

## Structure of the OH<sup>-</sup> stretching vibrational band in Sr<sub>x</sub>Ba<sub>1-x</sub>Nb<sub>2</sub>O<sub>6</sub>

C. David, A. Tunyagi, M. Ulex, M. Wöhlecke,<sup>a)</sup> and K. Betzler  
*Fachbereich Physik, Universität Osnabrück, Barbarastr. 7, D-49069 Osnabrück, Germany*

K. Lengyel and L. Kovács  
*Crystal Physics Department, Research Institute for Solid State Physics and Optics, Hungarian Academy of Sciences, 1121 Budapest, Konkoly-Thege M. út 29-33., Hungary*

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The stretching mode of the hydroxyl ions in Sr<sub>x</sub>Ba<sub>1-x</sub>Nb<sub>2</sub>O<sub>6</sub> crystals with  $x = 0.38$  to  $0.79$  has been measured by the Fourier transform infrared spectroscopy technique. The main absorption band at about  $3493\text{ cm}^{-1}$  is accompanied by a shoulder on the low energy side. The shape of the shoulder depends strongly on the Sr/Ba ratio of the crystal which allows a rough estimation of the composition. The main absorption band including the shoulder has been decomposed using Lorentzian and Gaussian curves and the parameters of three components have been determined. The components are attributed to OH<sup>-</sup> transitions in different cation environments strongly depending on the crystal composition. The temperature dependence of the OH<sup>-</sup> absorption band is approximately linear in the  $20\text{--}200\text{ °C}$  range and does not show any peculiarities at the phase transition temperature. © 2004 American Institute of Physics. [DOI: 10.1063/1.1712011]

### INTRODUCTION

Strontium barium niobate, Sr<sub>x</sub>Ba<sub>1-x</sub>Nb<sub>2</sub>O<sub>6</sub> (SBN) is a widely studied ferroelectric relaxor crystal with a high potential for applications due to its large electro-optic, pyroelectric, and piezoelectric coefficients.<sup>1</sup> SBN has a tetragonal unfilled tungsten bronze structure and is built by Nb–O octahedra linked by their corners in such a way that three different types of channels are formed along the tetragonal  $c$  axis.<sup>2</sup> One channel is always empty, the second is partially filled only by Sr atoms, while the third one is also partially occupied by Sr and Ba. The distribution of Sr and Ba atoms in the channels depends on the composition of the compound which will be henceforth characterized by the Sr fraction  $x$  of the crystal throughout the article. The structural disorder results in a large variety of oxygen environments in which protons can be captured forming hydroxyl ions with the oxygen. Charge compensation is most likely due to intrinsic and extrinsic defects.

Hydroxyl ions are often present in as-grown oxide crystals and were used to monitor the composition of compounds not grown from a congruent melt,<sup>3</sup> because their stretching vibrational mode can easily be detected by infrared (IR) absorption spectroscopy. OH<sup>-</sup> absorption bands have already been reported in many tungsten bronze type materials, e.g., SBN,<sup>4,5</sup> Pb<sub>x</sub>Ba<sub>1-x</sub>Nb<sub>2</sub>O<sub>6</sub> (PBN),<sup>6,7</sup> K<sub>x</sub>Li<sub>1-x</sub>NbO<sub>3</sub> (KLN),<sup>8–10</sup> Ba<sub>2</sub>NaNb<sub>5</sub>O<sub>15</sub> (BNN),<sup>11,12</sup> and Ba<sub>2</sub>LiNb<sub>5</sub>O<sub>15</sub> (BLN).<sup>13</sup> As-grown SBN crystals studied so far contained only a small amount of hydroxyl ions. For a deeper understanding of the vibrational properties of OH<sup>-</sup> ions their concentration was increased by different high temperature treatments.<sup>4,5</sup> The IR absorption of the stretching mode has been measured in pure and Ce-doped congruent (Sr<sub>0.61</sub>Ba<sub>0.39</sub>Nb<sub>2</sub>O<sub>6</sub>) crystals. A relatively broad absorption

band has been detected which is composed of a main band at about  $3495\text{ cm}^{-1}$  and a broad shoulder at the low energy side extending to wave numbers of about  $3100\text{ cm}^{-1}$ . The shoulder was assumed to contain at least two<sup>5</sup> or three<sup>4</sup> bands due to the above-mentioned different oxygen environments in the unfilled tungsten bronze structure. The aim of the present article is to investigate systematically the OH<sup>-</sup> band shape in Sr<sub>x</sub>Ba<sub>1-x</sub>Nb<sub>2</sub>O<sub>6</sub> crystals in a wide composition range ( $x = 0.38$  to  $0.79$ ) in order to obtain more information about the relation between the band components and the crystal structure, as well as the occupancy of the proton sites and the cation distribution in the structural channels.

