

X-Ray Powder Diffraction and Vibrational Spectra Studies of Rare Earth Borophosphates, $Ln_7O_6(BO_3)(PO_4)_2$ ($Ln = La, Nd, Gd, \text{ and } Dy$)

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The crystal structure of the isomorphical rare earth borophosphate compounds, $Ln_7O_6(BO_3)(PO_4)_2$ ($Ln=La, Nd, Gd$ and Dy), has been studied by a combination of X-ray powder diffraction (XRD) and vibration spectroscopic techniques. The Raman and infrared spectra of these compounds have been investigated, and their interpretation is discussed on both theoretical and experimental bases. Assignments have been deduced from the systematic investigation of pure compounds and isotopic species. A comparison of vibrational frequencies in La, Na, Gd, and Dy borophosphates reveals that the internal vibrations of the BO_3 and PO_4 ions shift to higher frequency with the decrement of lattice parameters from La to Dy, indicating a strengthening of the phosphorus–oxygen and boron–oxygen bonding. © 1997 Academic Press

1. INTRODUCTION

Because of the complex and varied optical energy level structures of lanthanides, rare earth compounds have found their widest application in laser and luminescence materials. Considerable progress has been made in the field of stoichiometric laser materials (1,2). In contrast to other lasers where the active ion is dispersed in a crystalline or glassy host, the stoichiometric rare earth compounds can be called self-active lasers. The anion groups in these compounds should be large enough to separate active ions, in order to reduce the concentration quenching behavior caused by the ion–ion interactions (3). Therefore, the work of exploring and investigating new rare earth compounds consisting of large anion groups such as BO_3 , PO_4 , or WO_4 must be of significance.

Our previous work (4) about phase relations of La_2O_3 – B_2O_3 – P_2O_5 revealed that there is only one ternary compound $La_7O_6(BO_3)(PO_4)_2$ in this system. The crystal structure of the isomorphous compound $Nd_7O_6(BO_3)(PO_4)_2$ has been studied by Palkina (5), and

the X-ray powder diffraction patterns of other rare earth compounds $Ln_7O_6(BO_3)(PO_4)_2$ ($Ln = Gd$ and Dy) were also reported, but the indexing results were not given.

Spectroscopy is an important technique for the characterization of inorganic anion groups and may be used in conjunction with X-ray diffraction for determination of crystal structure. Although several collections of IR and Raman spectra of borate and phosphate compounds have been published (6–10), no vibrational spectra investigation or rare earth borophosphate compounds has been carried out. In order to separate the internal modes of BO_3 triangles and PO_4 tetrahedra and to propose a detailed interpretation of the spectra, the borate isotopic $^{10}B^*$ species of $La_7O_6(BO_3)(PO_4)_2$ is synthesized and its vibrational spectra are investigated.

2. EXPERIMENTAL PROCEDURE

2.1. Synthesis of the Compounds

All the compounds including isotopic compounds were synthesized by a standard solid-state reaction technique by heating mixtures of rare earth oxides (purity > 99.99%), H_3BO_3 (99.5%) and $NH_4H_2PO_4$ (99.0%), according to stoichiometric composition. The starting materials were weighed on an analytical balance to an accuracy of 0.05 mg and thoroughly mixed in an agate mortar. The powders were pressed at about 10^8 Pa into 10×2 mm³ diameter pellets and heated to 400°C for 4 h in covered Pt crucibles for elimination of volatility. The specimens thus obtained were reground and pressed into pellets, then calcined at $1350 \pm 10^\circ C$ for about 72 h, and furnace-cooled to room temperature. Solid-state reaction was done in a SiC Global muffle furnace. Temperature was measured and controlled with a Pt–PtRh (10%) thermocouple.

Boron was available either as natural B (essentially ^{11}B) or ^{10}B -rich. P is a monoisotopic element (100% ^{31}P), and isotopic replacement is not possible. The isotopic purity data are collected in Table 1.

TABLE 1
Isotopic Purity Data

| Element | Isotopic composition (in mol%) | |
|-----------------|--------------------------------|-------|
| B (natural) | ^{10}B | 18.83 |
| | ^{11}B | 81.17 |
| ^{10}B | ^{10}B | 89.99 |
| | ^{11}B | 10.01 |

2.2. X-ray Powder Diffraction Analysis

The XRD structural analyses of the compounds were performed using a M18AHF X-ray diffractometer with graphite monochromator and $\text{CuK}\alpha$ radiation (50 kV \times 200 mA). The XRD data were collected at ambient temperature. The scattering slit is 0.50° , the divergence slit 0.50° , and the receiving slit 0.15 mm. The scanning step width is 0.02° in 2θ from 10° to 80° .

2.3. Vibration Spectrum

The room temperature Raman scattering (RS) spectra of the compounds were obtained with a Spectra Physics Ar ion laser excitation. The Raman system includes a SPEX-1403 double monochromator with 1800 lines/mm holographic grating, a cooled R3103402 photomultiplier, and photon counting electronics. All RS spectra were obtained at 200 mW of 5145 and 4880 Å laser lines, in order to eliminate misidentification of our Raman data due to possible fluorescence from trace impurities. The spectral band pass was 2 cm^{-1} .

Infrared transmittance spectra were measured at room temperature in KBr disks using a PE-983 G IR spectrophotometer in the frequency range $200\text{--}1500\text{ cm}^{-1}$. Wavenumber accuracy is within $\pm 2\text{ cm}^{-1}$ for narrow bands.

3. X-RAY POWDER DIFFRACTION INDEXING RESULTS

The rare earth borophosphate compounds $\text{Ln}_7\text{O}_6(\text{BO}_3)(\text{PO}_4)_2$ ($\text{Ln} = \text{La}, \text{Nd}, \text{Gd}, \text{and Dy}$) are isostructural and belong to monoclinic structure with space group $P2_1/n$. The structure of $\text{Nd}_7\text{O}_6(\text{BO}_3)(\text{PO}_4)_2$ determined by the monocystal method (5) indicates that this crystal has laminar structure with one lamina consisting of neodymium polyhedra and PO_4^{3-} tetrahedra, and the next lamina built of Nd polyhedra and BO_3^{3-} triangles. These folded layers are parallel to the y axis. The PO_4^{3-} and BO_3^{3-} groups are isolated from each other.

