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Crystal growth and morphology of Nd:YVO$_4$ under hydrothermal conditions

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Neodymium doped yttrium orthovanadate single crystals have been obtained from hydrothermal solutions. Systematic investigations of the role of pH of the growth media, mineralizer type and experimental temperature have been carried out with reference to the growth of Nd:YVO$_4$ crystals. The crystal growth mechanism has been proposed for the growth of Nd:YVO$_4$ crystals from hydrothermal solutions. The crystals obtained have been subjected to powder X-ray diffraction, morphological, EDAX and FTIR studies.

1. Introduction

After the advent of ruby laser in the year 1960, laser, an unprecedented light source has brought a revolution in optics, and has a far-reaching influence in various branches of science and technology. Though solid-state lasers—still retain greater advantages over other media due to their regularity in the crystal structure and the extraordinary wide range of physical parameters, striking advances in quantum electronics have been accomplished mainly based on the optically high quality single crystals. At present hundreds of laser active ions have been demonstrated as successful lasers and are being operated both experimentally and commercially. Amongst them the Nd:YVO$_4$ is a very attractive material for use as a phosphor [1], polarizer [2, 3] or laser host material [4]. As a single crystal it has excellent mechanical properties such as higher chemical stability and higher laser induced damage threshold, 3.3 ± 0.4 GW/Cm^2 [2, 5]. For example, the laser cross-section in Nd:YVO$_4$ is 2.7 times greater than that of Nd:YAG at 1064 nm and it has also been demonstrated that Nd:YVO$_4$ exhibits a very high slope efficiency (requiring half of the threshold power of Nd:YAG) [6]. Therefore, Nd:YVO$_4$ is a desirable crystal for diode-pumped laser systems, micro-lasers and deep space communications.

The objective of this paper is to obtain good quality single crystals of Nd:YVO$_4$ under hydrothermal conditions and explain the possible morphology and mechanism of Nd:YVO$_4$ crystallization.

2. Growth of Nd:YVO$_4$ crystals

The growth of Nd:YVO$_4$ single crystals was carried out under hydrothermal conditions. Experiments were carried out in General-Purpose hydrothermal autoclaves made up of stainless steel (SS316), designed and fabricated at the University of Mysore, India. These autoclaves were provided with teflon liners of capacity 30 ml. Fig. 1 shows the schematic representation of the autoclave.

The starting materials such as V_2O_5 (99.99% GR grade, LOBO Chem. Ltd. India), Y_2O_3 (99.99% GR grade, LOBO Chem. Ltd. India) and Nd_2O_3 (99.99% GR grade, LOBO Chem. Ltd. India) were taken in an appropriate molar proportion in the teflon liners.

A suitable mineralizer $HNO_3 + HCl$ with a known molar concentration and ratio was added into the teflon liner and the entire mixture was stirred well till a

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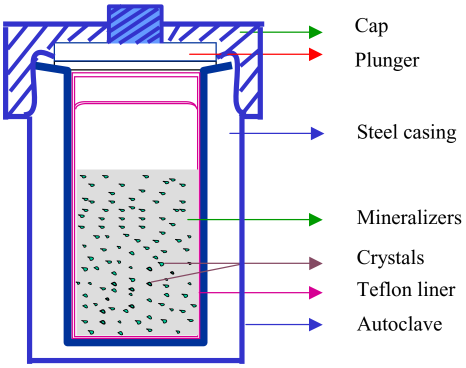


Figure 1 Schematic diagram of hydrothermal autoclave.

homogeneous and relatively less viscous solution was obtained. Such a solution was heated at 80°C for 1 hour in the constant temperature water bath. Then the whole complex solution was transferred into a teflon liner. The complex solution was found to be highly acidic in nature. The authors have made an emphasis on the growth of the title compound from the hydrothermal solutions at much reduced temperature and consequently lower pressure conditions than our previous experiments by the conventional hydrothermal technique [7]. The teflon liner was placed inside the autoclave and heated to the desired temperature using a tubular furnace provided with a temperature controller.

The experimental temperature and duration have a positive influence on the rare earth yttrium orthovanadate crystallization process. The rising experimental temperature will increase both the nucleation rate and growth rate. The crystallinity of the product normally increases with both experimental temperature and experimental duration. The $Nd:YVO_4$ crystals are governed by the occurrence of phase transformation. The thermodynamically least favorable phase will crystallize first, and will be successively replaced with time by more stable phases.

