

RAMAN PHONONS IN RPO₄ CRYSTALS*

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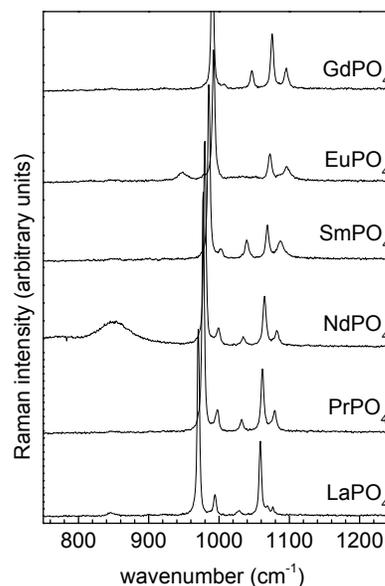
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Orthophosphates formed by elements in the first half of the lanthanide transition series (La, Pr, Nd, Sm, Eu and Gd) are structural analogs to the monoclinic mineral monazite. This mineral is characterized by an almost unique combination of properties that make its synthetic forms attractive as possible hosts for the long-term storage of actinide wastes. Crystals of lanthanide orthophosphates were grown by dissolving and by reacting lanthanide oxides in molten lead pyrophosphate at high temperatures. The LnPO₄ crystals which formed on cooling were separated by dissolving the lead phosphate matrix in boiling concentrated nitric acid. Lanthanide oxides highly pure were used in all measurements.

Raman spectra were recorded with a JY T64000 triple spectrometer equipped with N₂-liquid CCD. The spectra were excited with the 514.5 nm line of a Spectra-Physics model 164 argon ion laser. All spectra recorded are not polarized. The lanthanide orthophosphates crystallize in the monoclinic monazite structure C_{2h}⁵ with four molecules per unit cell. Only 18A_g+18B_g Raman active modes are expected to be observed, where 9A_g+9B_g are due to internal vibrations of PO₄ group and 9A_g+9B_g are due to external vibrations. Of 36 modes expected, an average of 25 were observed for the crystals investigated. Besides typical distribution of Raman phonons in monazites [1-3], we have observed a systematic trend in the behavior of internal PO₄ vibration frequencies with the Ln atomic number (see Fig.1).

Fig. 1 – Part of Raman spectrum of RPO₄.



The phonon densities of states of LaPO_4 and PrPO_4 were characterized by inelastic neutron scattering. The combined Raman and neutron data enable an analysis not only the nature of Raman phonons but also of the systematics in the variation of the phonon frequencies with respect to the Ln ionic radii and interatomic distances. The high-frequency shift of internal modes when the atomic number is increased is related to the decreasing of crystal radii for these compounds. This leads to a closer packing of PO_4 ion groups. The compression of PO_4 group shortens the P-O distance higher stretching and bending frequencies for highest atomic number lanthanide orthophosphates. Also, an interesting feature is observed in the spectrum of NdPO_4 when the laser wavelength changes (see Fig.2). The broadening of the width of bending modes indicates that an electron-phonon interaction takes place.

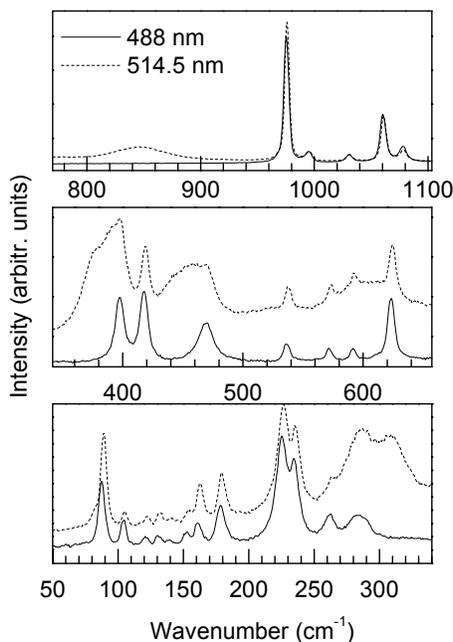


Fig.2 – Raman spectrum of NdPO_4 for two laser wavelengths.

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