The Elemental Doping Effects on the Vibronic Properties of Nd: KTP Nanocrystallites

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Abstract:
In this work the synthesization process of nanocrstallite Nd:KTP powders by modified Pechini method was studied. The results of XRD studies indicate that KTP nanocrystallites doped by Nd has orthorhombic phase. The structural and lattice modes of the synthesized nanocrystallite products were investigated by using Micro Raman back scattering and FT-IR transmission spectroscopies. SEM imaging technique was applied for the observation of grain sizes and the morphology of the nanoparticles. The Debye-Scherrer formula was used to confirm the grain sizes determined by the SEM slides. In overall conclusion, it can be claimed that XRD, SEM and back scattering Raman spectroscopy are suitable methods to study the quality and characterization of nanocrystallite materials such as KTP family nanocrystals.
Keywords: *Nd-KTP, Nanocrysallite, Pechini method, Raman scattering, XRD.*

1. INTRODUCTION

The synthesis and study of nanocrystallite materials have been a major research interest in the last years due to expectations of new or enhanced optical, electronic or structural properties related to the size of the synthesized materials in the nanometers regime.

Potassium titanyl phosphate, KTP, is a standard material in industrial, medical and army applications [1]. KTP is an excellent non-linear optical, NLO, crystal and one of the most commonly used materials for frequency doubling of laser wavelengths such as Nd: doped lasers [2,3].

During the last two decades, many attempts have been made to improve the properties of KTP family crystals and to develop new applications. Rare earth elements are very attractive to use as doping elements for KTP, [4]. Studies on KTP family crystals have so far been predominantly restricted to single crystals and single phase KTP thin films and very little is reported on the preparation of nanocrystallite KTP powders.

Some investigations have reported the KTP synthesis by sol-gel method, [5]. The alternative modified Pechini method [6] because of its low cost, easy control of the stoichiometry, its simplicity, low processing temperatures, high degree of homogeneity due to the reagents which are mixed at the molecular level, has been preferred to sol-gel method. In this work the synthesization process of the KTP nanocrstallite powders by modified Pechini method is reported.

Furthermore the morphological, structural and phononic characterization of the synthesized nanocrystllites is discussed by using SEM, XRD, FTIR and back-scattering Raman spectroscopy.

