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The Effect of Polyvinyl Alcohol Concentration on the Growth Kinetics of $KTiOPO_4$ Nanoparticles Synthesized by the Co-precipitation Method

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Abstract

$KTiOPO_4$ nanoparticles are known as the best candidates to be utilized for second-harmonic generation in multiphoton microscopes and bio labels. Size and shape are important and effective parameters to control the properties of nanoparticles. In this paper, we will investigate the role of capping agent concentration on the size and shape control of KTP nanoparticles. We synthesized KTP nanoparticles by the co-precipitation method. Polyvinyl alcohol with different mole ratios to titanium ion (1:3, 1:2, 1:1) was used as a capping agent. Products were examined by X-ray diffraction patterns and scanning electron microscopy analyses. The X-ray diffraction patterns confirmed the formation of the KTP structure. The biggest (56.36 nm) and smallest (39.42 nm) grain sizes were obtained by using 1:3 and 1:1 mole ratios of capping agent, respectively. Dumbly, spherical and polyhedral forms of KTP nanoparticles were observed by the change in capping agent mole ratio. The narrowest size distribution of $KTiOPO_4$ nanoparticles was obtained at a 1:1 mole ratio of capping agent.

Keywords: Co-precipitation Method; Nanoparticles; Potassium Titanyl Phosphate; Size Control; Shape Control.

1. Introduction

Potassium Titanyl Phosphate ($KTiOPO_4$ or KTP) single crystals are excellent nonlinear optical materials [1-3]. They also have important technological applications in laser frequency mixing and waveguides [4]. They are good ionic conductors [5, 6] and piezo-optic materials [3]. Many valuable properties of this crystal have made it a standard material in many industrial, medical, and other applications. A study on the growth conditions of KTP single crystals to improve their properties for different applications [7-9], especially for SHG, started in the late nineteenth century. These crystals are industrialized, but there are a few reports of the same studies on KTP nanocrystalline. In recent years, nanoscience and technology have had potential applications in the fields of science and technology. Because of it, the attention of scientists has been focused on the production of KTP nanostructures. Different applications were reported for these nanoparticles, such as second harmonic generation [10], charged nanofiltration membranes [11], and bio-labels [12]. The size and shape of nanocrystals act as critical parameters for determining material properties. Therefore, precise control of the size and shape of nanocrystals results in the desired chemical and physical properties. Pechini [13], Sol-gel [14], mechanochemical mixing [15], combustion [16], co-precipitation [17, 18], and hydrothermal [19] methods have been used to prepare KTP nanostructures. Mechano chemical, sol-gel, and pechini are primitive methods for the synthesis of KTP nanoparticles. Among these methods, there are problems such as

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expensive raw materials, the presence of OH^- ions in products, and weaknesses in the shape control of nanoparticles. Co-precipitation is known as an appropriate, cheap, and simple method for controlling the size and shape of nanoparticles [20-22].

In this method, by controlling the relative rate of nucleation and growth during the nanoparticles synthesis process, shape, size, and distribution will be controlled. A capping agent is generally added to nanocrystals prepared by solution-based chemical methods to control the size and shape of the nanocrystals. Capping agents with selective adsorption to specific crystal faces could be used to kinetically control the single-crystalline growth. Also, it plays an important role in the formation of nanocrystal morphology. When we use polymers as capping agents, the length of their polyol's hydrocarbon chain can determine solution viscosity. Therefore, using polymers as a capping agent can greatly control the diffusion, growth process, and morphology of obtained nanoparticles. In this paper, we report a low-temperature aqueous solution-based co-precipitation method for the synthesis of KTP nanoparticles and selected polyvinyl alcohol (PVA) as capping agents. PVA generally acts as a holding matrix and is expected to control the size of nanoparticles and their distribution. The average grain size, particle size, and morphology of obtained nanoparticles were studied by X-ray diffraction (XRD) patterns and scanning electron microscopy (SEM) analysis.