The experimental temperature in the present work was varied form 100–250°C, but good quality crystals are obtained at 240°C, the pressure was maintained through an appropriate % fill. The pH of the growth medium was measured before and after for each experimental run. The crystallization was carried out through a spontaneous nucleation. Table I gives the experimental conditions for the growth of $Nd:YVO_4$ crystals. The characteristic photographs of $Nd:YVO_4$ crystals are shown in Fig. 2.

TABLE I Experimental conditions for the growth of $Nd:YVO_4$ crystals

			pH			
Sl.no	Nutrients	Mineralizers	Initial	Final	Size(mm)	Remarks
1.	V_2O_5, Y_2O_3, Nd_2O_3-5wt% 2:1	0.75 M HCl 1.5 M HNO_3 3:1	0.02	0.4	—	Amorphous powder
2.	V_2O_5, Y_2O_3, Nd_2O_3-2wt% 2:1	3M HCl 2M HNO_3 2:1	0.5	4.65	0.10–0.25	Thin plate-like crystals
3.	V_2O_5, Y_2O_3, Nd_2O_3-5wt% 2:1	1M HCl 2 M HNO_3 3:1	0.20	5.15	0.5–1.0	Plate-like pseudo monoclinic symmetry crystals
4.	V_2O_5, Y_2O_3, Nd_2O_3-10wt% 2:1	1.5 M HCl 3 M HNO_3 3:1	0.18	6.7	1–0.5	Plate-like rhombohedral thicker crystals
5.	V_2O_5, Y_2O_3, Nd_2O_3-5wt% 2:1	1.5 M HCl 3M HNO_3 3:1	0.10	6.73	1.5–2	Well developed plate-like rhombohedral thicker crystals
6.	V_2O_5, Y_2O_3, Nd_2O_3-10wt% 2:1	2M HCl 4M HNO_3 3:1	0.04	3.3	0.5–2	Irregular shaped thicker crystals
7.	V_2O_5, Y_2O_3, Nd_2O_3-5wt% 2:1	1.5M HCl 3M HNO_3 3:1	0.07	2.6	1–2	Not well developed crystals
8.	V_2O_5, Y_2O_3, Nd_2O_3-5wt% 2:1	1 M HCl 1 M HNO_3 3:1	0.24	3.9	0.5–1	Thin irregular crystals
9.	V_2O_5,Y_2O_3, Nd_2O_3-5wt% 2:1	0.5M HCl 1M HNO_3 3:1	0.32	0.9	—-	Crystalline powder

Temperature = 240°C. **Experimental** duration = 10 days

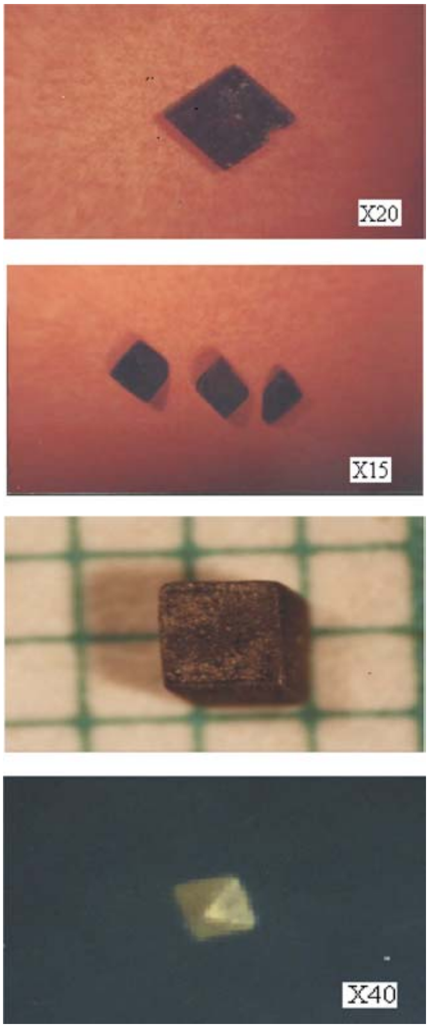


Figure 2 Characteristic photographs of Nd:YVO_4 crystals.

