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Micro Raman scattering and structural investigation of nanocrystalline Nd:KTP

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Abstract:

In this work we report the synthesization process of nanocrstalline Nd:KTP powders by modified sol-gel method. The results of XRD studies indicate that KTP nanocrystallines doped by Nd has orthorhombic phase. By using micro Raman back scattering and FT-IR transmission spectroscopies, the lattice modes of the synthesized nanocrystalline products have been investigated. The structural and the grain sizes determination for the synthesized samples were measured using the XRD patterns and the Debye-Scherrer formula. These data are in close agreement with the grain sizes determined by the SEM slides. It can be claimed that XRD analysis and micro Raman backscattering spectroscopy are suitable methods to study the quality of nanocrystalline materials including KTP family.

Keywords: Nd-KTP; nanocrysallite; modified sol-gel method; Raman scattering; XRD.

1. Introduction

The growth, synthesis and study of nanocrystalline materials have been a major research interest in the last years due to expectations of advent of new or enhanced optical, electronic or structural properties related to the size of the material in the nanometers regime. Potassium titanyl phosphate (KTP) is a very attractive 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 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 for these structures. Rare earth elements are very attractive to use as doping for KTP [4]. Studies on KTP have so far been predominantly restricted to single crystals and single phase KTP thin films and very little is reported on the preparation of nanocrystallines. Some reports have been synthesized KTP nanocrystalline by the well-known sol-gel method, [5]. However, the alternative modified sol-gel method [6] because of its low cost, easy control of the stoichiometry, its simplicity, low processing temperature, high degree of homogeneity due to the reagents which are mixed at the molecular level, has been prefered to the sol-gel method. In this work we have synthesized the nanocrstallite KTP by modified sol-gel method.

2. Experimental

K_2CO_3, TiO_2, EDTA, EG, $(NH_4)2HPO_4$ and Nd_2O_3 were used as starting precursor materials. Because of strong chelating power of EDTA, we used it for chelating metallic ions, [7]. The precursor solution of Ti; K and P were prepared by adding raw materials into aqueous solution of EDTA and EG by heating and stirring. By increasing the temperature of solution to 373 K in a steady stage and within several hours, the solution changes to a resin like material with high viscosity. A further calcinations process at 575 K for several hours breaks 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 sizes of the products. In the present work we adapted the ratio as 1:2:6 for the metallic ions, EDTA and EG, respectively. The reported percent of doping is according to the weight of the final synthesized product.

3. Results and discussions

3.1. Micro Raman Spectra Analysis

Micro Raman spectra of the grown nanocrystallines of KTP were collected at the Spectroscopy Laboratory, TM University (I.R. Iran) by using a micro Raman scattering spectrometer operating from the second harmonic of a Nd:YLF Laser in a backscattering configuration.

The active Raman modes in the recorded spectra can be assigned according to the standard procedures and in comparison with the Raman spectra for the similar structures. The mode at 273 cm^{-1} has been assigned to ν_5 mode of TiO_6. For the PO_4 unit, one Raman active mode at 440 cm^{-1} has been assigned to ν_2 mode of the unit [8]. By increasing the doping percentage, the intensity of the Raman modes starts to weaken. If the doping amount is very high, the structure will be completely decomposed, (Fig.1.). Which is for the synthesized sample of KTP doped with 10% by Nd in weight. However, with much higher doping in compare with the threshold doping value, clearly the modes of additional structures, such as TiO_2, can be seen. The doping threshold depends to the atomic radius of doping element in compare with the Ti radius.

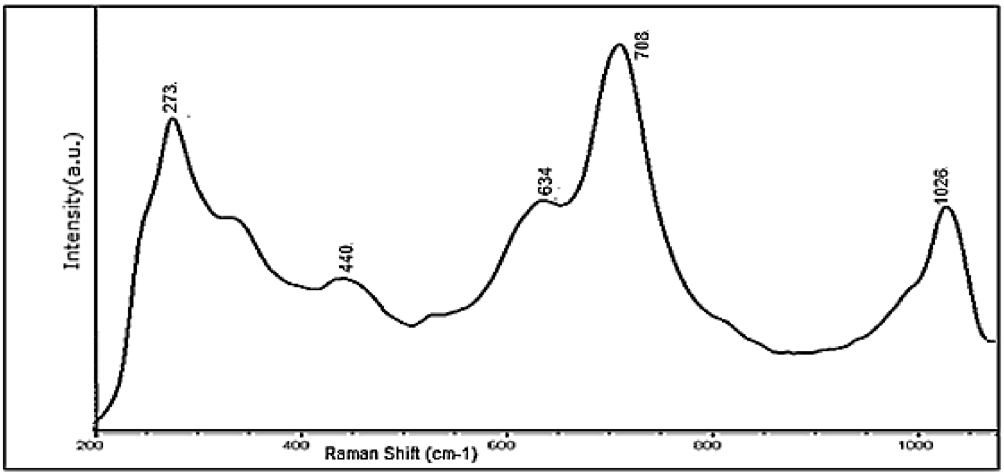

Fig. 1: Raman spectrum of Nd:KTP (doped by 10% of Nd by weight) in the spectral region of 200-1050 cm^{-1}.