2. Materials and Methods

The aqueous solution of titanyl chloride, high purity of potassium dihydrogen phosphate (KH_2PO_4), potassium carbonate (K_2CO_3) and PVA as capping agent in different mole ratios to titanium ion (1:3,1:2 and 1:1) were used for the synthesis of KTP nanoparticles. The aqueous solution of titanyl chloride was produced by dissolving $Ti(OH)_4$ powder in HCl (6 N) solution. Capping agent-mixed titanyl chloride solution was reacted with an aqueous solution of KH_2PO_4 with solution concentration equal to 0.5M. Solution pH was regulated at pH≈6 using K_2CO_3 to obtain white precipitate. The obtained powders were washed by distilled water several times to remove chloride ion from them and finally dried at 100˚C under ambient condition. The initial amorphous phase, after precipitation, was calcined at 700 ˚C for 2h. The synthesis steps to obtain $KTiOPO_4$ nanoparticles are shown in Figure 1.

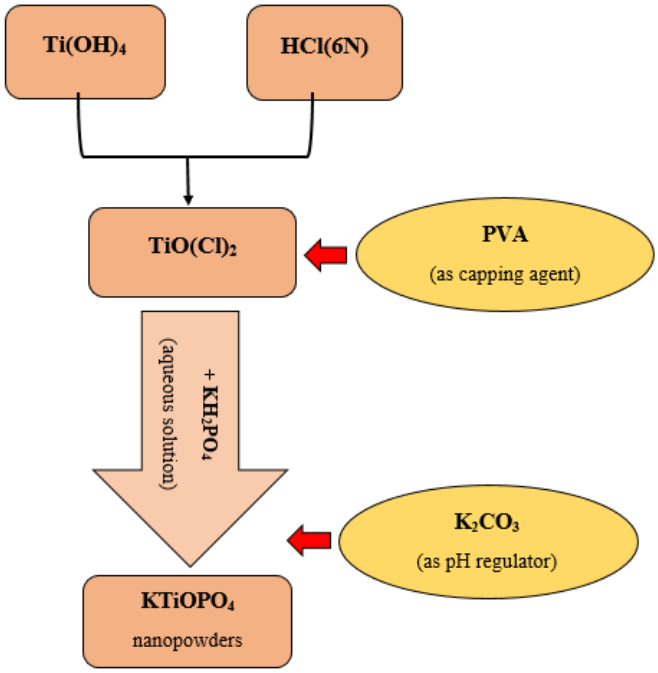


Figure 1. The synthesis diagram of KTP nanoparticles by co-precipitation method

