

RESEARCH PAPER

## Theoretical and experimental investigation of the effect of Acetic and formic acids as capping agents on the morphology of KTiOPO<sub>4</sub> nanoparticles

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### ABSTRACT

KTiOPO<sub>4</sub>(KTP) nanoparticles were synthesized using acetic and formic acids as capping agents by the co-precipitation method for the first time. X-Ray diffraction (XRD) and Fourier Transform Infrared (FT-IR) analyses confirmed the formation of the KTP structure with an orthorhombic phase. The effect of capping agents on the structural and morphological properties of obtained KTP nanoparticles was also studied. The largest grain size (66 nm) and lattice strain (0.0056) were obtained using acetic acid and formic acid, respectively. Using acetic and formic acids resulted in the rotation of the crystal lattice and an increase in the grain size. Acetic acid prevented the agglomeration of synthesized KTP nanoparticles after calcination and resulted in uniform size distribution. Theoretical computations and FE-SEM analysis were used for morphological studies. FE-SEM analysis showed that acetic acid resulted in the spherical form of nanoparticles, and using formic acid led some nanoparticles' morphology to oriented growth. Theoretical computations confirmed these results. The structural energy of the most stable KTP nanostructures obtained using formic acid as a capping agent was  $\Delta E = -202.6518584$  kJ/mol and  $\Delta E = -196.613208$  kJ/mol. The first formation energy belonged to the oriented template of the nano-particles.

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### INTRODUCTION

Properties of nanoparticles depend strongly on their shape and size. Therefore, understanding the effective parameters of nucleation and growth process of nanoparticles and their optimization is essential in fabricating the desirable properties of nanoparticles. Over the last two decades, many approaches have been developed to achieve control over shape and size of nanoparticles. One effective method among them involves the use of various ligands to control the surface energy of nanoparticles [1]. The growth rate in different crystal directions can be tailored by modulating

the relative surface energies of crystal planes using surface-selective ligands [2].

KTiOPO<sub>4</sub>(KTP) is known as a highly desirable material due to its high nonlinear optical, high optical damage threshold, thermally stable phase-matching, large linear electro-optic, and low dielectric constants which make it a useful and ideal material for second harmonic generation in lasers and various electro-optical applications such as modulators and Q switches [3-5].

To improve KTP single crystals' properties for various applications, especially for SHG, their growth conditions were studied in the late nineteenth century. Nowadays, these crystals are industrialized, and in recent years, scientists have

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focused on producing KTP nanostructures for different applications such as second harmonic generation [6], biolabel [7], and charged nanofiltration membranes [8]. The properties of nanoparticles change with their size and shape; therefore, the precise control of the size and shape of nanocrystals can manipulate their properties as desired for use as the building blocks in nanodevices.

The co-precipitation method is known as an appropriate, economical, and simple method to control the size and shape of nanoparticles [9]. A capping agent is generally added to control the size of nanocrystals and prevent agglomeration of synthesized nanocrystals. The selective adsorption of the capping agent to certain crystal helps to kinetically control single-crystal growth. The capping agent also plays a key role in the morphology of nanocrystals.

Formic acid (HCOOH) is an organic compound and the simplest carboxylic acid, the structure of which is H-C(=O)-O-H. It is an important intermediate in chemical synthesis [10, 11]. Formic acid is also known as a capping agent and an effective reductant for producing nanocrystals with well-controlled shapes [11]. Nanocrystals with controlled shapes were engineered for bioimaging, biomedical, sensing applications, and energy storage [12].

On the other hand, several monodentate binders, such as acetic acid [13,14] and benzoic acid [15], are used as capping agents. These monocarboxylate ligands were utilized to control the morphology and crystal size of nanoparticles [16]. Further, acetic acid plays a vital role in improving the structural properties.

The optimal synthesis of nanoparticles is a challenging process, influenced by various experimental conditions, such as reaction time, reagent concentrations, temperature, solution rotation, and pH solution along with the nucleation and growth process. The contribution of each experimental variable to the final product is generally determined by trial and error, resulting in a time-consuming and laborious identification of the most effective reaction parameters. Thus, we required more efficient and controlled approaches to synthesize the nanoparticles with specific properties [17].

