## Determination of the Thermal Expansion Coefficient and the Local temperature Measurements of BaTiO<sub>3</sub> Nanoparticles with Nanometer Resolution

Bibash Sapkota<sup>1</sup>, Emilio Ferral<sup>1</sup>, Serdar Ogut<sup>1</sup> and Robert F. Klie<sup>1\*</sup>

Our ability to determine the local temperature of a sample inside the electron microscope column is key in measuring the effects of electron-sample interaction and to control the beam-induced sample changes. According to the free electron model, the plasmon resonance energy of a material is related to the temperature through its electron density. Using this property, several experiments [1-2] have shown that the local temperatures can be measured by measuring the shift in the plasmon energy of the nanoparticles such as Si, Al, etc. with high resolution and high accuracy. However, these nanoparticles either have a low plasmon energy shift ( $\approx 0.1 \text{ meV}/^0\text{C}$  for Si [2]) resulting in a decrease in the accuracy of the measurement or a low melting point ( $\approx 660 \, ^0\text{C}$  for Al [3]) rendering them unable to be used in the high-temperature setting. Perovskite oxides such as BaTiO<sub>3</sub> (melting point  $\approx 1600 \, ^0\text{C}$  [4]) and SrTiO<sub>3</sub> (melting point  $\approx 2000 \, ^0\text{C}$  [5]) can be suitable alternatives for high-temperature local measurements because of their high melting point and moderate energy shift ( $\approx 0.4 \, \text{meV}/^0\text{C}$ ). However, the behavior of plasmon energy change with respect to the temperature of BaTiO<sub>3</sub> might be complicated due to the phase transition as well as oxygen vacancies generation.

In this work, we will compare the performance of BaTiO<sub>3</sub> nanocubes as a nano-thermometer for high-temperature measurement with that of Si and SrTiO<sub>3</sub>. We will explore the potential pitfalls and challenges encountered during the high-resolution nano-thermometry by using BaTiO<sub>3</sub> nanoparticles and we will explore the effects (if present) of the particle thickness, oxygen vacancies and contamination on this approach of measuring the local temperature. In addition, we will also utilize a novel approach of non-contact thermometry based on the combination of low-loss electron energy-loss spectroscopy (EELS) with the free electron model to measure the thermal expansion coefficient (TEC) of BaTiO<sub>3</sub> with nanometer resolution.

We will use the atomic-resolution imaging and electron spectroscopy technique with the help of an aberration-corrected scanning transmission electron microscope (JEOL-ARM200CF) at the University of Illinois at Chicago, equipped with a cold-field emission electron source and a Gatan Continuum Gif. We will use Protochips Fusion double-tilt stage for in-situ heating.

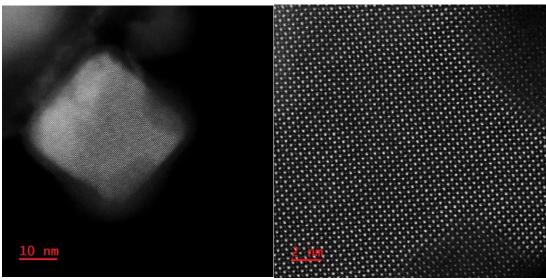
Figure 1 shows the low magnification as well as atomic resolution HAADF image of BaTiO<sub>3</sub> along the [100] direction at room temperature.

Figure 2 shows the low-loss EELS of  $BaTiO_3$  at different temperatures. For a 200  $^{0}$ C change in temperature, there is a shift of 12 meV in plasmon peak energy. The plasmon peak is fitted with the Lorentzian function to determine its center.

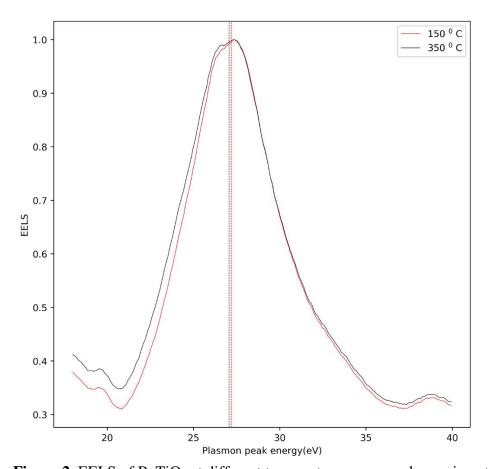
In the current presentation, we will measure the plasmon peak energy of BaTiO<sub>3</sub> nanocubes as a function of temperature (from 27 to 1000  $^{0}$ C) and use it to measure the local temperature as well as its linear thermal expansion coefficient. We will observe how the plasmon energy changes during phase transition. We will then compare the performance of BaTiO<sub>3</sub> as a nanothermometer with that of a range of nanoparticles including Al, Si, and SrTiO<sub>3</sub> [6].

<sup>&</sup>lt;sup>1.</sup> University of Illinois at Chicago, Chicago, IL, United States.

<sup>\*</sup> Corresponding author: rfklie@uic.edu



**Figure 1.** (a) Low magnification image of BaTiO3 nanocube (b) Atomic resolution HAADF image of BaTiO3 [100] at room temperature



**Figure 2.** EELS of BaTiO<sub>3</sub> at different temperatures measured experimentally. Plasmon peaks are normalized such that the maximum intensity of each peak is 1. Vertical dashed lines represent the plasmon peak center obtained by fitting the peak with the Lorentzian function.

## References:

- [1] Mecklenberg et al., Sci. 347 (2015), p. 6222.
- [2] Mecklenberg et al., Phys. Rev. Applied 9 (2018), p. 014005.
- [3] JB Sturgeon and BB Laird, Phys. Rev. B 62 (2000), p. 14720.
- [4] https://www.chemsrc.com/en/cas/12047-27-7\_244353.html
- [5] http://www.crystec.de/daten/srtio3.pdf
- [6] This work was supported by the National Science Foundation (DMR-18314061).