The powder XRD patterns of these rare earth borophosphates shown in Fig. 1 indicate that these compounds are isostructural. It is difficult to index so many reflections directly. Fortunately the structural data of

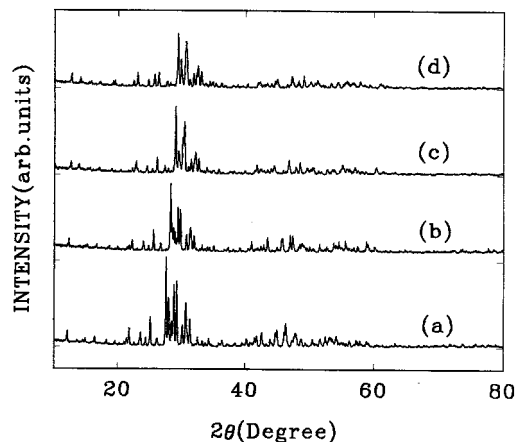


FIG. 1. X-ray diffraction patterns of $\text{Ln}_7\text{O}_6(\text{BO}_3)(\text{PO}_4)_2$ ((a) La, (b) Nd, (c) Gd, and (d) Dy).

$\text{Nd}_7\text{O}_6(\text{BO}_3)(\text{PO}_4)_2$ including lattice constants and atom coordinates could be used to index them approximately by the LAZY (11) program. Then the accurate lattice constants could be obtained by calculating these indexed reflections using the method of least squares. Thus the reflections of $\text{Ln}_7\text{O}_6(\text{BO}_3)(\text{PO}_4)_2$ ($\text{Ln} = \text{La}, \text{Nd}, \text{Gd}, \text{and Dy}$) could be indexed precisely using the calculating lattice constants by LAZY program again.

Table 2 gives the indexing results of the XRD patterns of the $\text{Ln}_7\text{O}_6(\text{BO}_3)(\text{PO}_4)_2$ ($\text{Ln} = \text{La}, \text{Nd}, \text{Gd}, \text{and Dy}$) compounds. The lattice parameters and volumes of the compounds are given in Table 3. Figure 2 suggests that there is a good linear correlation between the lattice parameters of $\text{Ln}_7\text{O}_6(\text{BO}_3)(\text{PO}_4)_2$ ($\text{Ln} = \text{La}, \text{Nd}, \text{Gd}, \text{and Dy}$) and the radius of rare earth cations with 8 coordination (12, 13), which also verified the accuracy of our X-ray powder indexing results.

4. ANALYSIS OF VIBRATIONAL SPECTRA

4.1. Site Group Analysis

The structure of rare earth borophosphate compounds $\text{Ln}_7\text{O}_6(\text{BO}_3)(\text{PO}_4)_2$, determined by X-ray diffraction (5), is described by the space group $C_{2h}^5(P2_1/n)$; the primitive unit cell is centrosymmetric with 4 formula units per unit cell. All the atoms in this crystal occupy the site symmetry C_1 .

The $\text{Ln}_7\text{O}_6(\text{BO}_3)(\text{PO}_4)_2$ cell contains therefore $27 \times 4 = 108$ atoms and there exist $(108 \times 3) - 3 = 321$ principal variations.

The irreducible representation of rare earth borophosphate compounds can be obtained by the site group analysis (SGA), which relies on the transformation of the irreducible representation when passing from the site group of a given ion or atom to the factor group (C_{2h} in the present case (5)). This treatment can be carried out by assuming the

TABLE 2
List of d , Diffraction Intensity, and the Results of Indexes of $Ln_7O_6(BO_3)(PO_4)_2$ ($Ln=La, Nd, Gd, \text{ and } Dy$)