### EXPERIMENT

Sr<sub>x</sub>Ba<sub>1-x</sub>Nb<sub>2</sub>O<sub>6</sub> crystals were grown by the Czochralski method from melts with a Sr fraction in the range of  $0.3$  to  $0.8$ , which corresponds to  $0.38$  to  $0.79$  in the samples. The composition  $x$  of the corresponding crystals was determined by x-ray fluorescence with an accuracy better than  $0.01$  and will be used throughout this work, details will be reported elsewhere.<sup>14</sup> For each composition,  $c$ -plates, about  $2\text{ mm}$  thick, were cut and polished, while  $a$ -cut plates were only prepared for certain compositions. To allow a conclusive analysis of the OH<sup>-</sup> spectral band shape we raised the hydroxyl ion concentration of the as-grown crystals by about one order of magnitude modifying the well-known treatments.<sup>4,5</sup> We treated the samples at  $900\text{ °C}$  for  $10\text{ h}$  with wet oxygen, which flows through a water bottle held at  $80\text{ °C}$ . This method guaranteed a strong OH<sup>-</sup> doping, but avoided significant reduction of the crystals resulting in disturbing polaron absorption.

The absorption spectra of  $a$ - and  $c$ -cut samples were measured in the range of the OH<sup>-</sup> stretching vibrational frequency with a spectral resolution of  $1\text{ cm}^{-1}$  by a Bruker 120HR Fourier transform infrared spectroscopy spectrometer

<sup>a)</sup>Electronic mail: manfred.woehlecke@uos.de

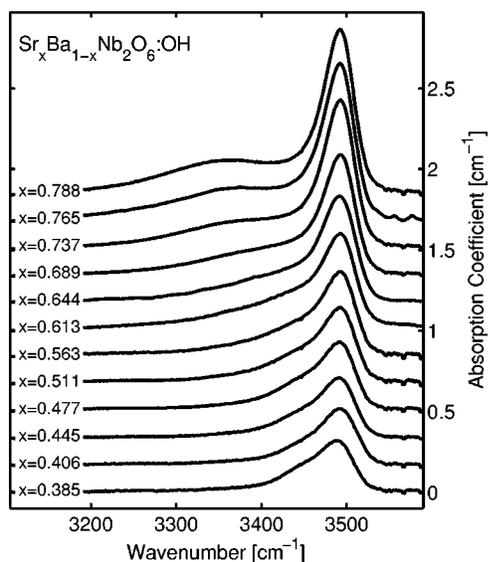


FIG. 1. Ordinarily polarized absorption spectra of the  $\text{OH}^-$  stretching mode for various  $\text{Sr}_x\text{Ba}_{1-x}\text{Nb}_2\text{O}_6$  crystals treated with wet oxygen at  $900^\circ\text{C}$  for 10 h.

at about  $25^\circ\text{C}$  in an evacuated sample chamber. In tetragonal SBN the majority of the absorption is observed for light polarized perpendicular to the optical  $c$ -axis. Therefore all evaluations were restricted to this ordinary polarization observed only in  $c$ -cuts. The  $a$ -cuts were used for checking the extraordinary polarization, i.e., light polarized along the  $c$ -axis and propagating perpendicular to  $c$ . The temperature dependence of the  $\text{OH}^-$  band shape of several crystal compositions were recorded by a Jasco FT/IR-300E spectrometer in the  $30$ – $200^\circ\text{C}$  temperature range, using a Specac sample heater and a spectral resolution in the range  $1$ – $4\text{ cm}^{-1}$ .

