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論　　文　　名	「Study on the development of $BiFeO_3$-based lead-free piezoelectrics （$BiFeO_3$ をベースとした非鉛圧電体の開発に関する研究）」
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論文要旨

$BiFeO_3$ (BFO) has attracted much attention due to its very high Curie temperature (T_C) (~820 ℃), large spontaneous polarization (~100 μC/cm^2) and multiferroic properties. While it is expected to have a wide range of novel applications, the d_{33} piezoelectric coefficient of BFO is as low as ~20 pm/V in spite of the excellent properties. Furthermore, difficulty in preparation of single phase by a ceramic process and a large coercive field of above 10 kV/mm restrict the applications to piezoelectric fields.

Therefore, various BFO-based solid solutions, such as $BiFeO_3$-$BaTiO_3$, $BiFeO_3$-(Bi,K)TiO_3, $BiFeO_3$-(Bi,Na)TiO_3, $BiFeO_3$-$BiCoO_3$, and $BiFeO_3$-$ReFeO_3$ (Re=rare-earth) have been investigated to solve these issues. Although extensive studies have been carried out using ceramics and thin films in recent years to enhance the piezoelectric properties at morphotropic phase boundary (MPB), the d_{33} coefficient remains at around 100 pm/V.

$(Bi_{0.5}K_{0.5})TiO_3$ (BKT) is the promising end-member to make solid solution with BFO, which has rhombohedral structure (R3c), because it has a high T_C (~370 ℃) and tetragonal structure (P4mm). The solid solution of BFO and BKT is expected to have a MPB between ferroelectric phases and to have a high ferroelectric and a piezoelectric activity. For this reason, the crystal structure and the electrical properties of BFO-BKT solid solutions have been of interested in recent years. It has been reported that dense BFO-BKT ceramics was prepared by using nanosized (~100 nm) powder and showed a large P_r of ~50 μC/cm^2 and a moderate electromechanical coupling factor (k_{33}) of ~0.35 with temperature stability up to 300 ℃.

$(Bi_{0.5}Na_{0.5})TiO_3$ (BNT) has ferroelectricity with a P_r of ~35 μC/cm^2 at room temperature, a high T_C (~ 320 ℃) and a rhombohedral symmetry (R3c). It was reported that the BFO-BNT system, which has rhombohedral structure throughout the composition, have the d_{33}*

piezoelectric coefficient above 180 pm/V. This might be a new approach towards the development of high performance piezoelectric thin films, because the piezoelectric response is significantly enhanced without using MPB. These results are explained by the manipulation of the lattice distortion.

In this thesis, to investigate the ferroelectric and piezoelectric properties of the BFO-based solid solutions, the thin film growth of the BFO-BKT and BFO-BNT binary system was presented. To understand the effect of substitution of BKT and BNT on the phase development, the surface morphologies and the dielectric, ferroelectric, and piezoelectric properties were discussed. This thesis consists of six chapters, and the outline of each chapter is described below.

In chapter 1, a short overview of the properties and current issues of BFO is provided.

In chapter 2, the effects of sintering conditions on the phase development and ferroelectric properties of BFO ceramics were investigated. The BFO ceramics were prepared by conventional solid-state reaction method. A pinched polarization electric-field (P-E) loop was observed in the sample sintered at high temperature for a short period (820 ℃ for 1 hour) because the domain wall motion is prohibited by a large amount of ionic defects such as oxygen vacancy. The BFO ceramic sintered at low temperature for a long period (760 ℃ for 6 hours) displayed well-saturated P-E loop, which suggests the decrease of the defect. The decrease in the polarization by ac electric field cycling, which is fatigue, was observed in the sample sintered at 760 ℃ for 6 hours. The fatigue by ac field cycling was started after the initial state increase in the polarization due to the depinning process in the sample sintered at 820 ℃ for 1 hour.

In chapter 3, multiple dielectric relaxations were observed in (1-x)BFO-xBKT (BFO-BKT). Temperature-dependent dielectric relaxations of BFO-BKT lead-free piezoceramics were investigated via impedance spectroscopic techniques. Regardless of the compositions, the dielectric maximum temperatures exhibit a frequency-dependent dispersion, origination from a Debye relaxation due to the presence of oxygen vacancies.
It was also observed that there exist local dielectric maxima due to the relaxation of polar nanoregions (PNR) as a shoulder on the lower temperature side. The onset temperature for the Debye-type relaxation decreased with decreasing BKT content, gradually overlapping with the low-temperature dielectric dispersion from the relaxation of PNR. It was proposed that the role of BKT in the BFO-BKT system is to enhance the random fields that favor a relaxor state and to suppress the Debye-type relaxation of oxygen vacancy related dipoles.

