Phonon and Magnetic Excitations in Neodymium Pentaphosphate

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Abstract

The structure of $\text{NdP}_5\text{O}_{14}$ consists of cross-linked double chains of corner-sharing PO_4 tetrahedra extending parallel to the crystallographic a-axis. Each Nd atom is coordinated by 8 O atoms. The NdO_8 polyhedra are isolated from each other and share no common O atoms. High-gain and long-lifetime laser action had been reported in $\text{NdP}_5\text{O}_{14}$ crystals. The neutron excitation spectra reveal a one-phonon density of states extended to about 180 meV with several distinct P-O stretching bands at high energies. This features reflect the existence of different P-O bond lengths among the terminal and bridging configurations and the associated atomic dynamics. Furthermore, magnetic scattering from Nd ions permitted the determination of the energy-level structure of the crystal-field-split $\text{Nd}^{4f_{9/2}}$ ground term.

Keywords: rare-earth pentaphosphate, ultraphosphate, crystal fields, PO_4 chains

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1. Introduction

Corner-sharing tetrahedra of PO_4 units are the basic building blocks of condensed phosphates. In ultra-, meta-, and pyrophosphates the linkage of the PO_4 units corresponds principally to 3-D networking, chain-like, and dimer configurations, respectively. In orthophosphates, the tetrahedra are disconnected. $\text{NdP}_5\text{O}_{14}$ belongs to the ultraphosphate category. Its crystal structure below ~ 420 K (monoclinic, space group $\text{P}21/c$) consists of corrugated, corner-sharing PO_4 tetrahedra chains extending parallel to the crystallographic a -axis in the ac -plane. The chains are cross linked by another PO_4 tetrahedron at every second PO_4 unit of the chains.[1] This double-chain structure is illustrated schematically in Fig. 1. This structure is of interest from the point of view of distribution of P-O terminal bonds versus O-P-O bridging bonds. Without other network modifying cations, the additional P $d\pi$ -O $p\pi$ bond among the other sp^3 σ -bonds within the branching PO_4 units is energetically unstable. Addition of certain modifying cations may change drastically the structural and chemical properties of phosphate materials. Such phenomenon is not well understood at present.

$\text{NdP}_5\text{O}_{14}$ is of interest also for the search of efficient laser materials. A seven-fold reduction in fluorescence quenching as compared to traditional Nd:YAG crystals has been found in $\text{NdP}_5\text{O}_{14}$. [2] In this paper we report the phonon and Nd crystal-field excitations in polycrystalline $\text{Nd}_{0.9}\text{La}_{0.1}\text{P}_5\text{O}_{14}$. The study was motivated by the accumulated knowledge of the rare-earth (R) orthophosphate system, RPO_4 , investigated previously by neutron-scattering. [3, 4]

2. Experimental

About 66g of polycrystalline sample was obtained by powdering small crystals of $\text{Nd}_{0.9}\text{La}_{0.1}\text{P}_5\text{O}_{14}$ prepared by a flux-grown method. The neutron inelastic-scattering experiments were carried out using the High-Resolution Medium-Energy Chopper Spectrometer (HRMECS) at the Intense Pulsed Neutron Source (IPNS) of Argonne National Laboratory. Experimental procedure for the phonon and magnetic scattering was described in detail in previous publications.[3, 4]

3. Results and discussion

The monoclinic unit cell of $\text{Nd}_{0.9}\text{La}_{0.1}\text{P}_5\text{O}_{14}$ contains four formula units (240 phonon branches). It is too complex to measure individual phonon dispersion curves even using large single crystals. A neutron spectrometer equipped with multiple detectors covering a wide range of scattering angles, such as HRMECS, is effective in phonon density-of-states (PDOS) measurements using polycrystalline samples. The observed spectrum is weighted by the neutron scattering cross sections of the atoms that participate in atomic motions over the energy range. Fig. 1 shows the neutron-weighted PDOS obtained from a run with an incident energy (E_0) of 200 meV. Only data corresponding to wavevectors $Q > 10 \text{ \AA}^{-1}$ were summed so that contribution from magnetic scattering of Nd ions was negligible. The spectrum shows broad phonon bands centered around 20, 57, 91 meV and sharp features at 145, 162, and 176 meV. From a previous study of phonons in LuPO_4 , [4] we assign the band at 20 meV to mainly motions of Nd atoms and phonons between 20 to 100 meV to lattice vibrations involving P and O atoms. The sharp phonon peaks above 120 meV correspond to P-O stretch vibrations. The positions and the span of the P-O stretch modes provide important insights into the nature of