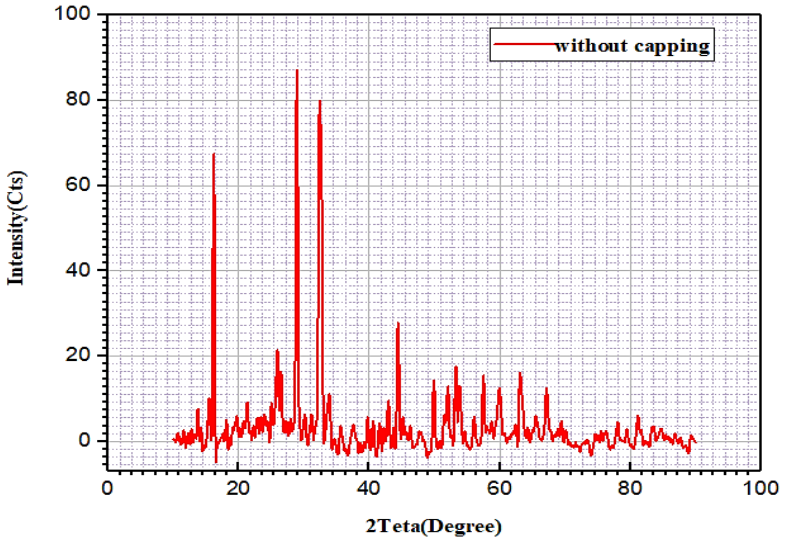
3. Results and Discussion

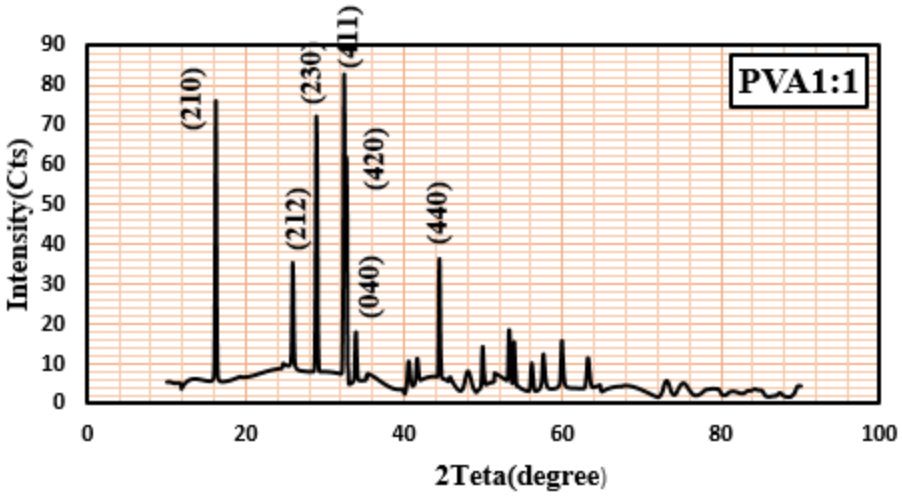
3.1. X-Ray Diffraction Studies

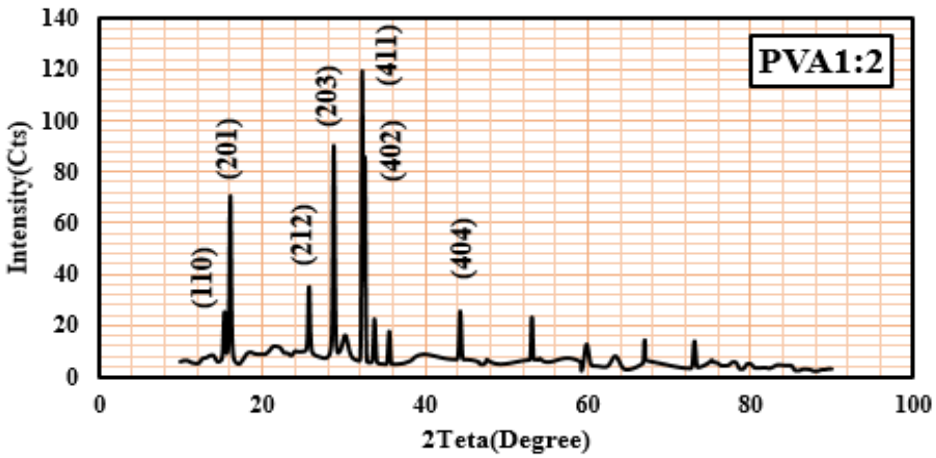
Figure 2 shows the XRD patterns of KTP nanoparticles synthesized without using capping agent and with different mole ratios of PVA as capping agent after calcination at 700˚C. For all the samples, diffraction peaks were well assigned to orthorhombic structure of KTP. X-ray analysis showed crystal lattice rotation at 1:2 mole ratio of PVA as capping agent. Lattice parameters were calculated equal to a= 10.58A˚, b= 12.81 A˚ and c=6.40 A˚ for 1:3 and 1:1 mole ratios of PVA, which are in consistent with the values in the standard card of ASTM (35-0802). One's values for PVA1:2 sample were obtained equal to a=12.82, b=6.40 and c=10.59 (card No. 01-079-1569). The average crystallite size of produced samples was calculated by measuring the broadening of the XRD peaks using the Scherrer equation.

