

# Hydrothermal Synthesis of Sodium Tantalate Nanocubes

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## Abstract

Experiments were conducted to optimize the growth parameters of perovskite structure of sodium tantalate in energy efficient hydrothermal process. We have successfully grown sodium tantalate nanocubes at low temperature of  $140^{\circ}\text{C}$  for 15 hours in rich alkaline atmosphere. It contains orthorhombic crystal system of perovskite structure with an average size of 80 nm. The morphological, compositional, structural, and thermal properties of as-synthesized nanocubes were characterized by scanning electron microscope (SEM), x-ray powder diffraction (XRD), and thermal gravimetric analysis (TGA) techniques.

## Introduction

Sodium tantalates are perovskite compounds of sodium bonded with tantalum and oxygen atoms with definite proportion. A material that obeys the crystallographic structure of calcium titanate ( $\text{CaTiO}_3$ ) is usually known as perovskite material. The perovskite structure simply consists of a large cation A with 12-fold coordination at the center of a cubic lattice. The corners of the cube is relatively smaller cation B with 6-fold coordination, and the midpoint of each edge are occupied by smaller anions C (halides or oxides). Alternately, cations A are at corners, cation B is at the center of the cube, and anions C ( $\text{O}^{2-}$ ) are located at the middle of each face as shown in figure 1. The majority of perovskite compounds are oxides but halides and cyanides also exist such as  $\text{MCNi}_3$  ( $\text{M} = \text{Al, Mg, Zn}$ ),  $\text{MAPbX}_3$ , ( $\text{MA} = \text{CH}_3\text{NH}_3$ ,  $\text{X}_3 = \text{halides}$ ), and  $\text{MTaO}_3$  ( $\text{M} = \text{Li, K, Na}$ ). They possess properties of semiconductor, ferroelectric, piezoelectric, and superconductor. Perovskite oxides of type  $\text{ABO}_3$ , however, are fascinating functional materials which exhibit range of stoichiometries and crystal structures. The filled and unfilled 3d shells of transition metal give dielectric, electronic, and magnetic behavior of these materials. The functionalities of these materials can be utilized in catalysis, fuel cells, and electrochemical sensing [1–3]. Tantalate based perovskite such as  $\text{NaTaO}_3$  exhibits fairly high activity for the photocatalytic decomposition of water under ultraviolet irradiation [3]. The flexible structure of oxide-perovskites with different A and B ions lead to the large number of known compounds. Most perovskites are distorted and do not have ideal cubic structure. Therefore, they are fascinating to be studied to exploit their special properties. Another relevant subject is to develop an environmental friendly chemical process to synthesize perovskite compounds.

