JOURNAL OF SOLID STATE CHEMISTRY **133,** 260–263 (1997)
ARTICLE NO. SC977452

FTIR and FT Raman Spectra of B_6O

H. Werheit and U. Kuhlmann

Solid State Physics Laboratory, Gerhard Mercator University Duisburg, D-47048 Duisburg, Germany

Received April 14, 1997; accepted April 28, 1997

The IR active phonon spectrum of B_6O is typical for the α-rhombohedral boron structure group. The number of phonons corresponds exactly to that predicted by group theory. The phonon bands in the spectrum are weakly damped, indicating that the structure is largely undistorted. Contrary to the IR spectrum the FT Raman spectrum exhibits no narrow lines but considerably broadened bands. This leads to the conclusion that the strong optical excitation by the Nd:YAG laser with about 2 W irradiation power causes a considerable distortion of the structure by fluctuations in consequence of the interaction between optically excited electrons and intraicosahedral phonons.
© **1997 Academic Press**

INTRODUCTION

B_6O belongs to α-rhombohedral boron structure group (1). In the rhombohedral unit cell, which is determined by B_{12} icosahedra at the vertices, two oxygen atoms are accommodated on the main diagonal saturating the external equatorial bonds of the three adjacent icosahedra. The distance between the oxygen atoms is so large that bonding between them can largely be excluded. The first IR transmission spectra were observed by Becher and Thévenot on B_6O powder (2). IR spectra with higher resolution obtained on bulk material were published by Werheit *et al.* (3, 4) and in particular by Kuhlmann *et al.* (5) in comparison with boron carbide spectra, however without interpretation. A group theoretical analysis of the lattice vibrations was made by Werheit and Haupt (3). Beckel *et al.* (6) calculated the phonon frequencies and intensities by a classical central force field model.

In the present paper highly resolved IR phonon spectra and FTIR Raman spectra of B_6O will be presented and discussed in some detail.

SAMPLE MATERIAL AND STRUCTURE

The investigated B_6O was obtained by hot pressing. Unfortunately no details about purity and preparation conditions have become known. It is assumed that the preparation essentially followed the procedure described by Brodhag and Thevenot (7). The sample contains numerous pores of typically about 1 to 3 μm diameter. Nevertheless, as can be deduced from the IR spectra shown below, the crystal structure is only weakly distorted.

B_6O (structure formula $B_{12}O_2$) belongs to the space group $R\overline{3}m$. Structure refinements by the Rietveld method have recently been performed by Bolmgren *et al.* (8) and Higashi *et al.* (9) and yielded the hexagonal cell parameters $a = 5.366(1)$ Å, $c = 12.331(3)$ Å and $a = 5.374(2)$ Å, $c = 12.331(3)$ Å respectively. The interatomic distance between the oxygen atoms found to be 3.06(2) and 3.08(2) Å respectively was confirmed by Kawai *et al.* (10) by oxygen $K\alpha$ X-ray-emission spectroscopy. Since the distance between the oxygen atoms is more than twice that in free O_2 molecules (1.21 Å), bonding between them is largely excluded.

EXPERIMENTAL

Reflectivity spectra of the samples were obtained with a fourier transform IR spectrometer 113v (Bruker, Karlsruhe) in the spectral range between 20 and 5000 cm^{-1} with a resolution of 2 cm^{-1}. By use of the Kramers–Kronig relation (KKR) the absorption spectra were calculated. Toward high frequencies the prerequisite for KKR was fulfilled, because the measurements were extended to the approximately dispersion-free range between absorption edge and lattice vibrations. Toward low frequencies there is no dispersion-free range in B_6O because of the dynamical conductivity leading to a monotonous increase of the reflectivity toward low frequencies. However, using a suitable extrapolation, which takes this behavior into account, the prerequisite for the allowable application of the KKR could be realized.

The Raman spectra were measured with a commercial FT Raman supplement equipment of the FTIR spectrometer (Bruker). It contains a Nd:YAG laser (1.07 μm = 1.16 eV) for excitation. This laser allows irradiation powers up to 4 W. The measurements were performed largely in back scattering geometry.