$$D = \frac{k\lambda}{\beta \cos\theta} \quad (1)$$

Where D is the crystallite size, λ is the wavelength of the CuKα radiation (1.542Å), K is a constant (0.9), β is the full-width at half-maximum and θ is the Bragg angle. The crystallite size of obtained KTP nanoparticles under different conditions is given in Table 1. Crystallite size decreased with an increase in the mole ratio of the capping agent. At 1:2 and 1:3 mole ratios of PVA, the number of ligands is fewer than Ti^{+2} ions. This parameter results in fewer nucleation and bigger grain size. Optimum condition to kinetically control the nanoparticle grain size was observed at the 1:1 mole ratio of PVA. This concentration showed the smallest grain size of the obtained KTP nanoparticles.







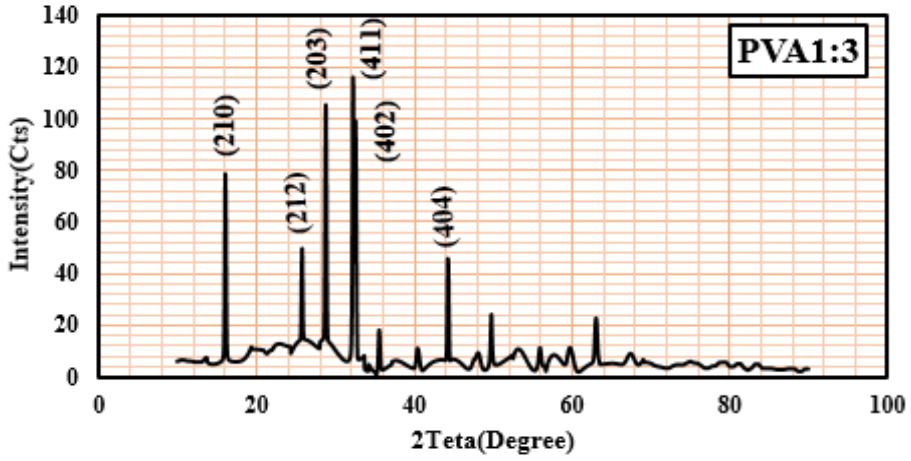


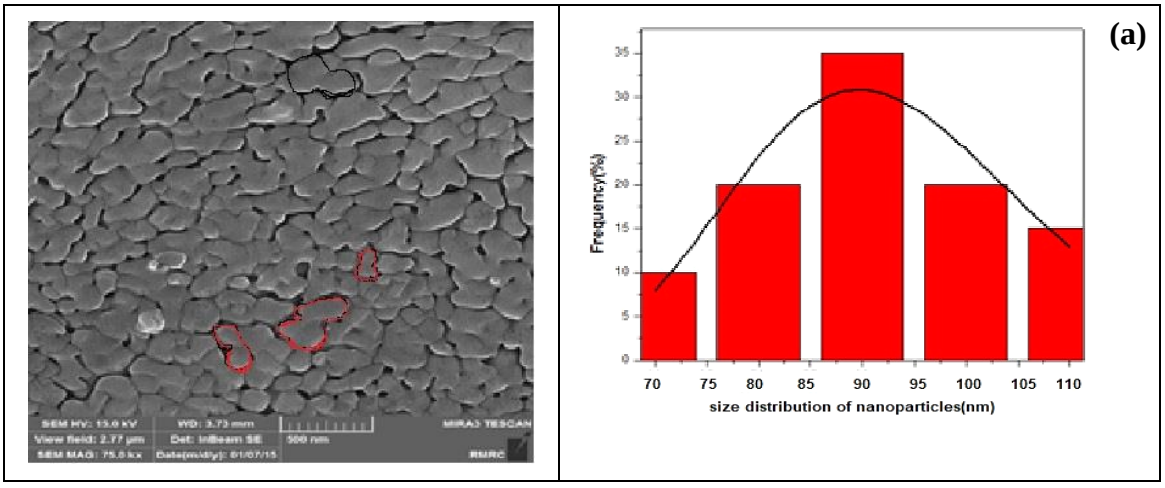
Figure 2. XRD patterns of KTP nanoparticles synthesized without and with different mole ratios of PVA as capping agent

