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# Solid-state-growth of lead-free piezoelectric $(Na_{1/2}Bi_{1/2})TiO_3$-$CaTiO_3$ single crystals and their characterization

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ABSTRACT

Single crystals in the $(Na_{1/2}Bi_{1/2})TiO_3$-$CaTiO_3$ system have been grown for the first time using the solid state crystal growth method. Seed crystals of $SrTiO_3$ were buried in $0.96(Na_{1/2}Bi_{1/2})TiO_3$-$0.04CaTiO_3$ (NBT-4CT) powder which was then pressed into pellets. Pellets were sintered and single crystals of NBT-4CT grew on the seeds. Electron probe micro analysis shows that the chemical composition of the single crystal is close to the nominal composition. X-ray diffraction and micro-Raman scattering analysis shows that the single crystal has the rhombohedral $(Na_{1/2}Bi_{1/2})TiO_3$ structure. Single crystals were also grown by bonding a seed crystal to a pre-sintered NBT-4CT pellet and annealing. The single crystal shows dielectric behavior similar to that of NBT-4CT ceramics and other $(Na_{1/2}Bi_{1/2})TiO_3$ -based ceramics and single crystals. Characteristic dielectric transitions can be related to the rhombohedral-tetragonal and tetragonal-cubic phase transitions. The NBT-4CT single crystal has improved ferroelectric and piezoelectric properties compared to the bulk polycrystalline ceramic.



## 1. Introduction

Piezoelectric ceramics find an increasing number of applications as transducers, actuators and sensors [1]. The most popular piezoelectric ceramic is $Pb(Zr,Ti)O_3$ due to its excellent properties and versatility [2,3]. However, recent legislation from several countries and regions e.g. China, Japan and the European Union, restricting or prohibiting the use of lead in electronic products has provided a strong impetus to the study of lead-free piezoelectric materials [2,4,5]. At present, the majority of research into lead-free piezoelectric materials is concerned with ceramics based on $(K_{0.5}Na_{0.5})NbO_3$ and $(Na_{1/2}Bi_{1/2})TiO_3$ (NBT) [2,4,6,7].

Pure NBT is difficult to pole due to its high coercivity and large leakage current [8]. The electrical properties of NBT can be improved by forming solid solutions with other perovskites such as $BaTiO_3$ and $SrTiO_3$ [9,10]. The addition of a second component to NBT leads to the formation at a particular composition of a morphotropic phase boundary (MPB) between two phases. The piezoelectric properties of compositions close to the MPB are improved [2]. The $(Na_{1/2}Bi_{1/2})TiO_3$-$BaTiO_3$ system (NBT-BT) has an MPB between rhombohedral and tetragonal phases at ~6–10 mol% $BaTiO_3$ addition [9,11]. The NBT-BT system has been comprehensively studied [2,12–14]; however, the $(Na_{1/2}Bi_{1/2})TiO_3$-$SrTiO_3$ (NBT-ST) and $(Na_{1/2}Bi_{1/2})TiO_3$-$CaTiO_3$ (NBT-CT) systems have received less attention [15–17]. The NBT-ST system has an MPB between rhombohedral and pseudocubic phases at ~20–30 mol% $SrTiO_3$ addition [10,16]. Large electric field-induced strains were found in compositions close to the MPB [10,18]. The NBT-CT system has an MPB between rhombohedral and orthorhombic phases at ~8–14 mol% $CaTiO_3$ addition [17,19]. The composition $0.96(Na_{1/2}Bi_{1/2})TiO_3$-$0.04CaTiO_3$ was found to have the optimal value of $d_{33}$ by Du et al. [20].