0022-4596/97 $25.00

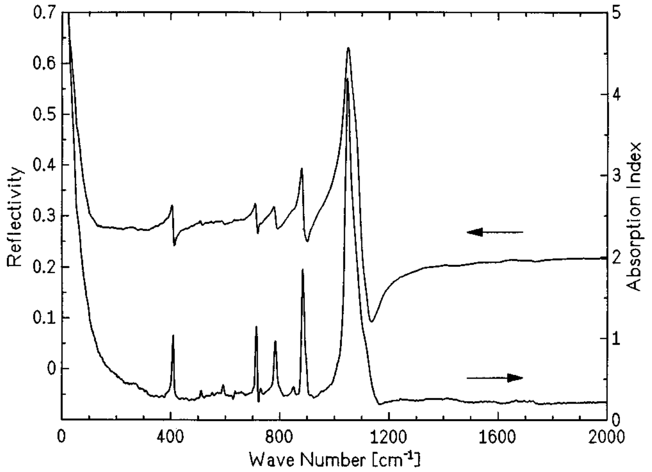

FIG. 1. (a) Reflectivity and (b) absorption index of B_6O.

RESULTS

Reflectivity and absorption index of B_6O measured at room temperature are shown in Fig. 1. The resonance frequencies, the oscillator strengths, and the damping constants derived from the spectra are listed in Table 1. Since the measurements were performed on polycrystalline material the symmetry type of the phonons could not be determined by experiment. Therefore in Fig. 2 the experimentally determined phonon frequencies are correlated with those determined theoretically by Beckel *et al.* (6). For the five strong phonons this correlation is inevitable. The others are attributed to one another in the sequence of frequencies.

TABLE 1
Resonance Frequencies $\tilde{\nu}$ (Error Margin 2 cm^{-1}), Oscillator Strenghts $\Delta\varepsilon$ (Error Margin 0.005), and Damping Constants γ (Error Margin 1.6 cm^{-1}) of the IR Active Phonons of B_6O

$\tilde{\nu}$	$\Delta\varepsilon$	γ	Symmetry type
(270)			
(301)			
408.9	0.099	8.2	E_u
511.6	0.008	6.8	A_{2u}
592.1	0.012	9.6	E_u
713.6	0.080	9.6	E_u
731.0	0.011	7.7	E_u
783.1	0.063	11.6	A_{2u}
850.6	0.009	11.6	A_{2u}
883.4	0.137	11.6	A_{2u}
(897)			
1047.3	1.506	40.5	E_u
1117			E_u

Note. Uncertain resonance frequencies in parentheses. Probable symmetry types of the phonons as obtained by the correlation to calculations (6) in Fig. 2.

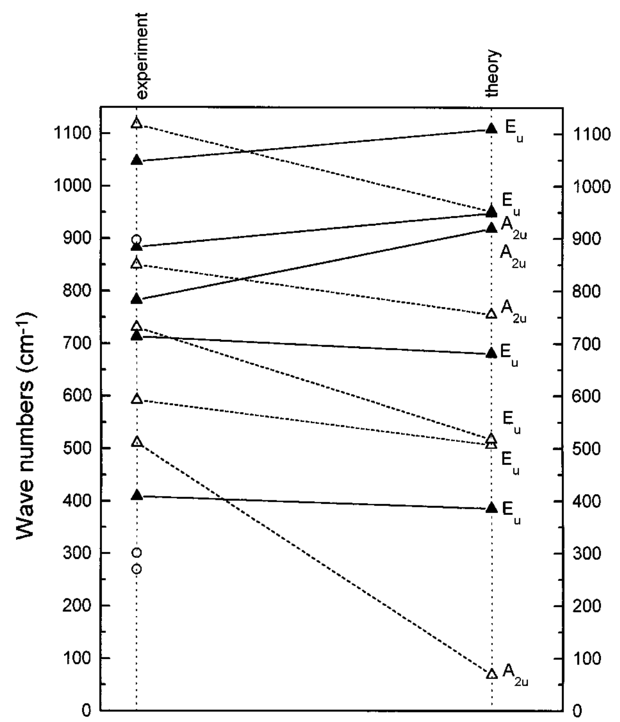

FIG. 2. Correlation between the experimentally determined phonon resonance frequencies and those theoretically calculated by Beckel *et al.* (4). The attribution of the five strongest phonons (▲) was inevitable. The weak phonons (△) were attributed according to their sequence in frequency. The uncertain phonons in the experimental spectrum are marked by open circles (○).