Table 1. Crystallite size, particle size and PDI for KTP nanoparticles obtained under different conditions

sample	Type of capping agent	Mole ratio of capping agent	Grain size (nm)	Particle size (nm)	PDI
S	Without capping agent	-	39/49	100	1/26
PVA1:3	PVA	1:3	56/36	115	2/25
PVA1:2	PVA	1:2	42/50	110	2/23
PVA1:1	PVA	1:1	39/42	90	1/53

3.2. Scanning Electron Microscopy (SEM) Studies

The FE-SEM images of KTP nanoparticles synthesized without and with using different mole ratios of capping agent are shown in Figure 3. Poly dispersity index (PDI) [18] was calculated via Image-J software. PDI and particle size of obtained KTP powders with different mole ratios of polyvinyl alcohol are given in Table1. It is observed that size, size distribution, and the shape of produced nanoparticles have been affected by mole ratios variation of PVA. The particle size of the obtained KTP nanoparticles increased with a decrease in the mole ratio of PVA. Table.1 shows using PVA as a capping agent only at 1:1 mole ratio results in a decrease in grain size and particle size compared with the S sample. Morphology of KTP nanoparticles for the S sample was dumbly-form but using PVA as a capping agent resulted in spherical-form for PVA1:3 and PVA 1:2 samples and polyhedral-form for PVA1:1 sample. PDI decreased with increasing the PVA mole ratio for obtained samples. PVA generally has the role of the holding matrix. The OH functional group of PVA may temporarily bind with the metal ions through Vander Waals forces [23]. The amount of PVA as a capping agent plays a definite role in determining the growth habit of the various crystal faces, so in determining the morphology of KTP nanocrystals. The selective adsorption of capping agents on the crystal surface results in the formation of nanoparticles with certain morphology.



