NEUTRON DIFFRACTION EXPERIMENTS ON THE MODULATED STRUCTURE OF $Sr_xBa_{1-x}Nb_2O_6$

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$Sr_xBa_{1-x}Nb_2O_6$ ($0.25<x<0.75$) is a very attractive material for technological applications and basic research because of its high electro-optic, piezoelectric and pyroelectric coefficients and its favorable photorefractive properties, for example holographic data storage (Fig. 1).

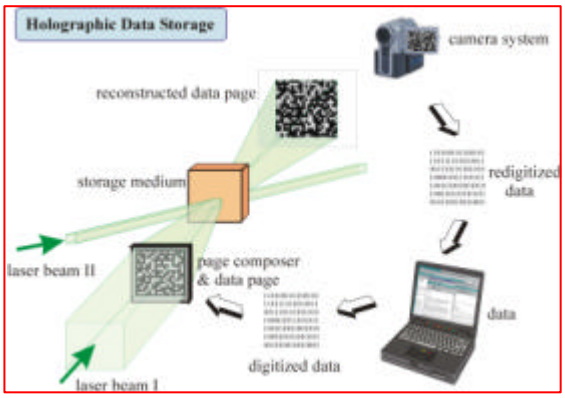

Figure 1. Schematic layout for holographic data storage. The holograms are written from different direction into the crystal, therefore taking advantage of 3-dimenstional data storage

It belongs to the class of oxygen octahedral ferroelectrics possessing tetragonal potassium tungsten bronze structure [1]. The average structure of congruently melting $Sr_{0.61}Ba_{0.39}Nb_2O_6$, space group P4bm, has been determined by X-ray diffraction [2], showing that the structure is a three-dimensional network of NbO_6 octahedra linked by their corners forming alternating five- and four-membered rings (see Fig. 2). The five Sr/Ba atoms are statistically distributed over 6 possible lattice places.
Two full data sets on a poled (300V/mm) single crystal of $Sr_{0.61}Ba_{0.39}Nb_2O_6$ (size: a=b=4mm, c=5mm) were measured on the two four-circle diffractometers TriCS at the Swiss Neutron Spallation Source SINQ at PSI, Villigen/Switzerland and 5C2 at the Laboratoire Léon Brillouin (LLB) in Saclay/France. We were interested in the origin of the modulated structure, especially if it is due to occupational or distortional modulation, and if this modulation is harmonic or not (appearance of higher order satellites).

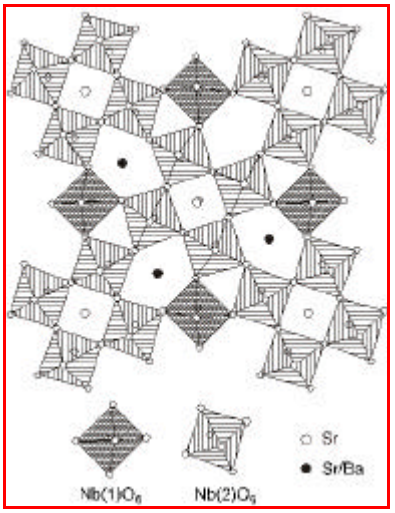

Figure 2. Average structure of $Sr_{0.61}Ba_{0.39}Nb_2O_6$, projected onto the ab-plane.

Modulated crystal structures are characterized by appearance of reflections at non-Bragg positions. The positions of these reflections in reciprocal space can be described using

$$\mathbf{Q}(h,k,l,m_i) = h\mathbf{b}_1 + k\mathbf{b}_2 + l\mathbf{b}_3 + \sum_{i=1}^{n} m_i \mathbf{Q}_i$$

where

$$\mathbf{Q}_i = Q_{i,a}\mathbf{b}_1 + Q_{i,b}\mathbf{b}_2 + Q_{i,c}\mathbf{b}_3$$

are called modulation vectors. The modulation is called commensurate if all $Q_{i,j}$ (j=a,b,c) are rational and incommensurate if at least one of the $Q_{i,j}$ is irrational. Reflections with $m_i=0$ are called main reflections (Bragg positions), whereas diffraction spots with $m_i\neq0$ are called satellites (non-Bragg positions). The Fourier transform of the main reflections is the average structure in real space. Taking into account the satellite reflections, the Fourier transform yields a structure in real space, which does not exhibit translation symmetry anymore. To overcome this problem de Wolff and Janner [3] developed the so-called superspace

approach. Thereby the reciprocal lattice is embedded in a higher dimensional space R_{d+n} (d= dimension of average structure, n=number of modulation vectors). The measured reflections are considered as the projection of this higher dimensional lattice onto R_d. The Fourier transform of this projection is a section of a higher dimensional structure, which possesses again the full translational symmetry in real space.

