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Structural and optical effects induced by gamma irradiation on $NdPO_4$: X-ray diffraction, spectroscopic and luminescence study

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ABSTRACT

Rare earth orthophosphate ($NdPO_4$) monazite single crystals were grown using high temperature flux growth method employing $K_6P_4O_{13}$ (K_6) as molten solvent. Their structural parameters were studied using single crystal X-ray diffraction (XRD) method. The grown crystals were examined by SEM and EDX techniques for their homogeniousity and inclusion in the crystals. The influence of gamma irradiation in structural and optical absorption properties were studied by the powder XRD, FTIR and reflectance spectroscopy. The effect of gamma irradiation on luminescence properties was recorded. No significant structural change is observed up to 150 kGy gamma dose. The gamma ray induced charge trap in the crystal was saturated to 40 kGy dose. The luminescence intensity decreases with an increase in the irradiation. The emission of luminescence intensity stabilizes above 40 kGy gamma dose.

1. Introduction

The immobilization factor and optical applications are of immense interest to the researcher to analyze the neodymium orthophosphate ($NdPO_4$). In general, lanthanide phosphate crystallizes in xenotime structure having tetragonal phase and the monazite structure having monoclinic phase. The monazite phase of lanthanide phosphate highly resists the radiation induced by amorphization [1]. Natural monazite ore contains radioactive actinide (U, Th) and their disintegration products [2,3]. Admittance of significant amounts of Th and U in the monazite mineral over a long period makes it feasible for radiation resistance [4,5]. The vested interest on monazite for immobilization of actinide is due to its higher thermal stability, storage capability for actinides, chemical lastingness and resistance to radiation damage effects [6–8]. Minor actinides Np, Am and Cm presented in high-level nuclear waste, with long half-lives (~100,000 years) produces hazardous long term vulnerable ionizing radiation [9]. The ceramic and crystalline phosphate materials have overcome the demerits of oxide glasses such as low melting temperature, high dissolution and poor radiation stability and high corrosion for high level nuclear waste storage [1,10,11]. For these reasons, the monazite rare earth phosphate is a suitable host material to immobilize the long term radioactive minor actinides due to its radiation resistance, chemical permanence, thermal resistance, aqueous durability, mechanical durability and high melting point [10,12,13].

Recently, self activated stoichiometric neodymium (Nd) laser materials attracted the researchers due to its less concentration quenching of the materials [14,15]. The high Nd concentration of neodymium in the crystal gives the high yield emission of 1064 nm due to its efficient absorption of pump radiation at short distances (~50–100 μm) [13]. In the Nd based phosphate complex materials (NdP_5O_{14}, $LiNdP_4O_{12}$ and $KNdP_4O_{12}$) the concentration quenching is similar, which is significantly less than Nd:YAG [15–17]. $NdPO_4$ has a high Nd concentration in the order of 13.7×10^{21} cm^{-3} [18]. In the crystal, the luminescence is associated with high concentration of neodymium, so it can be used to detect the minor radioactive damage in the crystal.

Due to its high melting point (2173 K), $NdPO_4$ is hard to obtain monazite phase by direct single crystal growth from melt method [19]. The $NdPO_4$ was grown and processed by various methods namely hydrothermal, heating, chemical reaction, flux growth, microwave assisted growth and solid state reaction method [18,20–24]. Very few have achieved single crystal of $NdPO_4$ using molten fluxes as a solvent at a high temperature of about 1293 K and 1623 K [18,25].

The present investigation deals with the growth of single crystal $NdPO_4$ by flux method and the effect of gamma ray irradiation on structural and optical properties. The crystal was grown using potassium poly phosphate molten flux at 1273 K by flux growth method. The structural properties were assessed by XRD and Raman spectroscopy. The optical properties were evaluated by diffused reflectance spectroscopy and photoluminescence studies.

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2. Experimental method

2.1. Crystal growth

The phenomenon behind the flux growth technique is that, the crystallization temperature reduces with an increase of the solvent in the solution [26]. In this technique, the growth of crystals (solute precursors to be crystallized) is reduced to liquid form in a suitable flux, and the growth of crystal starts when the solution attains critically supersaturation. The resultant supersaturation and crystal growth are made by cooling the molten solution. The $K_6P_4O_{13}$ flux has been chosen for the growth of $NdPO_4$. The $K_6P_4O_{13}$ flux has low melting point, non-volatile, hygroscopic at room temperature, no toxic evaporation and less corrosion on the growth vessel compared to the flux used by Wang et al. and Cherniak et al. [18,25].

