

Precession Electron Diffraction Studies of $\text{Sr}_x\text{Ba}_{1-x}\text{Nb}_2\text{O}_6$ and $\text{Ca}_x\text{Ba}_{1-x}\text{Nb}_2\text{O}_6$ Single Crystals

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Crystal structures of two single crystals $\text{Sr}_x\text{Ba}_{1-x}\text{Nb}_2\text{O}_6$ and $\text{Ca}_x\text{Ba}_{1-x}\text{Nb}_2\text{O}_6$ have been reinvestigated using automated electron diffraction tomography method with beam precession. 3D reciprocal space has been reconstructed based on recorded tilt series. For both samples the crystal structure was refined and the tetragonal symmetry with space group $P4bm$ was confirmed. The three dimensional reciprocal space allowed to observe and to study satellite reflections in both materials.

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1. Introduction

The crystals of ferroelectric niobates with an open tetragonal tungsten bronze structure such as strontium barium niobate $\text{Sr}_x\text{Ba}_{1-x}\text{Nb}_2\text{O}_6$ (SBN) and calcium barium niobate $\text{Ca}_x\text{Ba}_{1-x}\text{Nb}_2\text{O}_6$ (CBN) are technologically important due to their pyroelectric, dielectric, and photorefractive properties [1, 2].

SBN (CBN) shows a crossover from normal to relaxor ferroelectric behavior with increasing Sr (Ca) content because of the enhancement of random fields mostly originating from the missing charges at A (i.e. A1 and A2) unoccupied sites in the tetragonal tungsten bronze (TTB) structure (Fig. 1) [3]. Upon heating from room temperature, they undergo a ferroelectric phase transition from $4mm$ to $4/mmm$ symmetry [4].

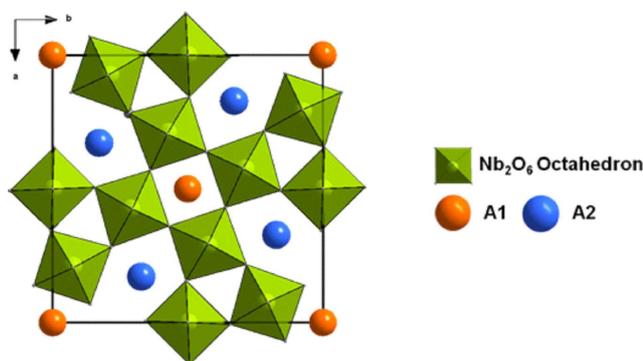


Fig. 1. The projection of the tetragonal tungsten-bronze unit cell along the c axis.

Automated electron diffraction tomography (ADT) is a recently developed method for electron diffraction acquisition and analysis [5–7]. Differently from traditional acquisition based on oriented patterns, ADT is able to sample the whole reciprocal space inside the tilt range of the microscope and to reduce dynamical effects, so that intensity data can be used for *ab initio* structure determination by a simple kinematical approximation ($I \approx F^2$).

Precession electron diffraction (PED) is a measurement technique with increasing interest and applications. The method was proposed in 1994 by Vincent and Midgley [8] for *ab initio* structure determinations. PED patterns usually contain more Bragg peaks than diffraction patterns collected without beam precession — conventional selected area diffraction (SAED) patterns. This fact is explained by the geometrical consideration that during PED measurements bigger volume of the reciprocal space is sampled [7]. Using that technique intensity of the diffracted beams is integrated over selected region of reciprocal space increasing data completeness. Due to these features PED pattern contain more complete data with more reliable intensities suitable for structural studies. Additional benefit of beam precession is the reduction of dynamical interactions [6] so kinematical approximation can be used during crystal structure determination and refinement.

The aim of presented work was the reinvestigation of crystal structure down to nanoscale. For both samples crystal structure was refined and the tetragonal symmetry with space group $P4bm$ was confirmed. Additionally, the three-dimensional reciprocal space allowed to observe and to study satellite reflections in both materials.

2. Experimental

$\text{Sr}_x\text{Ba}_{1-x}\text{Nb}_2\text{O}_6$ where $x = 0.50$ (SBN50) and $\text{Ca}_x\text{Ba}_{1-x}\text{Nb}_2\text{O}_6$ where $x = 0.28$ (CBN28) single crystals were grown by the Czochralski method [9]. Single crystals were prepared as standard thin foil used in transmission electron measurements. Samples were cut to plates along [100] and [001] with optically polished $5\text{ mm} \times 5\text{ mm}$ surfaces with 1 mm thickness. Next they were polished and thinned by sand paper, mechanical grinder and finally thinned by focused Ar ion beams.

Transmission electron microscopy (TEM) measurements were performed and electron diffraction patterns with beam precession were recorded sequentially (Figs. 2 and 3) while tilting a crystal around an arbitrary crystallographic axis with 1° steps [5]. After each rotation

crystal was tracked in image mode to ensure that data collection is performed always from the same region.

Data collection for both crystals was performed on JEM 3010 electron microscope with $2k \times 2k$ CCD camera within tilt range of 36° (for SBN 50) and 52° (for CBN 28). High tension was 300 kV and Nanomegas DigiStar electron beam precession attachment was used.

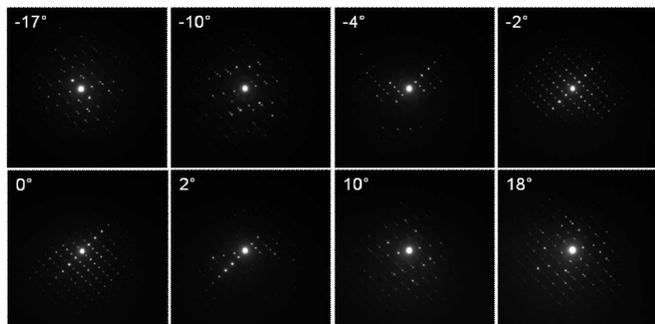


Fig. 2. Electron diffraction tilt series taken for sample $\text{Ca}_x\text{Ba}_{1-x}\text{Nb}_2\text{O}_6$.