From the exactly measured reflectivity in the spectral range between absorption edge and lattice vibrations the real part of the optical dielectric constant was determined. R (2000 cm^{-1}) = 0.22 yields n (2000 cm^{-1}) = 2.77 and $\varepsilon_\infty = 7.7(1)$. This value is between those of β-rhombohedral boron ($\varepsilon_\infty = 8.9$ (see (11)) and boron carbide ($\varepsilon_\infty = 7.3$) (12).

FT Raman spectra of B_6O measured at two different excitation intensities are shown in Fig. 3. While the weaker excitation intensity is about 1 W and the higher one is larger by a factor of about 1.3 only, the Raman signal increases by about one order of magnitude. Nevertheless the noise is much lower. Contrary to the IR spectrum the Raman phonon peaks are broad, indicating high damping constants. Moreover, starting at a Raman shift of about 1170 cm^{-1} (equivalent absolute energy 1.02 eV compared with the energy of the laser radiation of 1.17 eV) at high excitation intensities a strong luminescense increasing toward lower energies is found. The resonance frequencies of the Raman active phonons are listed in Table 2.

DISCUSSION

According to group theory (5), 10 IR active phonons (4 A_{2u} and 6 E_u), and 11 Raman active phonons (5 A_{1g} and

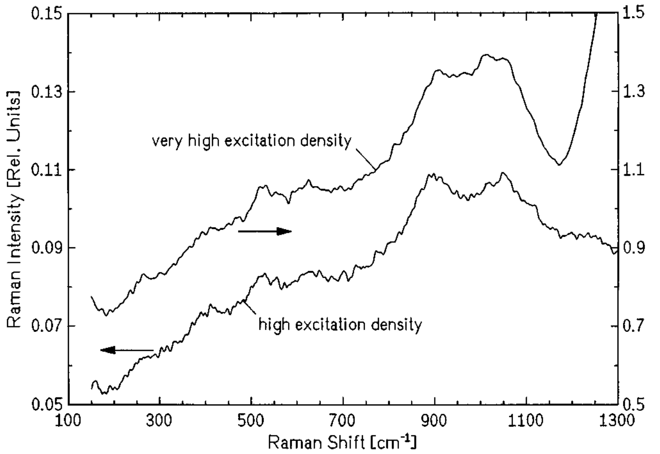

FIG. 3. FT Raman spectra of B_6O measured at different excitation powers of the Nd:YAG laser. The weaker intensity was about 1 W, the higher one about 1.3 W.

6 E_g) are expected. The IR and the Raman spectra yield the predicted number of resonance peaks each. Apparently no accidental degeration occurs.

Since the distances of icosahedral atoms are nearly the same in B_6O and boron carbide, the according phonon spectra are expected to be closely related. However, the strong phonon of boron carbide at $1430\,\text{cm}^{-1}$ due to the stretching mode of the three-atomic chain (5) is missing in the spectrum of B_6O as in that of α-rhombohedral boron (13). On one hand this is in agreement with group theory, according to which the stretching mode of a two-atomic arrangement is not IR active but Raman active only. On the other hand, according to the structure investigations there is no bond between both oxygen atoms, and for this reason no vibration will occur. This is confirmed by the observed Raman spectrum measured, where the highest resonance frequency is at 1243 cm^{-1}. This vibration is attributed to intericosahedral phonons like in α-rhombohedral boron (11).

TABLE 2
Resonance Frequencies $\tilde{\nu}$ of the Raman Active Phonons of B_6O

$\tilde{\nu}$ (weak excitation) (cm^{-1})	$\tilde{\nu}$ (strong excitation) (cm^{-1})	Raman scattering intensity
264(5)	264(5)	Weak
398(6)	396	Weak
521	519	Weak
530	534	Weak
556	555	Weak
639(10)	627	Weak
(773)		
902(10)	909	Strong
1034(16)	1034(20)	Strong
1119		Medium
(1243)		Weak

Note. Strong and weak excitation intensities differ by a factor 1.3. Uncertain resonance frequencies and error margins in parentheses.

Like in the spectra of all other representatives of the α-rhombohedral boron structure group the intraicosahedral vibrations of B_6O are found in the spectral range between about 400 and $1100\,\text{cm}^{-1}$. The strong vibration at $407\,\text{cm}^{-1}$ in boron carbide is attributed to an accidental degeneration of the mode of the free icosahedron shifted in the crystal field and the bending mode of the three-atomic chain (3). Since this vibration is missing in B_6O, its related phonon at 408.9 cm^{-1} is much weaker.