the PO_4 network and P-O bonding. In RPO_4 compounds of zircon-type structure where the PO_4 units are not connected with each other and all the P-O bonds are terminal, σ -type with only two distinct bond lengths, there are 8 stretch modes resulting in two sharp peaks in the PDOS at about 128 and 135 meV.[4] In RP_5O_{14} there are 8 terminal P-O bonds (bond lengths from 1.455 to 1.477Å) and 12 bridging ones (1.550 to 1.618Å).[1] This gives rise to many more characteristic stretch frequencies ranging from 120 to 180 meV. In the case of phosphate glasses, the distribution of the P-O stretch vibrations reflects the intermediate-range order intrinsic to the glass structure.[5]

Each of the Nd atoms in $\text{Nd}_{0.9}\text{La}_{0.1}\text{P}_5\text{O}_{14}$ is coordinated by 8 oxygen atoms forming a PO_8 polyhedron, as shown in Fig. 2. The Nd^{3+} ionic ground multiplet, $^4\text{I}_{9/2}$, is split by the crystal electric fields of the ligands into 5 Kramers doublets. The transitions between these crystal-field (CF) states were measured using E_0 of 40, 60 and 150 meV. Fig. 2 displays the observed scattering function at low Q ($< 3 \text{ \AA}^{-1}$) for $E_0 = 60 \text{ meV}$ at 10 K which is dominated by magnetic excitations. The four peaks labeled A to D correspond to CF excitations from the ground state to the upper states of the $^4\text{I}_{9/2}$ multiplet. At higher temperatures, transitions among the populated excited states (E to G) were also observed (not shown). The energy level scheme of the $\text{Nd}^{3+} \text{ } ^4\text{I}_{9/2}$ term is shown in Fig. 2. The result agrees very well with those obtained previously from an optical study by Blätte and co-workers.[6] The neutron intensities, in principle, should provide a more straightforward comparison with the calculated transition strengths using a CF model. However, the very low point symmetry (C_1) of the rare-earth site requires 26 CF parameters. Obviously, a simplified treatment of the CF model will

be necessary in any attempt to analyze the neutron data. Such analyses in conjunction with additional measurements of other RP_5O_{14} members are presently underway.

Acknowledgment

Work performed at Argonne National Laboratory is supported by the U. S. DOE-BES under Contract No. W-31-109-ENG-38.

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Figure captions

Fig. 1. (Top) The $(\text{P}_5\text{O}_{14}^{3-})_\infty$ chains in $\text{NdP}_5\text{O}_{14}$. (Bottom) The observed neutron-weighted phonon density of states of $\text{Nd}_{0.9}\text{La}_{0.1}\text{P}_5\text{O}_{14}$.

Fig. 2. (Top left) The NdO_8 polyhedron and neighboring PO_4 units in $\text{NdP}_5\text{O}_{14}$. (Top right) The energy level scheme of Nd^{3+} : $^4\text{I}_{9/2}$ ground multiplet of $\text{Nd}_{0.9}\text{La}_{0.1}\text{P}_5\text{O}_{14}$. (Bottom) The observed scattering function at low Q for $\text{Nd}_{0.9}\text{La}_{0.1}\text{P}_5\text{O}_{14}$.

Figure 1, Loong et al., "Phonon and Magnetic..."

Figure 2, Loong et al., "Phonon and Magnetic..."

Estimation of the length of this paper

a) Title, authors, affiliation and 117-word abstract	350 words
b) Two figures, fitting a single column	300 words
c) Manuscript text	854 words
d) References (4)	90 words

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