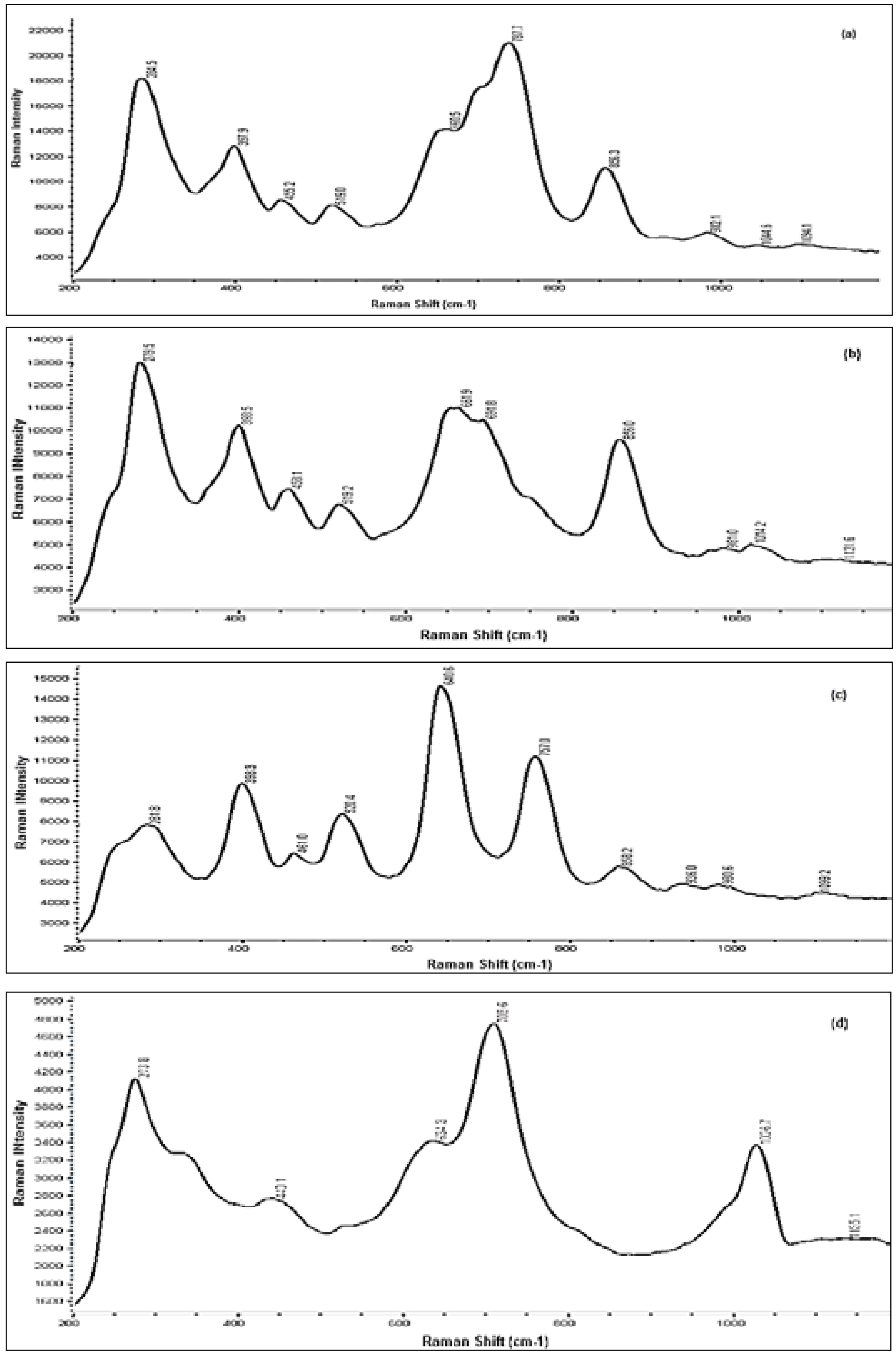

Figure 1: *Raman spectra of the synthesized nanocrystallites, from the top to the bottom: a) Nd-KTP 1% ; b) Nd -KTP 3%; c) Nd -KTP 5% d); Nd -KTP 10% in the spectral region of 200-1300 cm^{-1}*

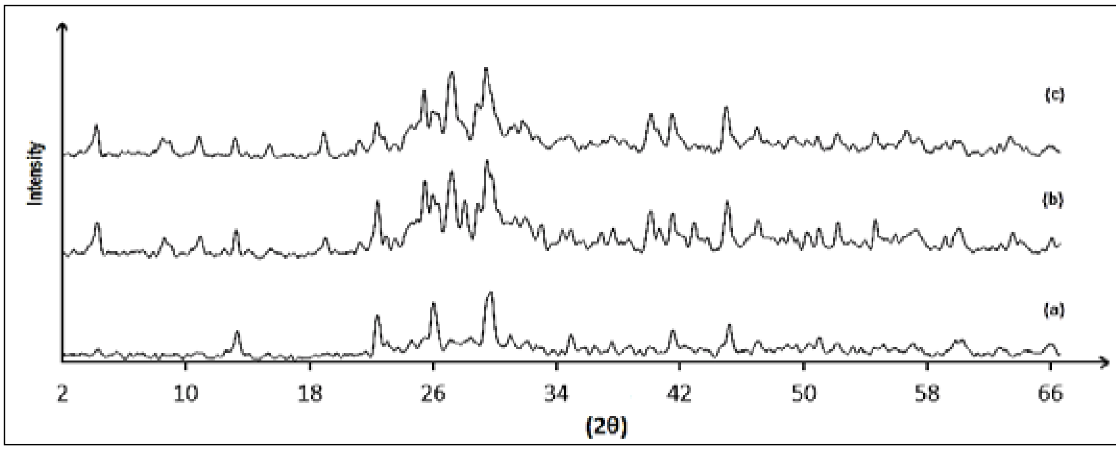

Figure 2: *XRD patterns, intensity versus 2θ diffraction angles for the synthesized Nd-KTP nanocrystallites with Nd doping of : a) 1%; b) 3% and c) 5%*

2. EXPERIMENTAL

K_2CO_3 (Merck 99.5%), TiO_2 (Merck 99.5%), EDTA (Merck 99.5%), EG (Merck pure), $(NH_4)2HPO_4$ (Merck 99.5%) and Nd_2O_3 were used as starting precursor materials. EDTA was used for chelating metallic ions due to its strong chelating power [7]. The precursor solution of Ti; K and P were prepared by adding raw materials into aqueous solution of EDTA and EG with heating and stirring. By increasing the temperature of solution to 373 K in a steady stage and within 1-2 h, the solution changed to resin with high viscosity. A further calcinations process at 575 K for 2 hours broke the resin and it followed by another calcinations process at 973 K for several hours. The molar ratio of the metallic ions, EDTA and EG is a very important factor for an optimum grain size of the products. In this work the ratio was adapted as 1:2:6. Here the percentage of the doping element was the final weight of the product.