The small half-width of the phonon bands in the IR spectrum proves that the crystal structure of the investigated B_6O sample is only slightly distorted. In contrast, the phonon bands in the FT Raman spectrum are considerably broadened. A similar result is known from $B_{12}P_2$ (14), where the FT Raman spectrum could be compared with a conventional Raman spectrum using a much lower irradiation power and yielding narrow phonon bands comparable with the IR active phonons. This leads to the conclusion that the broadening of phonon bands in the FT Raman spectra of both representatives of the α-rhombohedral boron structure group is caused by the high irradiation power of the Nd:YAG laser. We attribute the strong damping to the distortion of the B_{12} icosahedra by electron–phonon interaction similar to that in β-rhombohedral boron (15–17).

The strong luminescence proves that the energy of the Nd:YAG laser is sufficient to excite electrons into higher states, probably into the conduction band. These electrons generate intrinsic trapping states by interaction with intraicosahedral phonons. In consequence of the high excitation power the reallocation of these states by trapping and optical reexcitation leads to a considerable fluctuation in the distortion of the icosahedra. This fluctuation is assumed to be the reason for the strong damping of the phonon bands in the FT Raman spectrum. That explanation is supported by the fact that when excitation density is increased further the damping decreases (see Fig. 3) as expected for the case that the density of occpied traps approaches saturation.

The reflectivity of B_6O strongly increasing toward low frequencies in the FIR part of the spectrum is due to the dynamical conductivity. As in other boron-rich solids it can be described by a superposition of Drude type and hopping type transport.

ACKNOWLEDGMENT

The authors are grateful to Dr. K. A. Schwetz, Elektroschmelzwerk Kempten (ESK) for providing the B_6O sample.

REFERENCES

1. T. Lundström, *AIP Conf. Proc.* **231,** 186 (1990).
2. H. J. Becher and F. Thévenot, Z. *Anorg. Allg. Chem.* **410,** 274 (1974).
3. H. Werheit and H. Haupt, *Z. Naturforsch A* **42,** 925 (1987).
4. H. Werheit, *Prog. Cryst. Growth Charact.* **16,** 179 (1988).
5. U. Kuhlmann, H. Werheit, and K. A. Schwetz, *J. Alloys Compd.* **189,** 249 (1992).
6. C. L. Beckel, B. S. Abbott, T. J. Schilling, B. L. Zink, *in* "Proc. 11th Int. Symp. Boron, Borides and Related Comp., Tsukuba 1993, "JJAP Series 10, p. 76, (1994).
7. C. Brodhag and F. Thevenot, *J. Less-Common Met.* **117,** 1 (1986).
8. H. Bolmgren, T. Lundström, and S. Okada, *AIP Conf. Proc.* **231,** 197 (1990).
9. I. Higashi, M. Kobayashi J. Bernhard, C. Brodhag, and F. Thévenot, *AIP Conf. Proc.* **231,** 201 (1990).
10. J. Kawai, K. Maede, I. Higashi, M. Takami, Y. Hayashi, and M. Uda, *Phys.* Rev. *B* **42,** 5693 (1990).
11. H. Werheit, *in* "Landoldt Börnstein, Numerical Data and Functional Relationships in Science and Technology" (O. Madelung, M. Schulz, and H. Weiss, Eds.), New Series, Vol. 17e, p. 9. Springer–Verlag, Berlin/New York, 1983.
12. U. Kuhlmann, Thesis, University of Duisburg, 1994.
13. H. Werheit, U. Kuhlmann, N. E. Solov'ev, G.P. Tsiskarishvili, and G. Tsagareishvili, *AIP Conf. Proc.* **231,** 350 (1990).
14. H. Werheit, U. Kuhlmann, K. Shirai, and Y, Kumashiro, *J. Alloys Compd.* **233,** 121 (1996).
15. H. Werheit and U. Kuhlmann, *Solid State Commun.* **88,** 421 (1993).
16. H. Werheit, M. Laux, and U. Kuhlmann, *Phys. Status Solidi B* **176,** 415 (1993).
17. H. Werheit, U. Kuhlmann, M. Laux, and T. Lundström, *Phys. Status Solidi* B 179, 489 (1993).