3. Growth mechanism for Nd:YVO_4 under hydrothermal conditions

The choice of the solvent was determined by the solubility of the components of the most complex-equilibrium systems. In the complex systems considered here, consisting of more than four components, it is extremely difficult to understand precisely the formation of such coordination compounds like the title compound. The hard bases H_2O, OH and NO_3 act upon the dissolution of the solute and solvated complexes determining the solubility of the final resultant stable complex.

The following reaction series can be proposed for the formation of YVO_4:

$$V_2O_5 + NH_4OH \rightarrow NH_4VO_3 + HVO_3 \tag{1}$$

$$NH_4VO_3 + HNO_3 \rightarrow NH_4NO_3 + HVO_3 \tag{2}$$

$$Y_2O_3 + 3HCl \rightarrow Y(OH)_3 + YCl_3 \tag{3}$$

$$Y(OH)_3 + HVO_3 \rightarrow YVO_4 + 2H_2O \tag{4}$$

$$YCl_3 + HVO_3 \rightarrow YVO_3Cl_2 + HCl \tag{5}$$

$$YVO_3Cl_2 + 2H_2O \rightarrow YVO_3(OH)_2 + 2HCl \tag{6}$$

$$YVO_3(OH)_2 \rightarrow YVO_4 + H_2O \tag{7}$$

OR

$$Y_2O_3 + 6HCl \rightarrow 2YCl_3 + 3H_2O \tag{8}$$

$$YCl_3 + HVO_3 \rightarrow YVO_3Cl_2 + HCl \tag{9}$$

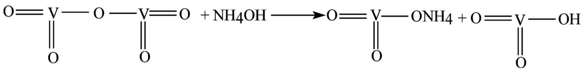
$$YVO_3Cl_2 + 2H_2O \rightarrow YVO_3(OH)_2 \tag{10}$$

$$YVO_3(OH)_2 \rightarrow YVO_4 + H_2O \tag{11}$$

The reactions shown above are those possible, but not necessarily the operative ones. It is further presumed that the formation of the stable complex, i.e. YVO_4 for example, at 240°C and corresponding pressure, must have undergone several intermediate stages of solvation, forming stable and unstable solvated complexes, at different temperatures (room temperature to 240°C) and pressure between 1 atm and 100 atm. It is not possible to write precisely all the intermediate stages of solvation taking place in such a complex system.

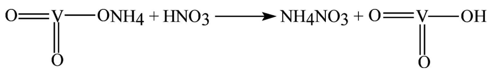
4. Reaction mechanism of YVO_4

1) $V_2O_5 + NH_4OH \longrightarrow NH_4VO_3 + HVO_3$



$$O{=}\underset{\underset{O}{\|}}{V}{-}O{-}\underset{\underset{O}{\|}}{V}{=}O + NH_4OH \longrightarrow O{=}\underset{\underset{O}{\|}}{V}{-}ONH_4 + O{=}\underset{\underset{O}{\|}}{V}{-}OH$$

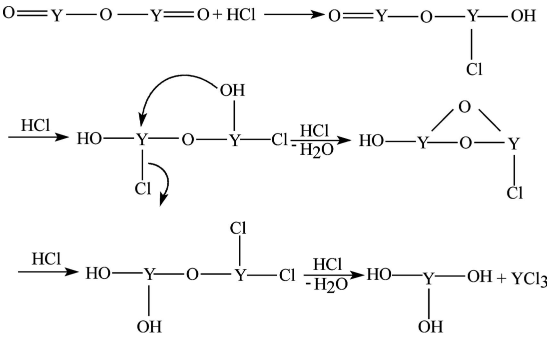
2) $NH_4VO_3 + HNO_3 \longrightarrow NH_4NO_3 + HVO_3$



$$O{=}\underset{\underset{O}{\|}}{V}{-}ONH_4 + HNO_3 \longrightarrow NH_4NO_3 + O{=}\underset{\underset{O}{\|}}{V}{-}OH$$

The V_2O_5 reacts with one molecule of NH_4OH, the NH_4VO_3 and HVO_3 are formed. Again add one molecule of HNO_3 with NH_4VO_3, the HVO_3 is formed.

