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SEM Investigation of Domain Structure in (Ba,Ca,Pb)TiO$_3$

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Abstract

In the present paper the microstructure and domain structure in modified BaTiO$_3$ with Pb and Ca as additives have been investigated using SEM technique. The (Ba,Pb)TiO$_3$ and (Ba,Ca,Pb)TiO$_3$ ceramics show a slight difference in grain size, being smaller in composites with Ca additives which acts as grain growth inhibitor. The domain configuration is almost the same. The small grain microstructure with tiny domains have been observed in specimen sintered at 1300°C and the average grain size is in the range 1–3 μm. For those specimens sintered at 1320°C the homogenous microstructure is also obtained with grain size around 2–4 μm. For both types of specimens, the single domain structure is associated with grain which size is lower than 2 μm. The banded domain structure could be observed in grains with size bigger than 3 μm. The bar shape grains and elongated grains together with some large region in microstructure are free of domain structure. The observed domain patterns reveal mainly the straight domain boundary lines with 90° domains walls. The wall thickness ranged from 0·03 μm to 0·15 μm, while the domain width is in the range of 0·1 μm–1 μm. © 1999 Elsevier Science Limited. All rights reserved

Keywords: sintering; electron microscopy; microstructure-final; grain size; BaTiO$_3$ and titanates.

1 Introduction

The ferroelectricity is fundamentally associated with domain structure and domain motion, which affect to a great extent the nonlinear electronic properties, particularly their positive temperature coefficient of resistivity in ferroelectric materials such as BaTiO$_3$ and related BaTiO$_3$ ceramic composites.[1–4] The domain structure, which is formed during the cubic to tetragonal phase transformation at Curie temperature, enables the release of stresses induced into crystal. The configuration and type of domains depend not only on the presence of additives but also on the microstructure obtained during sintering process. The homogeneous and small grained microstructure with single domain structure enables the stable and uniform ferroelectric behavior of BaTiO$_3$ ceramic composites. In coarse grained microstructure, apart from the single domain, the banded domain structure is the predominate structure.[5] Two types of domain configuration, the herringbone and the square net patterns are the most common in BaTiO$_3$ ceramics.[2,5,6] The fine parallel lines were identified as 90° walls which are [101] planes, and the herringbone pattern with watermarks are described as 180° walls separating the regions with different polarization.[6] Tiwari *et al.*[2] gave some details of domain patterns in Ca doped BaTiO$_3$. They observed the 90° domain walls even in grains smaller than 1 μm size, where the average width of each domain is nearly 0·1–0·3 μm.

In polycrystalline BaTiO$_3$, besides simple lamellar domains associated with small grain size, a banded domain structure in large grains is frequently formed.[1] The banded domain structure affects the ferroelectric properties, the permittivity becomes inhomogeneous within the crystal, and therefore it is of great interest to obtain the uniform small grained microstructure with a single domain grain structure.

The purpose of the present study is to correlate the microstructure with the domain configuration

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in various $BaTiO_3$ based ceramics using SEM and EDS technique.

2 Experimental

Conventional ceramic sintering process is used for preparation of $(Ba,Ca,Pb)TiO_3$ and $(Ba,Pb)TiO_3$ ceramics. High purity $BaCO_3$, $CaCO_3$, TiO_2, PbO and small quantities of Al_2O_3, SiO_2 and TiO_2 (AST) were used as raw materials. The nominal compositions of powders were: $Ba_{0\cdot84}Pb_{0\cdot16}TiO_3$ and $Ba_{0\cdot84}$ $Pb_{0\cdot06}$ $Ca_{0\cdot10}$ TiO_3 with 5 mol% of AST. Powders of proper compositions were mixed 30 h, pressed in pellets, calcinated at 1050°C for 1 h in air and then remilled with polyvinyl alcohol. After granulated the green pellets were formed by pressing (green density was $d = 3{\cdot}5\,\mathrm{g\,cm^{-3}}$) and sintered for 2 h at 1300 and 1320°C in air. The sintered densities were in the range $5{\cdot}1$–$5{\cdot}6\,\mathrm{g\,cm^{-3}}$. For comparison purposes the $BaTiO_3$ without additives was also used. The microstructure was investigated by scanning electron microscope JEOL, SEM 5300 equipped with EDS. For the examination of the domain structure the samples were etched in 10% HCl with 5% HF.