## RESULTS

Treating a dozen  $c$ -cut samples of different crystal compositions ( $0.38 < x < 0.79$ ) at  $900^\circ\text{C}$  for 10 h with wet oxygen yields a pronounced increase of the  $\text{OH}^-$  absorption depending on the composition. This doping at moderate temperature and pressure produces a composition dependent absorption coefficient of about  $0.3$ – $1\text{ cm}^{-1}$  for the main band, which is comparable to other procedures.<sup>4</sup> In Fig. 1 we have shown the ordinarily polarized absorption of  $c$ -cut samples after background subtraction. The spectra were shifted vertically for better viewing.

It is evident from Fig. 1 that the intensity of the main band at about  $3493\text{ cm}^{-1}$  increases with  $x$ , and the shape is definitely influenced. The integral absorption being proportional to the  $\text{OH}^-$  ion content of the crystals increases in an almost linear manner as a function of  $x$ , see Fig. 2. Sr-rich samples ( $x > 0.74$ ) accept approximately three times more hydrogen than Ba-rich ones ( $x < 0.45$ ) when treated under equal conditions.

The  $\text{OH}^-$  spectra of congruent material taken with extraordinarily polarized light reported previously<sup>4,5</sup> have shown a strongly reduced absorption. Moreover, the  $\text{OH}^-$  band for the ordinary polarization at  $3495\text{ cm}^{-1}$  disappeared and a higher frequency band emerged at about  $3510\text{ cm}^{-1}$ . It

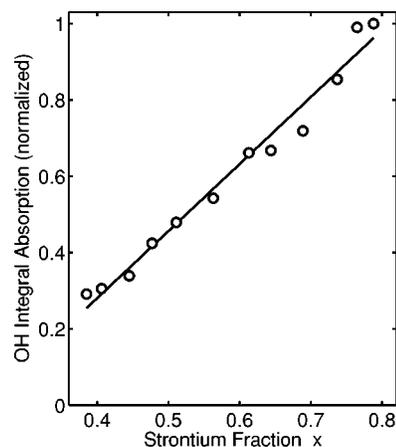


FIG. 2. Normalized integral absorption of the  $\text{OH}^-$  stretching mode for various  $\text{Sr}_x\text{Ba}_{1-x}\text{Nb}_2\text{O}_6$  crystals treated with wet oxygen at  $900^\circ\text{C}$  for 10 h.

has been concluded that the preferred plane of vibration of the hydroxyl ions is the plane perpendicular to  $c$ , while a small amount of  $\text{OH}^-$  ions vibrates along the  $c$  axis. This result has been confirmed for congruently melting SBN by us and we have proved that it holds for other  $x$  compositions, too. This is in contrast to PBN<sup>6,7</sup> and KLN<sup>9,10</sup> where a comparably strong absorption has been observed for extraordinarily polarized light, too. In the following sections we discuss only the  $\text{OH}^-$  spectra for ordinary light polarization.

A search for the influence of the ferroelectric phase transition on the  $\text{OH}^-$  stretching mode spectrum failed. The spectra of four samples with different  $x$  values (i.e.,  $0.477$ ,  $0.511$ ,  $0.563$ , and  $0.644$ ) in the range  $30 < T < 200^\circ\text{C}$  revealed a linear red-shift of about  $13 \pm 1\text{ cm}^{-1}$  with increasing temperature. The observations reported recently<sup>5</sup> were confirmed for not congruently melting samples. No remarkable broadening was observed, but the maximum absorption decreased with increasing temperature and the spectrum became more symmetric.

## DATA FITTING

The shape of the  $\text{OH}^-$  absorption bands is complex for each composition. It can be characterized by a main component peaking at about  $3493\text{ cm}^{-1}$  and a shoulder at the low energy side. While the main component is present in samples of all compositions, and only its intensity increases with  $x$ , as emphasized above, the shoulder changes more drastically. At low  $x$  (e.g.,  $x = 0.385$ ) the shoulder is present at about  $3450\text{ cm}^{-1}$ , while at high  $x = 0.788$  it appears as a sideband at about  $3350\text{ cm}^{-1}$ . The higher the  $x$ -values, the more symmetrical the main band.

