Hydrothermal Synthesis of Sodium Tantalate Nanocubes

Priya Karna, M.Ghimire*, S. Mishra*, and S. Karna

Department of Natural Science, Union College, Barbourville, KY

* Department of Physics, University of Memphis, Memphis, TN

Abstract

Experiments were conducted to optimize the growth parameters of perovskite structure of alkali tantalate in energy efficient environment friendly hydrothermal process. Here we are presenting Sodium tantalates outof Lithium, Sodium, and Potassium Tantalates perovskite which were grown at 140^oC for 15 hours in rich alkaline atmoshphere. Sodium tantalates contains monoclinic crystal phase of perovskite structure with an average size range of 70 nm. The morphological, compositional, structural, and thermal properties of as synthesized nanocubes were characterized by using scanning electron microscope (SEM), x-ray powder diffraction (XRD), and thermal gravimetric analysis (TGA) techniques.

Introduction

Alkali tantalates are perovskite compounds of group I element bonded with tantalum and oxygen atoms. A material that obeys the crystallographic structure of calcium titanate $(CaTiO_3)$ 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 $C(O^{2-})$ 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 $MCNi_3$ (M = Al, Mg, Zn), $MAPbX_3$, $(MA = CH_3\,NH_3$, X_3 = halides), and $MTaO_3$ (M = Li, K, Na). They possess properties of semiconductor, ferroelectric, piezoelectric, and superconducting. Perovskite oxides of type 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 $NaTaO_3$ 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.

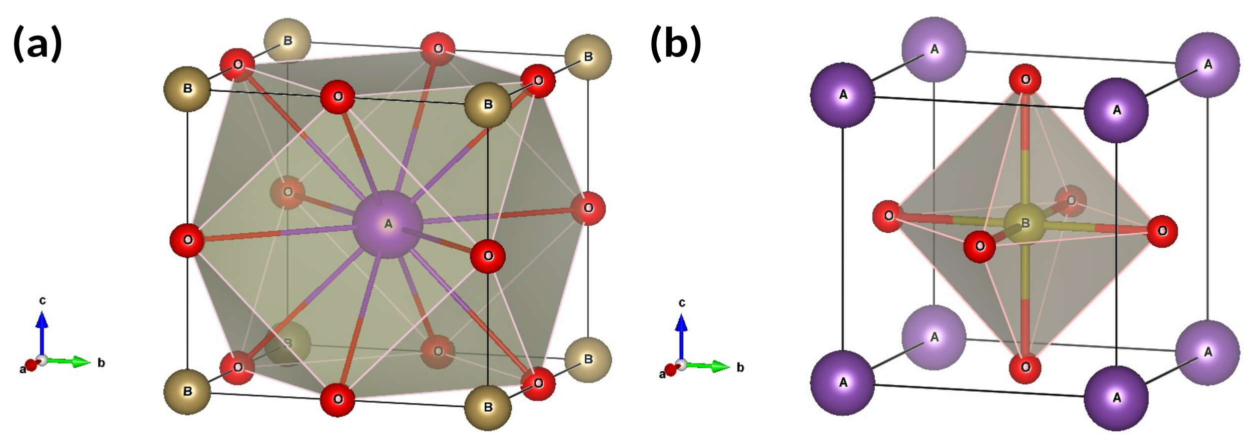

Figure 1: Perovskite cubic crystal structures of type ABO_3. In figure 1a cation A occupies at the body center, and in figure 1b cations A are located at the corners of Bravice unit cell.

Main Objectives

1. To develop an environmental friendly chemical process to synthesize nanparticles.
2. To optimize growth parameters such as temperature, duration, and chemical concentrations to synthesize alkali nanocubes at low temperature hydrothermal process.
3. 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

Among various methods such as mechanochemical synthesis, gas phase synthesis, and wet chemical synthesis (sol-gel process, and hydrothermal process) to synthesize tantalates perovskite [1]. Hydrothermal process is one of the most suitable, energy efficient, and environmental friendly chemical process. We have used this process to optimize growth parameters of $NaTaO_3$ 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. $NaTaO_3$ nanocubes were synthesized by reacting a Tantalate powder Ta_2O_5 as a suitable precursor in high alkaline NaOH environment under hydrothermal conditions. The reaction mechanism is given as $2NaOH + Ta_2O_5 \xrightarrow{t^oC} 2NaTaO_3 + H_2O$. we have dissolved 0.44 g of Ta_2O_5 powder in 0.75 M of NaOH and 50 mL of this solution was kept in 100 mL Teflon lined autoclave and heated for 15h at 140^oC. The milky-white products were centrifuged and washed with water and ethanol many times and dried at 80^oC for 6 hours after reaction time is complete.

