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Interband Transitions and Phonon Spectra of Si-Doped $B_{12}P_2$

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Optical absorption and FT Raman spectra of polycrystalline $B_{12}P_2$ prepared by CVD on silicon substrates are presented. The silicon content is rather high, and we assume that a ternary compound with the structure formula $B_{12}(P_2)_{1-x}(Si_2)_x$ is formed. The absorption edge yields indirectly allowed transitions at 1.62, 1.80, 2.17, 2.46, and 2.75 eV, the energies of which are considerably lower than those reported by G. A. Slack *et al.* (1983, *J. Phys. Chem. Solids* 44, 1009) for pure $B_{12}P_2$. Six gap-state related transitions have ionization energies, which agree with those of electron traps in β-rhombohedral boron. The number of one-phonon resonance frequencies agrees exactly with that predicted from group theory. The two-phonon spectra are quantitatively determined. Strong luminescence radiation superimposes the FT Raman spectrum, which differs qualitatively from that traditionally measured. This difference is explained by fluctuating distortions of the icosahedra related to the strong optical excitation of trapped electrons. © 1997 Academic Press

INTRODUCTION

In idealized $B_{12}P_2$ the P atoms saturating the outer bonds of the equatorial atoms of the adjacent icosahedra form a two-atom chain on the main diagonal in the typical unit cell of the α-rhombohedral boron structure (1). The existence of a homogeneity range with excess and deficite P atoms has been proved (1–4). $B_{12}P_2$ is p-type with hole mobilities up to $700\,\mathrm{cm^2\,v^{-1}\,s^{-1}}$ and extremely high Seebeck coefficients of 10 to $20\,\mathrm{mVK^{-1}}$ (5). Experimental optical investigations were published by Slack *et al.* (2) on the band gap, by Tallant *et al.* (6), and Shirai *et al.* (7) on the phonon spectra, and by Werheit *et al.* (8) on the optical properties in general. Theoretical studies on lattice vibrations were made by Beckel *et al.* (9) and Shirai *et al.* (7). In the present paper we present results of optical measurements in different spectral ranges on $B_{12}P_2$ highly doped with silicon.

SAMPLE MATERIAL

The samples were prepared by CVD on Si(100) surfaces under optimized conditions at 1100°C. The Si substrate was chemically removed with a HF–HNO_3 solution. For details see Ref. (10). The initial layer thickness ($\sim 65\,\mu$m) was reduced by mechanical grinding and polishing to plane-parallel samples 25, 45, and 50 μm thickness. From a SIMS analysis on a much thinner layer it is known that the Si concentration at the interface is about 10^{21} atoms/cm^3 (8). Since only material from the interface side is removed, the Si content in the actual samples is assumed to be considerably lower, probably $\lesssim 10^{19}\,\mathrm{cm^{-3}}$. The concentration of other impurities (Na, K, Ca, and Sn) does not exceed $10^{15}\,\mathrm{cm^{-3}}$.

From the different thinkable possibilities to accommodate the Si atoms we prefer the formation of a ternary compound $B_{12}(P_2)_{1-x}(Si_2)_x$, which would be similar to the accommodation of Si atoms in boron carbide. For a more detailed discussion on this question see Ref. (8).

EXPERIMENTAL

The optical absorption spectra of $B_{12}P_2$ have been measured for photon energies between about 6 meV and 3.3 eV. For lower energies ($\lesssim 0.7$ eV) a FTIR spectrometer was used. For higher energies ($\gtrsim 0.5$ eV) we used a commercial grating spectrometer with the sample position behind the double monochromator to avoid optical excitation of the

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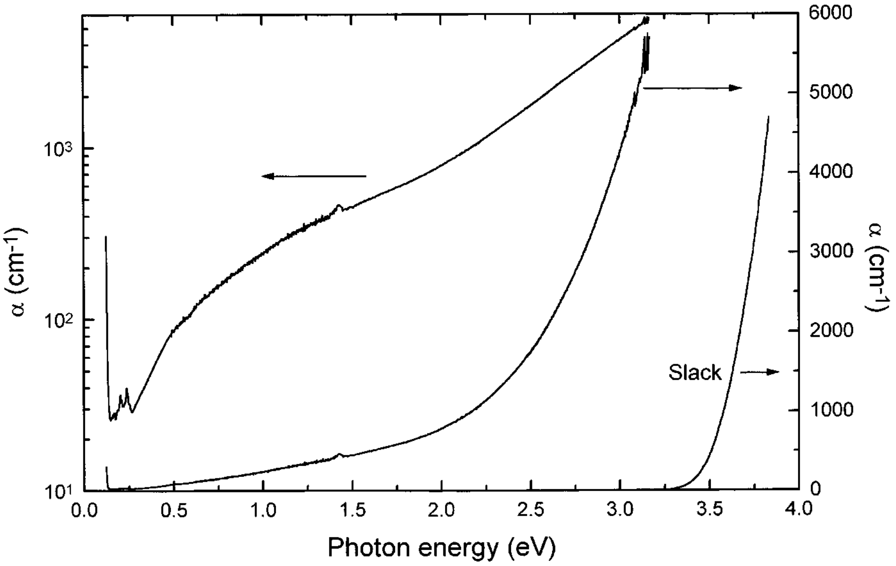