Computations based on the quantum mechanics of electronic structure is commonly used to study the structures of molecules and materials and to

predict a range of atomic-scale properties [18].

In this research, KTP nanoparticles were synthesized using acetic and formic acids as capping agents by the co-precipitation method. The structure and morphology of the obtained nanoparticles were studied using XRD, FT-IR and FE-SEM analyses. In addition, the effect of the capping agents on the shape of primary nucleation was investigated by Gaussian software using Hartree-Fock method. The calculated theoretical data and obtained experimental results confirm each other.

## EXPERIMENTAL METHOD

### *Synthesizing potassium titanyl phosphate nanoparticles (KTPNPs)*

(a) Aqueous solution of titanyl chloride, which was produced by dissolving freshly precipitated Ti(OH)<sub>4</sub> in HCl (6N) solution, (b) potassium dihydrogen phosphate (KH<sub>2</sub>PO<sub>4</sub>), (c) potassium carbonate (K<sub>2</sub>CO<sub>3</sub>), (d) HCl (35%), (e) acetic acid and formic acid as capping agents with high purity were used as raw materials.

To produce KTP nanoparticles, aqueous titanyl chloride solution was mixed well with a selected capping agent in 1:1 mole ratio with respect to titanium ion. Then the aqueous solution of potassium dihydrogen phosphate with the solution concentration of 0.5M was added to the reaction solution dropwise. At the end, potassium carbonate was added to obtain white precipitate at pH≈6. The precipitate was washed with distilled water several times and dried at 100 °C under ambient conditions. Produced amorphous powder was calcined at 700 °C for 2h. The schematic of the synthesis process is shown in Fig. 1.

### *Characterization*

The obtained samples were characterized by X-Ray powder diffraction (XRD) using an Advanced Bruker D8 X-ray diffractometer with CuK $\alpha$  radiation ( $\lambda = 1.5405$ ) at a scan rate of 0.065° min<sup>-1</sup>. The grain size, lattice strain, structural phase, and lattice parameters of obtained KTP nanoparticles were calculated using XRD patterns. Fourier transforms infrared (FTIR) spectra of the samples were obtained using the KBr pellet technique. The spectra were recorded on an 8400S- SHIMADZU infrared spectrometer. The samples were scanned between 400 and 4000cm<sup>-1</sup>. The formation of KTP structure for obtained nanoparticles was confirmed by FT-IR analysis. The morphology of

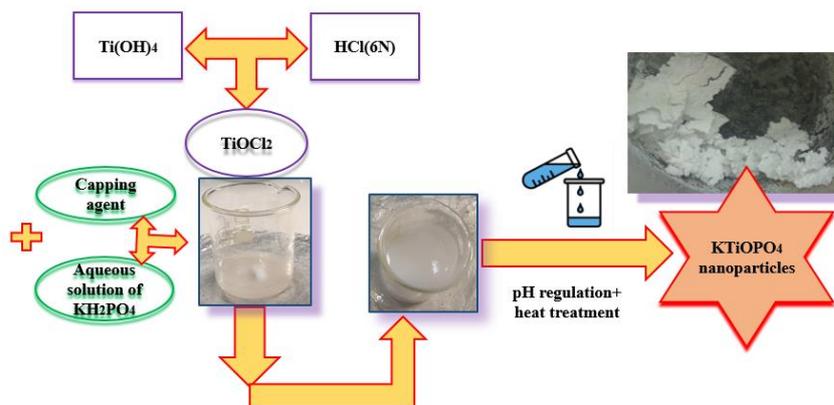


Fig.1. The schematic of synthesis process

Table1. Structural properties of obtained KTP nanoparticles.

sample	Crystal lattice constant			Grain size(nm)- Scherer	Grain size(nm)- William-Son	Lattice strain
	a	b	c			
S	10.58	12.81	6.40	51.17	55.44	0.0016
FO1:1	12.81	6.39	10.58	57.34741	64.3	0.0056
AC1:1	12.81	6.39	10.58	66.16197	66	0.0028

nanostructures was viewed by HITACHI S4160 scanning electron microscope. The samples were sputtered on a copper substrate and then coated with gold-palladium to make them conductive before SEM analysis.