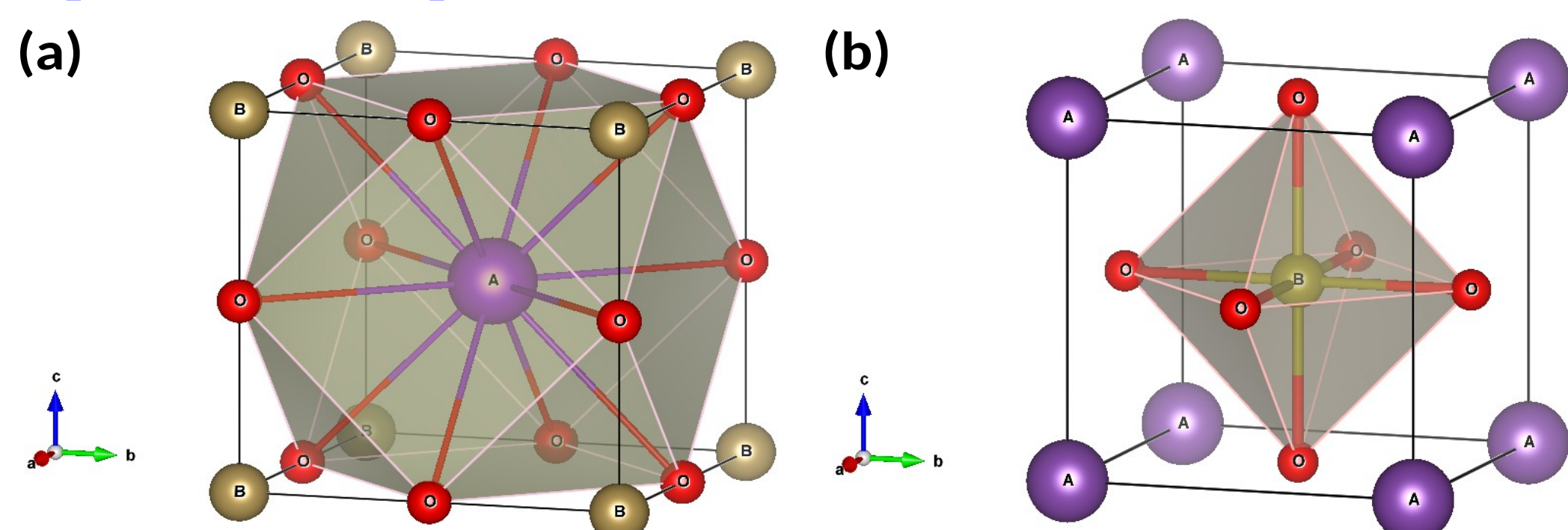


Figure 1: Perovskite cubic crystal structures of type  $\text{ABO}_3$ . In figure 1a cation A occupies at the body center, and in figure 1b cations A are located at the corners of Bravice unit cell.

## Main Objectives

1. To optimize growth parameters such as temperature, duration, and chemical concentrations to synthesize alkali nanocubes at low temperature hydrothermal process.
2. To understand how the oxygen stoichiometry and lattice distortion are introduced as a result of doping another type of cation with different valence state.

## Materials and Methods

Various methods such as mechanochemical synthesis, gas phase synthesis, and wet chemical synthesis (sol-gel process, and hydrothermal process) are available to synthesize tantalate perovskite [1]. Hydrothermal process (HTs) is one of the most suitable, energy efficient, and environmental friendly chemical process. We have used this process to optimize growth parameters of  $\text{NaTaO}_3$  nanocubes and control their size range. Size and chemical compositions of oxides type perovskite in HTs process can be controlled by adjusting the concentration of precursors, reaction time and temperature.  $\text{NaTaO}_3$  nanocubes were synthesized by reacting a Tantalate powder  $\text{Ta}_2\text{O}_5$  as a suitable precursor in high alkaline NaOH environment under hydrothermal conditions. The reaction mechanism is given as  $2\text{NaOH} + \text{Ta}_2\text{O}_5 \xrightarrow{t^\circ\text{C}} 2\text{NaTaO}_3 + \text{H}_2\text{O}$ . we have dissolved 0.44 g of  $\text{Ta}_2\text{O}_5$  powder in 0.75 M of NaOH with 6 hours of magnetic stirring in closed container. A 50 mL of this solution was then kept in a 100 mL Teflon lined autoclave and heated for 15 hours at  $140^{\circ}\text{C}$ . The milky-white products were centrifuged and washed with water and ethanol many times and dried at  $80^{\circ}\text{C}$  for 6 hours after reaction time is complete.

## Results & Discussion

The average size of nanocubes are 80 nm as measured from full width at half maximum (FWHM) value of prominent XRD peaks between ( $30^{\circ}$  to  $45^{\circ}$ ) of  $2\theta$  peak position using Scherrers formula,

$$\beta(2\theta) = \frac{K * \lambda}{L * \cos\theta} \quad (1)$$

where  $K = 0.89$  for cubical symmetry, FWHM ( $\beta$ ) is in radian unit, and  $\lambda = 0.1540598\text{nm}$ . TGA curve was obtained to determine thermal stability and decomposition behavior of synthesized nanocubes. Continuous weight loss after  $500^{\circ}\text{C}$  may indicate no thermal stability in this experimental temperature range.

