

Investigation of the absorption of OH vibrations in oxide crystals

Abstract of the PhD thesis

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1. Preliminaries and objects

This PhD work was accomplished in the Crystal Physics Department of the Research Institute for Solid State Physics and Optics of the Hungarian Academy of Sciences. This group has been engaged for a long time in growing and investigating non-linear optical crystals having important potential applications. Understanding the relations between non-linear effects, crystal structure and defect structure helps to produce crystals with better quality.

The OH^- ions, introduced into the crystal during the growth process, are frequent defects in inorganic crystals containing oxygen. The characteristic absorption bands of their bond-stretching vibrations in the infrared region have been observed to have shapes and positions strongly dependent on the environment of OH^- ions. So making infrared absorption measurements one can get information about the structure and composition of crystals as well as the properties and quantities of defects in the lattice. OH^- ions and water molecules can be used as detectors to examine a large number of physical effects. Using this method, in my PhD work I have investigated the OH vibrations in three oxide crystals (LaGaO_3 , $\text{CsLiB}_6\text{O}_{10}$ and LiNbO_3), all of which have excellent non-linear or structural properties.

The LaGaO_3 crystal is a possible substrate of the $\text{YBa}_2\text{Cu}_3\text{O}_7$ high-temperature superconductor because of the good fit of lattice parameters. Quantum mechanical calculations show that incorporation of hydroxyl ions into the LaGaO_3 crystal lattice is unfavourable. I have made infrared absorption measurements to establish whether the incorporation of a small quantity of OH^- ions could be detected. The application of LaGaO_3 crystals is made difficult by an orthorhombic–rhombohedral phase transition about 140–150 °C changing the lattice parameters. To investigate the effect of the phase transition on the vibrational properties of OH^- ions I made temperature dependent infrared absorption measurements in this temperature region.

$\text{CsLiB}_6\text{O}_{10}$ is an excellent non-linear optical material. The fifth harmonic of

a Nd:Yag laser was produced using this crystal. However, its open-air application is limited by the hygroscopic property: first surface cracks appear deteriorating the optical properties, followed by crumbling of the crystal into pieces. The effect of moisture on the crystal had been investigated previously by X-ray diffraction, DTA and thermogravimetry measurements. In my PhD work I studied the hygroscopic properties of the $\text{CsLiB}_6\text{O}_{10}$ crystal by means of infrared absorption measurements.

The LiNbO_3 crystal has excellent non-linear optical, photorefractive, ferroelectric qualities and a huge refractive index therefore it can be used for lots of applications (holographic memories, frequency converters, optical switches, optical waveguides etc.). Holograms can be written into the crystal using the photorefractive effect, however they get partly erased during the read-out process. To prevent erasure the sample is annealed at about 100–200 °C with subsequent illumination with homogeneous light; this treatment results in a new hologram which is no more sensitive to read-out. Protons becoming mobile at high temperature were expected to play an important role in the fixing process. To prove this assumption I made time dependent infrared absorption measurements at different temperatures in a nearly stoichiometric LiNbO_3 crystal to determine the thermal activation energy of OH^- ions and to compare it with the value obtained from the thermal fixing of holograms.

For other applications of the LiNbO_3 crystal its laser damage resistance has to be as high as possible. Doping the congruent LiNbO_3 crystal with more than 5 mol% Mg increases its laser resistance by two orders of magnitude, which is of basic importance for the enhancement of the second harmonic generation efficiency. Along with this effect the absorption spectrum of OH^- ions in the crystal is also found to change. The Mg concentration threshold, where these changes happen, strongly depends on the stoichiometry of the crystal. Several theoretical models have been suggested to explain this effect. In my PhD work I present absorption measurements in the infrared, visible and ultraviolet wavelength regions and also Raman spectroscopy experiments in LiNbO_3 samples for wide composi-

tion and Mg concentration ranges to investigate the validity of theoretical models.

2. Experimental methods

The infrared absorption spectra were measured by a JASCO-FT 300E FTIR apparatus in the $400\text{--}7000\text{ cm}^{-1}$ wavenumber region with 0.5 cm^{-1} maximum resolution and a BRUKER IFS66/v FTIR spectrophotometer in the same wavenumber region with 0.1 cm^{-1} maximum resolution. Crystals cooled to $-185\text{ }^{\circ}\text{C}$ could be investigated in a SPECAC cryostat working with liquid nitrogen. To measure crystals at elevated temperatures (maximum $250\text{ }^{\circ}\text{C}$) I used a SPECAC, water cooled, electrically heatable sample holder. The stability of the temperature was $\pm 0.5\text{ }^{\circ}\text{C}$ at low and $\pm 0.1\text{ }^{\circ}\text{C}$ at high temperature. A KRS-5 wire-grid polarizer was used to determine the orientation of OH^{-} dipoles.