The components of the complex absorption band in  $\text{Sr}_x\text{Ba}_{1-x}\text{Nb}_2\text{O}_6$  crystals are assumed to originate from vibrations of  $\text{OH}^-$  ions in different environments. In order to find correlation between the structure of SBN and the possible hydrogen sites in the crystals the change of the band shape has to be described analytically for different compositions. In other words, the occupancy of the  $\text{OH}^-$  defect sites can be deduced from the intensities of the band components.

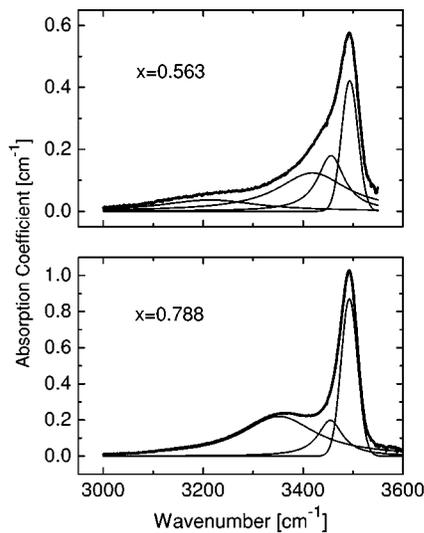


FIG. 3. Decomposition of ordinarily polarized absorption spectra of the OH<sup>-</sup> stretching mode in Sr<sub>x</sub>Ba<sub>1-x</sub>Nb<sub>2</sub>O<sub>6</sub> crystals with two different compositions. Different scales have been used for the ordinates.

For this purpose the absorption bands have been decomposed into several components using a nonlinear least squares method.

First of all the decomposition procedure requires some knowledge about the number of components and the shape of each band. This is not obvious for strongly overlapping bands like in our case. A first hint can be obtained by an inspection of the high energy wing of the main band. This clearly points to a Gaussian band shape, while the broad feature shifting from about 3450 to 3350 cm<sup>-1</sup> suggests a Lorentzian shape. The asymmetry of the main band for low and medium  $x$ -values led us to include another band at about 3455 cm<sup>-1</sup>, but we have no conclusive arguments for a particular band shape, even if we take into account that typically homogeneous broadening causes a Lorentzian shape, as it is observed for most of the OH<sup>-</sup> stretching vibrational bands in other oxide crystals.<sup>3</sup>

As a first attempt, called fit 1, we fitted each spectrum with three bands by varying the relevant parameters like position, linewidth and height. As expected from Fig. 1, the position and halfwidth of the main band are practically constant, but to our surprise the same holds for the second band at about 3455 cm<sup>-1</sup>, too. As it is seen in Fig. 3, the third band is shifted to lower energy with increasing  $x$ . For several compositions in the range  $x = 0.5-0.6$  the contribution of a weak and broad fourth component was also observed at about 3220 cm<sup>-1</sup> (see the upper curve in Fig. 3). This band improved the quality of the fit, but did not influence strongly the parameters of the three other bands. Even more important was the observation that all parameters varied smoothly, allowing for a general fit of all data with few parameters. As a preparation for such a general fit each spectrum was smoothed using Savitzky-Golay filtering. Thus we get rid of noise without losing any spectral relevant information.

Taking into account the general trends of fit 1, we introduced as parameters the three line positions and widths  $\nu_i$  and  $\sigma_i$ , respectively, and in addition a shift of line position

TABLE I. The  $l_1$  norm for the different fits.

Fit	1	2	3	4
$l_1$ norm	0.0495	0.0926	0.0783	0.0757
Number of parameters	108	13	14	17

three, depending linearly on  $x$ , with the fit parameter  $d\tilde{\nu}_3$

$$\tilde{\nu}_3 = \tilde{\nu}_{30} - x \cdot d\tilde{\nu}_3. \quad (1)$$

Following the observation that the OH<sup>-</sup> band intensity increases linearly with  $x$ , for the line intensities linear dependencies in the form

$$S(x) = (a_1 + b_1x)G_1 + (a_2 + b_2x)L_1 + (a_3 + b_3x)L_2 \quad (2)$$

are assumed where  $G$  and  $L$  denote Gaussian and Lorentzian line shape, respectively.