3 Results and Discussion

During sintering of $(Ba,Ca,Pb)TiO_3$ and $(Ba,Pb)TiO_3$ at 1300 and 1320°C normal grain growth was observed, the average grain size being $1{\cdot}5\,\mu m$ for the lower temperature and approximately $3\,\mu m$ for the higher temperature. A nearly uniform microstructure is obtained as can be seen in Fig. 1, for $(Ba,Pb)TiO_3$ sintered at 1300°C as an example, which can be compared to the microstructure of pure barium titanate shown in Fig. 2. In general, the grain size in samples with Ca additive is smaller compared to that ones in $(Ba, Pb)TiO_3$ samples. Regarding the microstructure of modified barium titanate it could be pointed out that the needle shape crystals and some large elongated grains with less defined structure are randomly distributed in the sintered samples. The excess of Pb is not incorporated within the $BaTiO_3$ matrix, but is mainly present in these grains, as can be deduced from the EDS spectra (Fig. 3). As another feature of the obtained microstructure it should be noted, that the fracture surface reveals a grain size in the bulk in the range of 10–$15\,\mu m$ having a terrace structure (Fig. 4). Looking to the domain structure it can be observed that a single domain structure is associated with grains of less than $2\,\mu m$ in size. The SEM micrograph of the etched surfaces of a modified $BaTiO_3$ sintered at 1320°C (Fig. 5) shows that

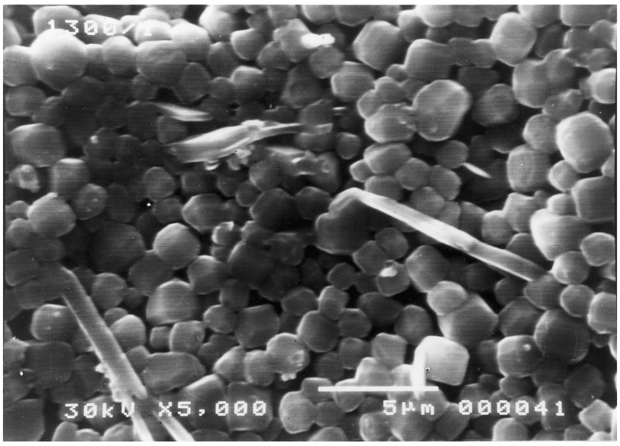

Fig. 1. SEM micrograph of $(Ba,Pb)TiO_3$ sintered at 1300°C.

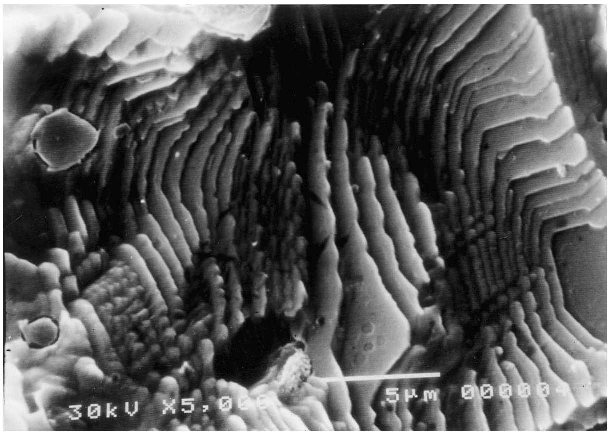

Fig. 2. SEM micrograph of $BaTiO_3$ sintered at 1240°C.

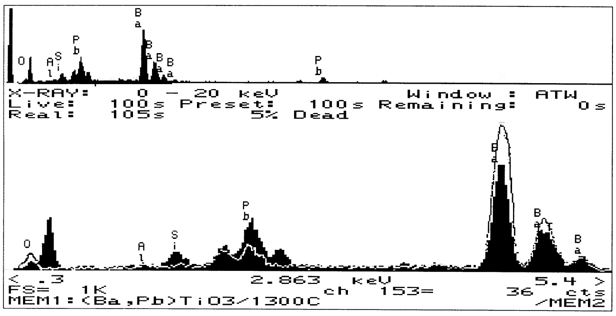

Fig. 3. EDS spectra of $(Ba,Ca,Pb)TiO_3$ sintered at 1300°C, the full black line is for elongated grains.