In chapter 4, the growth of 0.6BFO-0.4BKT thin films by rf-sputtering deposition was investigated. The (100)-oriented films with perovskite were grown on (100)-oriented $LaNiO_3$

(LNO) bottom electrodes at substrate temperatures of 475-575 ℃. It was found that the lattice constant of the films decreases with increasing growth temperature. Moreover, the films deposited below 505 ℃ show a dielectric permittivity of ~600 and a loss tangent of 0.02 at 1 kHz, whereas the films deposited above 540℃ show large frequency dispersion. It appears that these results are caused by A-site deficiency. Although ferroelectricity was observed at the growth temperatures of 475 and 505 ℃, the piezoelectric properties response was obtained only at 505 ℃. The obtained results suggest that BKT has an effect to reduce the growth temperature.

In chapter 5, the effect of BNT substitution on the phase development and ferroelectric and piezoelectric properties of BF films were investigated. Pure BFO and 1-*x*BFO-*x*BNT thin films with *x*=0.05 were grown on LNO/Si substrate by co-sputtering method. All films showed (100) orientation due to the (100) texture growth of LNO. It was found that BFO–BNT films showed better ferroelectric and piezoelectric properties than the BFO films deposited under the same condition, especially at the deposition temperature of 450 °C. The addition of small amount of BNT (*x*=0.05) to BF films increases the dielectric constant to ~480. The piezoelectric coefficient ($d_{33(\mathrm{AFM})}$) of the BF–BNT film deposited at 450 °C is ~100 pm/V, which is comparable to the best value of BF–based films with substitutions of other perovskite or rare-earth elements. Therefore, BFO-BNT is promising material for the development of lead-free piezoelectric films with potential for low temperature growth.

In chapter 6, the results obtained in this study were summarized. It is indicated that the electrical properties of pure BFO and BFO-based materials differ depending in the manufacturing process of the sample. Especially, it seems that low temperature preprocess appears to offer a solution to the fundamental problems of BFO to obtain enhanced electrical properties for both ceramic and thin films.

審査結果の要旨

鉛の有害性明らかになって以来、圧電材料の非鉛化の要求が高まっている。セラミックスを中心に多くの研究が行われているが、鉛系材料に匹敵する材料は未だ開発されていない。本論文は、$BiFeO_3$(BFO)をベースとした非鉛圧電体の開発を目的として研究を行ったものであり、以下の成果を得ている。

（１）BFO は約１０年前に良好な強誘電性を有することが見いだされた物質であるが、同時に絶縁性が低いという課題を有することも明らかになっている。その起源として酸素欠損が指摘されているため、焼結条件が BFO の電気的特性に及ぼす影響を調べた。その結果、標準的な焼結条件に比べて、低温(760℃)かつ長時間(6h)の焼結より、格子欠陥密度の減少

を示す誘電特性が得られることを見出した。

（2）圧電特性の向上において代表的な方法の一つに濃度相境界(MPB)の利用がある。MPB とは、結晶構造の異なる強誘電体材料の固溶体系において、結晶構造が変化する組成境界のことである。ここでは、菱面体構造を有する BFO に正方晶構造を有する$(Bi_{0.5}K_{0.5})TiO_3$(BKT)の固溶体のセラミックス試料を作製し、その誘電緩和特性を調べた。組成によらず酸素欠損の存在を示すデバイ型の誘電緩和現象が確認された。BKT 組成と誘電緩和特性との関係から、BFO-BKT 系における BKT の添加は、酸素欠損に起因した電気双極子のデバイ型緩和の抑制に対して効果を有することを明らかにした。

（3）BFO-BKT 系において、酸素欠損量の減少を示唆する結果が得られたため、MEMS 応用で重要となる薄膜の作製を行い、その結晶構造、強誘電特性および圧電特性を調べた。製膜方法にはスパッタ法を用い、基板には(100)配向成長した $LaNiO_3$ 電極を有する Si 基板を用いた。500℃程度の基板温度で製膜した試料は高い誘電率を有していること、製膜温度を上昇させると格子欠陥の存在を示す誘電緩和現象が現れることを見出した。これは K 揮発に起因していると考えられた。以上の結果から、BFO-BKT 薄膜においては、低温成長が必要であるが､その条件で作製した薄膜は BFO 薄膜よりも高い誘電電特性を有していることを明らかにした。

（4）BKT は K の揮発という課題を有していることが明らかになったので、K を Na に置換した系の薄膜の作製に取り組んだ。その結果、5%程度の BKT の添加により、誘電率および圧電応答が増大することを見出した。得られた圧電応答は希土類を添加した BFO 薄膜において得られた結果とほぼ同等であり、有望な圧電体薄膜材料であると結論付けた。

以上の成果は、$BiFeO_3$ をベースとする強誘電体材料が有望な非鉛圧電体薄膜になりうることを示したものである。また、申請者が自立して研究活動を行うのに必要な能力と学識を有することを証したものである。