3) $Y_2O_3 + 6HC1 \longrightarrow 2YC1_3 + 3H_2O$



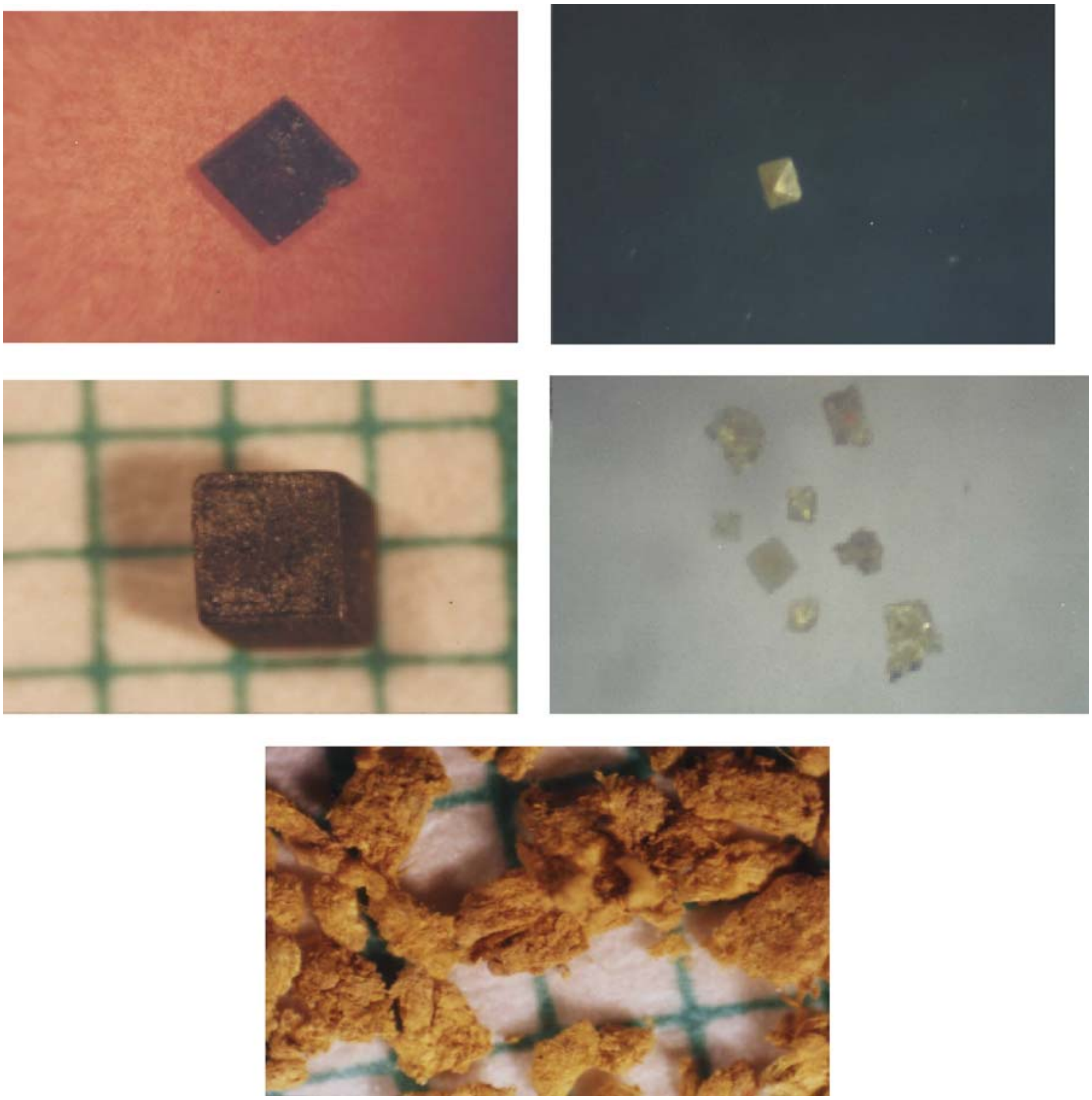


Figure 3 Diffrent crystal morphologies of Nd: YVO_4 crystals.

