HYDROXYL ION AS A PROBE OF THE STRUCTURE AND DEFECTS OF OXIDE CRYSTALS

L. Kovács

Crystal Physics Laboratory, Research Institute for Solid State Physics and Optics, Hungarian Academy of Sciences, Budapest, Hungary
E-mail: lkovacs@szfki.hu

The incorporation of hydrogen into synthetic wide band gap oxide crystals can remarkably influence e.g. their electrical and optical properties utilized for practical applications. The presence of hydroxyl ions (OH^-) in oxides has been widely studied in many papers and summarized recently [1].

It is widely accepted that OH^- ions or protons captured by oxygen ions enter the lattice from the ambient atmosphere during the preparation process, when the crystals are grown in air at high temperatures (~ 600 – 1600^{o}C) from melt or solution. The relatively low concentration of OH^- ions in as-grown crystals makes it possible to study them as isolated diatomic molecules in the lattice. Due to the light hydrogen atom the frequency of the localized vibrational mode (3200 – 3700 cm^{-1}) is higher than the vibrational frequencies of the host matrix. The OH^- absorption band can be measured with high resolution ($\Delta\nu \leq 0.1$ cm^{-1}) by the Fourier Transform Infrared (FTIR) spectroscopic technique.

Hydroxyl ions are assumed to occupy oxygen sites compensating some other kinds of intrinsic or extrinsic defects by their surplus positive charge. This behaviour of OH^- ions allows probing the defect structure of the crystals by studying the vibrational properties of hydroxyl ions influenced by their surroundings. The information obtained from the pleochroism of the absorption bands can be used to determine the structural site of the hydroxyl defects in the crystal lattice. The effect of a structural phase transition on the O-H vibrational frequency in $LaGaO_3$ crystals is an example for the relation between the crystal structure and the OH^- vibration. The composition of some non-stoichiometric niobates and tantalates (e.g. $LiNbO_3$, $LiTaO_3$, $K_3Li_2Nb_5O_{15}$, and $Sr_xBa_{1-x}Nb_2O_6$) can be characterized by the shape of the OH^- absorption bands. The anharmonicity of the stretching mode obtained for O-H vibrations and the weak coupling to phonon bands derived from the temperature dependence of the OH^- band parameters has also been studied in some complex oxides such as sillenites, tungstates (e.g. $CdWO_4$), molybdates etc.

As an example for practical applications the role of hydroxyl ions in the thermal fixing of holographic gratings via their kinetic behaviour will be presented in photorefractive $LiNbO_3$ crystals.

References

[1] M. Wöhlecke and L. Kovács, *Critical Reviews in Solid State and Materials Sciences*, **26** (2001) 1-86.