$NdPO_4$ crystals were grown using lead free phosphate flux (molten solvent at high temperature). The high viscosity of potassium polyphosphate flux hampers the transportation of solute in molten solution. Molybdenum (VI) oxide (0.002 wt.%) is added to reduce the viscosity of the flux. The potassium phosphates of monobasic (KH_2PO_4) and dibasic (K_2HPO_4) were taken in the molar ratio 2:2 to synthesize $K_6P_4O_{13}$. Potassium poly phosphate powder was synthesized by heating potassium phosphate in a platinum crucible using resistive heating furnace at 1073 K. The molten form of potassium poly phosphate was then cooled down from 1073 K to room temperature. Rare earth oxide (Nd_2O_3) and KH_2PO_4 were taken in the molar ratio 1:2. The Nd_2O_3 was mixed thoroughly with KH_2PO_4 and flux ($K_6P_4O_{13}$). The solute ($NdPO_4$) and solvent ($K_6P_4O_{13}$) weight proportions was found to be 0.25. The mixed precursor compound exhibits frothing volatility (~723–773 K) during slow heating from room temperature to growth temperature. In order to avoid frothing volatility this mixed precursor is placed directly at 1113 K in a three zone home build resistive heating furnace. It is heated for 24 h at 1273 K for solution homogenization. After obtaining the homogenized transparent molten solution, temperature cooling program (Supplementary information Fig. A) is initiated by programmed temperature controller Pro 980. The cooling program was fixed to 2 K/day from 1273 K to 1233 K and then the cooling rate is increased 4.5 K/day for every 50 K decrease, up to 1133 K. The temperature is gradually reduced to room temperature by 50 K/day from 1133 K. The crucible was taken out of furnace and the crystals were bleached from flux using low concentrated H_2SO_4. The harvested crystals were rinsed many times thoroughly by boiling de-ionized water to remove the acid contamination. The grown inclusion free transparent pink colored crystals are shown in Fig. 1.

2.2. Analytical methods

X-ray diffraction (XRD) pattern was studied by powder X-ray diffractometer (X'Pert PRO, PANalytical, The Netherlands) using CuKα (1.5405 Å) radiation with nickel filter. The 2θ range is fixed between 18 and 60° with step size of 0.017°. The crystal system and structural parameters of the grown crystal were studied by Bruker Kappa APEXII X-ray diffractometer using MoKα (0.71073 Å) radiation at 303 K.

The absorption spectrum was recorded in the spectral range of 200–900 nm using a Shimadzu UV-2600 single monochromator. The diffused reflectance accessory was used with 0.5 nm resolution. Before collecting the data, baseline was noted for reference ($BaSO_4$) standard (Supplementary information Fig. B) and subtracted for $NdPO_4$ sample.

$NdPO_4$ samples were coated with a thin layer of evaporated carbon and secondary electron images were obtained using an FEI Quanta 200 scanning electron microscope (SEM).

Fig. 1. Flux grown $NdPO_4$ single crystals.

For EDX microanalysis, the grown samples were coated with a thin layer of evaporated carbon for conduction and the crystal was embedded to a stage pasted in araldite resin. The microanalysis of the EDX analyzes checks the elements present in the crystal and flux (alkali metal) inclusions in grown crystals.

2.0 g of $NdPO_4$ ground powder sample was taken for gamma irradiation analysis. A ^{60}Co gamma cell (14,000 Ci) was used as a gamma ray irradiation source with a dose rate of 66.66 Gy/min at temperature 303 K. Radial dose rate uniformity of +25% and axial dose rate uniformity of −25% was fixed as per instrument standard.

The infrared emission spectra and excitation spectra were recorded by Jobin Yvon Fluorolog-FL3-11 spectrofluorometer equipped with data max software. The xenon flash lamp (450 W) was used for excitation. The IR emission signal was detected by liquid nitrogen cooled InGaAs array detector with the resolution of 0.2 nm.

Infrared spectroscopic investigations were carried out for a wave number range of 400–1600 cm^{-1} using a Thermo Nicolet FT-IR spectrometer (model 6700). Approximately 1 mg of the sample is mixed with 250 mg KBr and pressed to pellets for the measurements.

The Raman shift study was implemented in backscattering geometry using a Renishaw InVia Raman spectroscope equipped with a confocal DM 2500 Leica optical microscope, thermoelectrically (TE)-cooled Ren-Cam CCD detector and Ar^+ ion laser working at the 514.5 nm wavelength. The unpolarized Raman shift was recorded in single scan for 60 s. The obtained Raman shift was calibrated with the reference sample (Silicon) as an internal standard (Supplementary information Fig. C).

3. Results and discussion

3.1. Structural characterization

The single crystal XRD analysis confirms the grown crystal belonging to monoclinic system with $P2_1/n$ space group. The unit cell parameters are $a = 6.770$ Å, $b = 6.986$ Å, $c = 6.408$ Å and $\beta = 103.62°$ (Supplementary information Fig. D). The grown single crystals were taken to the X-ray diffraction analysis. The XRD pattern with index is shown in Fig. 2. The XRD pattern showing the diffraction peaks at 2θ of 21.36°, 27.2°, 34.61°, 52.14°, 53.17° and 56.09° indexed miller indices (1 1 1), (2 0 0), (2 0 2), (3 2 2), (3 0 3) and (4 0 0) respectively. The XRD pattern shows consensus with