The Temperature Dependence of the Band Edge Energy in Calcium Barium Niobate

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The temperature dependent band edge energy of the novel tungsten bronze type calcium barium niobate (CBN) is measured over a temperature range from 80 K to 573 K.
CBN has been under investigation for serveral years and is believed to be a promising material for future applications. Czochralski-grown, colorless single crystals from the congruently melting composition with a calcium content of 0.281 were used. A numerical fit has been applied, comparing the results of CBN to those of the well known relaxor ferroelectric strontium barium niobate (SBN). The band edge energy of CBN was found to be higher than in SBN over the whole temperature range.

1 INTRODUCTION Over the past decades, ferroelectrics and relaxors in particular have been subject of extensive research. Due to their interesting physical properties, for example large nonlinear coefficients and a large dielectric constant over a wide temperature region near the ferroelectric phase transition, it is highly desirable to use them in technical applications. Several years ago, the novel tungsten bronze type calcium barium niobate ($Ca_xBa_{(1-x)}Nb_2O_6$, CBN) was grown for the first time as a single crystal with excellent optical quality [1,2]. The well investigated strontium barium niobate ($Sr_xBa_{(1-x)}Nb_2O_6$, SBN), as a related material, offers promising physical properties. This leads to the assumption, that CBN might also be an interesting material for future applications. The major advantage of CBN is a much higher phase transition temperature compared to SBN of about 539 K for the congruently melting composition with 28.1 mole% calcium (x = 0.281). This considerably widens the field of future applications. A detailed knowledge of the fundamental physical properties is of vital importance. In many of today's optical systems, short wavelengths and high pulse intensities are used. In these systems, all optical components have to be virtually transparent for those wavelengths to avoid optical damage. Thus, the band edge of contemplable materials is one of the significant limiting factors. Detailed measurements of the refractive indices and of the ferroelectric phase transition of CBN have been performed [3–7], but the band edge energy and its temperature dependence has not been investigated so far. We present detailed measurements over a temperature region ranging from 80 K up to 573 K.

2 EXPERIMENTAL DETAILS CBN crystals were grown by the Czochralski technique [1]. Single crystal (hk0)-oriented as-grown samples from the congruently melting composition were cut to a thickness of approximately 0.4 mm and polished to optical quality.

The measurements above room temperature were performed using a heatable crystal holder with a maximum temperature of 573 K and an accuracy of ± 0.5 K. Measurements below room temperature were carried out in a *Leybold* cryogenerator with a minimum temperature of about 80 K and an accuracy of ± 0.5 K. The sample was illuminated by a *Hamamatsu L2175* Xe-high-pressure lamp with a spectral range from 185 to 2000 nm. The transmitted intensity was detected using an *OceanOptics USB4000* spec-

trometer with a spectral resolution of about ± 1.5 nm in the short wavelength region.

Reflection correction has been applied using refractive indices calculated with the Sellmeier equation and the coefficients published in [8]. The absorption coefficient α was calulated from the measured fundamental and reflection-corrected transmitted intensities applying Beer's law.

For the temperature dependence of the band edge energy the phenomenological expression established by Johnson et al. [9,10] was used:

$$E_\alpha(T) = E_\alpha(0) - \frac{\beta k\theta}{exp(\frac{\theta}{T} - 1)}, \qquad (1)$$

with E_α as the energy corresponding to a fixed absorption coefficient α, β as a dimensionless lattice coupling constant, k as the Boltzmann constant, and $k\theta$ denoting the average phonon energy.
Equation (1) is a specialized version of the general form $E_g(T) = E_g(0) - K \cdot N$ with K as the electron-lattice coupling and N as the occupation number. The results are much more satisfying than those obtained from the equation proposed by Varshni et al. [11], especially in the low temperature regime.

Regarding K, the observed temperature dependence can usually be described by a single Einstein oscillator, since the internal energy of a set of optical phonon modes with different energies can be approximated by a single phonon mode with its energy being the average of the set [12]. The occupation number N is approximated using Bose-Einstein statistics.
Following the authors of [10], for a more complete description actually the absorption and emission of phonons would have to be taken into account. Since the authors did not find any noticeable differences in the results for SBN, we also adopted the simple form for our investigations, considering only absorption.

3 RESULTS AND DISCUSSION Figure 1 shows typical absorption spectra of CBN from the congruently melting composition for ordinary and extraordinary light polarization at two different temperatures. The measurements reveal a steep increase of the absorption in the high energy part and a flat shape in the low energy regime of the spectrum, both for ordinary and extraordinary light polarization.