Results & Discussion

The average size of nanocubes are 70 nm as measured from full width at half maximum (FWHM) value of prominent XRD peaks using Scherrers formula. TGA curve was obtained to determine thermal stability and to monitor decomposition behavior of synthesized nanocubes. Continuous weight loss after 500^oC may indicate no thermal stability in this experimental temperature range.

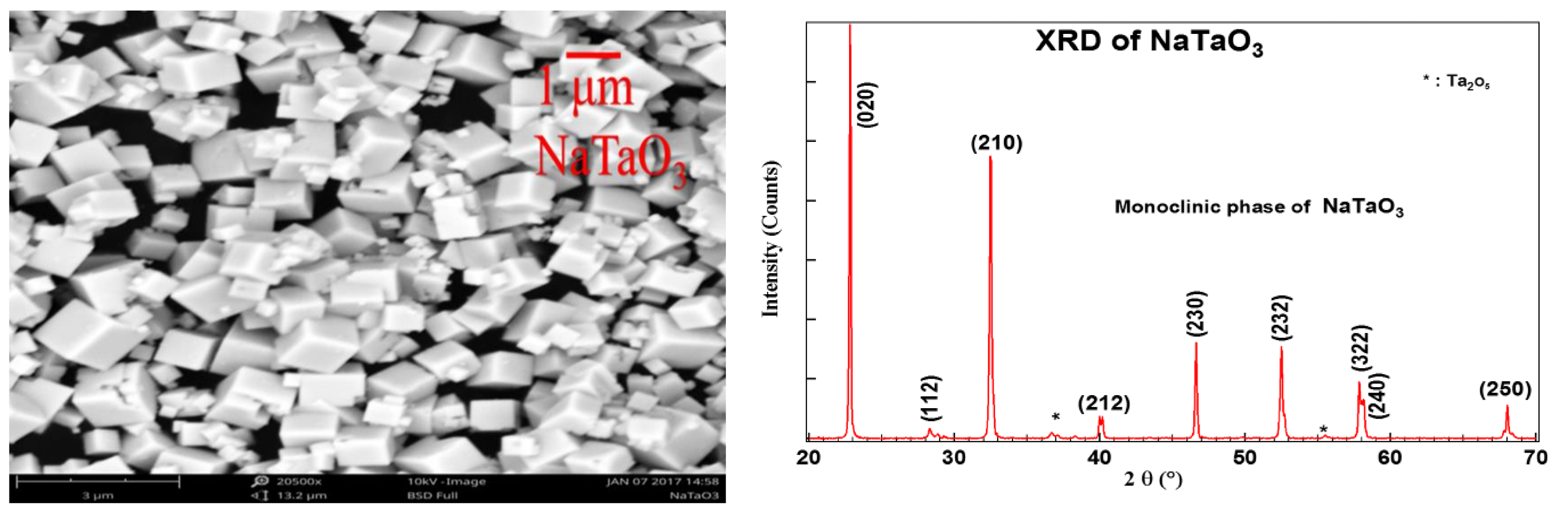

Figure 2: SEM images (figure 2a), and X-ray powder diffraction pattern (figure 2b), of perovskite phase of Sodium tantalate obtained under hydrothermal conditions at 140^oC for 15 hours. Average particle size is 70 nm.