In addition to choosing compositions near an MPB, the properties of NBT-based materials can also be improved by growing single crystals [12,21–24]. A polycrystalline ceramic consists of many randomly oriented micron-scale crystals (grains) whereas a single crystal is a large (several hundred micron scale or larger) crystal. In a polycrystalline ceramic, the grains are randomly oriented and it is not possible to align all of the ferroelectric domains with the

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electric field during poling. In a single crystal, the crystallographic orientation of the single crystal piece can be controlled and aligned with the poling field, allowing better alignment of the ferroelectric domains. Also, the lack of grain boundaries eliminates grain boundary pinning of the domains, making reorientation easier. The use of single crystals also allows domain engineering and poling in nonpolar directions to further improve the piezoelectric properties [25–27]. Again, many references exist regarding single crystal growth in the NBT-BT system but little or no work has been done on single crystal growth in the NBT-ST and NBT-CT systems to our knowledge. Therefore it would be of interest to grow single crystals of NBT-CT as a possible alternative to NBT-BT single crystals. Single crystals of NBT-BT and NBT-ST were previously grown by the solid state crystal growth method [23,28,29]. The present work describes the growth of single crystals of NBT-CT by the solid state crystal growth method, their structure and electrical properties.

## 2. Materials and methods

Powders of formula $0.96(Na_{1/2}Bi_{1/2})TiO_3$-$0.04CaTiO_3$ (NBT-4CT) were synthesized by the solid state reaction method. The starting materials were $Na_2CO_3$ (ACROS Organics, 99.5%), $Bi_2O_3$ (Alfa Aesar, 99.9%), $TiO_2$ (Alfa Aesar, 99.8%) and $CaCO_3$ (Alfa Aesar, 99.5%). All starting materials were dried at 250 °C for 5 h to remove adsorbed water before weighing. Stoichiometric amounts of the starting materials were ball milled in a polypropylene jar for 24 h with high purity (99.9%) ethanol and $ZrO_2$ milling media. The ethanol was then evaporated from the slurry by using a hot plate with magnetic stirrer. The dried powder cake was then crushed in an agate mortar and pestle and sieved through a 180 μm mesh to remove agglomerates. The powder was calcined in a high purity alumina crucible with lid at 850 °C for 3 h. The phase purity of the calcined powder was investigated by X-ray Diffraction (XRD X'Pert PRO, PANalytical, The Netherlands) using CuKα radiation, a scan range of 20–90° 2θ and a scan speed of $3°.min^{-1}$. The powder was ball milled as before to break up any agglomerates.

$SrTiO_3$ seed crystals (MTI Corp, Richmond, CA) of dimensions 3 mm × 3 mm × 0.5 mm and [0 0 1], [1 1 0] and [1 1 1] orientations were embedded into 0.7 g of powder and lightly pressed into pellets by hand in a stainless steel die of 10 mm diameter to form samples. The samples were then cold isostatically pressed at 1500 $kg.cm^{-2}$ (~147 MPa). Samples were sintered at 1200 °C for 20 h with heating and cooling rates of $5\ °C.min^{-1}$. To reduce volatilisation of Na and Bi during sintering, the samples were buried in a 2 wt% $Na_2CO_3$ – 2 wt% $Bi_2O_3$ – 96 wt% NBT-4CT packing powder in a double alumina crucible with lids.

Sintered samples were sectioned vertically using a diamond wheel saw, polished to a 1 μm finish with diamond paste and thermally etched. The microstructure of the specimens was examined by Scanning Electron Microscopy (SEM, S-4700, Hitachi, Tokyo, Japan) with an Energy Dispersive Spectrometer attachment with standardless quantification (EDS, EMAX Energy EX-200, Horiba, Kyoto, Japan). The grain size distribution of the ceramic matrix was measured from SEM micrographs using ImageJ v.1.46 software. For each sample, at least 200 grains were measured. Electron Probe Microanalysis (EPMA, EPMA-1600, Shimadzu, Kyoto, Japan) was used to measure the chemical composition of a polished and unetched sample. The sample was measured under an accelerating voltage of 15 kV. NaCl, Bi, Ti, Zr, $BaF_2$ and $CaF_2$ were used as standards with ZAF4 correction.