## RESULTS AND DISCUSSIONS

### The powder X-Ray diffraction (XRD)

Fig. 2 shows the XRD patterns and William-son curves of KTP nanoparticles synthesized without using a capping agent (Fig. 2.a) and using acetic acid and formic acid as capping agents (Figs. 2. b and 2. c) after calcination at 700°C for 2h.

The X-ray diffraction spectra for all the samples confirm the formation of KTiOPO<sub>4</sub> nanocrystals with an orthorhombic phase. The spectrum belonging to the sample synthesized without capping agent was adopted to 00-35-0802 card number with the lattice constant of a=10.58, b=12.81, c=6.40. Using acetic and formic acids as capping agents resulted in crystal lattice rotation. The obtained spectra were adopted to 01-080-0893 card number with the lattice constant of a=12.81, b=6.39, and c=10.58. The grain size and lattice

strain of obtained nanoparticles were calculated using Debby-Scherer and William-Son equations (eq-1 and eq-2), where D is the crystallite size, λ is the wavelength of the CuKα radiation (1.5405Å), K is a constant (0.9), β is the full-width at half-maximum, ε is lattice strain and θ is the Bragg angle [19,20]. The results are shown in Table 1.

$$D = \frac{K\lambda}{\beta \cos(\theta)} \quad \text{Eq. 1}$$

$$\beta \cos(\theta) = 4\epsilon \sin(\theta) \quad \text{Eq. 2}$$

Using acetic acid, the grain size of the KTP nanoparticles increases. The acetate molecules are small carboxylate ligands that bind to the primary nuclei surface. At a 1:1 mole ratio of ones, the concentration of molecules is not enough to decrease the surface energy, resulting in a kink state on nuclei surface; thus, the surface energy, growth rate, and grain size increase.

It is observed that using formic acid, rather than acetic acid, as a capping agent resulted in a smaller grain size. Using acetic and formic acids as capping agents led to an increase in the grain size while nanoparticles synthesized without a capping agent