To complete the infrared measurements in Mg doped LiNbO_3 crystals I also made Raman scattering as well as absorption measurements in the ultraviolet and visible regions ($190\text{--}900\text{ nm}$). Absorption spectra were measured using a two-beam JASCO V550 spectrophotometer with a best resolution of 0.05 nm . Raman spectra were recorded by a Renishaw 1000B micro-Raman device using a red laser beam of 785 nm wavelength providing a resolution of 1 cm^{-1} .

3. New scientific achievements

- I. The infrared absorption band of hydroxyl ions in the LaGaO_3 crystal was observed for the first time. Using proton–deuteron isotopic replacement I demonstrated that this band corresponds to the vibration of OH^{-} ions. The quantity of OH^{-} ions ($\approx 10^{15} - 10^{16}\text{ cm}^{-3}$) was calculated from the half-width ($\Delta\nu \approx 2\text{ cm}^{-1}$) and the absorption coefficient ($\alpha \approx 0.21\text{ cm}^{-1}$) of the absorption band, and was found to be smaller by two orders of magnitude than the usual concentration of OH^{-} ions in most other air-grown oxide

crystals. This value confirms the results of quantum mechanical calculations predicting that the incorporation of OH^- ions into the LaGaO_3 crystal is energetically unfavourable.

An abrupt decrease of the absorption band frequency of OH^- ions at the temperature of the orthorhombic–rhombohedral phase transition during heating has been demonstrated. This decrease was interpreted by a displacement of the oxygen nearest to the OH^- ion: it further approaches the hydroxyl ion. I also observed that the temperature dependence of the halfwidth of the absorption band is different from that expected from the phonon coupling model. Measuring the changes of the band position and halfwidth was found to be a suitable method for the investigation of the phase transition of LaGaO_3 crystals.

- II. Measuring the infrared absorption of $\text{CsLiB}_6\text{O}_{10}$ crystals stored in an atmosphere containing water or heavy water I showed that incorporation occurs in the form of water molecules and not as OH^- ions. The absorption bands belonging to the vibration of water molecules were interpreted as follows: 1650 cm^{-1} bending, 3413 cm^{-1} symmetrical stretching, 3581 cm^{-1} asymmetrical stretching vibrational modes, 5080 cm^{-1} and 5213 cm^{-1} combination bands of stretching and bending modes. Absorption bands due to D_2O molecules were identified after heavy water treatment: the 2517 cm^{-1} and 2650 cm^{-1} bands are assigned to symmetrical and asymmetrical stretching vibrations, respectively. From polarization dependent absorption measurements I concluded that water molecules replace Cs ions. Using time dependent absorption measurements in $\text{CsLiB}_6\text{O}_{10}$ crystals stored in air I demonstrated that the initial stage (4–5 hours) of water incorporation can be described by a simple diffusion process, which is followed by a stage where the growth of infrared bands becomes faster. This was explained by the hydration of the crystal hampering the out-diffusion of water molecules.

- III. I made the observation that for a given temperature the infrared absorption spectrum of undoped LiNbO_3 crystals changes with time, while the area of bands in the OH^- vibrational region remains constant. I showed that for every temperature between 40 and 120 °C there is a wavelength where the absorption remains constant in time. The existence of such an isosbestic point proves that the motion of protons detached from OH^- ions is subjected to first order kinetics with the protons having two states in the crystal lattice, a stable one at lower energy and a metastable one at higher energy. I demonstrated that stable and metastable states correspond to defects (related to the congruent composition) and more perfect stoichiometric type environments, respectively. An activation energy of $\varepsilon_a = 0.67 \pm 0.03$ eV characteristic for temperatures below 80 °C was determined by the isosbestic point method and assigned to the mobility of Li^+ ions. Another activation energy $\varepsilon_a = 1.01 \pm 0.15$ eV characteristic for temperatures above 80 °C belongs to the mobility of protons and shows good agreement with the value obtained from the thermal fixing of holograms. I concluded that the energy difference between stoichiometric and congruent states is: $\varepsilon_s - \varepsilon_k = 90 \pm 30$ meV which is comparable with the thermal energy kT confirming the thermal activation model of the motion of protons.
- IV. The models of Mg incorporation were experimentally confirmed by infrared absorption measurements carried out on $\text{LiNbO}_3\text{:Mg}$ samples for wide composition (with $(\text{Li}_2\text{O})_{50-x}(\text{Nb}_2\text{O}_5)_{50+x}$ formula: $x = 0 \dots 1.4\%$) and Mg concentration ($[\text{MgO}] = 0 \dots 8\%$) ranges. I concluded that in samples doped above the photorefractive threshold the frequency of the OH^- band position increases according to a square root function of the Mg concentration and does not depend on the Li/Nb ratio of the crystal. I interpreted the increase of the OH^- band frequency in above-threshold samples in terms of a defect structure of $\text{Mg}_4\text{Nb}_2\text{O}_9$ type.

