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Crystal structure and spectroscopic studies of $NaGd(PO_3)_4$

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Abstract

Single crystals of gadolinium–sodium polyphosphate $NaGd(PO_3)_4$ were grown for the first time using a flux method and characterized by X-ray diffraction. This phosphate crystallizes in a monoclinic system with $P2_1/n$ space group and with the following unit-cell dimensions: $a = 9.767(3)$ Å, $b = 13.017(1)$ Å, $c = 7.160(2)$ Å, $\beta = 90.564(5)^\circ$, $V = 910.3(4)$ Å^3 and $Z = 4$. The crystal structure was solved from 3451 X-ray independent reflections with final $R(F^2) = 0.0219$ and $R_w(F^2) = 0.056$ refined with 164 parameters ($F_0^2 > 4\sigma(F_0^2)$). The atomic arrangement can be described as a long chain polyphosphate organization. Two infinite $(PO_3)\infty$ chains with a period of eight tetrahedra run along the [0 1 1] direction. The structure of $NaGd(PO_3)_4$ consists of GdO_8 polyhedra sharing oxygen atoms with phosphoric group PO_4. Each Na^+ ion is bonded to eight oxygen atoms.

Keywords: A. Inorganic compounds; A. Optical materials; B. Crystal growth; D. Crystal structure

1. Introduction

In recent years, rare-earth phosphates crystals have attracted much attention due to the possibilities of using them in miniature laser materials [1–6], colour lumiphors, optic fiber communication [7–9], etc. The common chemical features of these polyphosphates indicate that they are relatively stable under

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normal conditions of temperature and humidity. They can be kept for many years in a perfect state of crystallinity, they are not water soluble as may be inferred from their estimated molecular weights and they all produce glasses when heated to their melting points [10].

Many double condensed phosphates of rare-earth and sodium are reported in the literature $NaLn(PO_3)_4$ (Ln = Pr [11], Nd [12], Ce [13]). These phosphates are obtained by flux method or by study of the phase-equilibrium diagrams of the M^IPO_3–$Ln(PO_3)_3$ systems (M^I: monovalent cation, Ln: rare-earth element).

A literature inspection indicates that the crystallographic data and the spectroscopic properties of $NaGd(PO_3)_4$ has not been carried out so far. This work enters within the framework of a systematic investigation of the crystal structures and luminescent properties of the double polyphosphate of the type $M^ILn(PO_3)_4$ [14–16]. This paper deals with the synthesis and single crystal structure of $NaGd(PO_3)_4$ by X-ray diffraction. Infrared and Raman spectroscopy are reported.

2. Experimental

2.1. Synthesis and characterization

Single crystal of $NaGd(PO_3)_4$ was prepared by a flux method. At room temperature, 5 g of Na_2CO_3 and 0.4 g of Gd_2O_3 were slowly added to 12 ml of phosphoric acid H_3PO_4 (85%). The mixture was then slowly heated to 573 K and kept at this temperature for 24 h. After 7 days of decreasing temperature, transparent and parallelepiped crystals were separated from the excess phosphoric acid by washing the product in boiling water. Subsequently, a second washing with nitric acid is necessary to eliminate the remaining oxide Gd_2O_3. It is noted that this compound is stable in air and its formula is determined by chemical analysis and confirmed by refinement of the crystal structure. For the spectroscopic study, $NaGd(PO_3)_4$:Eu^{3+} was prepared in the same way by adding Eu_2O_3 to the reaction mixture in the appropriate ratio.

2.2. Luminescence apparatus

The luminescence spectra were performed either at 300 K. The sample excitation has been carried out via a XeCl excimer laser (308 nm) and dye laser (337 nm) delivering pulses of 10 ns duration and 0.1 cm^{-1} spectral width. The pulse energy has been maintained to about 10 mJ. Time-resolved spectroscopy investigations were performed with Instaspec equipment composed of a Stanford delay generator, an Oriel 125 monochromator with a grating of 1200 grooves/mm and an Andor detector-type-intensified CCD camera.

2.3. Infrared spectroscopy

The infrared spectrum of $TlGd(PO_3)_4$ were recorded in the 250–1500 cm^{-1} range with a Perkin-Elmer FTIR Spectrum 1000 using sample dispersed in KBr pellets. The Raman spectrum was recorded at room temperature using a Raman microprobe combined with a Dilor XY spectrometer, with the 514.5 nm radiation from an argon ion laser as the excitation beam. A microscope allowed selection of a region of good optical quality in the crystalline sample.