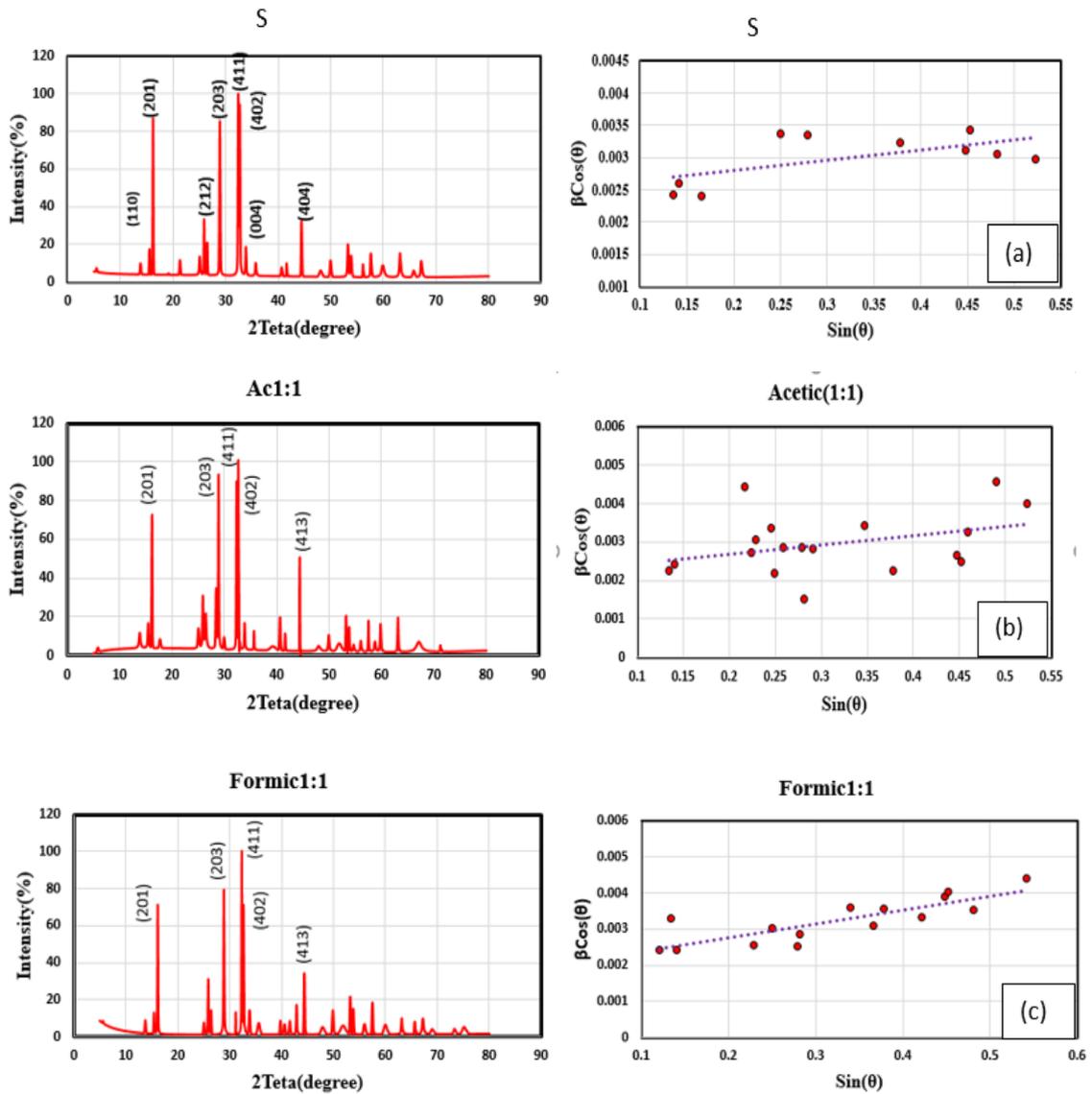


Fig. 2. XRD patterns of KTP nanoparticles synthesized (a) without capping agent, and using 1:1 mole ratio of (b) acetic acid, (c) formic acid as capping agent

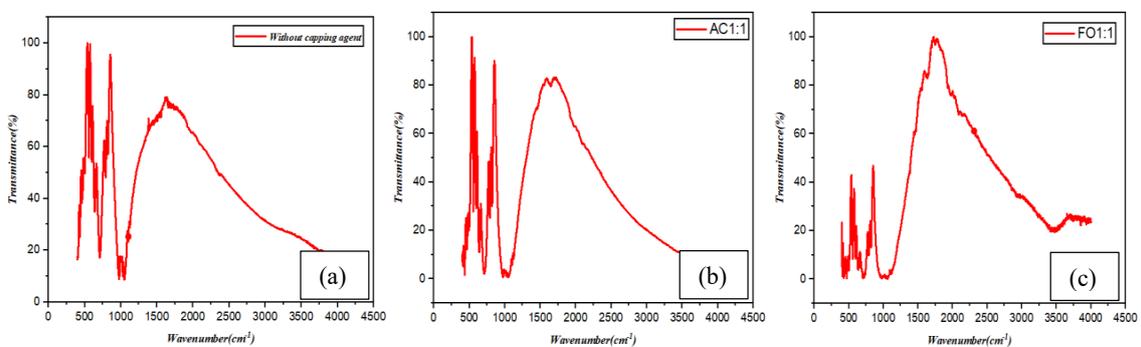


Fig.3. FT-IR spectra of samples synthesized (a)without capping agent and using (b) acetic acid, (c) formic acid as capping agent.