Thus the complete simulation of all 12 spectra, called fit 2, depends on 13 parameters, as compared to the  $12 \times 9 = 108$  parameters of fit 1, see Table I. The relatively good fit obtained by using only 13 parameters reflects that the assumption of fixed wave numbers and halfwidths for the components was realistic. The right side of Fig. 4 shows, however, that some deviation between the measured and fitted data occurs mainly for the main component of the absorption spectrum. The deviations can be removed by introducing a quadratic term in the composition dependence of the main band

$$S'(x) = (a_1 + b_1x + c_1x^2)G_1 + (a_2 + b_2x)L_1 + (a_3 + b_3x)L_2. \quad (3)$$

Figure 4 (left side) shows the result of fit 3 taking into account the nonlinear term for the Gaussian band. The parameter values of fits 2 and 3 are given in Table II. The quality of the fit was quantitatively characterized by the well known  $l_1$  norm (the sum of the absolute differences between the theoretical curve and the experimental points). Lower values mean better quality here. Table I summarizes the quality factors obtained for the different fits. It is clearly seen that the quadratic dependence of the amplitude of the Gaussian band

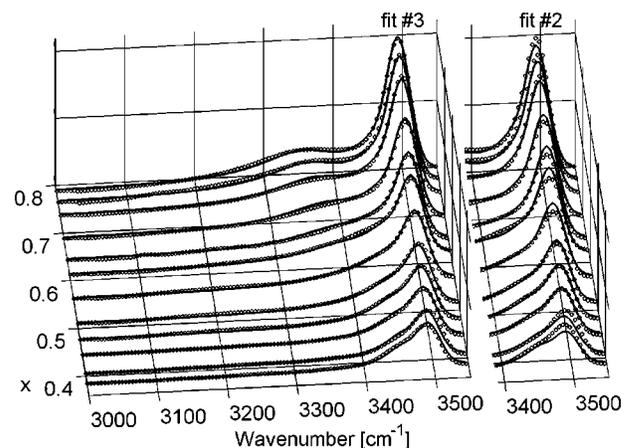


FIG. 4. Three-band fits for the OH<sup>-</sup>-bands in SBN as a function of the composition. Solid black bands indicate fits, measured spectra are represented by the dots.

TABLE II. Values of all necessary fit parameters for the full global fits 2 and 3. The parameters  $\tilde{\nu}_i$  and  $\sigma_i$  represent the frequency and halfwidth of the components, respectively.

Parameter	Fit 2 (cm <sup>-1</sup> )	Fit 3 (cm <sup>-1</sup> )
$\tilde{\nu}_1$	3492.5	3492.3
$\tilde{\nu}_2$	3455.6	3454.1
$\tilde{\nu}_{30}$	3546.3	3558.0
$d\tilde{\nu}_3$	244.3	259.4
$\sigma_1$	22.9	23.2
$\sigma_2$	28.8	30.0
$\sigma_3$	73.1	76.2
$a_1$	-0.430	0.574
$a_2$	0.046	0.099
$a_3$	-0.126	-0.161
$b_1$	1.608	-1.998
$b_2$	0.232	0.137
$b_3$	0.411	0.458
$c_1$	n.a.	3.072

on composition improves the quality factor. A further, but very weak improvement could be achieved by assuming a fourth component of the absorption band at the low energy side (fit 4). This will be neglected further on.

## DISCUSSION

Let us summarize the main results of our extended curve fitting with the help of Fig. 5, where we used the parameters in Table II to plot the dependence of the wave number and amplitude of the bands on the strontium fraction. Two bands do not depend on  $x$  with respect to the band position, while the frequency of the third component decreases with increasing Sr fraction. The amplitude of the main band is always much stronger than that of the other bands and shows a slightly nonlinear dependence on  $x$ . The amplitude of the second band is almost constant, while the contribution of the third band is remarkable at high Sr fraction. It is worth to stress again, although not plotted, that the halfwidth of the bands was found to be unchanged in the whole composition