| h | k | l | $La_7O_6(BO_3)(PO_4)_2$ | | | | $Nd_7O_6(BO_3)(PO_4)_2$ | | | | $Gd_7O_6(BO_3)(PO_4)_2$ | | | | $Dy_7O_6(BO_3)(PO_4)_2$ | | | |
|-----|-----|-----|-------------------------|-----------|-----------|-----------|-------------------------|-----------|-----------|-----------|-------------------------|-----------|-----------|-----------|-------------------------|-----------|-----------|-----------|
| | | | d_{obs} | d_{cal} | I_{obs} | I_{cal} | d_{obs} | d_{cal} | I_{obs} | I_{cal} | d_{obs} | d_{cal} | I_{obs} | I_{cal} | d_{obs} | d_{cal} | I_{obs} | I_{cal} |
| 0 | 2 | 1 | 7.30 | 7.29 | 17 | 23 | 7.17 | 7.15 | 17 | 24 | 7.01 | 7.02 | 16 | 17 | 6.96 | 6.96 | 23 | 17 |
| 0 | 1 | 2 | 5.92 | 5.92 | 8 | 7 | 5.81 | 5.80 | 10 | 7 | 5.66 | 5.67 | 8 | 5 | 5.62 | 5.61 | 11 | 5 |
| 0 | 3 | 1 | 5.40 | 5.39 | 10 | 10 | 5.30 | 5.29 | 10 | 10 | 5.20 | 5.20 | 8 | 7 | 5.16 | 5.16 | 7 | 7 |
| 1 | 2 | 1 | 4.85 | 4.85 | 7 | 4 | 4.76 | 4.76 | 8 | 5 | 4.68 | 4.67 | 7 | 3 | 4.62 | 4.62 | 11 | 3 |
| 1 | 3 | 0 | 4.53 | 4.53 | 5 | 3 | 4.45 | 4.44 | 7 | 4 | 4.35 | 4.36 | 5 | 3 | 4.32 | 4.32 | 7 | 3 |
| 1 | 3 | 1 | 4.16 | 4.15 | 9 | 11 | 4.08 | 4.07 | 9 | 12 | 3.99 | 4.00 | 9 | 8 | 3.96 | 3.96 | 13 | 8 |
| 0 | 1 | 3 | 4.08 | 4.07 | 21 | 25 | 3.99 | 3.99 | 15 | 26 | 3.90 | 3.90 | 18 | 17 | 3.86 | 3.86 | 27 | 17 |
| 1 | 4 | 0 | 3.77 | 3.77 | 16 | 17 | 3.70 | 3.69 | 13 | 18 | 3.63 | 3.63 | 12 | 12 | 3.59 | 3.59 | 16 | 12 |
| 0 | 4 | 2 | 3.65 | 3.64 | 10 | 10 | 3.58 | 3.57 | 8 | 11 | 3.50 | 3.51 | 7 | 7 | 3.48 | 3.48 | 15 | 7 |
| 1 | 4 | 1 | 3.54 | 3.54 | 34 | 36 | 3.48 | 3.47 | 33 | 37 | 3.41 | 3.41 | 22 | 25 | 3.38 | 3.38 | 30 | 25 |
| 1 | 0 | 3 | 3.40 | 3.39 | 8 | 9 | 3.33 | 3.33 | 14 | 10 | 3.26 | 3.26 | 12 | 7 | 3.22 | 3.23 | 13 | 7 |
| 2 | 0 | -2 | 3.23 | 3.23 | 100 | 100 | 3.15 | 3.15 | 100 | 100 | 3.07 | 3.07 | 100 | 67 | 3.04 | 3.03 | 100 | 67 |
| 1 | 5 | 0 | 3.18 | 3.18 | 53 | 47 | 3.13 | 3.13 | 42 | 48 | | 3.07 | | 33 | | 3.04 | | 33 |
| 2 | 1 | -2 | | 3.18 | | 29 | 3.10 | 3.10 | 36 | 29 | 3.02 | 3.02 | 31 | 19 | 2.988 | 2.986 | 56 | 19 |
| 1 | 4 | 2 | 3.13 | 3.13 | 30 | 23 | 3.08 | 3.07 | 32 | 23 | | 3.02 | | 16 | | 2.991 | | 16 |
| 1 | 5 | -1 | | 3.13 | | 11 | | 3.07 | | 11 | | 3.01 | | 7 | | 2.988 | | 7 |
| 0 | 5 | 2 | | 3.11 | | 10 | | 3.05 | | 10 | 2.997 | | 7 | | 2.972 | 2.973 | 23 | 7 |
| 0 | 1 | 4 | 3.09 | 3.09 | 70 | 76 | 3.03 | 3.02 | 68 | 77 | 2.957 | 2.958 | 55 | 52 | 2.925 | 2.926 | 74 | 52 |
| 1 | 5 | 1 | 3.046 | 3.044 | 77 | 85 | 2.990 | 2.988 | 66 | 86 | 2.934 | 2.935 | 71 | 58 | 2.912 | 2.911 | 86 | 58 |
| 0 | 2 | 4 | 2.959 | 2.960 | 23 | 24 | 2.901 | 2.898 | 24 | 24 | 2.836 | 2.837 | 21 | 16 | 2.806 | 2.806 | 27 | 16 |
| 1 | 5 | -2 | 2.910 | 2.911 | 43 | 32 | 2.855 | 2.852 | 27 | 33 | 2.796 | 2.797 | 23 | 22 | 2.773 | 2.771 | 28 | 22 |
| 1 | 4 | -3 | | 2.903 | | 41 | 2.843 | 2.840 | 36 | 43 | 2.779 | 2.780 | 31 | 29 | 2.751 | 2.751 | 44 | 29 |
| 2 | 0 | 2 | 2.886 | 2.886 | 14 | 16 | | 2.831 | | 17 | | 2.772 | | 11 | | 2.743 | | 11 |
| 2 | 1 | 2 | 2.850 | 2.850 | 30 | 39 | 2.796 | 2.795 | 26 | 40 | 2.738 | 2.737 | 23 | 27 | 2.707 | 2.709 | 32 | 27 |
| 2 | 4 | 0 | 2.748 | 2.747 | 10 | 6 | | 2.692 | | 6 | 2.639 | 2.637 | 11 | 4 | 2.609 | 2.611 | 13 | 4 |
| 1 | 5 | -3 | 2.611 | 2.610 | 9 | 11 | 2.557 | 2.556 | 10 | 12 | 2.503 | 2.504 | 8 | 8 | 2.481 | 2.480 | 10 | 8 |
| 1 | 6 | 3 | 2.240 | 2.242 | 10 | 9 | 2.199 | 2.200 | 17 | 9 | 2.160 | 2.160 | 14 | 6 | 2.143 | 2.142 | 12 | 6 |
| 3 | 3 | -1 | 2.176 | 2.175 | 11 | 10 | 2.128 | 2.128 | 10 | 10 | 2.080 | 2.080 | 8 | 7 | 2.055 | 2.056 | 10 | 7 |
| 2 | 1 | -5 | 2.159 | 2.159 | 12 | 11 | 2.106 | 2.106 | 10 | 11 | 2.054 | 2.055 | 10 | 7 | 2.030 | 2.029 | 14 | 7 |
| 1 | 3 | 5 | 2.121 | 2.120 | 16 | 18 | 2.079 | 2.079 | 23 | 18 | 2.035 | 2.037 | 13 | 12 | 2.015 | 2.017 | 19 | 12 |
| 1 | 4 | 5 | 2.060 | 2.060 | 10 | 8 | 2.016 | 2.017 | 8 | 8 | 1.975 | 1.974 | 7 | 5 | 1.952 | 1.952 | 9 | 5 |
| 3 | 4 | 0 | 2.023 | 2.023 | 18 | 18 | 1.984 | 1.984 | 21 | 18 | 1.944 | 1.945 | 15 | 12 | 1.922 | 1.926 | 24 | 12 |
| 1 | 6 | 4 | 2.014 | 2.014 | 22 | 24 | 1.976 | 1.976 | 19 | 24 | 1.938 | 1.939 | 21 | 16 | | 1.922 | | 16 |
| 0 | 9 | 1 | 1.966 | 1.966 | 18 | 20 | 1.930 | 1.930 | 30 | 20 | 1.897 | 1.898 | 11 | 13 | 1.883 | 1.884 | 16 | 13 |
| 3 | 5 | -1 | 1.957 | 1.957 | 30 | 34 | 1.915 | 1.915 | 29 | 34 | 1.875 | 1.874 | 20 | 23 | 1.854 | 1.854 | 27 | 23 |
| 2 | 1 | 5 | 1.908 | 1.908 | 12 | 10 | 1.872 | 1.872 | 12 | 10 | 1.835 | 1.834 | 11 | 7 | 1.816 | 1.816 | 13 | 7 |
| 2 | 1 | -6 | 1.895 | 1.895 | 14 | 11 | 1.850 | 1.849 | 9 | 11 | 1.805 | 1.805 | 10 | 7 | 1.782 | 1.782 | 17 | 7 |
| 2 | 5 | 4 | 1.869 | 1.869 | 9 | 7 | 1.834 | 1.834 | 8 | 7 | 1.799 | 1.799 | 8 | 5 | | 1.782 | | 5 |
| 2 | 2 | -6 | 1.864 | 1.864 | 8 | 10 | 1.819 | 1.819 | 10 | 10 | 1.777 | 1.776 | 7 | 7 | 1.753 | 1.754 | 7 | 7 |
| 3 | 5 | 2 | 1.804 | 1.804 | 8 | 7 | 1.769 | 1.769 | 14 | 7 | 1.734 | 1.734 | 9 | 5 | 1.715 | 1.717 | 12 | 5 |
| 3 | 4 | 3 | 1.768 | 1.768 | 10 | 13 | 1.734 | 1.734 | 10 | 13 | 1.700 | 1.699 | 8 | 9 | 1.683 | 1.683 | 11 | 9 |
| 4 | 0 | 0 | 1.740 | 1.740 | 12 | 11 | 1.702 | 1.702 | 16 | 11 | 1.664 | 1.664 | 15 | 7 | 1.645 | 1.644 | 14 | 7 |
| 0 | 10 | 2 | 1.724 | 1.723 | 10 | 6 | 1.691 | 1.691 | 12 | 6 | | 1.662 | | 4 | 1.650 | 1.650 | 13 | 4 |
| 1 | 6 | -6 | 1.705 | 1.706 | 8 | 9 | 1.669 | 1.670 | 9 | 9 | 1.634 | 1.635 | 9 | 6 | 1.617 | 1.617 | 12 | 6 |
| 3 | 4 | -5 | 1.691 | 1.691 | 14 | 16 | 1.650 | 1.651 | 19 | 16 | 1.612 | 1.612 | 12 | 11 | 1.592 | 1.592 | 15 | 11 |