3. RESULTS AND DISCUSSION

3.1. Raman spectra analysis

Raman spectra of the grown nanocrystallites of KTP were collected at the Spectroscopy Laboratory, Atomic and Molecular group, Physics Department, Tarbiat Modares University by using a Thermo Nicolet Almega dispersive Raman scattering spectrometer operating by a 532 nm line from the second harmonic of a Nd:YLF laser in a back-scattering configuration. A set of four recorded Raman spectra for 1, 3, 5 and 10 percent of the

Table 1: *Calculated grain sizes of the synthesized 3% Nd-KTP nanocrystallites by Debye-Scherrer equation*

Angle (2θ)	FWHM (a)	□	B	D
25.427	0.252	0.177	0.179	45.6 nm
28.621	1.918	1.907	0.179	4.3 nm
30.205	0.356	0. 307	0.179	26.4 nm
32.547	0.821	0.801	0.179	10.2 nm
43.090	0.655	0.630	0.179	13.7 nm

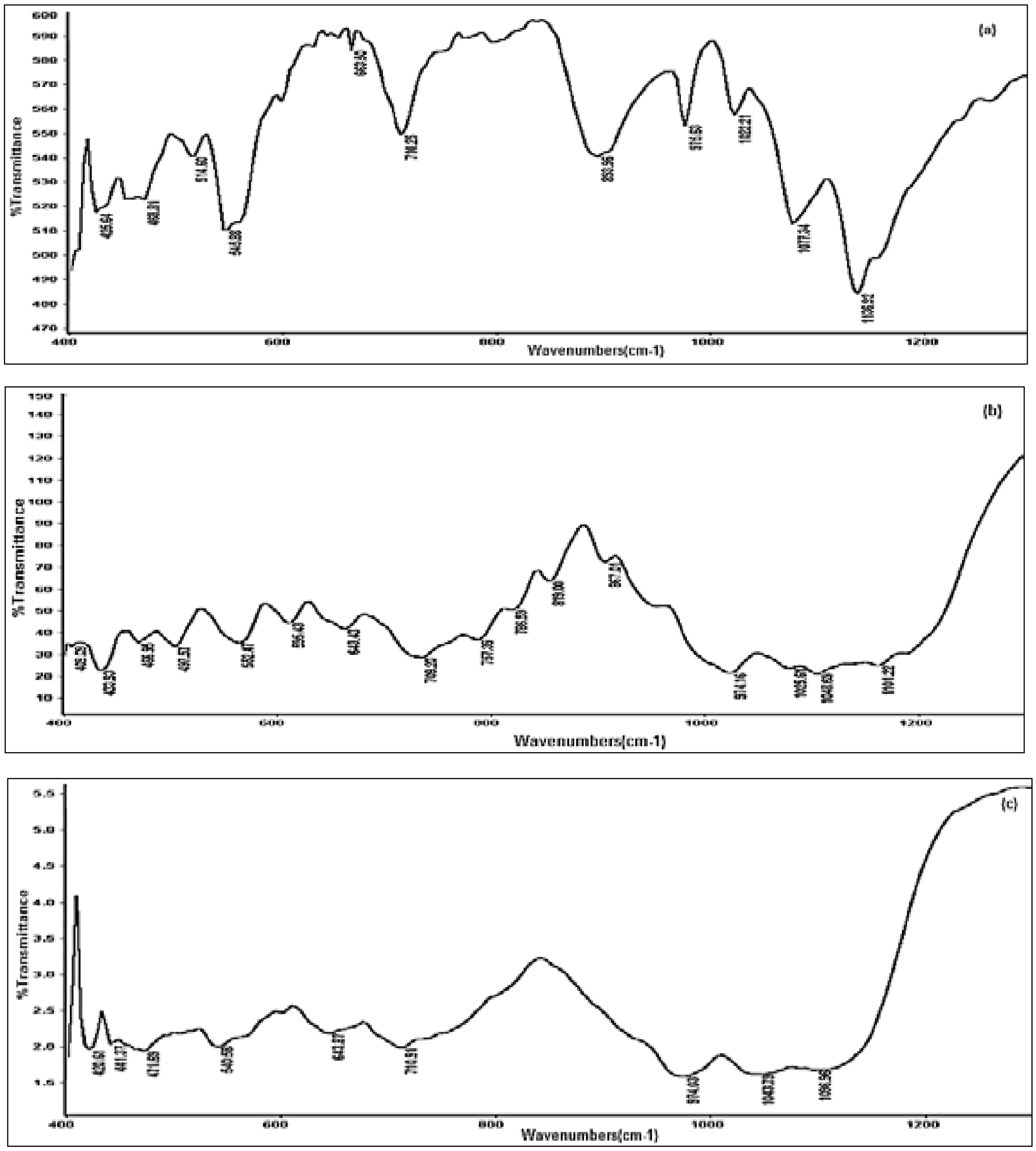

Figure 3: *FT-IR transmission spectra of the synthesized KTP nanocrystallites with Nd doping of: a) 1%; b) 3% and c) 5%.*

doping Nd element by weight of the synthesized nanocrystallites are presented in Figure 1, from the top to the bottom, respectively.