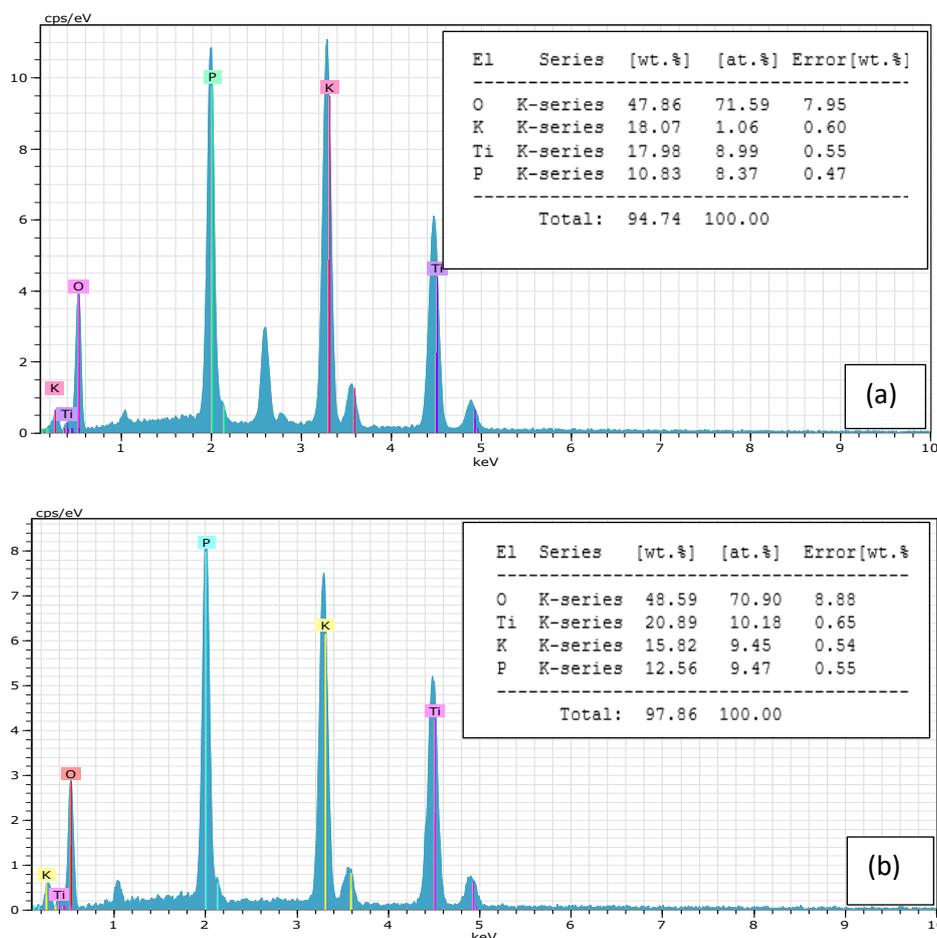


Fig.4.EDX analysis of samples synthesized using 1:1 mole ratio of (a)acetic acid, (b)formic acid as capping agents.

do not undergo such increase in the grain size.

The highest lattice strain belongs to the FO1:1 sample. Formic acid results in the oriented growth of KTP nanoparticles; thus, this sample shows the highest lattice strain.

#### Fourier Transform Infrared spectroscopy

Fig. 3 shows the FT-IR spectra of synthesized nanoparticles without and with using capping agents after calcination at 700°C for 2h. The characteristic bands of KTP structure appeared in the wavelength range of 1200 to 600 cm<sup>-1</sup> for all the samples. Six resolved bands at 974,995, 1027, 1050, 1100 and 1126 cm<sup>-1</sup> are associated with the asymmetric stretching vibrations of PO<sub>4</sub> units [21]. The three bands at 820, 785 and 712 cm<sup>-1</sup> are attributed to Ti-O vibrations of the distorted TiO<sub>6</sub> octahedral. The peaks in the region between 660-350 cm<sup>-1</sup> are assigned to the splitting of degenerate and PO<sub>4</sub> modes [22]. The absorption

peaks in our recorded FT-IR spectra confirmed the formation of KTiOPO<sub>4</sub> structure for all the obtained nanoparticles. The characteristic bands of KTP structure were observed in all the spectra. Recorded spectra showed a broad peak between 3000-4000 cm<sup>-1</sup> that are assigned to O-H stretching band absorbed on the surface of nanoparticles. Formic acid modified the Ti-O and P-O bands and resulted in weakening the characteristics peaks of Ti-O vibrations in TiO<sub>6</sub> octahedral and asymmetric stretching vibrations in PO<sub>4</sub> units.

#### Energy-dispersive X-ray analysis (EDX)

Energy-dispersive X-ray spectra of obtained nanoparticles using capping agents are given in Fig. 4.