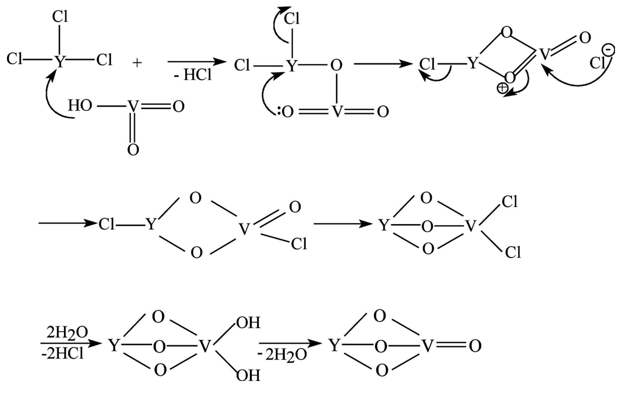
Yttrium oxide reacts with two molecules of HCl forming hydroxyl yttrium chloride, which isomers to new dihydroxy yttrium chloride via cyclic oxonium intermediate complexes. This rearranged molecules further reacts with two molecules of HCl forming $Y(OH)_3$ and YCl_3.

$$4)\qquad YCl_3 + HVO_3 \rightarrow YVO_3Cl_2 + HCl$$

$$YVO_3Cl_2 + H_2O \rightarrow YVO_3(OH)_2 + 2HCl$$

$$YVO_3(OH)_2 \rightarrow YVO_4 + H_2O$$

Yttrium chloride reacts with HVO_3 forming YVO_3Cl_2 and one molecule of HCl, add two molecules of water with YVO_3Cl_2, remove the two molecules of HCl and forming an intermediate molecule of YVO_3 $(OH)_2$. This reaction mechanism continues and finally forms YVO_4, as shown below:



5. Morphology

The crystals obtained in all the experiments were subjected to a systematic morphological analysis. Also the authors have studied the morphology with respect to the growth conditions. The experimental temperature has been varied from 100°C to 250°C.

The Nd:YVO_4 crystals obtained usually exhibit plate like, irregular, pseudo-monoclinic, rhombohedral, octahedral shape, and fibres like habits with vitreous lustre. The size of the crystals varies from 0.1 mm to 2.5 mm. The experimental duration of the growth was kept constant (8–10 days) for all the experiments. Using a phase contrast binocular microscope, the crystal morphology of the representative crystals was studied and also the interfacial angles were measured for the characteristic crystals. A number of factors such as degree of supersaturation, starting pH of the solution, growth temperatures, type of cation, etc, play an important role in determining the morphology of Nd:YVO_4 crystals.

The above studies on the Nd:YVO_4 crystal morphology show that when HCl is in surplus than HNO_3 in the nutrient, well developed crystals form with well facetted, honey yellow colour, vitreous lustre. In contrary when HNO_3 is more and HCl is less, irregular crystals form. With a moderate concentration of HCl and surplus HNO_3, thicker irregular crystals are obtained. When HCl is absent in the solvent, the crystallization of Nd:YVO_4 ceases. So also when HNO_3 is absent in the solvent, the crystals of Nd:YVO_4 ceases. All the above crystallization conditions shown when HCl is more than HNO_3, the well-developed crystals are formed. When HNO_3 is more then HCl is less irregular crystals are formed. When HNO_3 is surplus and HCl is moderate, the thicker irregular crystals are obtained. No crystals are formed when HCl is absent or less. Similarly when HNO_3 is absent no crystals are formed as shown in the figures.

TABLE II Cell parameters for Nd:YVO_4 crystals obtained under mild hydrothermal conditions

Compound	a, Å	c, Å	V, Å 3	Ref
YVO_4	7.123	6.292	319.24 (6)	[7]
Nd:YVO_4	7.118	6.289	318.64	P

P- present work

6. Characterization of Nd:YVO_4 crystals

A systematic characterization of neodymium yttrium orthovanadate crystals was carried out by employing different instrumental techniques like powder XRD, FTIR-spectroscopy and EDAX.

6.1. Powder X-ray diffraction

The powder X-ray diffraction patterns were recorded for the representative samples of Nd:YVO_4 crystals using Siemens X-ray diffractometer Model D-5000, Germany. The X-ray source was CuKα ($\lambda = 1.54060$ Å). The characteristic X-ray patterns were indexed (using reciprocal lattice method) and all the cell parameters were calculated. The powder X-ray diffraction pattern obtained in the present work for the representative samples of Nd:YVO_4 match closely with the literature data JCPDS File No. 72-0274 [8, 9]. The cell parameters are given in Table II. Any small variation in the values of cell parameters is due to the presence of Nd in different concentration.