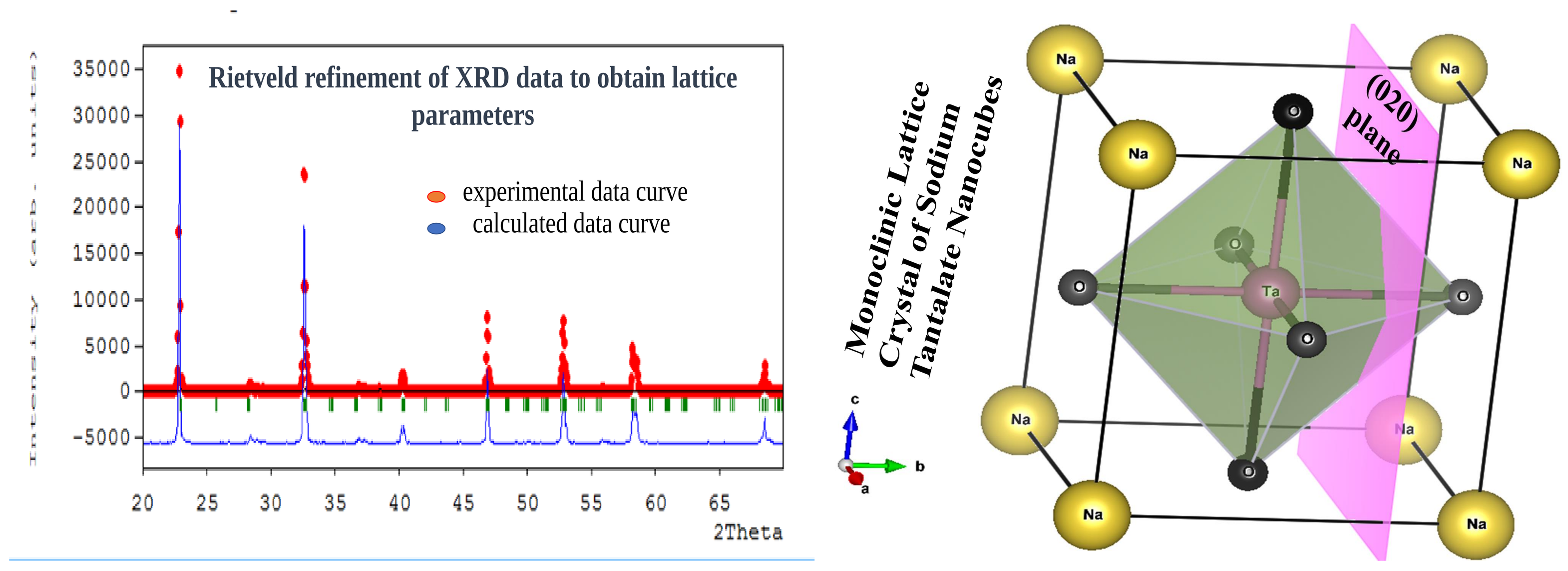

Figure 3: Monoclinic crystal system of $NaTaO_3$, space group P121 (no. 3), and cell parameter a = 5.8866 Å, b = 7.7952 Å, and c = 8.2426 Å, $\alpha = 90^o = \gamma$, $\beta = 92.277^o$, obtained by the least square fitting to the observed XRD data using rietveld method in FullProf suite, RexCell, and PowderX. Red curve represents experimental data and blue curve represents rietveld theoretical curve which matches with each other at high accuracy as shown in Figure (3a). Figure (3b) represents monoclinic crystal system of sodium tantalate perovkite structure ploted using VESTA-software, pink color plane in figure (3b) represents (020) plane of the crystal.