separation of the vibrations into internal (BO_3 and PO_4 ion groups) and external (lattice vibrations and librations) modes. The internal modes consist of vibrations of one planar BO_3 anion group (which belongs to the group D_{3h}) and two tetrahedral PO_4 anion groups with molecular symmetry T_d . The external modes include the translations (lattice vibrations) of one BO_3 and two PO_4 ion groups,

seven rare earth, the leaving six oxygen atoms, and the rotations (librations) of BO_3 triangles and PO_4 tetrahedra.

The essential steps of the correlation method are given in Tables 4 and 5 for the external and the internal modes, respectively. The labels applied to the "internal" modes of the BO_3 (14) and PO_4 (15) groups, $\nu_1, \nu_2, \nu_3, \nu_4$, are defined in standard text books.

TABLE 3
Lattice Constants of Rare Earth Borophosphate Compounds
 $Ln_7O_6(BO_3)(PO_4)_2$ ($Ln = La, Nd, Gd,$ and Dy)

| $Ln_7O_6(BO_3)(PO_4)_2$ | $a(\text{\AA})$ | $b(\text{\AA})$ | $c(\text{\AA})$ | $\beta(^{\circ})$ | $V(\text{\AA}^3)$ |
|-------------------------|-----------------|-----------------|-----------------|-------------------|-------------------|
| $La_7O_6(BO_3)(PO_4)_2$ | 7.019 | 17.915 | 12.653 | 97.52 | 1577.27 |
| $Nd_7O_6(BO_3)(PO_4)_2$ | 6.862 | 17.591 | 12.375 | 97.18 | 1482.12 |
| $Gd_7O_6(BO_3)(PO_4)_2$ | 6.704 | 17.299 | 12.100 | 96.94 | 1393.11 |
| $Dy_7O_6(BO_3)(PO_4)_2$ | 6.623 | 17.172 | 11.960 | 96.76 | 1350.84 |

After summing up, the irreducible representation corresponding to the $Ln_7O_6(BO_3)(PO_4)_2$ crystal is as follows:

$$\Gamma_{\text{cryst}}^{Ln_7O_6(BO_3)(PO_4)_2} = 81A_g + 81B_g + 81A_u + 81B_u.$$