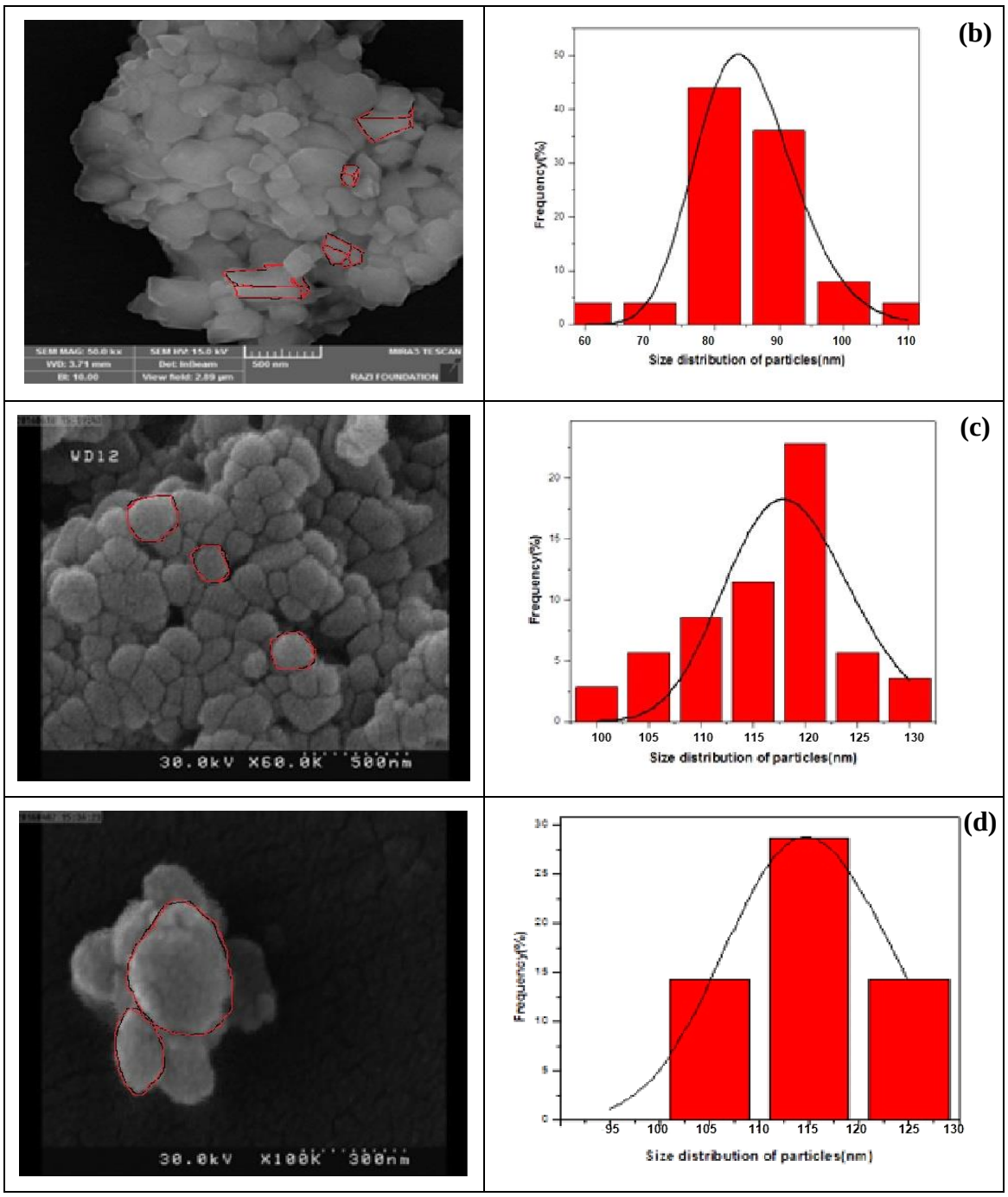


Figure 3. FE-SEM images of KTP nanoparticles synthesized (a) without capping agent and with PVA as capping agent with mole ratio, (b)1:1, (c) 1:2, (d) 1:3, accompanied by size distributions curve of obtained samples with different mole ratio

From another perspective, viscosity is increased by increasing the PVA solution concentration. An increase in the viscosity results in difficult diffusion and migration of ions within the solution. So, the nucleation process became slower and the nucleation number decreased. Decreasing the nucleation alongside the used stirring rate can provide the required conditions for steady growth at an appropriate PVA concentration. In this work, increasing the amount of capping agent and using relatively high-speed stirring lead to a decrease in the grain and particle size and an increase in the structural quality of the obtained nanocrystals in the PVA1:1 sample. In the absence of a capping agent, we will usually have a dumbly-formed nanoparticle. In the crystal growth process, the capping agent effectively reduces the surface energy of crystal faces, which can effectively decrease the grain adhesion. As a result, agglomeration is reduced and KTP nanoparticles with certain crystal faces are obtained at the 1:1 mole ratio of PVA. On the other hand, the shape of the nanoparticles is very sensitive to the stirring rate. Low capping agent concentration and relatively high stirring rates result in a spherical form of KTP nanoparticles at 1:3 and 1:2 mole ratios of PVA.