The elements of KTiOPO<sub>4</sub> composition were identified using EDX. The weight percentages of elements confirmed the formation of KTP

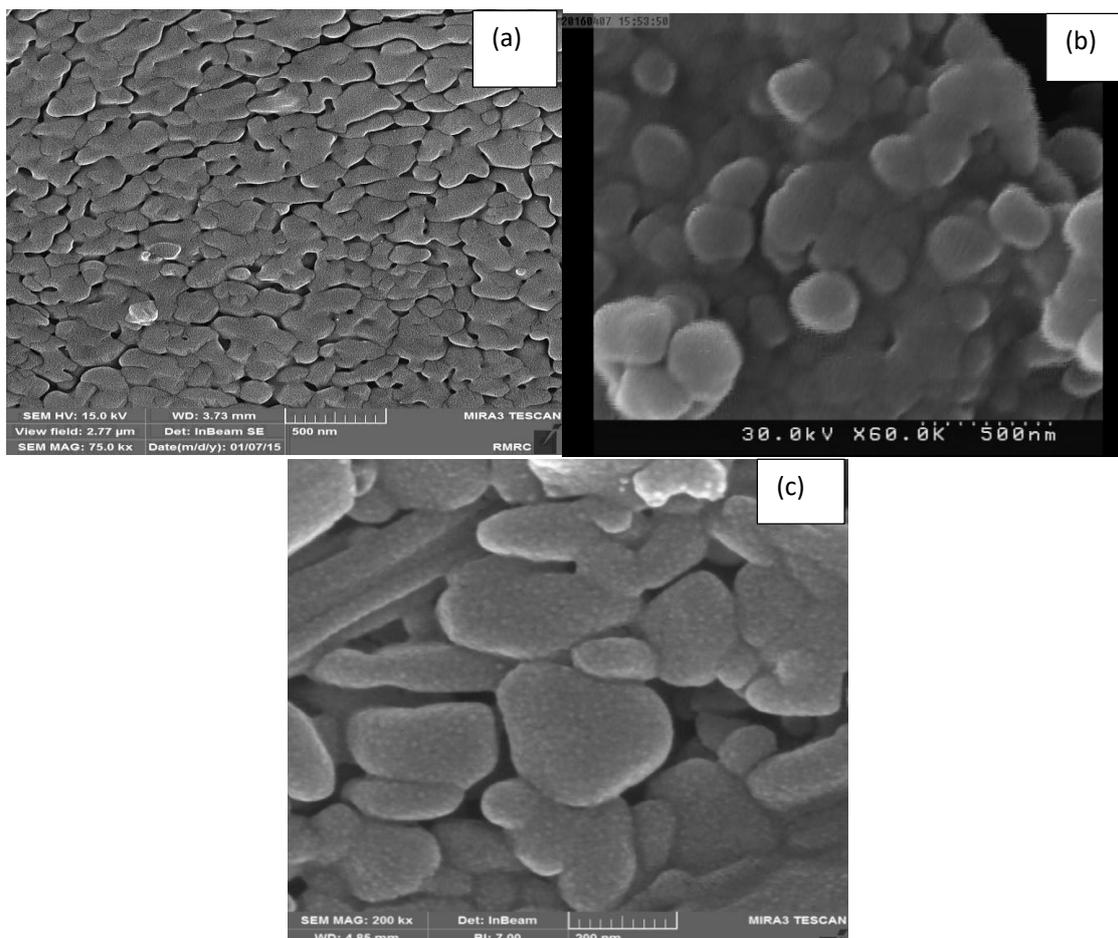


Fig. 5. FE- SEM images of KTP nanoparticles synthesized (a) without capping agent and using (b) acetic acid, (c) formic acid as capping agent

structure. Only a low error of 7-8% in the oxygen weight percentage was observed. Those elements with the atomic number below 11 were hard to be detected using EDX. By looking at the total weight percentage given in Fig. 4, we guess extra oxygen elements belong to absorbed O-H groups on the surface of nanoparticles, while hydrogen elements could not be detected using EDX analysis.

#### Scanning electron microscopy (SEM) study

Fig. 5 shows the FE-SEM images of KTP nanoparticles synthesized without (Fig. 5.a) and using capping agents (Figs. 5.b and 5.c).

The nanoparticles synthesized without capping agent were dumbbell-shaped, and had a uniform size distribution. The high surface energy of the synthesized nanoparticles resulted in attaching the spherical nanoparticles together and formation of dumbbell-shaped nanoparticles.