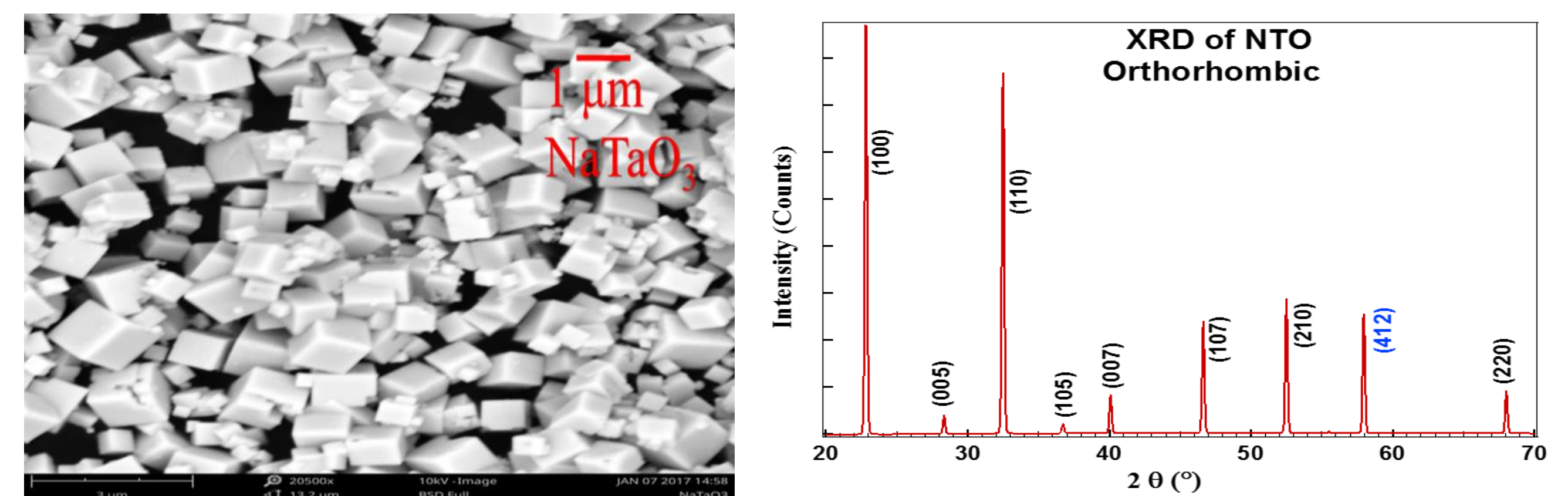


Figure 2: SEM images (figure 2a), and X-ray powder diffraction pattern (figure 2b), of perovskite phase of sodium tantalate obtained under hydrothermal conditions at  $140^{\circ}\text{C}$  for 15 hours. Average particle size is 80 nm.