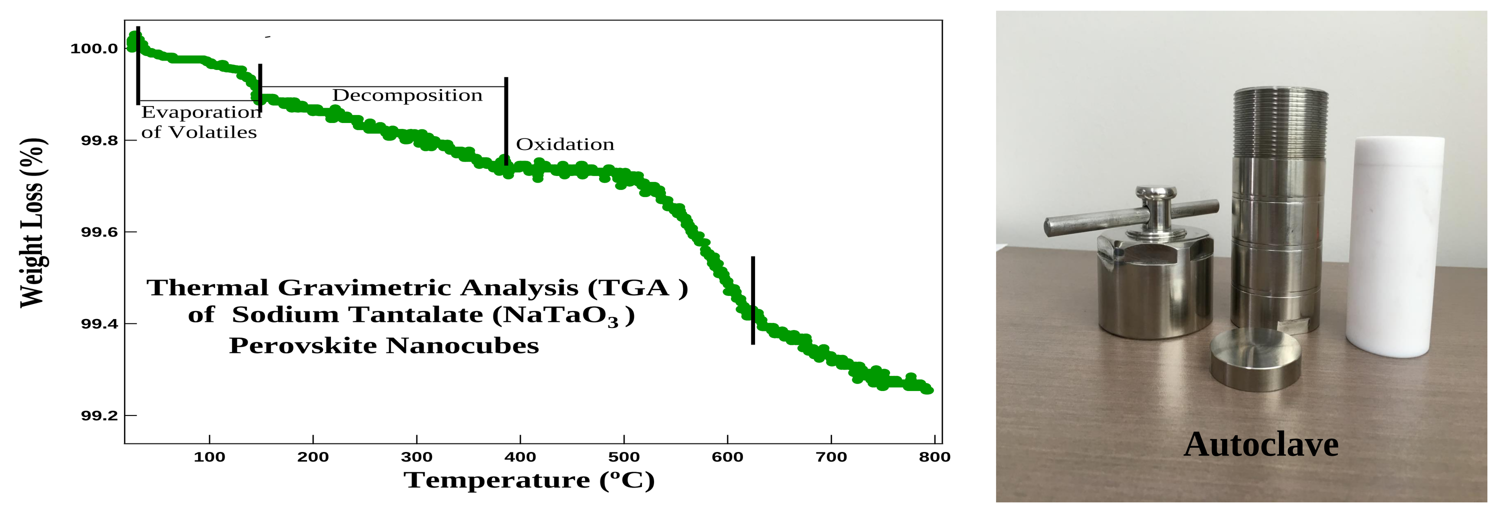

Figure 4: TGA curves of sodium tantalates nanocubes taken in air atmosphere at a heating rate of $20^oC/min$, figure 4a. Gradual weight loss upto 150^oC indicative of water or volatile substance evaporation. Slow but steady weight loss up to 380^oC may be due decomposition reaction. At 380^oC sample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

Conclusions

We have synthesized Sodium Tantalates nanocubes at 140^oC for 15 hours of growth process in rich alkaline atmoshphere by hydrothermal process. This compound contains monoclinic crystal phase of perovskite structure. The nanocubes were about 70 nm in size and have shown phase transition state between 250^oC to 600^oC, without any thermal stability within our experimental range of TGA study.

Research in our Lab

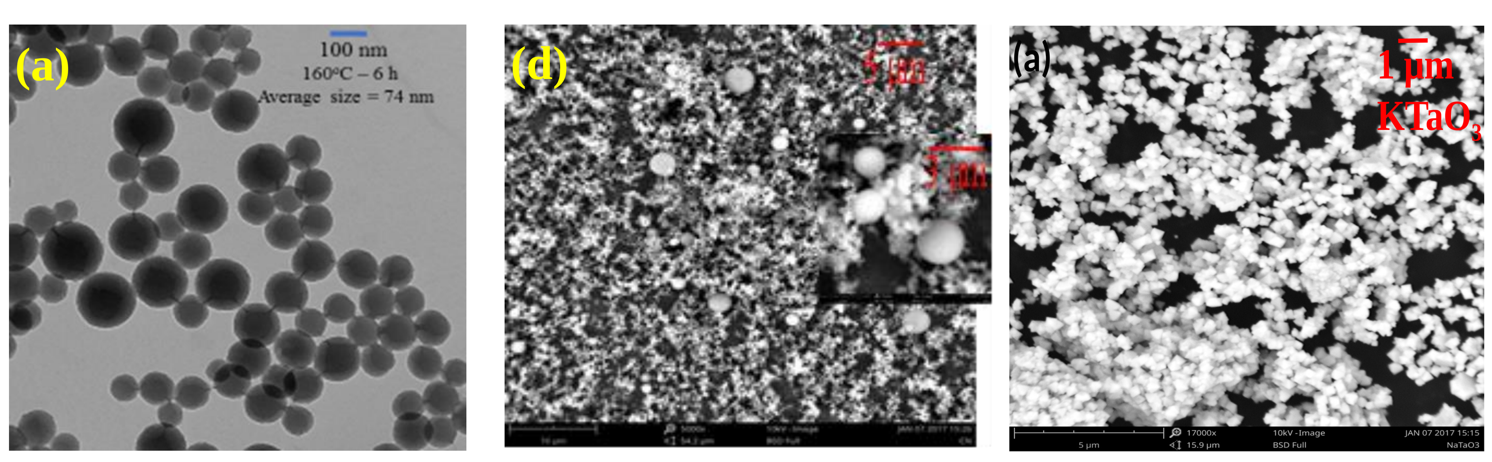

Figure 5: TEM image of Carbon nanospheres, figure 5a. SEM image of carbon nanospheres, figure 5b, and SEM image of Potassium tantalate nanocubes, figure 5c. All particles were synthesized in our lab via hydrothermal process.

References

1. W. Karachie (2005), *"Oxidation Chemistry of Some Early Transition-Metal Layered Perovskites"*
2. M. Johnson (2008), *"Crystallography and chemistry of perovskite"*, Journal of Physics: Condensed Matter, Volume 20, Number 26.
3. J. Angeles (2016), *"Synthesis of Perovskite Oxides by Hydrothermal Processing from Thermodynamic Modelling to Practical Processing Approaches"*, Intech Ch 2 (2016).

Acknowledgements: I would like to thank Faculty Research Committee, Department of Natural Science, and Physical Plant of Union College, Barbourville, KY to provide help during this project.