4. Conclusion

Nanoparticles' properties are affected by different parameters such as size, shape, and structural quality. These parameters have been controlled by growth kinetics. $KTiOPO_4$ nanoparticles were synthesized by the co-precipitation method, a known method for shape and size control of the nanoparticles. To control the growth kinetics, PVA as a capping agent was selected. Changes in PVA concentration resulted in a variety of sizes, morphologies, and size distributions of nanoparticles. For KTP nanoparticles synthesized with 1:3, 1:2, and 1:1 mole ratios of PVA, grain size and particle size were obtained in the range of 39.42–56.36 nm and 90–115 nm, respectively. The smallest grain and particle size belong to the 1:1 mole ratio of the capping agent. At a constant stirring rate, at the 1:1 mole ratio of PVA, the growth conditions were more stable than at other concentrations. This mole ratio resulted in the development of crystal faces and the polyhedral-form of KTP nanoparticles. Other concentrations of PVA showed spherical-form nanoparticles. The shape of KTP nanoparticles synthesized without a capping agent was dumbly-formed. Size distribution increased with a decrease in the capping agent mole ratio. The narrowest size distribution was obtained by a 1:1 mole ratio of PVA.

5. Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

6. References

[1] Canalias, C., Nordlöf, M., Pasiskevicius, V., & Laurell, F. (2009). A KTiOPO4 nonlinear photonic crystal for blue second harmonic generation. Applied Physics Letters, 94(8), 081121. doi:10.1063/1.3093798.

[2] Zukauskas, A., Pasiskevicius, V., & Canalias, C. (2013). Second-harmonic generation in periodically poled bulk Rb-doped KTiOPO_4 below 400 nm at high peak-intensities. Optics Express, 21(2), 1395. doi:10.1364/oe.21.001395.

[3] Galceran, M., Pujol, M. C., Carvajal, J. J., Tkaczyk, S., Kityk, I. V., Díaz, F., & Aguiló, M. (2008). Synthesis and characterization of KTiOPO4nanocrystals and their PMMA nanocomposites. Nanotechnology, 20(3), 035705. doi:10.1088/0957-4484/20/3/035705.

[4] Risk, W. P. (1991). Fabrication and characterization of planar ion-exchanged KTiOPO4waveguides for frequency doubling. Applied Physics Letters, 58(1), 19-21. doi:10.1063/1.104436.

[5] Sorokin, N. I., Novikova, N. E., Shaldin, Y. V., & Tseitlin, M. (2018). Structural Conditionality of the Ionic Conductivity of MTiORO4 (M = K, Rb; R = P, As) Single Crystals. Crystallography Reports, 63(2), 207–211. doi:10.1134/s106377451802027x.

[6] Sorokin, N. I., & Shaldin, Y. V. (2018). Ionic Conductivity of KTiOPO4 Single Crystals Grown by Flux Crystallization under Different Conditions. Crystallography Reports, 63(5), 780–783. doi:10.1134/s1063774518050292.

[7] Gharibshahian, E., Tafreshi, M. J., & Fazli, M. (2009). Growth of $KTiOPO_4$ crystals by flux technique and their characterization. J. Pure. Ap. Phy 47, 356-361.

[8] Elaheh, G., & Majid, J. T. (2015). The effect of cooling rate on size, quality and morphology of KTiOPO4(KTP) crystals grown by different nucleation techniques. Crystal Research and Technology, 50(8), 603–612. doi:10.1002/crat.201500002.

[9] Zhang, C., Huang, L., Zhou, W., Zhang, G., Hou, H., Ruan, Q., … Wang, G. (2006). Growth of KTP crystals with high damage threshold by hydrothermal method. Journal of Crystal Growth, 292(2), 364–367. doi:10.1016/j.jcrysgro.2006.04.036.

[10] Le Xuan, L., Zhou, C., Slablab, A., Chauvat, D., Tard, C., Perruchas, S., … Roch, J.-F. (2008). Photostable Second-Harmonic Generation from a Single KTiOPO4Nanocrystal for Nonlinear Microscopy. Small, 4(9), 1332–1336. doi:10.1002/smll.200701093.

[11] Abrabri, M., Larbot, A., Persin, M., Sarrazin, J., Rafiq, M., & Cot, L. (1998). Potassium titanyl phosphate membranes: surface properties and application to ionic solution filtration. Journal of Membrane Science, 139(2), 275–283. doi:10.1016/s0376-7388(97)00259-7.