From UV absorption measurements on LiNbO_3 crystals with different Mg

content and Li/Nb ratio I concluded that the UV absorption edge of above-threshold samples depends on the Mg concentration linearly and does not depend on the stoichiometry of LiNbO_3 . I demonstrated that the blueshift of the UV edge up to the threshold is caused both by the decreasing Nb_{Li} and the increasing Mg content.

From Raman spectroscopic measurements on $\text{LiNbO}_3\text{:Mg}$ crystals doped both below and above the threshold I established that the halfwidth of the $A_1(\text{TO}_2)$ Raman mode increases with increasing Mg content, while the halfwidth of the $A_1(\text{TO}_4)$ mode in under-threshold samples is constant and that in over-threshold samples increases with increasing Mg content. The broadening of the $A_1(\text{TO}_2)$ mode was explained by the increase of the number of Li vacancies and Mg_{Li} ions. The behaviour of the $A_1(\text{TO}_4)$ band was interpreted to be due to the practically unchanged oxygen sublattice below the threshold and to its distortion caused by the $\text{Mg}_4\text{Nb}_2\text{O}_9$ defect structure above the threshold.

4. Articles related to the topic of this thesis

1. **K. Lengyel**, L. Kovács, A. Baraldi, R. Capelletti, M. Berkowski, W. Ryba-Romanowski, „The stretching vibration of hydroxyl ions in LaGaO_3 ”, *Radiation Effects and Defects in Solids*, 158 (2003) 61.
2. L. Kovács, **K. Lengyel**, A. Baraldi, R. Capelletti, M. Berkowski, W. Ryba-Romanowski, „Hydroxyl ion absorption in LaGaO_3 single crystals”, *Journal of Physics and Chemistry of Solids*, 64 (2003) 741.
3. L. Kovács, **K. Lengyel**, Á. Péter, K. Polgár, A. Beran, „IR absorption spectroscopy of water in $\text{CsLiB}_6\text{O}_{10}$ crystals”, *Optical Materials*, 24 (2003) 457.
4. E. Hartmann, Á. Péter, **K. Lengyel**, L. Kovács, „Effect of melt composition on the electrical conductivity and IR absorption of $\text{CsLiB}_6\text{O}_{10}$ crystals”,

Crystal Research and Technology, 38 (2003) 331.

5. **K. Lengyel**, L. Kovács, G. Mandula, R. Rupp, „Kinetics of OH^- ions in nearly stoichiometric LiNbO_3 crystals”, *Ferroelectrics*, 257 (2001) 255.
6. G. Mandula, **K. Lengyel**, L. Kovács, M. A. Ellaban, R. A. Rupp, M. Fally, „Thermal fixing of holographic gratings in nearly stoichiometric LiNbO_3 crystals”, *Proceedings of SPIE, International Conference on Solid State Crystals 2000*, 4412 (2000) 226.
7. L. Pálfalvi, J. Hebling, G. Almási, Á. Péter, K. Polgár, **K. Lengyel**, R. Szipőcs, „Nonlinear refraction and absorption of Mg doped stoichiometric and congruent LiNbO_3 ”, *Journal of Applied Physics*, 95 (2004) 902.
8. **K. Lengyel**, Á. Péter, K. Polgár, L. Kovács, G. Corradi, „UV and IR absorption studies in $\text{LiNbO}_3\text{:Mg}$ crystals below and above the photorefractive threshold”, *Physica Status Solidi C*, accepted (2004).

5. Other articles

1. C. Bäumer, C. David, K. Betzler, H. Hesse, **K. Lengyel**, L. Kovács, M. Wöhlecke, „Composition dependence of the OH-stretch-mode spectrum in lithium tantalate”, *Physica Status Solidi A* 201 (2004) R13.
2. C. David, A. Tunyagi, M. Ulex, M. Wöhlecke, K. Betzler, **K. Lengyel**, L. Kovács, „Structure of the OH^- stretching vibrational band in $\text{Sr}_x\text{Ba}_{1-x}\text{-Nb}_2\text{O}_6$ ”, *Journal of Applied Physics*, 95 (2004) 5522.