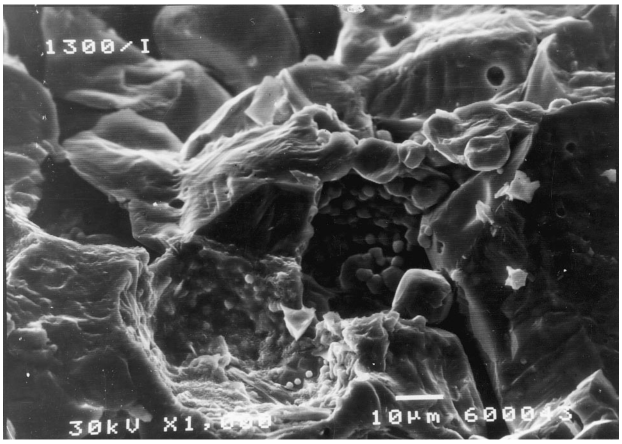

Fig. 4. The fracture surface of $(Ba,Pb)TiO_3$ sintered at 1300°C.

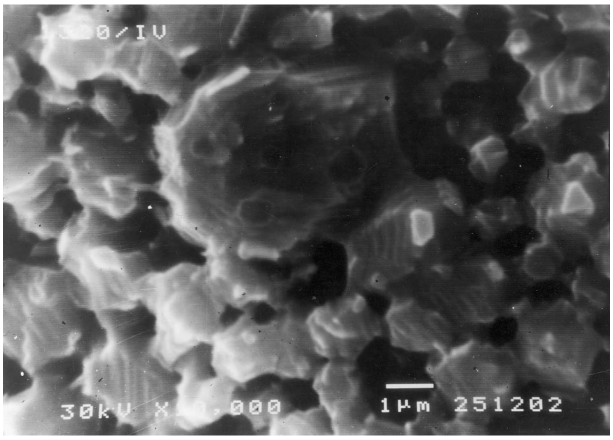

Fig. 5. SEM micrograph of single domain structure in (Ba,Ca,Pb)TiO$_3$ sintered at 1320°C.

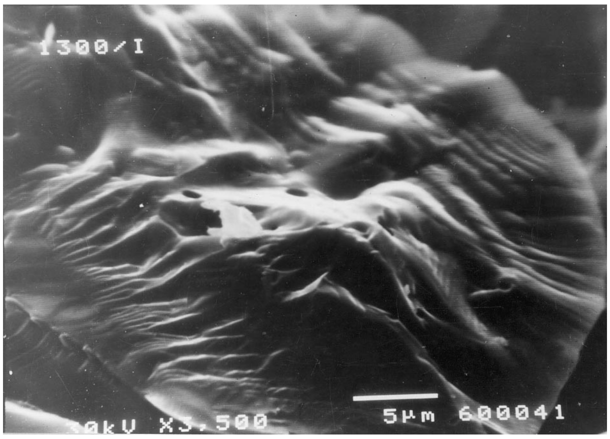

Fig. 6. The banded domain structure in (Ba,Pb)TiO$_3$ sintered at 1300°C.

the grains consist of a set of parallel lines with 90° domain boundaries. The wall thickness ranges from 0·03 μm to 0·15 μm while the domain width is nearly 0·15 μm. Independently of the sintering temperature for those grains, which size is larger than 3 μm a banded domain structure is observed and the domain width is approximately 1 μm, as can be seen in Fig. 6.

4 Conclusion

The observed domain structures in modified BaTiO$_3$ ceramics mainly reveal 90° domain boundaries. The wall thickness ranged from 0·03 μm to 0·15 μm, while the domain width ranged from 0·15 to 1 μm depending on the grain size. A single domain is associated with those grains which size is smaller than 2 μm. The domain banded structure is observed in larger grains independent from the sintering temperature, and with a domain width of approximately 1 μm. The bar shape grains and randomly distributed elongated grains together with some larger regions in the microstructure are free of a domain structure.

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