Available online at www.sciencedirect.com
ScienceDirect
ELSEVIER
JOURNAL OF RARE EARTHS, Vol. 33, No. 5, May 2015, P. 535
JOURNAL OF RARE EARTHS
www.re-journal.com/en/

Preparation by chemical co-precipitation, spectral and electrical characteristics of neodymium orthophosphate nanoparticles

Seema Verma, K.K. Bamzai*

(Crystal Growth and Material Research Laboratory, Department of Physics & Electronics, University of Jammu, Jammu 180006, India)

Received 17 May 2014; revised 6 February 2015

Abstract: Nanoparticles of neodymium orthophosphate ($NdPO_4$) were prepared through a facile wet co-precipitation technique. The X-ray diffraction (XRD) studies revealed the material belonging to monoclinic monazite phase with crystallite size of 30.8 nm. Scanning electron microscopic studies showed that the material was composed of a large number of agglomerated spherical particles having grain size of 92 nm. Thermogravimetric analysis suggested that the structural phase transition was seen above 800 °C. The spectroscopic investigations were carried out using Fourier transform infrared spectroscopy (FTIR). UV-VIS-NIR absorption spectrophotometer showed various transitions from the ground state $^4I_{9/2}$ to various excited states within the 4f shell and the optical band gap came out to be 3.3 eV. The dielectric constant (ε'), dielectric loss (tan δ) and ac conductivity ln(σ_{ac}) were measured in the frequency range of 5 kHz to 1 MHz and in the temperature range of 40 to 500 °C. The dielectric measurement suggested that there was a shift in the value of transition temperature (T_c), thereby indicating relaxor behaviour of the material. The activation energy value decreased with increase in frequency, thereby suggesting the role of mixed ionic-polaronic conductivity.

Keywords: nanoparticles; spectroscopic; dielectric properties; rare earths

Neodymium orthophosphate is interesting material because of technological applications on account of their ferroelectric, piezoelectric, optical and other important properties. Therefore, they have a wide range of applications either in the form of powder, or dense sintered parts such as phosphors, sensors, proton conductors, ceramic materials, catalysts and heat resistant materials[1–3]. In lanthanide series, the orthophosphates having larger ionic radii ranging from La to Gd are characterized by the monoclinic (monazite) structure while the orthophosphates having smaller ionic radii ranging from Dy to Lu have the tetragonal (zircon) structure[4]. In general rare earth orthophosphates ($REPO_4$) have three different structure types, hexagonal, tetragonal and monoclinic. The hexagonal is a low temperature phase and can transform into monoclinic after calcinations at 800 ºC or hydrothermal reaction at 200 ºC, while the tetragonal maintains its structure after calcinations at 900 ºC[5–7]. Neodymium orthophosphate has two phases, which are hexagonal and monoclinic exhibiting different properties.

The properties of a given material depend on the preparation route, which includes chemical composition, the crystalline structure, the grain size and the morphology. Several authors reported the synthesis of neodymium orthophosphate via different methods such as direct chemical reaction[8], flux assisted[9], heating[7], hydrothermal[10] and microwave assisted[11]. Hexagonal and monoclinic $NdPO_4$ nanowires were prepared through hydrothermal reaction by Guan and Zhang[12]. Wang et al.[13] reported the absorption and the fluorescence spectra of neodymium orthophosphate crystals. Many laser crystals of neodymium stoichiometric compositions were reported such as NdP_5O_{14}(NdPP)[14], $LiNdP_4O_{12}$(LNP)[15,16], $NdAl_3(BO_3)_4$ (NAB) and $KNdP_4O_{12}$ (KNP)[17]. Wong et al.[18] studied the structural and luminescent properties of europium ions in lithium aluminium borophosphate glasses. Jerbi et al.[19] reported the synthesis and structural characterization of new yttrium phosphate ($Na_{2.5}Y_{0.5}Mg_7(PO_4)_6$) with fillowite-like structure. Neodymium orthophosphate synthesized by simple method such as co-precipitation method has not been attempted in detail in literature. The advantages of this technique include a rapid reaction rate, the controllable reaction conditions and the ability to form nanomaterials with uniform shapes, narrow size distributions and high purity. Therefore, an attempt was made to synthesize neodymium orthophosphate through co-precipitation method as nanoparticles and then studies on its detailed characteristics were carried out. To the best of author's knowledge there is no such detailed study on the preparation of $NdPO_4$ by co-precipitation method and its spectroscopic and dielectric behaviour.

* **Corresponding author:** K.K. Bamzai (**E-mail:** kkbamz@yahoo.com; **Tel.:** +91-191-2450939)

DOI: 10.1016/S1002-0721(14)60453-1

1 Material and methods

1.1 Material preparation

Neodymium nitrate hexahydrate ($Nd(NO_3)_3·6H_2O$) 99.9% pure (M/S Indian Rare Earths Ltd., India) and ammonium dihydrogen phosphate ($NH_4H_2PO_4$) 99.9% pure (Alfa Aesar) were used as precursor material for the preparation of neodymium orthophosphate nanoparticles. Fig. 1 illustrates the schematic diagram of neodymium orthophosphate ($NdPO_4$) via co-precipitation method. 0.5 mol/L solution of neodymium nitrate hexahydrate was prepared in deionised water and was kept under stirring using a mechanical stirrer. Ammonium dihydrogen phosphate of the same molarity was added slowly to the above solution in the 1:1 molar ratio. Ammonium hydroxide (NH_4OH) was then added drop by drop to adjust the pH value at 12 for the flocculation of the precipitate and kept under vigorously stirring at 80 ºC for half an hour for complete precipitation. A pale violet precipitate was obtained in the beaker and was allowed to settle down for 24 h at room temperature. These precipitates were filtered and washed with distilled water and ethanol for several times to remove the nitrate ions. The pale violet slurry of neodymium phosphate thus obtained was dried, ground well in an agate mortar and further calcinated in a furnace at 800 ºC for 2 h under air atmosphere. The following reaction is expected to take place leading to the formation of neodymium orthophosphate ($NdPO_4$) nanoparticles:

$$Nd(NO_3)_3·6H_2O+NH_4H_2PO_4+2NH_4OH\rightarrow NdPO_4+3NH_4NO_3+8H_2O\uparrow \quad (1)$$

1.2 Characterization

The characterization techniques used to understand the neodymium orthophosphate nanoparticles include X-ray diffraction analysis, particle size analysis, scanning electron microscopy coupled with energy dispersive X-ray analysis (SEM-EDAX), optical properties include UV-VIS-NIR spectroscopy, and electrical properties include dielectric constant, dielectric loss and conductivity. The phase identification was carried out by X-ray diffraction patterns using a PANalytical X'Pert Pro diffractometer with Cu Kα radiation (λ=0.154060 nm), the intensities of the diffraction beam were obtained in the 2θ range between 20º–70º. Debye-Scherrer relation was used to determine the crystallite size. The particle size was measured with a Zeta Sizer Nano ZS (Malvern Instruments Ltd., UK) analyzer. In order to see the microstructure a scanning electron microscope of JEOL Model JSM-6390 LV supplemented with energy dispersive X-rays analysis (EDAX) of model No. JEOL JED-2300 was used. Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) curves were recorded simultaneously on the thermal analyzer (Shimadzu make DTG-60) over the temperature range from room temperature to 1000 ºC at the heating rate of 10 ºC/min at a flow rate of 30 mL/min. Fourier transform infrared (FTIR) spectrum was obtained on an IR Prestige-21 (Shimadzu) spectrophotometer in the region from 400 to 3500 cm^{-1} using KBr pellet. The optical absorption of the grown material in the UV-VIS-NIR regions was measured with a Varian Carry 5000 spectrophotometer. The dielectric studies were carried out with the help of an automated impendence analyzer (LF 4192A model) interfaced with USB GPIB converter 82357 B (Agilent) and further automated by using a computer for data recording, storage and analysis. For dielectric studies, the agglomerated nanoparticles were powdered in an agate mortar and then about 1%–2% PVA (poly vinyl alcohol) was added which served as a binder. The fine powder was then pressed into circular pellets of 13 mm diameter and thickness of 1.075 mm using a hydraulic press by apply-

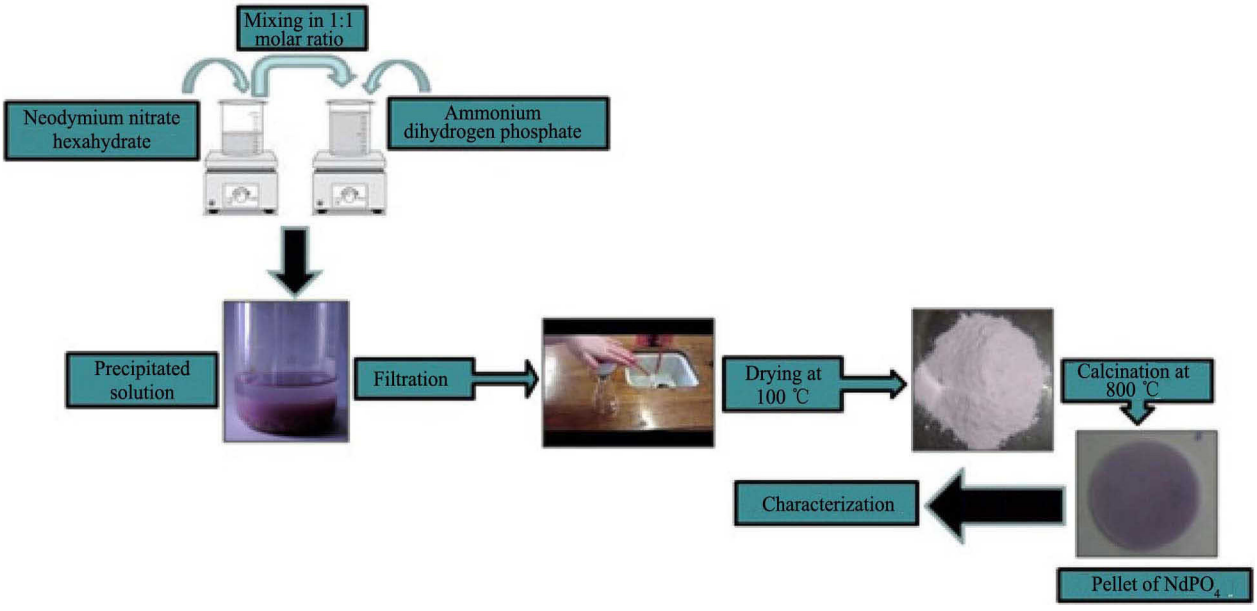

Fig. 1 Schematic diagram for synthesis of neodymium orthophosphate ($NdPO_4$) via co-precipitation technique