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Structural and electrical properties of barium strontium calcium titanate thick films for uncooled IR sensors

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$(Ba_{0.6}Sr_{0.3}Ca_{0.1})TiO_3$ powders, prepared by the sol-gel method, were mixed organic binder and the BSCT thick films were fabricated by the screen printing techniques on alumina substrates. The structural and pyroelectric properties were investigated with variation of Pr_2O_3 contents. All BSCT thick films, sintered at 1420 °C, showed the typical XRD patterns of a cubic perovskite polycrystalline structure. The average grain size of the thick film doped with 0.1 mol% Pr_2O_3 is 2.4 μm and the thickness of all BSCT specimens was about 50 μm. Relative dielectric constant and dielectric loss of the thick film doped with 0.1 mol% Pr_2O_3 were 4714 and 5.9%, respectively. All BSCT thick films showed the maximum pyroelectric coefficient at around the Curie temperature, and the specimen doped with 0.1 mol% Pr_2O_3 showed the highest value of 65.3×10^{-9} C/cm^{2}K. The figure of merit F.M.D* for specific detectivity of the specimen, doped with 0.5 mol% Pr_2O_3, showed the good values lager than 1.0×10^{-9} Ccm/J at around room temperature.

Key words: $BaTiO_3$, Pyroelectric properties, Thick film, Screen-printing, IR detector.

Introduction

IR detection has become an increasingly important technology in fields of security, energy-saving, cooking, medical appliances, human environment and others. Infrared detectors are classified as either photon types or thermal detectors [1]. Generally, photon detectors have high sensitivity and resolution. It is easier to identify a human body from a thermal image than from a conventional visual image obtained by charge coupled device. However, the sensor must be cryogenically cooled down during operation to maintain high sensitivity. Also, the apparatus is large and costly, and the sensitivity is dependent on IR wavelength. Uncooled thermal detectors have attracted much attention because they operated at room temperature. Relative to photon detectors of medium and long wavelength IR, these devices offer the advantage of low cost fabrication and broadband of 8-12 μm operation coupled with a performance adequate for many applications, especially in the consumer field.

Recently, the application of thick film technology to ferroelectric ceramics has been performed in a wide range of industrial field because of the simplicity and flexibility of thick film technology. Thick film technologies offer many advantages over the use of bulk ceramics in ferroelectric micro-system devices [2, 3]. Various thick film techniques, such as tape casting, sputtering, and screen printing method, can be used for successful deposition of thick films. Among these technologies, the screen printing method is one of the best for thick film preparation that involves high productivity and good cost performance brings the films to the stage of commercial mass production with typical thickness in the range of 10-100 μm.

In this study, ferroelectric $BaTiO_3$ powders, partially substituted with Sr^{+2} and Ca^{+2} ions at the A-sites (Ba^{+2} ions), were prepared by sol-gel method in order to decrease the phase transition temperature and improve the dielectric properties at near the room temperature. $(Ba,Sr,Ca)TiO_3$ thick films, doped with Mn and Pr ions to improve the pyroelectric properties, were fabricated by a screen printing method on alumina substrates. The structural and pyroelectric properties were investigated for use as uncooled infrared detector materials.

Experimental

The chemical compositions of the samples are given by the formula: $(Ba_{0.6}, Sr_{0.3}, Ca_{0.1})$ TiO_3 + 0.1 mol% $MnCO_3$ + y mol% Pr_2O_3 (y = 0.1, 0.3, 0.5, 0.7). These BSCT compositions gave a transition temperature near the ambient room temperature. Doped BSCT specimens with 0.1 mol% $MnCO_3$ were selected for their basic composition on the basis of previous experiments [4]. BSCT powders, starting with a mixture of Ba acetate, Sr acetate, Ca acetate and Ti isopropoxide were prepared by a sol–gel method. Acetic acid and 2-methoxyethanol were used as solvents. The calcined BSCT powders, doped with Pr_2O_3 and $MnCO_3$, were mixed and ground

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by planetary ball milling for 24 h. The screen-printable pastes were prepared by kneading the ground BSCT powder with 30 wt% of organic binder (α-terpineol, $C_{10}H_{18}O$) in a non-bubbling kneader (NBK-1, Kyoto Electro.). High purity alumina was used as a substrate. The bottom electrodes were prepared by a screen printing method with Pt paste and firing at 1450 °C for 2 h. After the BSCT paste had been screen printed using a 200 mesh screen mask, printed films were dried at 400 °C for 20 minutes. These processes from printing to drying were repeated 6-times to obtain the desired thickness. The thick films were sintered at 1420 °C for 2 h in air. The upper electrodes were fabricated by screen printing Ag paste.