One can see that the curvature of the absorption coefficient exhibits a temperature dependence with a steeper decrease for lower temperatures, which is in accordance to the Urbach rule [13].

In figure 2, the temperature dependence of the band edge energy is shown for both light polarizations. Squares denote ordinary, circles extraordinary polarization direction. As a measure for the band edge energy the wavelength for an absorption coefficient α of 50 cm^{-1} was used.

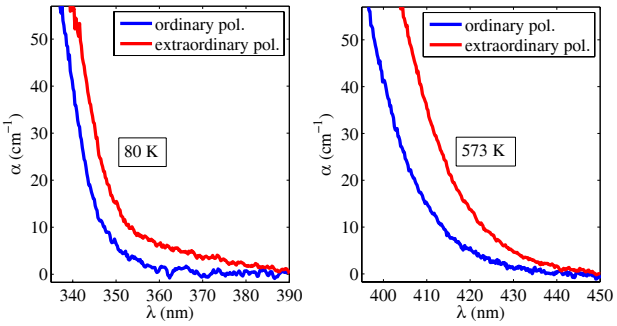

Figure 1 (color online) Absorption coefficient α as a function of the wavelength for T = 80 K and T = 573 K. The blue curves denote ordinary, the red curves extraordinary light polarization

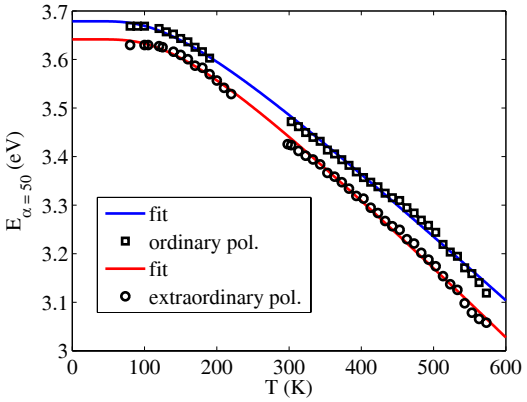

Figure 2 (color online) Temperature dependent UV band edge energy of CBN from the congruently melting composition for ordinary and extraordinary polarized light.

The experimental data were fitted using equation (1), the blue line denoting the fit for the ordinary light polarization, the red line for the extraordinary one. The fit with equation (1) obviously provides a good approximation for both light polarizations, in the flat low-temperature regime as well as in the linear high-temperature region.

The termination tolerance of the fitting procedure for both temperature and energy was set to $\chi^2 = 10^{-12}$. Errors were calculated by evaluating the maximum impact of variations in the experimental data within the grade of accuracy given in section 2 onto the fit results. The fit parameters for both light polarizations are summarized in table 1. For comparison, also the fit data for SBN from the congruently melting composition with 61 mole% strontium (x = 0.61), published by Meyer et al. [10], is listed. The fit in [10] was performed using equation (1) and an absorption coefficient α of 100 cm^{-1}.

To compare the results from [10] with the data for CBN, we calculated the value for the band edge energy if the authors would have used an α of 50 cm^{-1}.

We applied the approximation $E_\alpha(0) \approx E_\alpha(50)$, then the shift in the band edge energy for T = 50 K can be estimated from the data in figure 1,[10] (middle and right). The authors claim, that the shape of $E_g(T)$ remains the same, even when lowering the value of α down to 15 cm^{-1}. Therefore, only the shift of $E_\alpha(0)$ for $\alpha = 100\,cm^{-1} \rightarrow 50\,cm^{-1}$ was calculated, the values for β and θ were left unchanged. The resulting values of $E_{\alpha\,=\,50}(0)$ for SBN are presented in brackets.

	pol.	$E_{50}(0)$ (eV)	β	θ (K)
CBN	o	3.679±0.006	15.94±0.07	409±5
	eo	3.641±0.006	17.39±0.06	432±4
SBN	o	(3.572±0.005)	16.6±0.4	423±25
[10]	eo	(3.523±0.005)	18.4±0.4	451±24

Table 1 Fit parameters for CBN with x = 0.28 and SBN with x = 0.61 [10]. The values in brackets are derived from the data given in [10] for an α of 50 cm^{-1}.

In comparison to the values of CBN from [10], the values for $E_{50}(0)$ of CBN are increased about 0.11 eV for ordinary and 0.12 eV for extraordinary light polarization, i.e., the band edge in CBN is located at smaller wavelengths. This shift remains virtually constant over the whole temperature region for both polarization directions.

