Monitoring the crystallization of NaCl and NaI with THz ATR Spectroscopy

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***Abstract*— We monitor the crystallization of NaCl and NaI out of watery solution using THz attenuated total reflection (ATR) spectroscopy. The data give insight into the complex dielectric function of the solutions during the evaporation of the water.**

I. INTRODUCTION

Salts are important in the food industry and for physiological processes. The complex dielectric function of salt solutions has been studied for a wide range of the frequencies including the THz range [1], [2]. Yet, the transition of salt in watery solution from the dilute state to its crystal form has not been studied yet at THz frequencies. In this work we study the refractive index and absorption coefficient of the NaCl and NaI solutions during their transition to solid crystals. The entire measurements took about 45 hours.

II. MEASUREMENT METHOD

Pure NaCl crystals were dissolved in distilled water. The solution was inserted into a sample chamber on top of an ATR prism. The measurements were carried out until all water was evaporated and a NaCl crystal remained on the bottom of the sample chamber. The same procedure was carried for NaI.

To preform long term measurements with ATR THz spectroscopy, we introduced new configuration measurement [3]. In this technique, we divided the surface of the prism in to two chambers. The prism slides for sample and reference measurement via mechanical stage around the THz pulse focal point. This configuration helps us to record reliable data with less uncertainty from temperature drift in the lab environment [4] and angular misalignment between sample and reference measurements. Detailed information on the setup can be found in [3], [4].

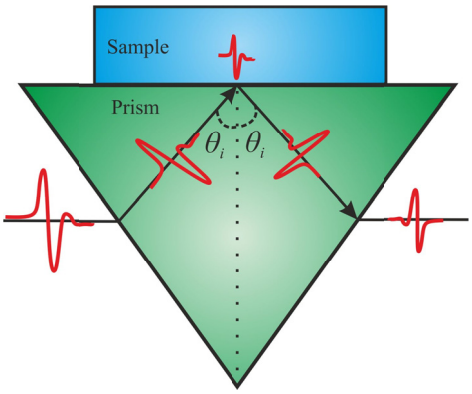


Figure 1: Schematic configuration of THz ATR

In THz ATR, optical parameters of the sample could be calculated as the following without considering any assumption:

$$\tilde{n}_{sample} = \frac{1}{Q}\sqrt{\frac{1}{2}\left(1 \pm \sqrt{1-(2\phi n_{silicon}\sin(\theta_i)^2)}\right)} \quad (1)$$

where $\tilde{n}_{sample}$ is the complex refractive index. In eq.1 Q equals to

$$Q = \frac{\cos(\theta_i)}{n_{sili}}\left(\frac{1-T.r^p_{sili-air}}{1+T.r^p_{sili-air}}\right) \quad (2)$$

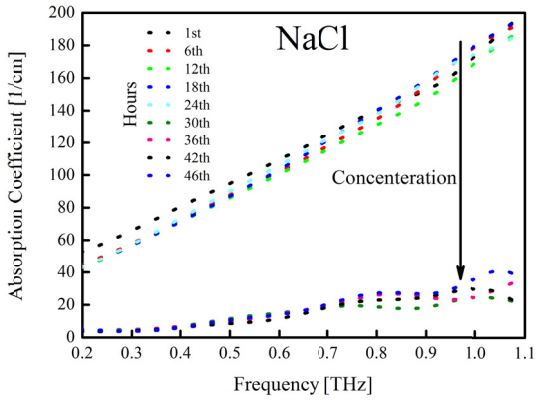
where θ_i is in the incident angle from prism to the sample (Fig.1). T also refers to transfer function as

$$T = \frac{E_{sample}(\omega)}{E_{ref}(\omega)} \quad (3)$$

In this equation, $E_{sample}(\omega)$ and $E_{reference}(\omega)$ are the Fourier transform of the sample and reference THz pulses.

III. RESULTS

Fig. 2 (a-b) show the frequency dependent of refractive index and absorption coefficient of the NaCl solution for different times. As expected water the effect of water dominates during the first hours and refractive index and absorption coefficient of the solution are close to that of bulk water. Fig. 2 (c-d) show the corresponding data for NaI. As water is highly absorbing the THz absorption decreases with increasing salt concentration for both solutions. On the other hand, NaI has a higher refractive index than water, so by increasing the concentration the refractive index of the solution increases. In contrast, the refractive index of NaCl is lower that of water. Therefore the refractive index of NaCl solution decreases by increasing the salt concentration.