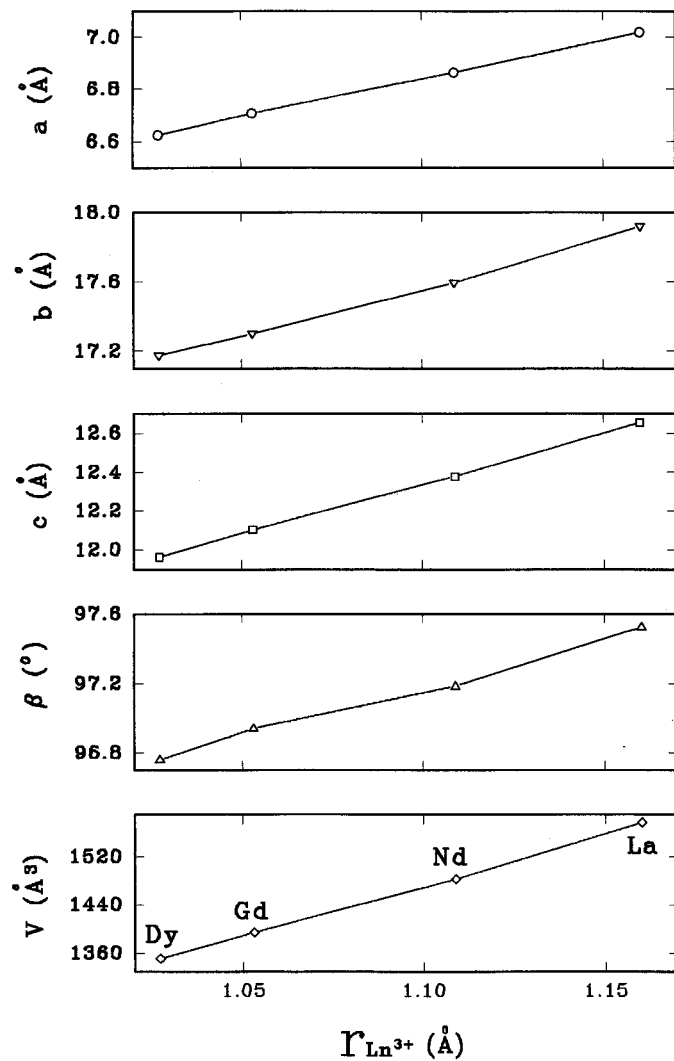


FIG. 2. Correlation between the lattice parameters of $Ln_7O_6(BO_3)(PO_4)_2$ ($Ln = La, Nd, Gd,$ and Dy) and the radius of rare earth cations with 8 coordination.

TABLE 4
Application of the Correlation Method to the External Modes
(Containing Translation and Rotation)

| $f^{\gamma} = n \cdot t^{\gamma}$ | t^{γ} | C_1 site symmetry species | C_{2h} factor group species | $C_{\xi} a_{\xi}$ |
|---|--------------------------------------|-----------------------------|----------------------------------|--------------------------|
| 12 | $3(T_{x,y,z} \text{ or } R_{x,y,z})$ | A | A_g B_g A_u B_u | 1 3 1 3 1 3 1 3 |
| $\Gamma_{Ln_7O_6(BO_3)(PO_4)_2}^{\text{extravib}} = \Gamma_{BO_3}^{\text{trans}} + 2\Gamma_{PO_4}^{\text{trans}} + 7\Gamma_{Ln^{3+} \text{ cation}}^{\text{trans}} + 6\Gamma_{O^{2-} \text{ ion}}^{\text{trans}} + \Gamma_{BO_3}^{\text{lib}} + 2\Gamma_{PO_4}^{\text{lib}}$ $= 57A_g + 57B_g + 57A_u + 57B_u$ | | | | |

Subtracting the three acoustical modes ($A_u + 2B_u$), the number and type of vibrations are given in Table 6.

4.2. Experimental Results and Assignments

4.2.1. General considerations. Because the compounds $Ln_7O_6(BO_3)(PO_4)_2$ ($Ln = La, Nd, Gd,$ and Dy) possess the same factor group, their spectral features, such as band shapes, relative intensities, and band numbers, are similar except for the band locations (Figs. 3 and 4). Therefore, we use the $La_7O_6(BO_3)(PO_4)_2$ compound as the example for which the isotopic species study was carried out and assignments of vibrational modes are discussed in detail below. The assignments for Nd, Gd, and Dy borophosphate compounds can be obtained without much difficulty by extending the results and conclusions of $La_7O_6(BO_3)(PO_4)_2$.

The spectra of the isotopic species $La_7O_6(^{10}BO_3)(PO_4)_2$ are also shown in Figs. 3 and 4. All the experimental results, including isotopic shifts, are collected in Table 7.

The spectra of $La_7O_6(BO_3)(PO_4)_2$ may be divided into three regions approximately:

- (1) A series of high-frequency bands which are observed in the $1350\text{--}900\text{ cm}^{-1}$ region: these are related to the stretching vibrations of the triangular BO_3 and tetrahedral PO_4 ions.
- (2) A pattern of bands in the $780\text{--}310\text{ cm}^{-1}$ region: these bands are expected to be due to the bending vibrations of the triangular BO_3 and tetrahedral PO_4 ionic groups.
- (3) The bands below 310 cm^{-1} correspond to the external modes.

Some comments should be made about these assignments: (i) The distinction between stretching and bending vibrations is in agreement with the general vibrational behavior of BO_3 triangular and PO_4 tetrahedral groups and is experimentally justified by the lack of bands in the intermediate $910\text{--}750\text{ cm}^{-1}$ Raman region and $900\text{--}780\text{ cm}^{-1}$ infrared region for $Ln_7O_6(BO_3)(PO_4)_2$ ($Ln = La, Nd, Gd,$ and Dy). (ii) The distinction 310 cm^{-1} limit between the

TABLE 5
Application of the Correlation Method to the Internal Modes (with BO_3 Triangles and PO_4 Tetrahedra)

| $f^\gamma = n \cdot \nu_{\text{vib}}$ | ν_{vib}^a | Molecular symmetry of BO_3 ion D_3 | Site symmetry C_1 | Factor group symmetry C_{2h} | C_ξ | a_ξ | |
|---------------------------------------|----------------------|--|------------------------|-----------------------------------|---------|---|---|
| 4 | 1(ν_1) | A'_1 | A | A_g | 1 | 6 | |
| 4 | 1(ν_2) | A''_2 | | B_g | 1 | 6 | |
| 16 | 4(ν_3, ν_4) | E' | | A_u | 1 | 6 | |
| | | | | | | 1 | 6 |
| | | | | | | $\Gamma_{\text{BO}_3}^{\text{intramol}} = 6A_g + 6B_g + 6A_u + 6B_u$ | |
| $f^\gamma = n \cdot \nu_{\text{vib}}$ | ν_{vib}^a | Molecular symmetry of PO_4 ion T_d | Site symmetry C_1 | Factor group symmetry C_{2h} | C_ξ | a_ξ | |
| 4 | 1(ν_1) | A_1 | A | A_g | 1 | 9 | |
| 8 | 2(ν_2) | E | | B_g | 1 | 9 | |
| 24 | 6(ν_3, ν_4) | F_2 | | A_u | 1 | 9 | |
| | | | | | | 1 | 9 |
| | | | | | | $\Gamma_{\text{PO}_4}^{\text{intramol}} = 9A_g + 9B_g + 9A_u + 9B_u$ | |
| | | | | | | $\Gamma_{\text{Ln}_7\text{O}_6(\text{BO}_3)(\text{PO}_4)_2}^{\text{intravib}} = \Gamma_{\text{BO}_3}^{\text{intramol}} + 2\Gamma_{\text{PO}_4}^{\text{intramol}} = 24A_g + 24B_g + 24A_u + 24B_u$ | |

internal and external modes is less clear-cut. (iii) No attempt was made to discriminate between translational and rotational modes.

