Preparation of lead-free ferroelectric $BaTi_2O_5$ large-sized single crystals by floating zone melting

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The transparent single crystalline $BaTi_2O_5$ about 6 mm in diameter was successfully grown along b-direction by floating zone melting. The effect of foreign element substitution on the dielectric properties of $BaTi_2O_5$ single crystals was investigated. $BaTi_2O_5$ is a promising lead-free ferroelectric material used at higher temperatures due to the high permittivity and the high Curie temperature.

Although the phase diagram of BaO-TiO_2 system has been studied for a long time, the ferroelectricity of $BaTi_2O_5$ (BT_2) has not been known until recently. Our group and Akishige *et al.* independently synthesized single-crystalline BT_2 and reported the significant ferroelectricity only in the *b*-direction. Since BT_2 can be easily decomposed into $BaTiO_3$ (BT) and $Ba_6Ti_{17}O_{40}$ (B_6T_{17}) above 1500 K, large-scaled single crystalline BT_2 can be hardly prepared. In order to apply BT_2 for practical applications, the process to prepare *b*-direction oriented BT_2 single crystal in large scale should be developed.

Dried $BaCO_3$ and TiO_2 powders (purity: 99.99%) were weighed and mixed at the molar ratio of 1 to 2 exactly. A floating zone (FZ) melting apparatus with a xenon heating lamp was used to prepare single crystalline BT_2. The crystal phase was identified by X-ray diffraction (XRD). The dielectric properties were measured in air with an impedance analysis (Hewlett Packard 4194A) from 293 to 1073 K in a frequency (f) range between 10^2 and 10^7 Hz. A gold paste and wire was used as electrodes.

The as-grown single crystalline BT_2 was transparent and its size was 6 mm in diameter and 30 mm in length. Figure 1 shows the appearance of single crystalline BT_2 prepared by FZ, which was cut perpendicular to the growth direction, *i.e.*, *b*-direction. $Ba_{0.99}Sr_{0.01}Ti_2O_5$ (BST_2) single crystal 4 mm in diameter and 16 mm in length was also obtained by the FZ. The SrO distribution in the as-grown single crystals prepared by FZ melting was almost uniform (±0.02%) except the initial and final growth regions.

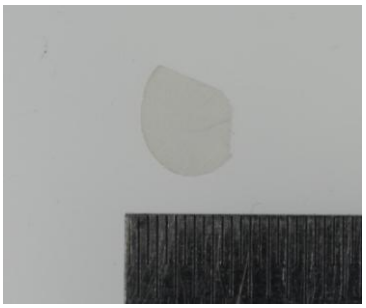

Fig. 1 Appearance of large-sized transparent BT_2 single crystal prepared by FZ.

The peak permittivity (ε_{max}) of single crystalline BST_2 at Curie temperature (T_c) changed depending on SrO content (x). The permittivity of the single crystalline BST_2 showed sharp peaks at the T_c and increased with increasing x until 0.01. Figure 2 demonstrates the effect of x on the T_c and the ε_{max} of single crystalline BST_2. The T_c of single crystalline BST_2 decreased from 748 to 742 K with increasing x from 0 to 0.03. The T_c of BST decreased linearly from 405 to 392 K with increasing x from 0 to 0.03, implying more sensitive to the Sr^{2+} substitution compared to that of BST_2. The solubility limit of Sr^{2+} in $BaTi_2O_5$ was much lower than that in $BaTiO_3$ because of the more complicated crystal structure of $BaTi_2O_5$. The smaller solubility of Sr^{2+} in $BaTi_2O_5$ may result in the smaller change of T_c than that in $BaTiO_3$. The maximum permittivity of single crystalline BST_2 had the highest value of 42190 at x = 0.01.

The remnant polarization (P_r) and coercive electric field (E_c) of single crystalline $BaTi_2O_5$ were 1.4×10^{-2} Cm^{-2} and 0.7×10^6 Vm^{-1}, respectively. The P_r and E_c of the single crystalline BST_2 at x = 0.03 were 4.8×10^{-2} Cm^{-2} and 1.7×10^6 Vm^{-1}, which were much larger than that of single crystalline BT_2, respectively.

Key Words

Lead-free ferroelectric $BaTi_2O_5$, Single crystal, Floating zone melting

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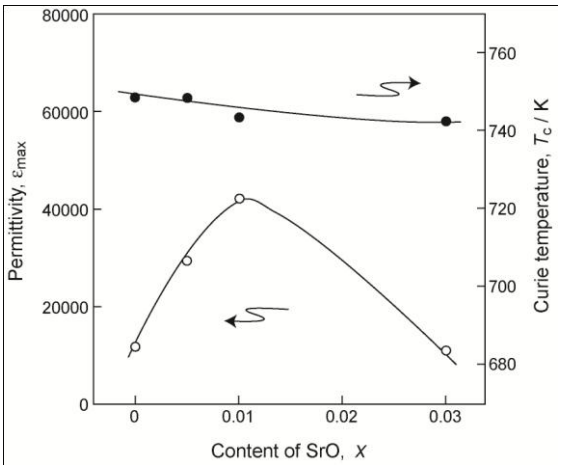

Fig. 1 Effect of SrO content in BST_2 single crystal on the highest permittivity and Curie temperature.