FIG. 1. Absorption edge of $B_{12}P_2$ doped with Si (present work) compared with results reproduced from Slack *et al.* (2) on probably pure $B_{12}P_2$. The small peak at 1.44 eV occurs at the switching point between two detectors of the spectrometer and is not real.

sample. Raman measurements were performed with a FT Raman spectrometer using a Nd:YAG laser for excitation. In Fig. 1 the absorption edge and its low-energy tail is shown. Compared with the result of Slack *et al.* (2) the edge is considerably shifted toward lower energies. The spectral range of IR active phonons is separated into one-phonon processes between about 300 and 1100 cm^{-1} (Fig. 2) and two-phonon processes extending up to between about 1200 and 2200 cm^{-1} (Fig. 3). Some of the one-phonon bands are split because of the slightly different resonance frequencies of ^{10}B ($\sim$19%) and ^{11}B isotopes ($\sim$81%). FT Raman spectra obtained for two different intensities (several watts) of the exciting Nd : YAG laser are shown in Fig. 4. These Raman spectra are obviously superimposed by a strong luminescence radiation. Moreover they are characterized by only few broadbands, and hence they differ qualitatively from a Raman spectrum obtained by the conventional method (excitation power 400 mW) (7).

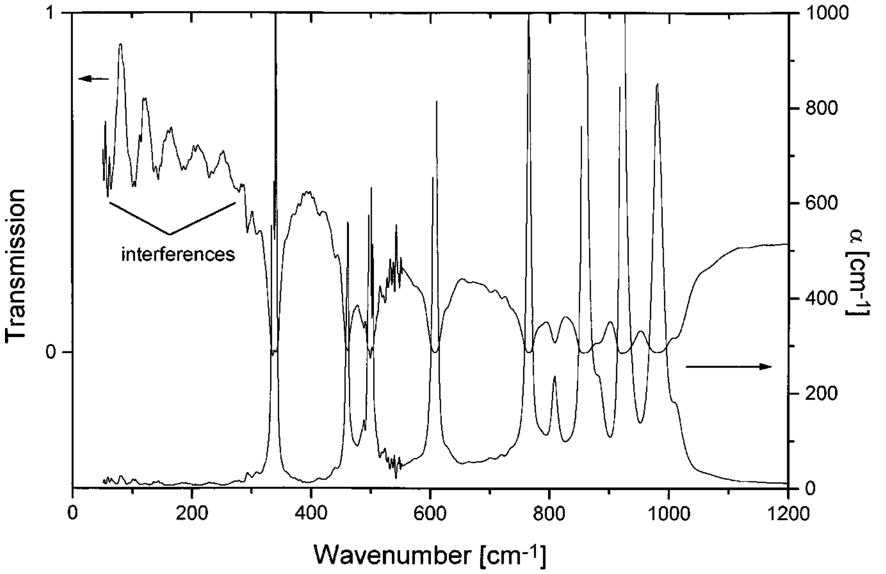

FIG. 2. One-phonon transmission and absorption spectra of $B_{12}P_2$. In the center of the strongest peaks, the transmission is too low to determine the absorption coefficients reliably. At low wave numbers interferences within the 45-μm-thick sample occur. The weak peaks in the ranges of low absorption (350–430 cm^{-1} and 650–730 cm^{-1}) are due to interferences as well. Because of the strong dispersion in these ranges, the evaluation is not meaningful.