The internal modes of BO_3 and PO_4 ions can be assigned on the basis of results obtained from vibrational spectra measurements of other borate and phosphate groups and

from the expectation that the internal modes of the “free” complex will be close in frequency to that of the parent mode. The fundamental vibrational frequencies for BO_3 and PO_4 ions are listed in Table 8.

TABLE 6
Types and Activities of the Normal Modes of Rare Earth Borophosphate Compounds

| Type | Raman active | Infrared active |
|---------------------------------|--------------------|--------------------|
| Internal modes BO_3 | $6A_g$ $6B_g$ | $6A_u$ $6B_u$ |
| Internal modes PO_4 | $18A_g$ $18B_g$ | $18A_u$ $18B_u$ |
| Rotations | $9A_g$ $9B_g$ | $9A_u$ $9B_u$ |
| Translations | $48A_g$ $48B_g$ | $47A_u$ $46B_u$ |
| Total | $81A_g + 81B_g$ | $80A_u + 79B_u$ |

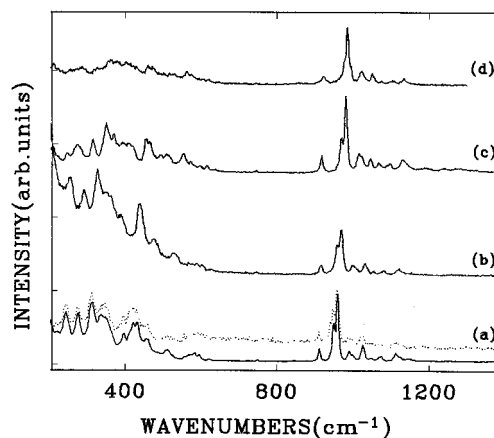


FIG. 3. Raman spectra of $\text{Ln}_7\text{O}_6(\text{BO}_3)(\text{PO}_4)_2$ ((a) La, (b) Nd, (c) Gd, and (d) Dy) showing the ^{10}B - ^{11}B isotopic shifts. The short dashed lines represent the spectra of ^{10}B isotopic species.

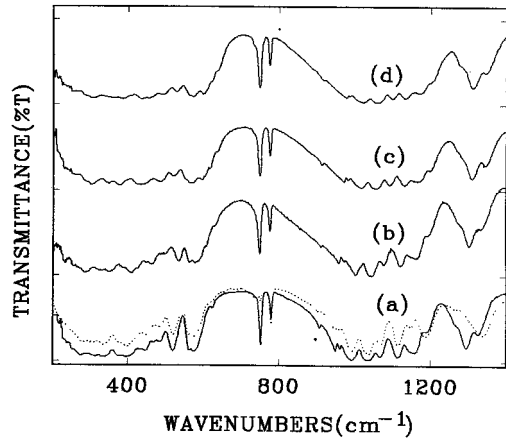


FIG. 4. Infrared spectra of $Ln_7O_6(BO_3)(PO_4)_2$ ((a) La, (b) Nd, (c) Gd, and (d) Dy) showing the ^{10}B – ^{11}B isotopic shifts. The short dashed lines represent the spectra of ^{10}B isotopic species.

4.2.2. *Vibrational assignment of BO_3^{3-} ions.* In a plane model of BO_3 , $\nu_1(A'_1)$ is totally symmetrical; $\nu_2(A''_2)$ is symmetrical about the symmetry axis but asymmetrical with respect to the plane of the molecule; and $\nu_3(E')$ and $\nu_4(E')$ are doubly degenerate, since the motion of the B atom is isotropic in the plane of the molecule. Therefore, the vibration $\nu_1(A'_1)$, unlike the other three, should not show an isotropic shift, because the B atom does not move in this vibration.

By application of the Teller–Redlich product rule (16) to the other three modes of a BO_3 group with D_{3h} symmetry, it can be obtained that

$$\frac{\nu_2^*}{\nu_2} = \frac{\nu_3^* \nu_4^*}{\nu_3 \nu_4} = \left(\frac{m_B}{m_{*B}} \cdot \frac{m_{*B} + 3m_O}{m_B + 3m_O} \right)^{1/2} = 1.029,$$

TABLE 7
Raman and Infrared Band Wavenumbers (cm^{-1}) and Assignments^a for $Ln_7BP_2O_{17}$ ($Ln = La, Nd, Gd, \text{ and } Dy$) Compounds