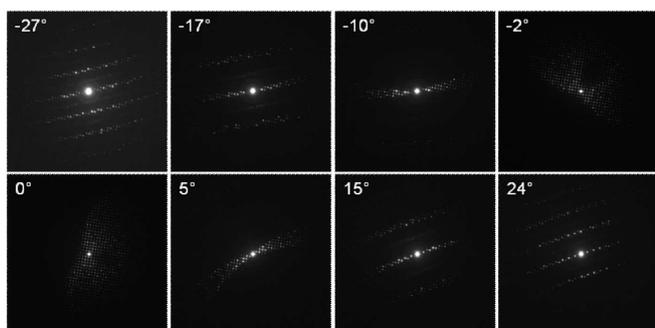


Fig. 3. Electron diffraction tilt series taken for sample $\text{Ca}_x\text{Ba}_{1-x}\text{Nb}_2\text{O}_6$.

Three-dimensional reciprocal space was reconstructed and diffraction intensities were extracted from tilt series by means of ADT3D software package [10]. Visualization of reciprocal space (Fig. 4) was performed by means of *Chimera* program [11].

3. Results and discussion

The goal of performed 3D reconstruction and investigation of reciprocal space is the determination of the unit cell parameters, crystal space group and extraction of intensities for the measured diffraction peaks. The accuracy of cell parameters determination from tilt series of electron diffraction patterns is influenced by the calibration procedures and other systematic errors during data reduction process (locating of the centre of individual diffraction pattern, correction for the tilt of rotation axis and background correction). The elongation of the Bragg peaks associated with the size effects and dynamical excitation causes additional ambiguity in the reflection's true position which influences lattice parameters [6, 12].

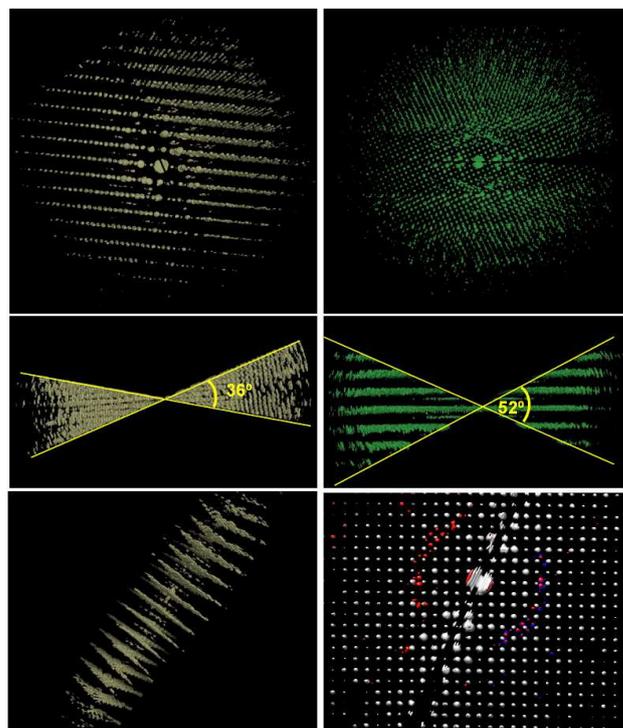


Fig. 4. Projections of 3D reciprocal space which allowed to observe and to study satellite reflections for sample $\text{Sr}_x\text{Ba}_{1-x}\text{Nb}_2\text{O}_6$ (left) and $\text{Ca}_x\text{Ba}_{1-x}\text{Nb}_2\text{O}_6$ (right).

TABLE I

Basic crystallographic information for studied crystal structures up to resolution of 0.8 Å.

Chemical formula	$\text{Sr}_x\text{Ba}_{1-x}\text{Nb}_2\text{O}_6$	$\text{Ca}_x\text{Ba}_{1-x}\text{Nb}_2\text{O}_6$
crystal system	tetragonal	
a [Å]	12.413	13.366
c [Å]	3.936	4.187
Unit cell volume [Å ³]	606.8	747.9
temperature	<i>RT</i>	
space group	<i>P4bm</i>	
No. of formula units per unit cell, Z	5	
radiation type	electron, 300 kV (0.0197 Å)	
tilt range [°]	36	52
No. of reflections measured	776	1555
No. of independent reflections	300	306
completeness [%]	52	76
R_{int}	0.3860	0.3146
final R_1 values ($I > 2\sigma(I)$)	0.3946	0.3338
final $wR(F^2)$ values ($I > 2\sigma(I)$)	0.7281	0.6583
final R_1 values (all data)	0.4170	0.3490
final $wR(F^2)$ values (all data)	0.7594	0.6769

Structures of two single crystals $\text{Sr}_x\text{Ba}_{1-x}\text{Nb}_2\text{O}_6$ where $x = 0.50$ (SBN50) and $\text{Ca}_x\text{Ba}_{1-x}\text{Nb}_2\text{O}_6$ where $x = 0.28$ (CBN28) were refined using full matrix least squares method by means of SHELXL97 [13] software. Obtained results are gathered in presented Table I.

For both samples $P4bm$ space group has been confirmed and no additional electron potential is observed in the unit cell. Refinement has been performed assuming kinematical approximation and this is the main reason for relatively large agreement factors ($R1$, $wR2$) in comparison to those usually obtained from X-ray measurements.

The aim of performed measurements was the reinvestigation of crystal structure down to nanoscale. The three-dimensional reciprocal space allowed to observe and to study satellite reflections in both materials.

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