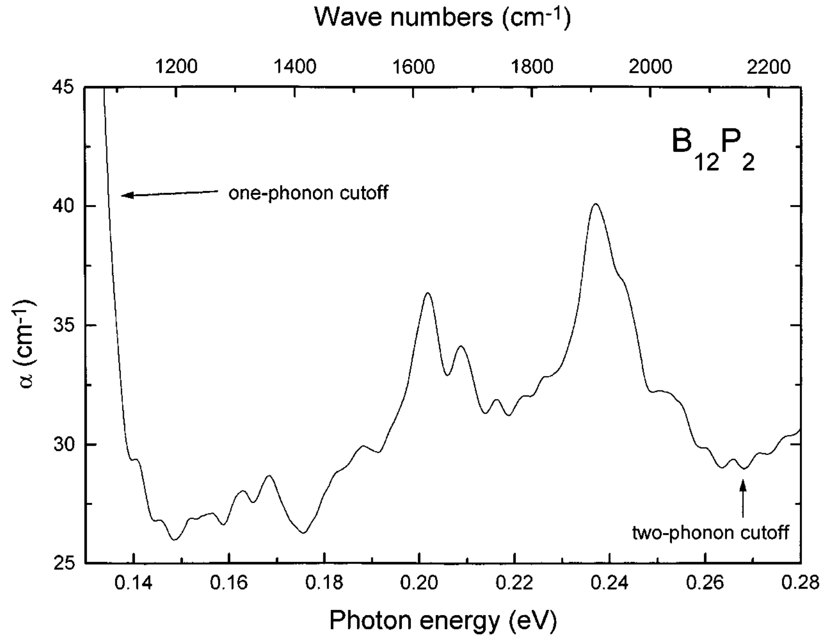

FIG. 3. Two-phonon spectrum of $B_{12}P_2$. The weak equidistant peaks at the high-energy of the spectrum are due to interferences.

DISCUSSION

a. Electronic Transition

The shift of the absorption edge relative to that published by Slack *et al.* (2) is by far too large to be explained by experimental error. Yang and Aselage (11) report on $B_{12}P_2$ samples, which are visually transparent contrary to ours, and therefore their samples seem to be closer to those investigated by Slack *et al.* (2). Obviously the band gap of $B_{12}P_2$ strongly depends on the specific material properties. In the case of our material the influence of Si doping seems to be prevailing.

Based on the theories of interband transitions (see, e.g., (12)) and deep level to band transitions (13) the absorption edge was decomposed by use of a local computer program. Transition energies from deep levels to parabolic bands

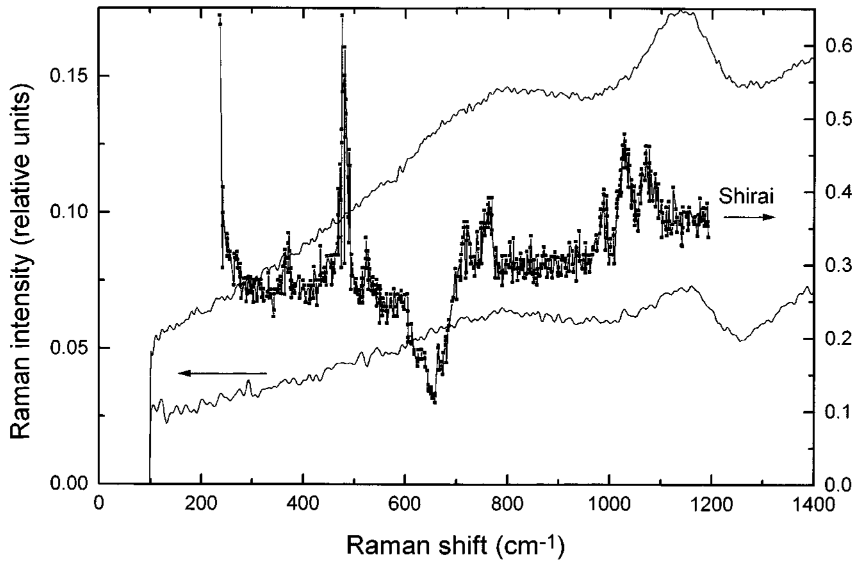

FIG. 4. FT Raman spectra of $B_{12}P_2$ obtained at different excitation intensities of the Nd : YAG laser. The conventionally measured Raman spectrum of a comparable sample (Shirai *et al.* (7)) is shown for comparison.

were determined at 0.075(5), 0.175(5), 0.27(1), 0.353(3), 0.423(3), 0.569(3), 0.749(3), 0.954(3), 1.187(5), and 1.49(2) eV. Those at 0.175, 0.353, 0.569, 0.749, 0.954, and 1.187 eV agree quite well with the sequence of electron traps in β-rhombohedral boron (14, 15). Energies of indirectly allowed interband transitions are 1.62(3), 1.80(2), 2.17(3), 2.46(1), and 2.75(1) eV. A more detailed characterization of the interband transitions requires a temperature-dependent investigation. Unfortunately there is no overlap with the transitions energies resulting from the spectrum published by Slack *et al.* (2). When the correct theory of interband transitions ($\sqrt{\hbar\omega \cdot \alpha} \propto \hbar\omega$) is applied on their spectrum, it yields transition energies of 3.18, 3.28, 3.36, and 3.46 eV.

b. IR Active Phonons

From interference patterns in the transmission and reflectivity spectra of a 45-μm sample the static and the optical dielectric constant were estimated (Table 1). In their difference $\Delta n = 0.03$ and $\Delta\varepsilon = 0.15$ respectively, the error essentially coming from the thickness measurement is cancelled. These results show that the integral oscillator strength of the IR-active phonons in $B_{12}P_2$ is low as typical for the boron-rich solids. Therefore the characterization of the oscillator strengths of one-phonon processes in Table 2 and two-phonon processes in Table 3 is to be taken as relative only.

