unity in $(Pb_{1-x}Ca_x)TiO_3$ ceramics, the lack of strain allows 90° domains to disappear. With a closer examination, however, it is found that a small concentration of the 90° domains are present in some grains. This effect may be a result of the low strain energy of the sample with a low c/a ratio. Consequently, it is evident that the sample with a high c/a ratio predominantly contains 90° domains and the sample with the low c/a ratio predominantly contains 180° domains.

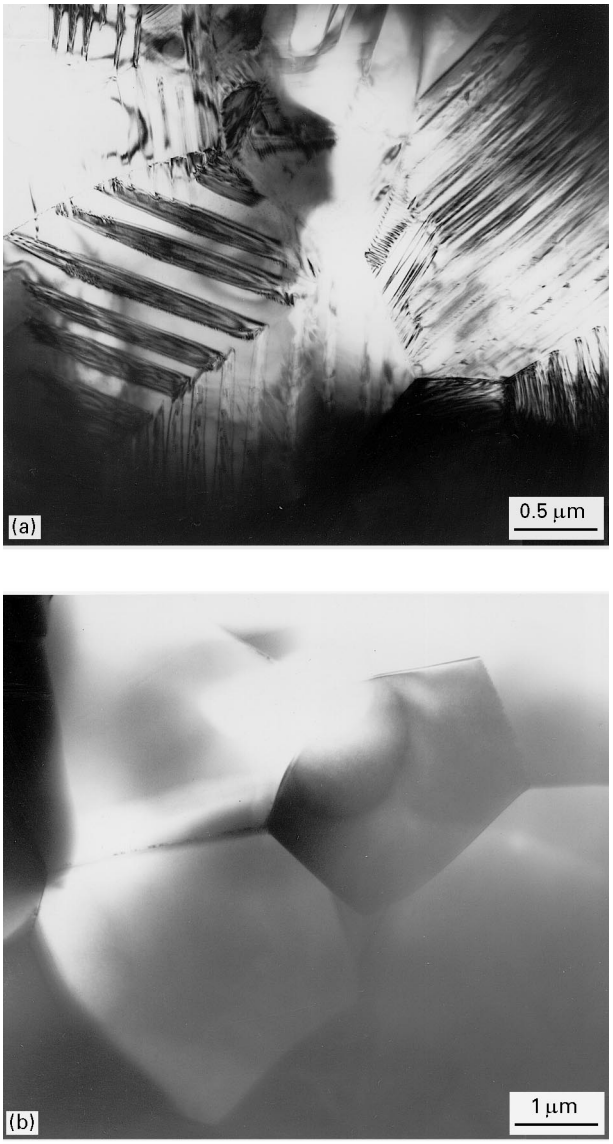

Figure 6 Bright field images obtained from (a) the sample PLTM15 and high tetragonality ratio ($c/a = 1.021$) and (b) sample PLTM24 with low tetragonality ratio ($c/a = 1.007$).

In short, it is concluded that the sample in which 90° domains are dominant shows a relatively larger amount of AE generation and 90° domain switching during poling compared with the sample where 180° domains are dominant. This fact suggests that most of the AE occurs due to 90° domain switching, and to a lesser extent 180° domain switching. It is believed that the sample where 90° domains are dominant has various threshold field levels to switch its 90° domains. In Fig. 3(a and b) the fact that the peaks of high energy are broader than those of low energy supports various field levels of 90° domain switching. This fact is also justified by remarkable burst emission in the case of the high c/a ratio sample as is shown in Fig. 2(a). On the other hand, the sample in which 180° domains are dominant shows little burst emission in the AE generation pattern.

4. Conclusion

The characteristics of electrically induced AE were investigated in order to study the dynamic behaviour of domains in tetragonal ferroelectric ceramics during poling. For this study, two kinds of La-modified $PbTiO_3$ ceramics in which 90° and 180° domains were respectively dominant, were prepared. One sample was a 15 mol % La-doped $PbTiO_3$ with a high tetragonality ($c/a = 1.021$) and the other was 24 mol % La doped $PbTiO_3$ where the tetragonality is close to unity ($c/a = 1.007$). The following conclusions are drawn:

(1) The AE spectrum of the sample where 90° domains were dominant consisted of burst emission in addition to continuous emission. In contrast, in the sample where 180° domains predominated the spectrum contained mainly continuous emission.

(2) An analysis of the energy distributions, enabled the identification of AE signals resulting from 90° and 180° domain switching.

(3) The difference in the amount of AE generation and 90° domain switching between the two samples confirmed that most of the AE occurred due to 90° domain switching, and to a lesser extent 180° domain switching.

(4) The introduction of an alternative switching behaviour for 90° domains, enabled the observed behaviour of AE generation during poling to be explained.

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