It was observed that using acetic acid, as a capping agent, resulted in powdery-form nanoparticles. The use of acetic acid as a weak acid allows for the control of the degree of condensation and the preferential crystallization of KTP nanoparticles, resulting in the most uniform size distribution. The small molecules of acetic acid can bind together on the surface of the nuclei, leading to the growth of primary nuclei into spherical nanoparticles. These results are corroborated by the findings of other researchers [1, 23].

The synthesis of KTP nanoparticles is highly sensitive to additives. Even small changes in the type or quantity of the additive can lead to a change in particles shape and size. Utilizing formic acid as a capping agent, almost all nanoparticles were seen to have an oriented growth. However, 1:1 mole ratio of formic acid was not sufficient to lead all primary nuclei to this growth, and only some nanorods are observed in Fig. 3. c.

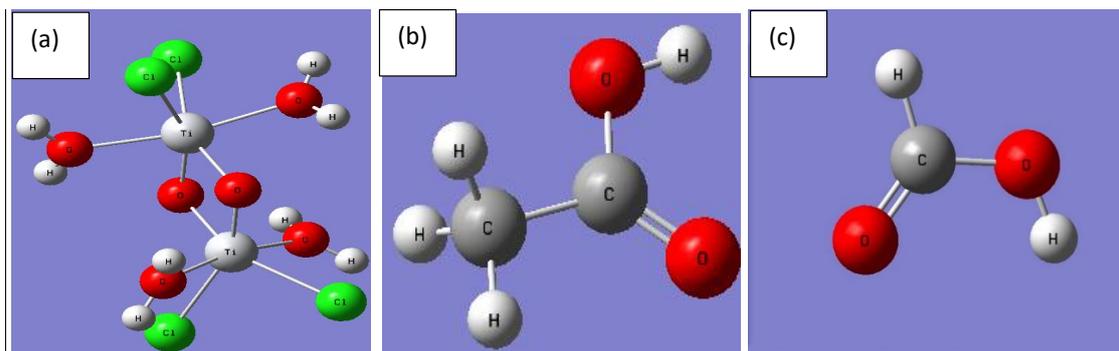


Fig. 6. Optimized structure of (a)  $\text{TiOCl}_2$  molecule in water solution, (b) acetic acid and (c) formic acid

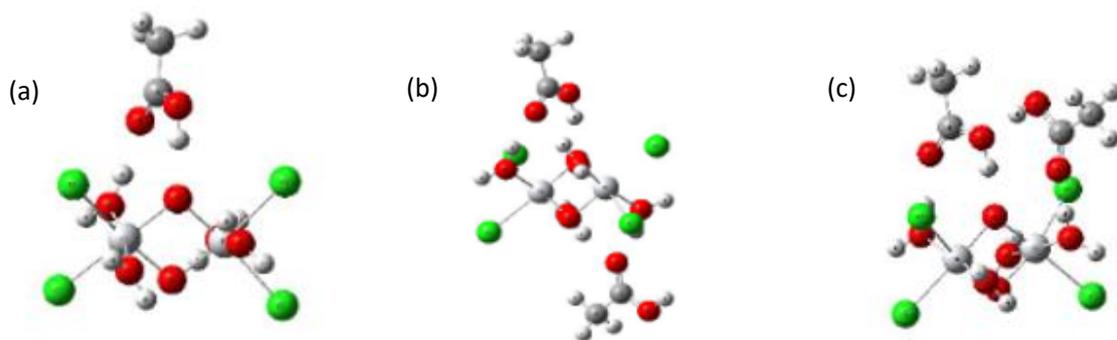


Fig. 7. The most stable structure after adding acetic molecule to water solution of  $\text{TiOCl}_2$ , in (a) 1:2 (b), and (c) 1:1 mole ratio with respect to Ti ion respectively