6.2. FTIR- spectroscopy

A systematic study of the FTIR spectroscopy of Nd:YVO_4 was carried out in order to study the variation in the internal structure. Since the variations in the internal structure

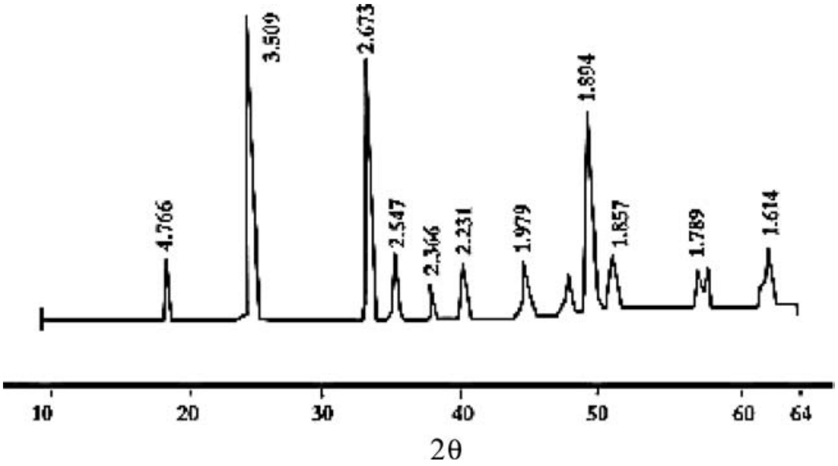


Figure 4 XRD pattern of Nd:YVO_4 crystals.

TABLE III Basic vibration frequencies (Cm^{-1}) of the VO_4 tetrahedra [10,11]

Coordination	$\gamma_1(A_1)$	$\gamma_2(E)$	$\gamma_3(F_2)$	γ_4 (F_2)
$[VO_4]^{3-}$	870	345	825	480

TABLE IV FTIR shift in Nd:YVO_4 crystals

Composition	$VO_4{}^{3-}$	γ (V - O)	δ(O - V - O)	γ (V = O)
Nd:Y VO_4	845	966	598	1370

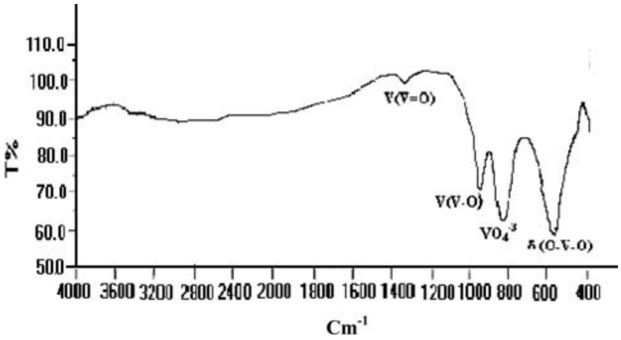


Figure 5 FTIR- spectrum of Nd:YVO_4 crystals.

and also the presence of water molecules in the structure may not be visible by the routine powder X-ray diffraction technique. The FTIR-spectra give minute structural details about the presence of various molecules (like corbonates hydroxyl compounds, etc.), distortion in the structure of $[VO_4]$ tetrahedra due to the presence of deliberate or accidental impurities.

The FTIR spectra of Nd:YVO_4 crystals obtained under hydrothermal conditions were registered in the range of 4000 to 400 cm^{-1} using a FTIR— spectrophotometer SHIMADZU model 8300E Japan. The Nd:YVO_4 crystals were ground and mounted on sodium chloride windows to record the infrared spectra.

It is well known that the orthovanadates, $[VO_4]^{3-}$ with tetragonal symmetry ($D_{4h}{}^{19}$) have four fundamental vibrations. The basic vibration frequencies (Cm^{-1}) of the $[VO_4]^{3-}$tetrahedra are given in Table III.