3.2. X Ray Diffraction Analysis:

The XRD patterns of the nanocrystalline KTP doped with Nd are shown in Fig. 2. It is clear from Fig. 2. the crystalline phase is present in the sample. However, in Nd:KTP with 10% doping, the formation of other structures will be increased and one more structure, TiO_2 in rutile phase, can be seen in the recorded XRD paptterns. It is apparent that by increasing the percentage of doping, the main structure starts to decompose and if the doping percentage further increases and become more than the threshold value, the original structure completely decomposes.

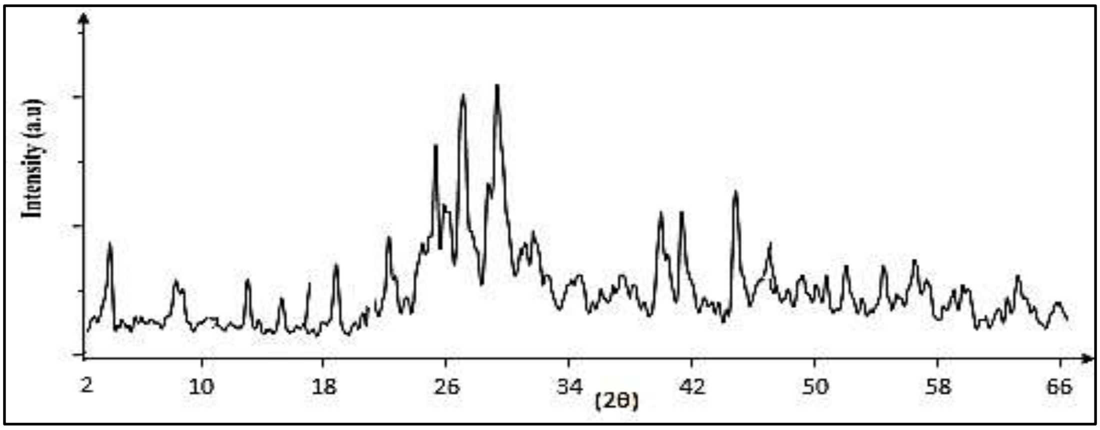

Fig. 2: XRD patterns, intensity versus 2θ angle for the synthesized Nd:KTP structure doped by 10%
of Nd in weight.

3.3. FTIR Spectroscopy

The band corresponding to the vibration of Ti=O fragment is observed at around 717 cm^{-1} in different doped KTP samples (Fig. 3.). It clearly shows two resolved bands at 939 and 1115 cm^{-1}, which are associated with the asymmetric stretching vibrations of PO_4 units. The bands that are at the lower part of 633 cm^{-1} are ascribed to the splitting of the degenerate PO_4 modes (415, 470 and 544 cm^{-1}). In comparison with pure KTP, because of doping some bands are missing, [9].

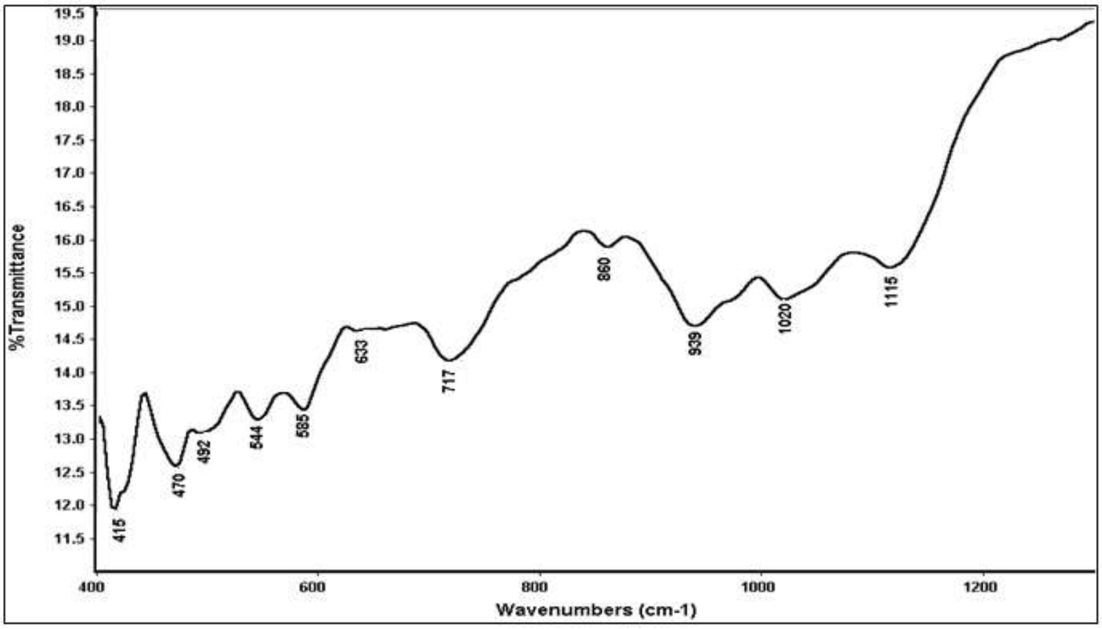

Fig. 3: FT-IR transmission spectrum of Nd:KTP nanocrystalline (10% Nd doping)

4. Conclusion

Nanocrystalline KTP samples with grain size in the nanometer regime have been successfully synthesized by modified sol-gel method as described. In the reaction, EDTA is a material as a chelating agent to produce nanoparticles. Nanocystallines with needle-shape shape and with medium sizes have been synthesized, [10]. Micro Raman backscattering spectroscopy, X-ray diffraction patterns and FTIR spectroscopy have been used to investigate the optical phonons, structure, morphology and transparency of the synthesized samples.

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