(a)

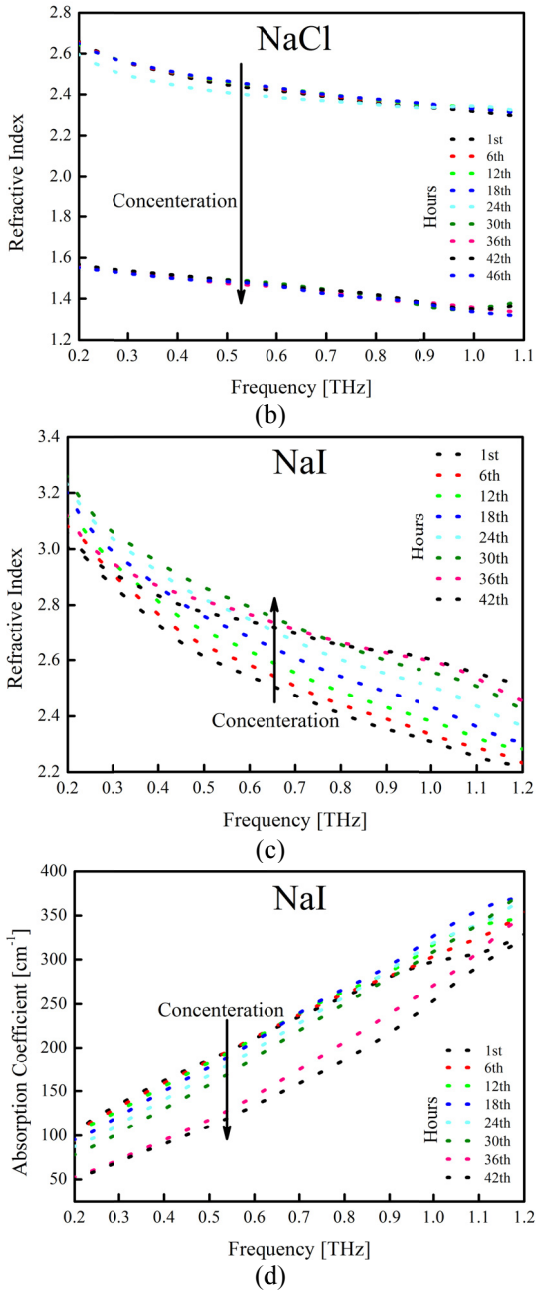


Figure 2: Refractive index and THz absorption for NaCl (a-b) and NaI (c-d) solutions.

IV. Conclusion

We have measured the refractive index and THz absorption spectrum of NaCl and NaI in watery solution during the transition from the dilute state to the crystal. This measurement scheme represents a new tool for studying crystallization processes at THz frequencies.

References

[1] P. U. Jepsen and H. Merbold, "Terahertz reflection spectroscopy of aqueous NaCl and LiCl solutions," *J. Infrared, Millimeter, Terahertz Waves*, vol. 31, pp. 430–440, 2010.

[2] R. Rungsawang, Y. Ueno, and K. Ajito, "Detecting a sodium chloride ion pair in ice using terahertz time-domain spectroscopy.," *Anal. Sci.*, vol. 23, no. July, pp. 917–920, 2007.

[3] A. Soltani, L. Duschek, S. F. Busch, T. Probst, E. Castro-Camus, and M. Koch, "A novel accurate method for attenuated total reflection spectroscopy," *Infrared, Millimeter, and Terahertz waves (IRMMW-THz), 2014 39th International Conference on*. pp. 1–2, 2014.

[4] A. Soltani, T. Probst, S. F. Busch, M. Schwerdtfeger, E. Castro-Camus, and M. Koch, "Error from Delay Drift in Terahertz Attenuated Total Reflection Spectroscopy," *J. Infrared, Millimeter, Terahertz Waves*, vol. 35, no. 5, pp. 468–477, Mar. 2014.