| $La_7BP_2O_{17}$ | | $Nd_7BP_2O_{17}$ | | $Gd_7BP_2O_{17}$ | | $Dy_7BP_2O_{17}$ | | Assignments |
|------------------|-------------------|------------------|----------|------------------|----------|------------------|----------|---------------|
| ^{10}B Raman | ^{11}B Infrared | Raman | Infrared | Raman | Infrared | Raman | Infrared | |
| | | | 1327 sh. | | 1335 sh. | | 1340 sh. | |
| | | 1339 s | 1295 s | | 1301 s | | 1310 s | $\nu_3(BO_3)$ |
| | | 1187 s | 1156 s | | 1162 s | | 1167 s | |
| 1110 w | 1114 m | 1115 s | 1113 s | 1122 m | 1120 s | 1130 m | 1132 s | |
| | 1074 w | 1068 m | 1066 m | 1082 w | 1076 m | 1098 w | 1092 s | |
| | 1044 vw | 1035 s | 1035 s | 1056 vw | 1044 s | 1068 w | 1058 s | $\nu_3(PO_4)$ |
| 1022 m | 1026 s | | | 1024 s | | 1046 m | | |
| 988 m | 988 s | 992 vs | 991 s | 1000 s | 1002 s | 1014 m | 1014 s | 1022 s |
| 958 s | 960 s | 959 sh. | 961 w | 970 s | 972 w | 980 vs | 985 w | 984 vs |
| 946 sh. | 950 sh. | 948 w | 948 m | 958 sh. | 957 m | 970 s | 971 s | 977 m |
| 910 m | 912 m | 909 vw | 907 m | 918 m | 912 vw | 918 m | 913 m | 922 m |
| | | 779 vs | 779 s | | 775 s | | 775 s | 774 s |
| | 756 w | 750 m | 751 vs | 746 w | 748 vs | 746 w | 749 vs | 748 vs |
| | | | 623 w | 632 w | | 616 w | | |
| | 626 w | | | 606 m | | | | |
| | 584 w | | | 588 w | | | | 598 w |
| | 572 w | 574 s | 574 s | 568 w | 576 m | 574 w | 591 sh. | 574 w |
| 512 w | 514 m | 520 s | 518 sh. | 530 m | 534 m | 556 m | 569 m | 529 m |
| | | 484 sh. | 487 sh. | | 496 w | 510 w | 521 m | 516 w |
| 460 sh. | 460 sh. | 448 sh. | 450 w | 474 m | 464 w | 494 w | 488 w | 496 w |
| | 432 s | | | 438 s | | 464 sh. | | 472 sh. |
| 422 s | 424 s | | | | | 454 m | | 460 m |
| 396 m | 396 m | 397 m | 396 m | 388 m | 411 m | 406 w | 431 w | 436 w |
| 340 m | 346 sh. | | | 358 sh. | | 392 w | | 402 w |
| | 334 w | 336 vw | 334 vw | 346 sh. | 353 w | 370 sh. | 376 m | 378 w |
| 310 s | 312 s | | | 326 s | | 350 s | | 360 w |
| 272 s | 276 s | 281 w | 276 m | 288 s | 288 m | 314 s | 300 m | 318 w |
| 240 s | 242 s | | | 250 s | | 272 m | | 284 m |
| 186 sh. | 186 sh. | | | | | 186 m | | 208 m |

^a Relative intensities: vs, very strong; s, strong; m, medium; w, weak; vw, very weak; sh, shoulder.

TABLE 8
Vibrational Frequencies of the Fundamental (in cm^{-1})
for BO_3 and PO_4 ions

| Ions | Ref. | ν_1 | ν_2 | ν_3 | ν_4 |
|---------------|------|---------|---------|---------|---------|
| BO_3 | (6) | 939 | 741 | 1330 | 606 |
| PO_4 | (16) | 980 | 363 | 1082 | 515 |

where ν^* and ν refer to the wavenumber of the light and heavy isotopic species, respectively. m_{O} is the mass of the oxygen atom; m_{*B} and m_B are the masses of the light and heavy boron isotopes, respectively. Average values of 10.10 (for m_{*B}) and 10.82 (for m_B) were used to take into account the actual isotopic compositions.

In the infrared spectrum of $\text{La}_7\text{O}_6(\text{BO}_3)(\text{PO}_4)_2$, two intense bands at about 1295 and 1156 cm^{-1} exhibit a very significant ^{10}B - ^{11}B isotopic shift, with ν_3^*/ν_3 being 1.034 and 1.027, respectively, and are thus unequivocally assigned to components of the $\nu_3(\text{BO}_3)$ vibrations. It is observed that the infrared spectra of the four rare earth borophosphates all contain a broad shoulder in the neighborhood of 1335 cm^{-1} , which are most probably due to the $\nu_3(\text{BO}_3)$ vibrations of $^{10}\text{BO}_3$ groups existing in boron with natural isotopic composition, and the corresponding band could be found at 1339 cm^{-1} in the spectrum of the isotopic species $\text{La}_7\text{O}_6(^{10}\text{BO}_3)(\text{PO}_4)_2$. The Raman bands of $\nu_3(\text{BO}_3)$ are so weak that they could not be observed at all.

As shown in Table 8, the bands $\nu_1(\text{BO}_3)$ due to the symmetric stretching mode of BO_3 should be observed around 939 cm^{-1} , and the $\nu_1(\text{PO}_4)$ often occurs approximately around 980 cm^{-1} . These two vibrational modes are too close to be separated by simply comparing them with the reported fundamental frequencies. However, another approach to this problem is to analyze the correlation between the vibrational frequency shifts of the same internal modes of $\text{Ln}_7\text{O}_6(\text{BO}_3)(\text{PO}_4)_2$ ($\text{Ln} = \text{La}, \text{Nd}, \text{Gd}, \text{and Dy}$) and the corresponding changes in lattice constants for La, Nd, Gd, and Dy borophosphates. This point will be discussed in detail later, and only the assignment results are given here. The medium Raman band at 912 cm^{-1} and the IR band at 907 cm^{-1} with negligible isotopic shifts are assigned to the $\nu_1(\text{BO}_3)$ vibrations of $\text{La}_7\text{O}_6(\text{BO}_3)(\text{PO}_4)_2$.

As discussed above, the $\nu_2(A_2'')$ of BO_3 groups should show an isotopic shift of 20 cm^{-1} in the neighborhood of 741 cm^{-1} , which is the reported fundamental frequency of $\nu_2(A_2'')(\text{BO}_3)$. In this region, the infrared spectrum of $\text{La}_7\text{O}_6(\text{BO}_3)(\text{PO}_4)_2$ consists of two intense and sharp bands at 779 and 751 cm^{-1} with the intensity ratio 2:5, which means that the band at 751 cm^{-1} is much stronger than the band at 779 cm^{-1} . Accordingly, the IR spectrum of its isotopic species contains one sharp and intense band at 779 cm^{-1} and another medium or nearly weak band at

750 cm^{-1} ; the intensity ratio of these two bands is about 2:1. Because the variation of their relative intensities is in relation with the isotopic ^{10}B composition of these samples, the two bands could be due to the $\nu_2(A_2'')$ of $^{10}\text{B}_3$ and $^{11}\text{BO}_3$ groups, respectively. The isotopic ratio is 1.039, which is higher than that calculated, but the latter is the result of an approximation. The rest of the bands in this region of the two infrared spectra can also be assigned to $\nu_2(\text{BO}_3)$ roughly. The ν_2 vibrations of BO_3 in the Raman spectrum are so weak that only a few bands can be observed in this region.