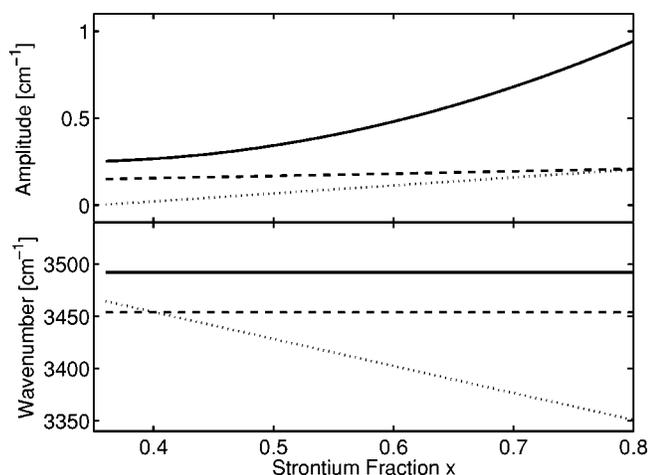


FIG. 5. Composition dependence of the wave number and the corresponding amplitude for the three bands used in fit 3. Solids bands belong to the Gaussian band 1, dashed to component 2, while band 3 is represented by dotted bands.

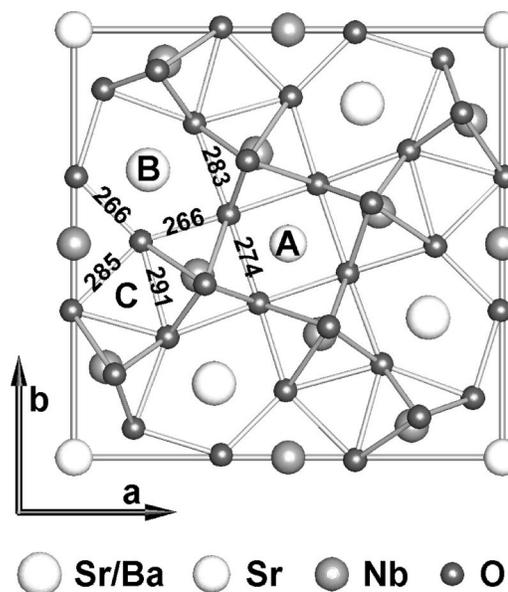


FIG. 6. Schematic drawing and O–O bond lengths (in units of pm) of the plane perpendicular to the tetragonal  $c$  axis of SBN. Tetragonal channel, partially occupied by Sr, A, pentagonal channel, partially occupied by Sr and Ba, B, and the empty triangular channel C.

range. The relatively broad bands are characteristic for the OH<sup>-</sup> absorption bands in crystals belonging to the LiNbO<sub>3</sub> family and other niobates having the tungsten bronze-type structure,<sup>3</sup> and are related to the high number of structural defects due to the random distribution of strontium over the corresponding sites.

Thus we are searching for different lattice sites for the OH<sup>-</sup> ions, which on one hand, are strongly influenced, and on the other hand, are nearly unaffected by the change of the Sr fraction. The SBN structure is built up of NbO<sub>6</sub> octahedra which are linked via oxygen corners as mentioned in the introduction.<sup>2</sup> Because there are two different NbO<sub>6</sub> octahedra, the tetragonal network has three kinds of structural channels running along the  $c$ -axis A, B, and C, see Fig. 6. The smallest one with a triangle shape is unoccupied in SBN, while the tetragonal and the pentagonal ones are partially filled. The medium-sized tetragonal channels contain Sr and the site occupancy is about 72%, a value which—due to Ref. 2—is virtually unchanged when  $x$ , the Sr fraction, varies. The large pentagonal channel is a host for both Ba and Sr. The Ba ions occupy a site with mirror symmetry, while the Sr site in the pentagonal channel has no symmetry, because it is shifted by about  $\pm 25.5(29.2)$  pm for  $x=0.75(0.61)$  out of the symmetry plane<sup>2</sup> depending on the composition. At low  $x$  values the pentagonal channel contains only Ba and no Sr.