X-ray diffraction (XRD) and scanning electron microscopy (SEM) were introduced in order to analyze the crystallinity and the microstructure of BSCT specimens, respectively. The dielectric properties of the specimens were measured using a LCR-meter (Fluke, PM6306). The pyroelectric properties were measured repeatedly using a digital electrometer (Keithley 6514) at a constant rate of temperature change of 5 °C/min for increasing and decreasing temperatures in the ranged from –25 °C to 60 °C.

Results and Discussion

Measurements of the thermogravimetry (TG) and the differential thermal analysis (DTA) curves of the dried BSCT powders were conducted, and the results are shown in Fig. 1. During the heat treatment processing, the total weight loss of the dried powder was about 44% at 1000 °C. The endothermic peaks due to evaporation of H_2O and volatilization of OH^- were observed at around 100 °C. The exothermic peaks were observed in the temperature range of 400 ~ 420 °C due to the combustion of organic residues and the weight loss was about 33.6%. The weight loss in the temperature range of 600 °C to 700 °C was attributed to the decomposition of barium carbonate, which was formed during heating [5]. The exothermic peak was observed at around 660 °C

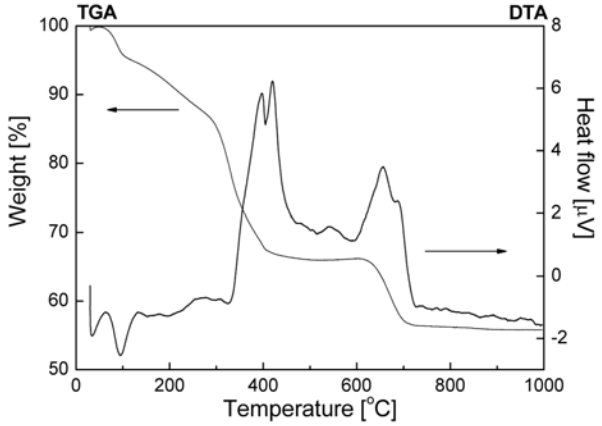

Fig. 1. DTA/TGA curves of the dried BSCT (60/30/10) powders.

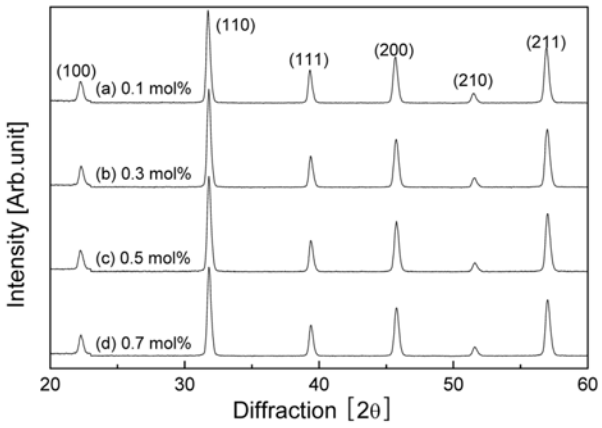

Fig. 2. XRD patterns of BSCT (60/30/10) specimens with various Pr_2O_3 contents.

due to the formation of the polycrystalline perovskite phase. It is can be concluded that the heat radiate to reach for stable state which was minimum activation energy. The calcining temperature was determined at 800 °C from the result of this TG-DTA analysis.

Figure 2 shows the X-ray diffraction (XRD) patterns of the Pr_2O_3-doped BSCT thick films. All the BSCT

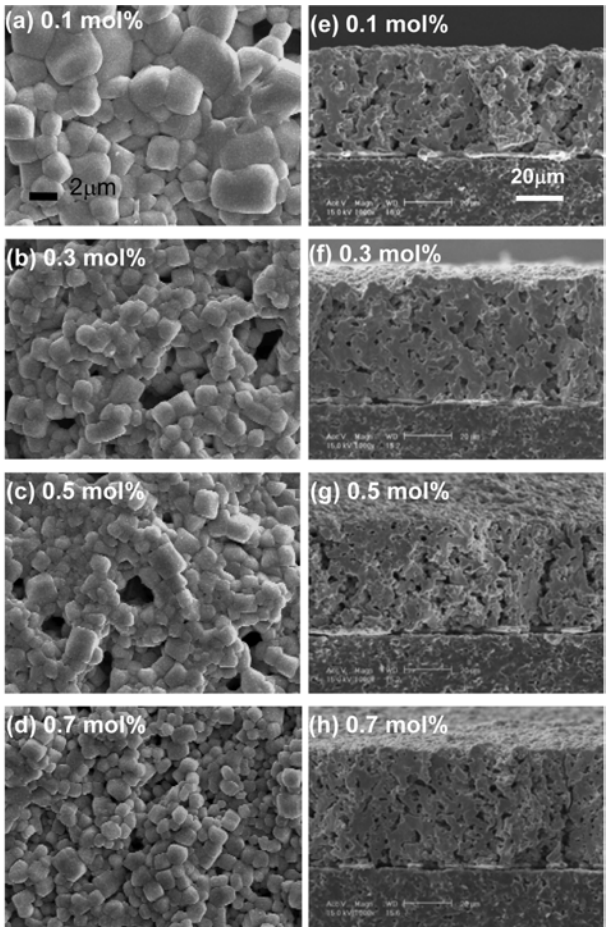

Fig. 3. Surface and cross-sectional SEM micrographs of BSCT specimens with various Pr_2O_3 contents.