The ν_4 vibrations are also very weak so only a few bands can be observed in the region 580–630 cm^{-1} of the Raman and infrared spectra of $\text{La}_7\text{O}_6(\text{BO}_3)(\text{PO}_4)_2$.

4.2.3. Vibrational assignment of PO_4^{3-} . As shown in Table 8, the bands due to the symmetric stretching mode of PO_4 should be observed around 980 cm^{-1} , and the $\nu_3(\text{PO}_4)$ often occurs at approximately 1082 cm^{-1} . Except the bands assigned to the vibrational modes of BO_3 , the remaining bands are simply assigned to the stretching motions (ν_1 and ν_2) of the PO_4 ion. Above 960 cm^{-1} , the five Raman bands and four infrared bands in the region 1120–980 cm^{-1} are assigned to $\nu_3(\text{PO}_4)$. Below, the symmetric PO_4 stretching mode (ν_1) gives an intense Raman band at 960 cm^{-1} with a shoulder at 950 cm^{-1} and two infrared bands at 961 cm^{-1} (weak) and 948 cm^{-1} (medium), respectively.

According to Table 8, the ν_4 bending vibrations of PO_4 ions usually occur at approximately 515 cm^{-1} , and $\nu_3(\text{PO}_4)$ should be observed around 363 cm^{-1} . Therefore, in the medium-frequency region of the spectra of $\text{La}_7\text{O}_6(\text{BO}_3)(\text{PO}_4)_2$, except the ν_2 and ν_4 vibrational modes of BO_3 ions which usually occur at the relatively higher frequencies, the remaining low-frequency bands are assigned to the ν_4 and ν_2 vibrations of PO_4 groups with a rough distinction at 400 cm^{-1} , according to their respective fundamental frequencies.

4.2.4. Low-frequency region. The low-frequency peaks (below 310 cm^{-1}) are assigned to external modes, either rotations or translations of the anions and cations. The assignments in this region are only very fragmentary.

5. DISCUSSION

Since only powder samples are available, no symmetry information of vibrational modes can be obtained. In order to extend the assignment results of $\text{La}_7\text{O}_6(\text{BO}_3)(\text{PO}_4)_2$ to other rare earth borophosphates, we must rely on the comparison of frequency and intensity of their spectra, i.e., discussing the correlations between the observed vibrational frequencies in $\text{Ln}_7\text{O}_6(\text{BO}_3)(\text{PO}_4)_2$ ($\text{Ln} = \text{La}, \text{Nd}, \text{Gd}, \text{and Dy}$) with the lattice parameters, especially for the parameters b , because the folded layers containing these two groups are parallel to the y -axis.

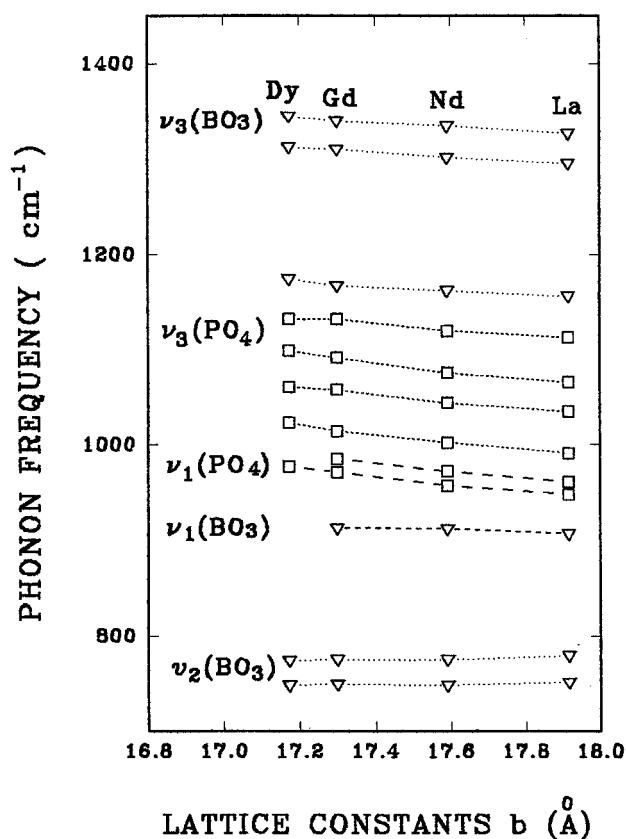


FIG. 5. Comparison of frequencies of infrared-active vibrational modes in La, Nd, Gd, and Dy borophosphates. Internal modes are labeled with the appropriate free borate and phosphate frequency (ν_i).

The relationship between the frequencies ($\geq 750 \text{ cm}^{-1}$) of infrared internal vibration bands in La, Nd, Gd, and Dy borophosphates and the lattice parameters b is present in Fig. 5. For the Raman spectra the relationship resembles the infrared spectra. In Fig. 5, broken lines connect bands of the same mode character according to the above assignments, the square symbols represent the vibrational modes of PO_4 tetrahedron, and the triangles represent those of BO_3 triangles.

It is obvious from Fig. 5 that the internal mode frequencies are lattice dependent. As the lattice parameter b of these rare earth borophosphates decreases from La to Dy linearly, the length of the phosphorus–oxygen and boron–oxygen bonds decreases, so the strength of these bonds increases, which leads to the internal vibrations of BO_3 and PO_4 ion groups shifting to higher frequency.

According to Palkina's structure model of $\text{La}_7\text{O}_6(\text{BO}_3)(\text{PO}_4)_2$, there are eight PO_4 tetrahedra and four BO_3 triangles in each unit cell, each kind of ion lying on individual lamina parallel to the y -axis. Therefore, the effect of lattice parameter contraction on the length decrement of the P–O bond is distinctly greater than that on the B–O bond. Accordingly, the incremental slope of PO_4 vibrational frequencies is obviously greater than that of corresponding BO_3 vibrational frequencies.

The ν_1 , ν_3 , and ν_4 modes involve some degree of bond stretching and shift in frequency accordingly. The contrasting remarkable insensitivity of the $\nu_2(\text{BO}_3)$ modes to the change of lattice parameters b can be understood in that, to a first approximation, these modes involve B–O bond angle deformation rather than a change in bond length. This supports our assignment of these modes.

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