[12] Mayer, L., Slablab, A., Dantelle, G., Jacques, V., Lepagnol-Bestel, A.-M., Perruchas, S., … Roch, J.-F. (2013). Single KTP nanocrystals as second-harmonic generation biolabels in cortical neurons. Nanoscale, 5(18), 8466. doi:10.1039/c3nr01251d.

[13] Dahaoui, S., Hansen, N. K., Protas, J., Krane, H.-G., Fischer, K., & Marnier, G. (1999). Electric properties of KTiOPO4and NaTiOPO4from temperature-dependent X-ray diffraction. Journal of Applied Crystallography, 32(1), 1–10. doi:10.1107/s002188989800497x.

[14] Barbé, C. J., Harmer, M. A., & Scherer, G. W. (1997). Sol-gel synthesis of potassium titanyl phosphate: Solution chemistry and gelation. Journal of Sol-Gel Science and Technology, 9(2), 183–199. doi:10.1007/bf02439398.

[15] Kanno, Y. (1994). Synthesis and sintering of KTiOPO4, via mechanochemical mixing route. Journal of Alloys and Compounds, 210(1-2), 45–52. doi:10.1016/0925-8388(94)90113-9.

[16] Arul Dhas, N., & Patil, K. C. (1993). Synthesis of A1PO4, LaPO4 and KTiOPO4 by flash combustion. Journal of Alloys and Compounds, 202(1-2), 137–141. doi:10.1016/0925-8388(93)90532-r.

[17] Biswas, S. K., Pathak, A., & Pramanik, P. (2007). Synthesis of Nanocrystalline KTiOPO4Powder by Chemical Method. Journal of the American Ceramic Society, 90(4), 1071–1076. doi:10.1111/j.1551-2916.2007.01591.x.

[18] Gharibshahian, E., Jafar Tafershi, M., & Fazli, M. (2018). Effects of solution concentration and capping agents on the properties of potassium titanyl phosphate noparticles synthesized using a co-precipitation method. Journal of Physics and Chemistry of Solids, 116, 241–249. doi:10.1016/j.jpcs.2018.01.015.

[19] Gharibshahian, E., Tafreshi, M. J., & Behzad, M. (2020). The effects of solution pH on structural, optical and electrical properties of KTiOPO4(KTP) nanoparticles synthesized by hydrothermal method. Optical Materials, 109, 110230. doi:10.1016/j.optmat.2020.110230.

[20] Houshiar, M., Zebhi, F., Razi, Z. J., Alidoust, A., & Askari, Z. (2014). Synthesis of cobalt ferrite (CoFe2O4) nanoparticles using combustion, coprecipitation, and precipitation methods: A comparison study of size, structural, and magnetic properties. Journal of Magnetism and Magnetic Materials, 371, 43–48. doi:10.1016/j.jmmm.2014.06.059.

[21] Shen, L., Qiao, Y., Guo, Y., Meng, S., Yang, G., Wu, M., & Zhao, J. (2014). Facile co-precipitation synthesis of shape-controlled magnetite nanoparticles. Ceramics International, 40(1), 1519–1524. doi:10.1016/j.ceramint.2013.07.037.

[22] Ali, S., Khan, S. A., Yamani, Z. H., Qamar, M. T., Morsy, M. A., & Sarfraz, S. (2018). Shape- and size-controlled superparamagnetic iron oxide nanoparticles using various reducing agents and their relaxometric properties by Xigo acorn area. Applied Nanoscience, 9(4), 479–489. doi:10.1007/s13204-018-0907-5.

[23] Sadeghi, B., Sadjadi, M. A. S., & Pourahmad, A. (2008). Effects of protective agents (PVA & PVP) on the formation of silver nanoparticles. International Journal of Nanoscience and Nanotechnology, 4(1), 3-12.