To study the structure of the single crystals, a polished and unetched sample was examined using micro-Raman scattering with a 514 nm $Ar^+$ ion laser and output power of 10 mW (LabRam HR800 UV Raman microscope, Horiba Jobin-Yvon, France). Raman spectra were recorded at room temperature in back scattering geometry with a resolution of ~0.5 $cm^{-1}$. The diameter of the laser spot on the sample was 1–2 μm. One measurement point was taken on the seed crystal, two points on the NBT-4CT single crystal and two points on the polycrystalline matrix. Peak fitting of Gaussian peaks was carried out using the program fityk 0.9.8 [30].

For measurement of the electrical properties, single crystals of NBT-4CT were grown using the top seeded growth method. 0.5 g of NBT-4CT powder (without a seed crystal) was pressed by hand in a stainless steel die of 10 mm diameter to form a pellet, then cold isostatically pressed as before. The pellet was sintered at 900 °C for one hour with heating and cooling rates of $5\ °C.min^{-1}$. The top face of the sintered pellet was polished to a 1 μm finish with diamond paste. A screen printing paste was prepared by mixing 3 g of NBT-4CT powder, 10 g of alpha-terpinol (Alfa Aesar, 96%), 1.5 g of ethyl cellulose (Sigma-Aldrich, 48.0–49.5% w/w ethoxy basis) and 50 ml of ethanol in a mortar and pestle. Two or three layers of the paste were painted on the top face of the sintered pellet and the paste was then partially dried in an oven at 80 °C. A [110]-oriented $SrTiO_3$ seed crystal was then pressed onto the top face of the sample. After drying, the sample was heat-treated at 350 °C for 1 h to burn out the organic materials in the paste. The sample was then buried in Na and Bi-excess NBT-4CT packing powder as before and annealed at 1200 °C for 20 h, with heating and cooling rates of $2\ °C.min^{-1}$. The screen printing paste fixes the seed crystal to the sintered pellet, making sample handling more convenient, and provides a good bond between the seed crystal and the sintered pellet. This is necessary for uniform single crystal growth across the whole face of the seed crystal.

After annealing, the samples were sectioned vertically and polished as before. One half of a sample was thermally etched and then examined by SEM. To prepare a single crystal sample for XRD, the sample used for SEM analysis was ground on its top face with SiC grinding paper to remove the $SrTiO_3$ seed crystal. The top and side faces were then ground with #2000 SiC paper to remove the Pt coating applied before SEM analysis. The top face of the sample was analysed by XRD as before.

To measure the dielectric properties, one half of a sample was polished to expose the single crystal on both sides (but not thermally etched). Pt pastes were symmetrically applied to both the single crystal and polycrystalline matrix regions of the sample by annealing at 900 °C for 10 min, allowing separate measurement of both regions of the sample, which are hereafter referred to as "SC" and "PM," respectively. Dielectric properties were measured using an impedance analyser (HP4284A, Hewlett-Packard, Kobe, Japan) in $O_2$ in the temperature range 700–40 °C on cooling at $1\ °C.min^{-1}$. For comparison, a bulk polycrystalline NBT-4CT sample, which is notated as "BP", was prepared by sintering a 0.5 g pellet (without seed crystal) at 1200 °C for 1 h, with heating and cooling rates of $5\ °C.min^{-1}$. The sample was polished on both sides, and the temperature-dependent dielectric properties were measured similarly. The comparison of the electrical response of SC, PM and BP over the wide temperature is expected to show the effects of the thermal history as well as microstructure on the dielectric properties associated with phase transitions.

For polarization and strain hysteresis measurements, an NBT-4CT single crystal sample was grown using the top seeded growth method as before. The sample was horizontally sectioned using a low speed diamond wheel saw and parallel polished on both sides using SiC paper to a final finish of #4000 grade. The thickness of the sample was ~1 mm and the horizontal faces of the sample were approximately parallel to the (1 1 0) plane of the single crystal. The sample contained both single crystal and polycrystalline regions (due to the small size and fragility of the sample, it was not possible to remove all the polycrystalline matrix region surrounding the single crystal). A silver paste was screen printed on