The modes at 697.9 and 271.7 cm^{-1} were assigned to ν_1 symmetric and ν_5 modes of TiO_6, respectively. For the PO_4 unit, two Raman active modes at 422.6 and 1045.9 cm^{-1} were assigned to ν_2 and ν_3 modes of the unit, respectively, [8]. By increasing the doping percentage and passing the threshold value believed around 3%, the Raman modes started to decrease in intensity. If the doping amount is very high, the structure will be completely decomposed. In the lower spectrum of the Figure1, which is related to the synthesized sample of 10% Nd-KTP, with much higher doping in comparison with the threshold doping value, clearly the modes of additional structures, such as TiO_2, could be seen and certainly were present in the structure. By exchanging Ti atoms for Nd atoms via doping, the molecular structures and accordingly the phononic properties of the nanocrystalites were modified. Depending on the amount of doping and the atomic mass of the dopant element, the Raman spectra of the synthesized nanocrystallite can be changed. Increasing the amount of Nd dopant caused the shift toward the lower wavenumbers in the related Raman spectra.

3.2. XRD analysis

The XRD patterns of the synthesized nanocrystallites of KTP doped with Nd are shown in Figure 2. It is clear from Figure 2. that some degree of crystallinity were present in the samples. All peaks in XRD patterns with 1% Nd doping were assigned to Nd-KTP but for the 3% Nd doping, a new molecular structure with small percentages of other structures such as $K_2Ti_6O_{13}$ and $KNdP_4O_{12}$ could be assigned. However, in Nd-KTP with 5% doping, the formation of other structures increased and one more structure, TiO_2 in rutile phase, could be seen. It is apparent that by increasing the percentage of doping, the main structure started to decompose. If the doping percentage increased more than the threshold value, which is believed around 3%, the original structure completely decomposed.
Using the data obtained from XRD patterns in the Debye-Scherrer equation, [10], the average particle sizes of the 3%Nd-KTP nanocrystallites were calculated. They were found to be in the ranges of 12-70 nm. (Table 1). Because of doping, other structures also could be assigned in the XRD patterns and different overlapping patterns could be recorded. Accordingly, the calculated grain sizes of the nanocrystallites could carry some uncertainty.

3.3. Near normal FTIR transmission spectroscopy

The band corresponding to the vibration of Ti=O fragment was observed at around 706 cm^{-1} in different doped KTP samples, Figure 3. It clearly shows two resolved bands at 974 and 1124.8 cm^{-1}, which are associated with the asymmetric stretching vibrations of PO_4 units. The bands that are at the lower part of 660 cm^{-1} are assigned to the splitting of the degenerate PO_4 modes, i.e. bands at 432.1, 465.9 and 560 cm^{-1}). In comparison with the pure KTP nanocrystallite samples some bands were missing, due to doping, [9].

3.4. Scanning electron microscopy (SEM)

The SEM images of the synthesized nancrystallites showed that the grains of the powders were almost needle-shaped, Figure 4. In comparison with pure KTP nanocrystallite sample which has a round shape, doping caused change in the overall shape, but by considering the related XRD pattern, the orthorhombic crystal structure was survived. Determining the grain sizes of the synthesized nanocrystallite by SEM imaging technique faced with huge uncertainty. The sizes of the grains also were calculated by Debye-Scherrer equation, [10], using the XRD patterns and were found to be in the ranges of 12-70 nm which was different from the SEM imaging results.

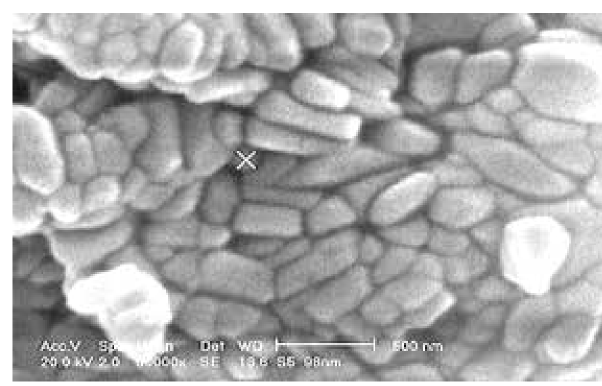

Figure 4: *SEM image of the synthesized nano-crystallite KTP doped by 3% Nd.*

4. CONCLUSION

Nanocrystallites of KTP with grain sizes in the nanometer regime were successfully synthesized by a modified Pechini method as described. In the reaction, EDTA was a chelating agent to produce nanoparticles. Nanocystallites with needle-shaped structure with calculated sizes in the range 0f 12-70 nm were synthesized. Micro Raman back-scattering, FTIR transmission spectroscopy, X-ray diffraction and SEM imaging were used to investigate the phononic, structural and morphological characterization of the synthesized nanocrystallites.

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