The split of some phonons (nos. 5, 8, and 10) attributed to different atomic masses of ^{10}B and ^{11}B isotope yields an average isotope-dependent shift of factor 1.03818. This deviates from the estimation $\omega_{^{10}\mathrm{B}}/\omega_{^{11}\mathrm{B}} = \sqrt{m_{^{11}\mathrm{B}}/m_{^{10}\mathrm{B}}} = 1.0488$ by -1.6% only, which can be attributed to the different zero-point energies of the boron isotopes. This value agrees satisfactorily with corresponding values estimated fro $LiAlB_{14}$ (-1.6%) (16) and -2.0% (17) and -0.9% (18) for β-rhombohedral boron. It is somewhat higher than the -0.4% estimated for the central atom in the three-atom chain in boron carbide (19).

The number of ten IR-active phonons agrees with that predicted from group theory ($4A_{2u}$ and $6E_u$) (20). Unfortunately in the spectra obtained on polycrystalline material the different symmetry types cannot be distinguished. However, obviously no accidental degeneration exists.

TABLE 1
Static and Optical Refractive Indices and Dielectric Constants of $B_{12}P_2$ Obtained from Interferences

Spectral range (cm^{-1})	n	ε_r
2121.58–2939.35	$n_\infty = 2.54(15)$	$\varepsilon_\infty = 6.45(70)$
62.2–275.8	$n_0 = 2.57(15)$	$\varepsilon_0 = 6.60(70)$

Note. The error is essentially caused by the thickness measurement with an accuracy of about ± 3 μm$\hat{=}$6%.

TABLE 2
$B_{12}P_2$, IR Active One-Phonon Modes Determined from the Absorption Spectrum

	Wave number (cm^{-1})	Attribution	Remarks
1	338		Strong
2	458		Strong
3	488		Weak
4	498		Strong
5a	608	^{11}B isotope	Strong
b	627	^{10}B isotope	Weak
6	764		Strong
7	808		Medium
8a	856	^{11}B isotope	Strong
b	882	^{10}B isotope	Weak
9	920		Strong
10a	980	^{11}B isotope	Strong
b	1013	^{10}B isotope	Weak

The two-phonon combination frequencies (Table 3) represent the phonon density at the boundary of the Brillouin zone. The small deviations from the sum frequencies of one-phonon processes indicate weak dispersion of the IR phonon branches in the Brillouin zone.

c. Raman-Active Phonons Luminescence

We explain the qualitative difference between the FT Raman spectra exhibiting only few broadbands super-

TABLE 3
$B_{12}P_2$, Two-Phonon (IR Active Modes)

	Wave number (cm^{-1})	Remarks
1	1130	
2	1169	
3	1225	
4	1255	
5	1310	
6	1354	
7	1471	
8	1514	
9	1572	
10	1624	Strong
11	1680	Strong
12	1740	
1	1790	
13	1822	
14	1908	Strong
15	1951	
16	2025	
17	2050	
18	2094	Probably interference peak

imposed by strong luminescence radiation and the conventionally measured Raman spectrum with narrow bands (see Fig. 4) as follows. Taking into account the results obtained on other boron-rich solids, in particular, β-rhombohedral boron, it seems sensible to attribute the tail of the absorption edge to high-density occupied intrinsic electron traps in the band gap. These traps are generated by interaction between electrons and intraicosahedral phonons, leading to a distortion of the icosahedra (see, for example, Refs. (14, 15)). If in thermal equilibrium the majority of the icosahedra is distorted as can be concluded from the strong absorption in the absorption edge tail, this structure may be largely homogeneously distorted, hence yielding a Raman spectrum like that of a largely undistorted crystal. However, if in the case of a very strong optical excitation a considerable portion of the electron traps is emptied, in connection with the retrapping processes a strong fluctuation of differently distorted and undistorted icosahedra in the whole structure results. If according to β-rhombohedral boron, six different distortions of the icosahedra are possible (14, 15), the Raman spectrum, which reacts very sensitively to local structural distortions, changes to that of a strongly distorted solid. This asumption is supported by similar features in the FT Raman spectra of amorphous boron (21) and YB_{66} (22). Accordingly we attribute the broad peaks in the FT Raman spectrum of $B_{12}P_2$ at 1140 and 810 cm^{-1} to the averaged intericosahedral B–B vibrations and intraicosahedral lattice vibrations respectively, which vary only slightly in the different structures of the boron-rich solids.

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