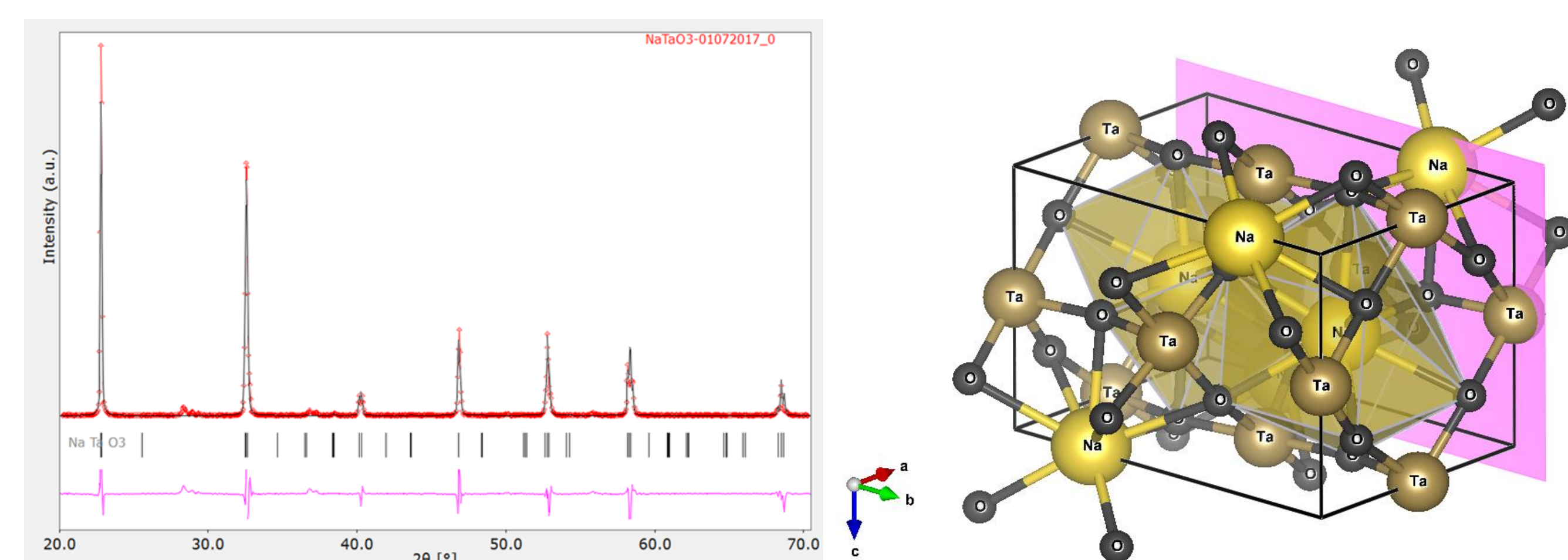


Figure 3: Orthorhombic crystal system of  $\text{NaTaO}_3$ , space group P cmn (no. 62), and cell parameter  $a = 5.4768 \text{ \AA}$ ,  $b = 7.7200 \text{ \AA}$ , and  $c = 5.5412 \text{ \AA}$ ,  $\alpha = \beta = \gamma = 90^{\circ}$ , obtained by the least square fitting to the observed XRD data using Rietveld refinement from Rex software as shown in Figure (3a). Figure (3b) represents unit cell of sodium tantalate plotted using VESTA-software, pink color plane in figure (3b) represents (100) reflection plane of the crystal.