thick films showed the typical XRD patterns of a cubic perovskite polycrystalline structure. The lattice constant, calculated from the XRD patterns, of thick films was independent of the Pr_2O_3 content. This can probably be explained by the fact that the Pr^{3+} (0.109 nm) ions irregularly substituted for Ba^{2+} (0.135 nm), Sr^{2+} (0.113 nm) and Ca^{2+} (0.099 nm) ions at the A-sites of ABO_3 perovskite structure. The lattice constants of the BSCT thick film doped with 0.1, 0.3, 0.5 and 0.7 mol% Pr_2O_3 are 0.3959, 0.3955, 0.3953 and 0.3953 nm, respectively.

Figure 3 shows the surface and cross-sectional SEM micrographs of the BSCT thick films with various Pr_2O_3 contents. The average grain size of BSCT thick film decreased with increasing Pr_2O_3 contents. This is due to the fact that Pr^{+3} ions act on the donor dopant in the BSCT specimens [6]. The average grain sizes of the BSCT thick film doped with 0.1 and 0.7 mol% Pr_2O_3 are 2.4 μm and 1.34 μm, respectively. The average thickness of all the specimens was about 50 μm.

Figure 4 shows the Curie temperature of BSCT thick films as a function of Pr_2O_3 content. The Curie temperature of the BSCT specimen decreased with increasing Pr_2O_3 contents, because it created cation vacancies in the lattice which is used for the maintenance of electroneutrality. These cation vacancies cause shrinkage of the lattice and affect the transition temperature [7]. The Curie temperature of the BSCT thick films doped with 0.1 mol% and 0.7 mol% were 25 °C and −5 °C, respectively.

Figure 5 shows the relative dielectric constant and the dielectric loss of BSCT thick films as a function of Pr_2O_3 content at 25 °C. The relative dielectric constant and dielectric loss decreased with increasing Pr_2O_3 contents. These properties may be understood in terms of the effects of decreasing grain size and the Curie temperature with the maximum dielectric constant, as shown in Fig. 4. Generally, the ferroelectric materials show the high dielectric constant and dielectric loss values at around the phase transition temperature due to increasing the displacement of the ions by the thermal energy [8]. Relative dielectric constant and dielectric loss of the BSCT specimen doped with 0.1 mol% Pr_2O_3 were 4714 and 5.9%, respectively.

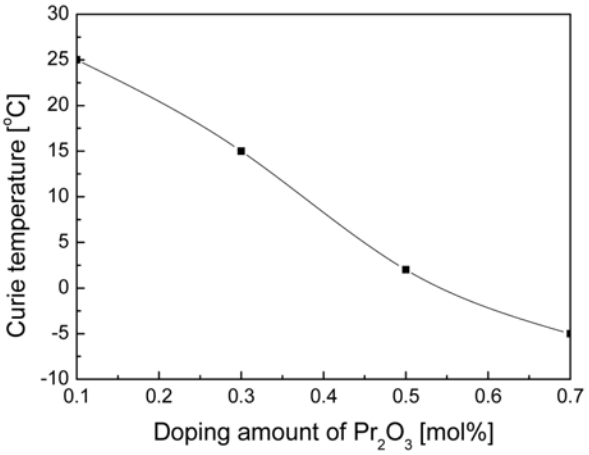

Fig. 4. Curie temperature of BSCT specimens as a function of Pr_2O_3 content.

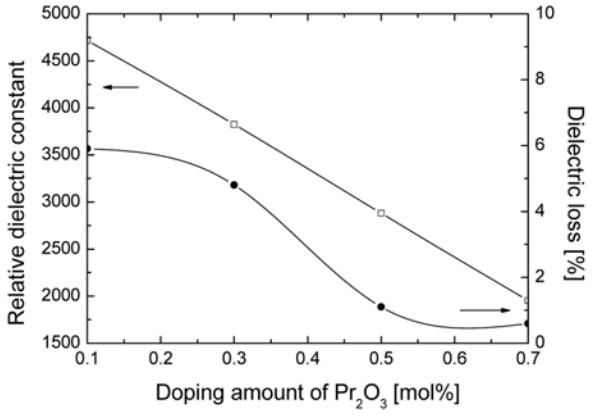

Fig. 5. Relative dielectric constant and dielectric loss of BSCT specimens with various Pr_2O_3 content.

