

Fabrication and Characterization of Perovskite Oxynitride Dielectrics

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Perovskite-type oxides (ABO_3) are the most widely used ferroelectric materials and their excellent dielectric properties have attracted much attention not only in the electroceramic industry but also in fundamental research. The polarization mechanism of dielectric properties and the origin of ferroelectricity are closely related to the covalency of A–O and B–O. Therefore, the anion substitution of the O-site is attractive for controlling the dielectric and ferroelectric properties. In this paper, we show a fabrication method and the dielectric properties of perovskite oxynitride dielectrics.

Strontium titanium oxynitride ($SrTiO_3:N$) single crystals were prepared by annealing $SrTiO_3$ single crystals at 1000 °C in gaseous ammonia. $SrTiO_3:N$ was assumed to have the chemical composition $SrTiO_{3-3x}N_{2x}$, which contained oxygen vacancies. To reduce the number of oxygen vacancies, $SrTiO_3$ crystals co-doped with nitrogen and niobium ($SrTiO_3:N,Nb$) were fabricated. Semiconducting Nb-doped $SrTiO_3$ crystals changed to dielectric N,Nb-codoped $SrTiO_3$ crystals with a resistivity of $6 \times 10^{12} \Omega \cdot cm$ with annealing in gaseous ammonia. XPS measurement indicated that niobium doping was effective for increasing the amount of dopant nitrogen. Figure 1 shows the dielectric permittivities and loss tangents of the $SrTiO_3$, $SrTiO_3:N$, and $SrTiO_3:N,Nb$ crystals. The relative permittivities of the $SrTiO_3:N$ and $SrTiO_3:N,Nb$ crystals were respectively 340 and 410 at 1 MHz, which were higher than that of the pure $SrTiO_3$ crystal (310). The dielectric permittivity increased with the amount of dopant nitrogen, indicating the effectivity of nitrogen doping for increasing the dielectric permittivity of perovskite oxides.

To understand the enhancement of the permittivity, we measured THz dielectric spectrum of the $SrTiO_3:N,Nb$ crystal using a far-infrared spectroscopic ellipsometer. As shown in Fig. 2, the Slater mode (soft mode) frequency shifted to a lower frequency, and therefore the ionic polarization was increased by the nitrogen substitution. Since nitrogen has a smaller electronegativity than oxygen, the covalency between Ti and O/N in $SrTiO_3:N$ should be higher than that between Ti and O in pure $SrTiO_3$. The high covalency weakens the short-range repulsion forces against long-range dipolar interaction. Therefore, substitution with nitrogen may enhance the ionic polarizability of $SrTiO_3$. Therefore, the ionic polarization might increase with nitrogen substitution.

References

- 1) T. Hoshina, A. Sahashi, H. Takeda, and T. Tsurumi, *Jpn. J. Appl. Phys.*, **54**, 10NB05 (2015).

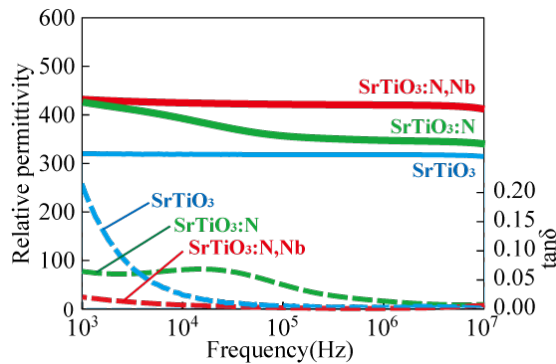


Fig. 1. Dielectric permittivities and loss tangents of $SrTiO_3$, $SrTiO_3:N$, and $SrTiO_3:N,Nb$ crystals.

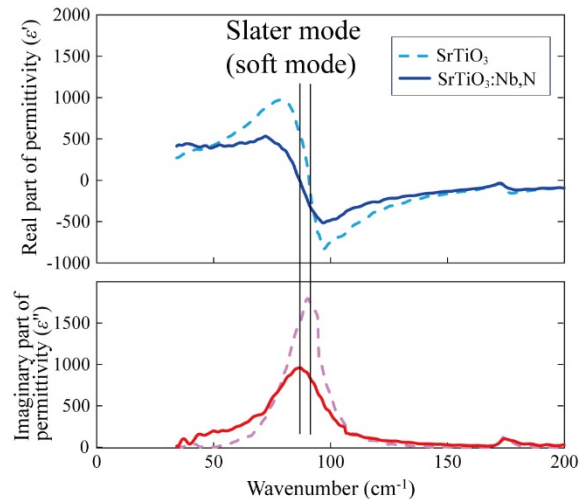


Fig. 2. THz dielectric spectrum of $SrTiO_3$ and $SrTiO_3:N,Nb$ crystals using a far-infrared spectroscopic ellipsometer.