Where γ_1 corresponds to the valence vibrations and γ_2 corresponds to the deformational vibrations. The γ_3 represents the symmetric valence vibrations and γ_4 is assigned to the asymmetric deformational vibrations. The vibration $\gamma_1(A_1)$ activates the irregularity in the tetragonal symmetry of the $[VO_4\ ]^{3-}$ tetrahedra. In the region γ_4 (F_2), we find a multiplication of the absorption bands, which may be due to the distortion of the $[VO_4]^{3-}$ tetrahedra [12].

The FTIR spectra of orthovanadate consist of absorption bands in the range 980–940 Cm^{-1}, 800–700 Cm^{-1} and 600–500 Cm^{-1}. The absorption bands for OH^- molecules were not seen in the spectra, the bands are attributed to γ (V—O), γ (V—O), $[VO_4]^{3-}$ and δ(O—V—O) respectively as shown in Table IV. which confirms the absence of water in spite of the mild hydrothermal conditions used for the growth of Nd:YVO_4 in the present work. Fig. 5 shows the FTIR spectra of Nd doped yttrium orthovanadates.

From the Table III, it is observed that γ (V—O) is same for all YVO_4 crystals as the concentration of dopants changes, but there is a slight shifted of bands for $VO_4{}^{3-}$, γ (V—O), δ (O—V—O).

6.3. Energy dispersive analysis of X-rays (EDAX)

Energy dispersive analysis was performed on the representative sample of Nd:YVO_4 crystals and the atomic percents of V, Y and Nd were determined. The characteristic X-ray radiation of the elements stimulated by electron

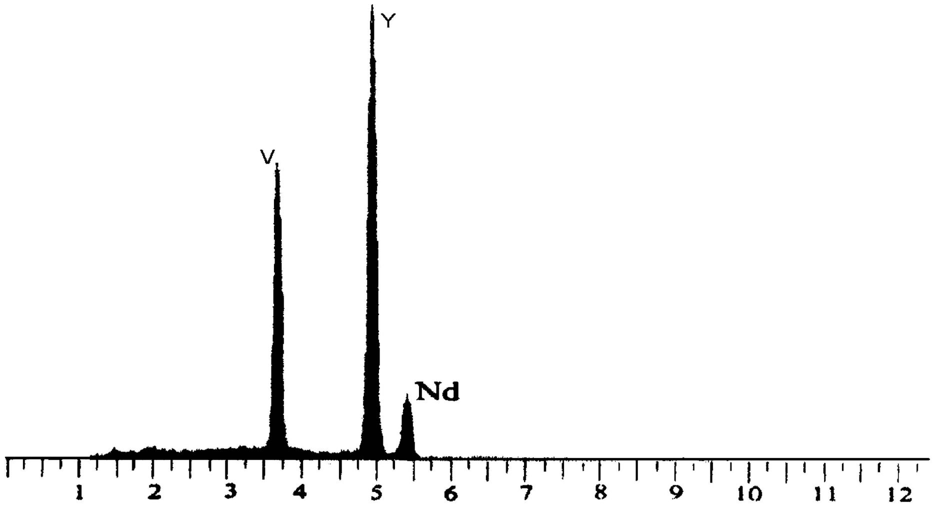


Figure 6 EDAX spectrum of Nd:YVO_4 crystal.

impact is detected up to a depth of several 1000 μm. The EDAX spectrum of Nd:YVO_4 crystal is shown in the Fig. 6.

7. Conclusions

The growth of Nd:YVO_4 crystals was carried out under hydrothermal conditions in the temperature range 100–250°C, and good single crystals were obtained at temperature 240°C and pressure autogenous. The crystals were obtained using $HNO_3 + HCl$ as the mineralizer. The crystallization was carried out through spontaneous nucleation. The type of mineralizer, experimental temperature and pH of the media play a vital role in obtaining good quality single crystals of Nd:YVO_4. The growth mechanism for Nd:YVO_4 have crystal morphology control and been worked out. The powder X-ray diffraction studies show that the cell parameters for Nd:YVO_4 obtained in the present work match well with the literature data.

The FTIR study shows that the Nd:YVO_4 structure has less distorted $[VO_4]^{3-}$ tetrahedra. Also there is an absence of hydroxyl molecules in the Nd:YVO_4, in spite of the fact that crystals were obtained under mild temperature and pressure conditions.

The crystal morphology could be well controlled through proper selection of crystal growth conditions.

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