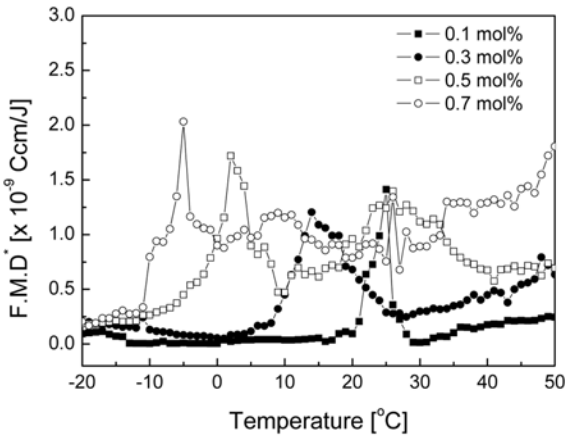

Fig. 6. Pyroelectric coefficient of BSCT specimen with various Pr_2O_3 content as a function of temperature.

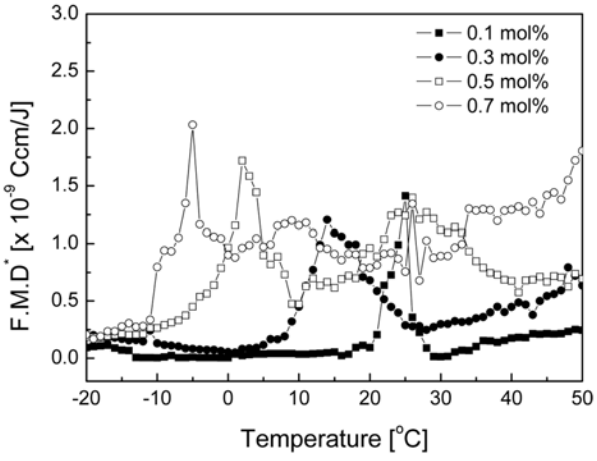

Fig. 7. Figure of merit F.M.D* of BSCT specimen with various Pr_2O_3 content as a function of temperature.

Figure 6 shows the pyroelectric coefficient of BSCT thick films as a function of temperature for the various Pr_2O_3 contents. All BSCT thick films showed the maximum values at around the Curie temperature because the specimens have the high dielectric constant and the large variation of the dielectric constant-temperature curve. The BSCT specimen doped with 0.1 mol% Pr_2O_3 showed the good value of 65.3×10^{-9} C/cm^{2}K at 25 °C.

Figure 7 shows the dependence of the figure of merit F.M.D* for specific detectivity D* (where F.M.D* = p/[c_v(K tanδ)$^{1/2}$], where, p = pyroelectric coefficient, c_v = volume specific heat (= 3.2 J/cm^{3}K) [9], K = dielectric constant, and tandδ = dielectric loss) on Pr_2O_3 content for BSCT specimens. The BSCT thick film doped with 0.5 mol% Pr_2O_3 showed the superior F.M.D* values lager than 1.0×10^{-9} Ccm/J at the temperature range from 20 °C to 35 °C. Even the BSCT specimens doped with 0.1 and 0.3 mol% Pr_2O_3 had good pyroelectric coefficient at around room temperature, and showed a low F.M.D*, due to their high dielectric constant and dielectric loss properties.

Conclusion

BSCT thick films doped with $MnCO_3$ (0.1 mol%) and Pr_2O_3 (0.1-0.7 mol%) have been fabricated by the screen-printing method and characterized for uncooled infrared detector materials. All BSCT thick films showed the typical XRD patterns of a cubic perovskite polycrystalline structure. The average grain size and Curie temperature of BSCT thick films decreased with increasing Pr_2O_3 amount. The average thickness of all the specimens was about 50 μm. The relative dielectric constant and dielectric loss decreased with increasing the Pr_2O_3 contents and the values of the specimen doped with 0.1 mol% Pr_2O_3 were 4714 and 5.9%, respectively. The BSCT specimen doped with 0.1 mol% Pr_2O_3 showed the good pyroelectric coefficient value of 65.3×10^{-9} C/cm^{2}K at 25 °C. The figure of merit F.M.D* for detectivity of the BSCT specimen doped with 0.5 mol% Pr_2O_3, however, showed the good values lager than 1.0×10^{-9} Ccm/J at around room temperature, because the specimen doped with 0.1 mol% Pr_2O_3 had a high dielectric loss.

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