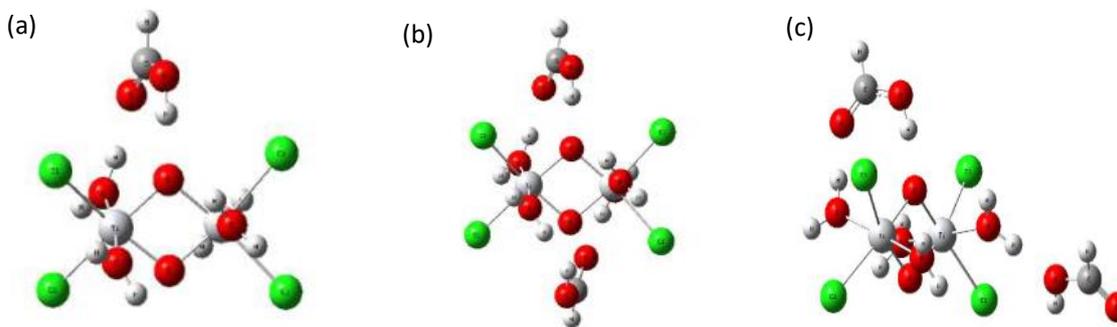


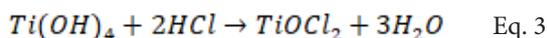
Fig. 8. The more stable structure after adding formic molecule to water solution of  $\text{TiOCl}_2$ , in (a) 1:2 (b), and (c) 1:1 mole ratio with respect to Ti ion, respectively

### THEORETICAL STUDIES

Computations based on the quantum mechanics of electronic structure was conducted using Gaussian software. The molecule structures were design using Gauss view, and were optimized using Gaussian software. The Hartree-Fock method and 6-31G basis set were used for the calculation.

The water solution of  $\text{TiOCl}_2$  formed after adding  $\text{HCl}(6\text{N})$  to  $\text{Ti}(\text{OH})_4$  powder (eq-3). To this

solution, acetic acid (or formic acid) as a capping agent was added in a 1:1 mole ratio with respect to Ti ion. The optimized structure of  $\text{TiOCl}_2$  molecule in water solution, acetic acid, and formic acid were calculated and are shown in Fig. 6.



Different modes of reaction between acetic acid molecules and  $\text{TiOCl}_2$  molecules after acetic acid mixing with a water solution of  $\text{TiOCl}_2$  were

investigated. The calculated energy for the stablest structure after adding acetic molecule in a 1:2 mole ratio was  $\Delta E = -99.12576005$  kJ/mol. This structure is shown in Fig. 6a. The most stable structures after adding a second acetic molecule (1:1 mole ratio) are given in Figs. 7. b and 7. c.  $\Delta E = -202.6518584$  kJ/mol and  $\Delta E = -196.613208$  kJ/mol are calculated for these structures, respectively. From Figs. 7.b and 7.c it is observed that acetic acid as a capping agent shows a tendency to bind together and cover the nuclei surface, leading the morphology of obtained nanoparticles to spherical form. This result was confirmed by FE-SEM images.

Different reaction modes after adding formic acid were investigated. The calculated energy for the most stable structure after adding acetic acid in a 1:2 mole ratio was  $\Delta E = -69.33420928$  kJ/mol. The more stable structures after adding the formic in 1:1 mole ratio are given in Figs. 8.b, and 8.c. For these structures  $\Delta E = -136.9880984$  kJ/mol and  $\Delta E = -124.724387$  kJ/mol are calculated, respectively. From Figs. 8.b and 8.c it can be seen that formic acid as capping agent make oriented templet for primary nucleation growth. This result was confirmed by FE-SEM images.

## CONCLUSION

The effects of acetic acid and formic acid as capping agents on the morphology of KTP nanoparticles were investigated. We used the co-precipitation method to synthesize the KTP nanoparticles, the formation of which were confirmed by XRD and FT-IR analyses. Using acetic and formic acids resulted in modifying the grain size, lattice strain, size distribution, and morphology of obtained nanoparticles. The morphology of obtained nanoparticles led to spherical form and oriented growth using acetic and formic acids, respectively. Theoretical studies on the morphology of the obtained nanoparticles confirmed the experimental results. The highest lattice strain (0.0056) was obtained using formic acid as a capping agent, while the largest grain size (66nm) was achieved using acetic acid. *Using acetic and formic acids resulted in the rotation of the crystal lattice and an increase in the grain size.*

## CONFLICT OF INTEREST

The authors declare no conflicts of interest.

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