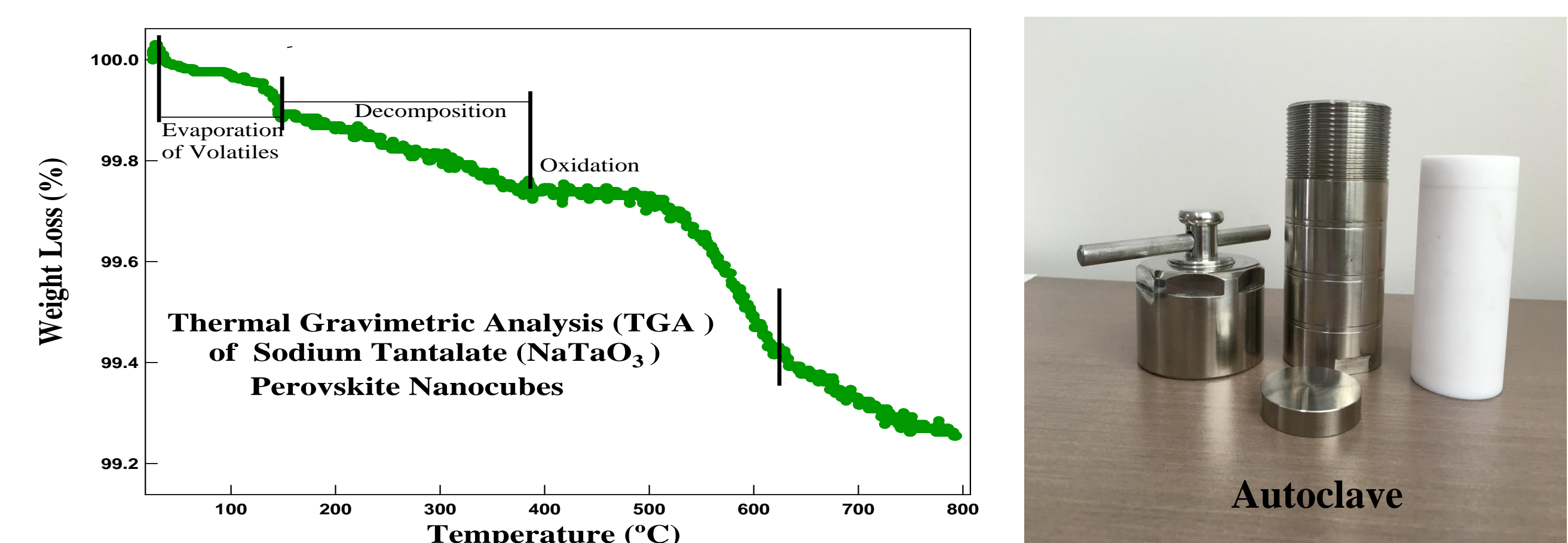


Figure 4: TGA curves of sodium tantalates nanocubes taken in air atmosphere at a heating rate of  $20^{\circ}\text{C}/\text{min}$ , figure 4a. Gradual weight loss upto  $150^{\circ}\text{C}$  indicative of water or volatile substance evaporation. Slow but steady weight loss up to  $380^{\circ}\text{C}$  may be due to decomposition reaction. At  $380^{\circ}\text{C}$  sample may go for oxidation reaction and started gaining weight till  $500^{\circ}\text{C}$ . Autoclaves with teflon linen pot for hydrothermal process, figure 4b.

## Conclusions

Sodium Tantalates nanocubes were grown at  $140^{\circ}\text{C}$  for 15 hours of growth period in rich alkaline atmosphere by hydrothermal process. The compound possesses orthorhombic crystal system of perovskite structure. The nanocubes were about 80 nm in size and have shown phase transition state between  $250^{\circ}\text{C}$  to  $600^{\circ}\text{C}$ .

## Research in our Lab

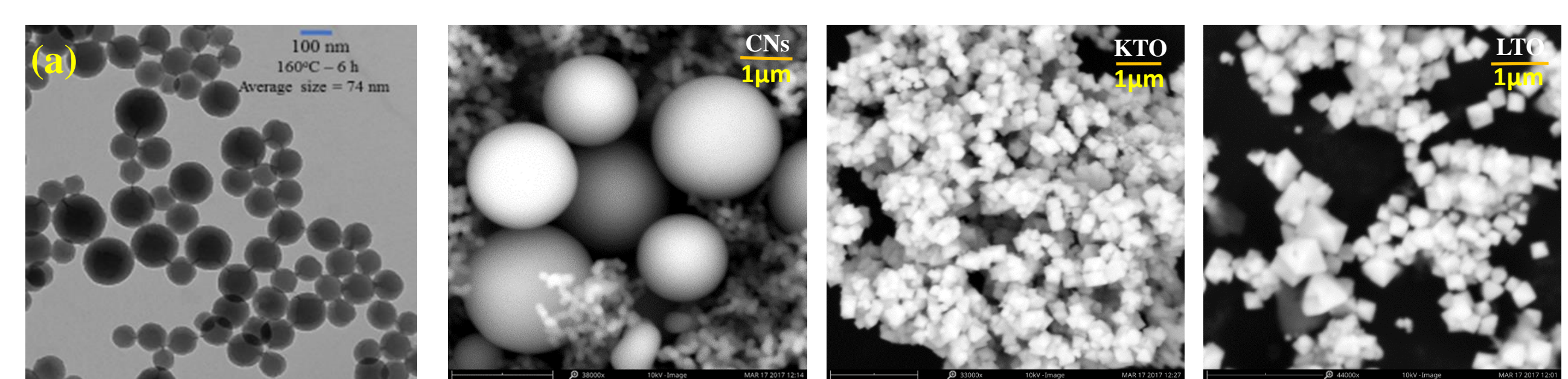


Figure 5: TEM images of carbon nanospheres, figure 5a, and SEM images of carbon nanospheres, Potassium tantalate and Lithium tantalate nanocubes, figures 5b, 5c, and 5d, respectively. All particles were synthesized in our lab via hydrothermal process.

## References

1. W. Karachic (2005), "Oxidation Chemistry of Some Early Transition-Metal Layered Perovskites"
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  3. J. Angeles (2016), "Synthesis of Perovskite Oxides by Hydrothermal Processing from Thermodynamic Modelling to Practical Processing Approaches", Intech Ch 2 (2016).
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