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Influence of manganese segregation on the grain size in (Ba,Sr)TiO_3-based ceramics

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1. Introduction

The donor/acceptor ratio is known to have a significant effect on the microstructure and dielectric properties of ceramic materials, and dopants can also be responsible for abnormal grain growth, for example Ti in TiO_2-doped $BaTiO_3$ [1]. In this work, we report an investigation of the dependence of grain size on the content of the acceptor dopant manganese in Mn-doped $Ba_{0.6}Sr_{0.4}TiO_3$ (BST) ceramics.

2. Experimental

$Ba_{0.6}Sr_{0.4}TiO_3$ (BST) bulk ceramics were prepared by conventional solid state methods. Stoichiometric barium titanate and strontium titanate powders (TPL, USA) with particle sizes of 69 to 80 nm were dry mixed on a ball mill. Manganese doping between 0-10 mol % Mn was introduced via manganese nitrate tetrahydrate. After drying, the powders were pressed into disks and sintered at 1450^{o}C for 2 h. Scanning electron microscopy (JEOL 6300) was used to examine the microstructure and grain size on fracture and polished surfaces. Transmission electron microscopy (FEI Tecnai F20) with EDX was used to characterize the microstructure and composition of the bulk ceramics.

3. Results and discussion

As the concentration of Mn increased, the grain size was observed first to increase, pass through a maximum and then finally decrease to a constant value (Fig.1 and Fig. 2). A similar dependence has been observed in the magnesium-doped BST system [2]. The SEM micrographs of the fracture surfaces (Fig.1) show that the fracture mode changes from intergranular failure to transgranular failure when the manganese concentration exceeds 3 mol%. EDX measurements showed that the solid solubility of manganese in BST grains is about 0.5 mol%. The remaining manganese segregates to the grain boundaries, Fig. 3, and, at the higher Mn concentrations, manganese oxide precipitates are observed at the grain boundaries (Fig.4.). We interpret these observations as follows.

It is well known that Mn can replace Ti on the B sites in the perovskite matrix and, at sintering temperatures above the eutectic temperature of 1332^{o}C [3], a titanium-rich liquid phase has been observed in the grain boundary regions [4, 5]. The presence of the liquid phase in these acceptor-rich samples could be responsible for the extensive grain growth, as observed in our samples. However, as the solubility limit of Mn in the grains is exceeded, MnO_2 begins to be precipitated at the grain boundary regions, thus reducing the atom mobility and hindering grain growth. Eventually the concentration and distribution of MnO_2 particles is such that the boundaries are effectively pinned resulting in a constant grain size. Thus it is proposed that the abnormal grain growth is controlled by a solution – diffusion - re-precipitation process [6].

4. Conclusion

The grain size of Mn-doped BST ceramics is reported. A maximum grain size is observed at 0.7 mol% Mn. It is proposed that Mn replaces Ti up to the solubility limit of about 0.5mol% leading to a Ti-rich liquid phase. At higher Mn concentrations discrete MnO_2 particles are observed which could restrict grain growth.

5. References

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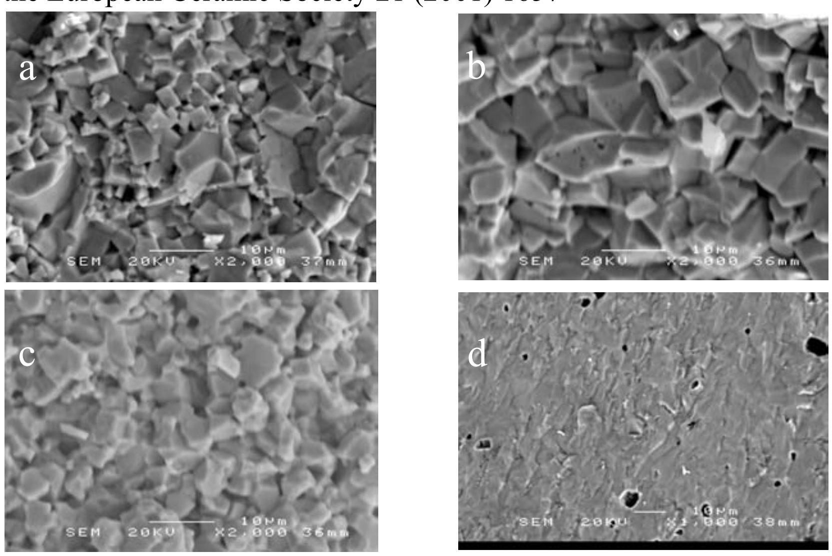

Fig.1. Scanning electron microscope micrographs of fracture surface of BST ceramics with different contents of Mn doping: (a) 0%, (b) 0.7%, (c) 1%, (d) 3%.

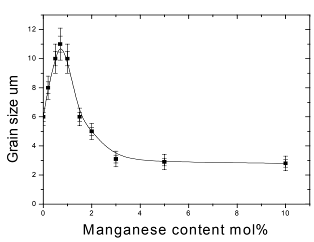

Fig.2. Dependence of grain size on Mn content in BST ceramics after 2h at 1450^{o}C.

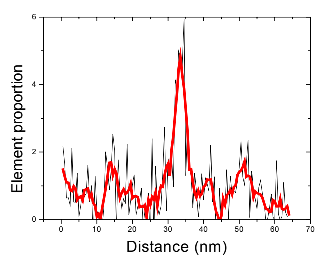

Fig.3. EDX linescan cross a manganese segregated grain boundary.

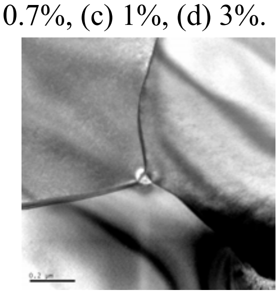

Fig.4. Nanometer size manganese oxide precipitate at grain boundary triple area.

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