The measurements were performed at room temperature well below the ferroelectric phase transition at 80º Celsius. The refinement was carried out with the program JANA2000 [4]. The average structure determined from the main reflections is shown in Fig. 2 and is in agreement with previous X-ray measurements [2].

From the positions of the satellites the modulation vectors $\mathbf{Q}_{1,2}$=(0.3075,±0.3075,0.5) found in X-ray experiments [5] could be verified. For the refinement of the modulated structure two modulation vectors $\mathbf{Q}_{1,2}$=(0.3075,±0.3075,0) in 5-dimensional superspace (space group X4bm with centering vectors (0,0,0,0,0) and (0,0,0.5,0.5,0.5)) were used. The third component of the modulation vectors was taken into account by doubling the cell along the c-axis (a=12.52 Å, c=7.87 Å). Because two modulation vectors are present, the modulation of position, occupation and temperature factors are described with two harmonic waves. The refinement of the positional parameters of the oxygen atoms resulted in a stronger modulation of O(4) than found with X-rays (Fig.3). The two oxygen atoms O(4) and O(5) show the largest modulation amplitude of all the atoms in this compound. The O(4,5) atoms are modulated mainly in the tetragonal plane while the O(1,2,3) atoms exhibit a strong modulation along z. This is due to the fact that O(4) and O(5) are lying in the same plane as the Sr and Ba atoms. They are therefore most affected by the statistical distribution of these atoms. The O(1,2,3)-atoms react on the deformation of the octahedra produced by the O(4,5) atoms and this results in a modulation along the z-direction [6]. Since the Nb atoms are positionally modulated only weakly, the whole modulation can be seen as a rotational modulation of almost rigid NbO_6 octahedra [7,8].

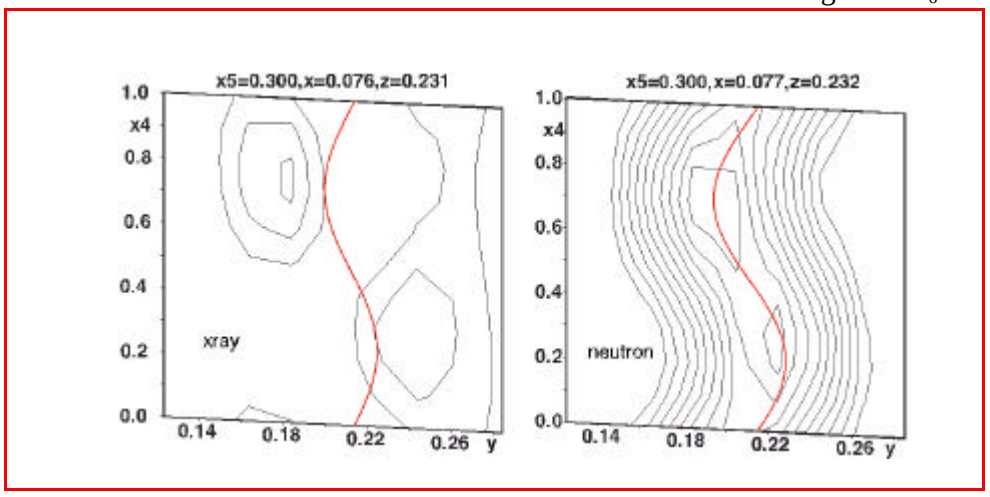

Figure 3. Modulation of O(4) obtained by X-rays (left) [5] and after refining the positional parameters of O(4) using the neutron data (right). Axes are given in fractional coordinates. x4=(**r**+**n**)$\mathbf{Q}_1$, x5=(**r**+**n**)$\mathbf{Q}_2$.

As we did not see higher order satellites, even in the Saclay measurement, we cannot refine any anharmonic distortions. Such a specialized refinement needs to be fixed not only quantitatively on the intensity of first order satellites, but also qualitatively on the appearance of second order reflections in order to allow such an advanced interpretation.

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