With the information deduced from the composition dependence of the OH<sup>-</sup> absorption spectra a more specific model for the hydrogen sites can be proposed. Sites for most of the hydrogen present in the crystal have to be restricted to the  $a, b$  plane, shown schematically in Fig. 6 because of the polarization behavior of the stretching mode absorption. The possible hydrogen sites are along the various O–O bonds in this plane. O–O bonds, whose length ranges from 265 to 291 pm form the equatorial planes of the two different NbO<sub>6</sub> octahedra. As a general trend, the longer the O–O bond, the

higher the frequency of the  $\text{OH}^-$  vibration along that bond.<sup>15</sup> Following this band, the main band at  $3493\text{ cm}^{-1}$  would correspond to  $\text{OH}^-$  vibrations in the unoccupied triangular channel having about 285–290 pm O–O bonds. The second band at  $3455\text{ cm}^{-1}$  which is practically independent of  $x$  may correspond to the tetragonal channel having 274 pm O–O bond lengths and nearly constant Sr occupancy,<sup>2</sup> while the third band with the lowest vibrational frequency may belong to the pentagonal channel. Three O–O bonds in the pentagonal channel are only 266 pm long. We may further assume that the  $\text{OH}^-$  vibrations responsible for the third band belong to those pentagonal channels which are occupied by Sr ions. On one hand the Sr occupancy of this site is proportional to  $x$  in agreement with the increasing  $\text{OH}^-$  band amplitude, and on the other hand the increasing shift of Sr out of the mirror plane with decreasing  $x$  causes a strongly changing environment and in turn a strong frequency shift of the  $\text{OH}^-$  band.

In conclusion, the infrared  $\text{OH}^-$  stretching mode absorption of various  $\text{Sr}_x\text{Ba}_{1-x}\text{Nb}_2\text{O}_6$  crystals with  $x$  ranging from 0.38 to 0.79 has been measured after increasing the proton concentration by a heat treatment in wet oxygen. A crystal with  $x=0.79$  incorporates three times more hydrogen than one with  $x=0.38$ . The shape of the spectra depends on the composition  $x$ . The spectra have been modeled using three components, two of them with fixed frequency while the frequency of the third broad band decreases with increasing  $x$ . The three bands have been assigned to  $\text{OH}^-$  vibrations in the  $a$ ,  $b$  plane of the crystal along the O–O bonds with different lengths and different cation environments.

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<sup>1</sup>A. M. Prokhorov and Y. S. Kuz'minov, *Ferroelectric Crystals for Laser Radiation Control* (Adam Hilger, Bristol, 1990).

<sup>2</sup>T. S. Chernaya, B. A. Maksimov, T. R. Volk, L. I. Ivleva, and V. I. Simonov, *Phys. Solid State* **42**, 1716 (2000).

<sup>3</sup>M. Wöhlecke and L. Kovács, *Crit. Rev. Solid State Mater. Sci.* **26**, 1 (2001).

<sup>4</sup>S. Hunsche, A. Gröne, G. Greten, S. Kapphan, R. Pankrath, and J. Seglins, *Phys. Status Solidi A* **148**, 629 (1995).

<sup>5</sup>M. Lee, H. S. Lee, and R. S. Feigelson, *J. Appl. Phys.* **84**, 1558 (1998).

<sup>6</sup>M. Lee, H. Lee, R. K. Route, and R. S. Feigelson, *J. Appl. Phys.* **81**, 917 (1997).

<sup>7</sup>M. Lee, R. S. Feigelson, A. Liu, L. Hesselink, and R. K. Route, *Phys. Rev. B* **56**, 7898 (1997).

<sup>8</sup>G. Y. Kang and J. K. Yoon, *J. Cryst. Growth* **193**, 615 (1998).

<sup>9</sup>Y. B. Kim, T. A. Kim, C. S. Kim, J. N. Kim, and J. H. Ro, *J. Korean Phys. Soc.* **32**, S603 (1998).

<sup>10</sup>T. H. Kim, Y. M. Yu, K. Lee, and J. H. Ro, *Phys. Status Solidi B* **227**, 485 (2001).

<sup>11</sup>L. C. Bobb, I. Lefkowitz, and L. Muldower, *Solid State Commun.* **7**, 937 (1969).

<sup>12</sup>S. Singh, H. J. Levinstein, and L. G. V. Uitert, *Appl. Phys. Lett.* **16**, 176 (1970).

<sup>13</sup>O. Bernecker, H. Matthes, and A. Marshall, *Phys. Status Solidi A* **17**, 453 (1973).

<sup>14</sup>M. Ulex *et al.* (unpublished).

<sup>15</sup>E. Libowitzky, *Monatsh. Chem.* **130**, 1047 (1999).