The values for θ in CBN correspond to average phonon energies $k\theta$ of about 284 cm^{-1} for the ordinary and 300 cm^{-1} for the extraordinary polarized light. These values are quite similar to the average wave number of 300 cm^{-1} published for SBN in [10] and the optical modes found in SBN by Amzallag et al. [14]. They also fit nicely into the Raman spectra for neodymium doped CBN published by Molina et al. [15] and Tan et al. [16].

The slope $dE_g(T)/dT$ in the linear high temperature regime is found to be -1.22 meV/K for the ordinary and -1.33 meV/K for extraordinary light polarization which matches the values published for SBN [17, 18].

Due to the increase of the band edge energy of CBN in comparison to SBN, the realization of optical applications using CBN single crystals from the congruently melting composition, even in the near-UV-regime, might move closer.

4 CONCLUSION In this work, we presented the temperature dependent shift of the band edge energy in the novel tungsten bronze calcium barium niobate. Single crystals from the congruently melting composition with a calcium content of 28.1 mole% have been used. The measurements were carried out over a temperature range from 80 K up to about 573 K. The data exhibit a flat part in the low temperature regime and a linear decrease at higher temperatures. A comparison to the well known relaxor SBN revealed an increased band edge energy over the whole temperature range and comparable average phonon energies. With increasing temperature, the value of $E_g(T)$ decreases with a steepness comparable to SBN.

Since the transmittivity of optical materials is of great interest regarding their usability in modern applications, CBN can be considered as a promising optical material, outranging SBN in its transparency, especially in the short wavelength spectral region.

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References

[1] M. EßER, M. BURIANEK, D. KLIMM, and M. MUEHLBERG, J. Cryst. Growth **240**, 1–5 (2002).
[2] M. BURIANEK, B. J. AN I. KERKAMM, T. SCHONEBECK, D. KLIMM, and M. MUEHLBERG, J. Cryst. Growth **299**, 413–417 (2007).
[3] H. SONG, H. ZHANG, X. XU, X. HU, X. CHENG, J. WANG, and M. JIANG, Mater. Res. Bull. **40**, 643–649 (2005).
[4] Y. J. QI, C. J. LU, J. ZHU, X. B. CHEN, H. L. SONG, H. J. ZHANG, and X. G. XU, Appl. Phys. Lett. **87**, 082904 (2005).
[5] H. SONG, H. ZHANG, Q. JIANG, X. XU, C. LU, X. HU, J. WANG, and M. JIANG, J. Cryst. Growth **290**, 431–435 (2006).
[6] B. JOSCHKO, PhD thesis, Universitaet zu Koeln, 2007.
[7] U. HEINE, U. VOELKER, K. BETZLER, M. BURIANEK, and M. MUEHLBERG, New J. Phys. **11**(8), 083021 (2009).
[8] M. EßER, M. BURIANEK, P. HELD, J. STADE, S. BULUT, C. WICKLEDER, and M. MUEHLBERG, Cryst. Res. Technol. **38**(6), 457–464 (2003).
[9] S. R. JOHNSON and T. TIEDJE, J. Appl. Phys. **78**, 5609–5613 (1995).
[10] M. MEYER, M. WOEHLECKE, and O. F. SCHIRMER, Phys. Status Solidi B **221**, R1–R3 (2000).
[11] Y. P. VARSHNI, Physica **34**, 149–154 (1967).
[12] D. REDFIELD and W. J. BURKE, J. Appl. Phys. **45**(10), 4566–4571 (1974).
[13] F. URBACH, Phys. Rev. **92**, 1324 (1953).
[14] E. AMZALLAG, T. S. CHANG, R. H. PANTELL, and R. S. FEIGELSON, J. Appl. Phys. **42**(8), 3524–3526 (1971).
[15] P. MOLINA, E. M. RODRIGUREZ, D. JAQUE, L. E. BAUS, J. GARCA-SOL, H. ZHANG, W. GAO, J. WANG, and M. JIANG, J. Lumin. **129**, 1658–1660 (2009).
[16] Y. TAN, F. CHEN, D. JAQUE, W. L. GAO, H. J. ZHANG, J. G. SOLE, and H. J. MA, Opt. Lett. **34**(9), 1438–1440 (2009).
[17] J. SEGLINS and S. KAPPHAN, Phys. Status Solidi B **188**, K43–K45 (1995).
[18] V. S. VIKHNIN, S. KAPPHAN, and J. SEGLINS, J. Korean Phys. Soc. **32**, S621–S623 (1998).