THz Spectrum and ionic polarizability of PbB_4O_7 Crystal

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***Abstract* —The terahertz refractive index n(ν) of lead tetraborate (PbB_4O_7) crystal decreases due to vanish of the ionic polarizabilities in sequence of the Pb^{2+}, O^{2-} and B^{3+} ions when the frequency increasing. The ionic polarizabilities are calculated by the Clausius-Mossotti relation, α_{Pb} is $0.428\times10^{-24}cm^3$ and α_O is $0.049\times10^{-24}cm^3$ respectively.**

I. INTRODUCTION

The crystals in the borates material family have various characters resulted from various configurations of the B-O bonds. It is significant to investigate the structures and properties of borate materials in different spectral region for novel device applications.

The time domain spectra in the range of 0.25-2.5 THz were measured for five borate crystals: Na_5 $[B_2P_3O_{13}]$, Zn_3BPO, SrB_4O_7, $Na_3La_9O_3$ and PbB_4O_7 at room temperature[1]. The power absorption coefficient α(ν) and refractive index n(ν) were studied. It is found that the refractive index spectra n(ν) of the four samples are more smooth and smaller than 3.5 in the range except lead tetraborate PbB_4O_7(PBO). We suppose that it was correlation to an effect of Pb^{2+} ion which is a heavy element.

II. EXPERIMENT

The lead tetraborate (PbB_4O_7) is orthorhombic crystal system, space group mm2 and two formula units per unit cell (*Z*=2). The lattice parameters are: a=0.4251nm, b=0.4463nm and c=1.086nm[2]. The sample was cut along the (001) plane and twin polished. The thickness is 0.845 mm.

The ultraviolet-visible-infrared spectra have been measured by ShiMaDZu Corporation's spectrum analyzer. The curves of reflectance R(λ) and transmission T(λ) of the PBO have been measured in a wavelength range from 200nm to 2000nm at room temperature.

The THz time domain spectrum is measured using transmission in a range from frequency 0.2THz to 3.0 THz.

III. RESULTS

The Fig. 1 is reflectance R(λ) and transmission T(λ) curves of the PBO crystal in a range 200nm-2000nm. The forbidden band energy E_g of PbB_4O_7 is 5.64 eV (λ=220nm) and the dielectric function ε_1=6.0 from the transmission R(λ) and T(λ) curves.

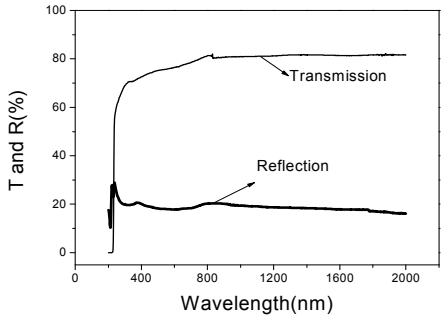

Fig. 1 The reflectance R(λ) and transmission T(λ).

THz time-domain spectrum of the PBO crystal was measured in room temperature. Absorption coefficient α(ν) of was obtained from the Fourier transform and data calculated. The refractive indix n(ν) was calculated from the relations between optical constants. The absorption coefficient α(ν) is smaller than $20cm^{-1}$ in the regions from 0.3THz to 1.5 THz, and it is larger than $40cm^{-1}$ in the regions from 1.7THz to 3.0 THz as shown in Fig. 2. The refractive index n(ν) is shown in Fig.3. There are three peaks in the n(ν) curve.

The dielectric function $\varepsilon_1(\nu)$ curve can be got from the n(ν) curve, it is conform to the n(ν), and two $\varepsilon_1(\omega)$ peaks value are 34.28 (at 1.56THz) and 29.95 (at 2.34THz). The imaginary part of dielectric function $\varepsilon_2(\nu)$ is smaller than 1.0 in the regions from 0.3THz to 3.0 THz.

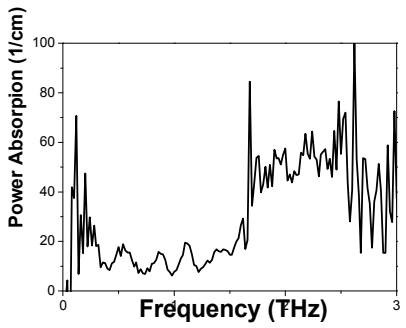

Fig. 2 The absorption coefficient α(ν) curve..

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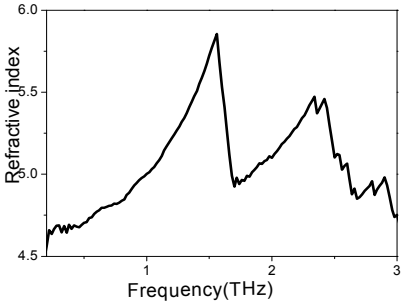

Fig. 3 The refractive index n(ν) curve.

The dielectric function $\varepsilon_1(\nu)$ of a sample is a macroscopic measured quantity, it is the representation of microcosmic polarizability $\alpha(\nu)$ of electric charge particles. And $\varepsilon_1(\nu)$ change is due to the $\alpha(\nu)$ as shown in the Clausius- Mossotti relation[3].

$$\frac{n^2-1}{n^2+2}=\frac{\varepsilon-1}{\varepsilon+2}=\frac{4\pi}{3}\sum N_k\alpha_k$$

The polarizabilities may usually be separated into three parts: electronic, ionic, and dipolar[4]. The dipolar contribution to the polarizabilitiy is small and vanished at about microwave band, so it can be neglected here. The ionic contribution is reduces and vanishes at about infrared band because of the inertia of the molecular and ion. The decrease of the dielectric function $\varepsilon(\nu)$ is from vanish of the contribution in sequence of the Pb^{2+}, O^{2-}, and B^{3+} ions when the frequency increasing.

For the lattice parameters of the PBO crystal a=0.4251nm, b=0.4463nm, c=1.086nm and Z=2, the volume of a molecule is

$$V=\frac{abc}{Z}=0.1030\times10^{-21}cm^3$$

$N=N_{Pb}=1/V=9.708\times10^{21}cm^{-3}$,

$N_O=7N$, and $N_B=4N$.

Suppose a value A included Pb^{2+}, $O^{2-}$and B^{3+}ions and electrons in the CLausius- Mossotti relation(CGS),

$$\frac{n^2-1}{n^2+2}=\frac{4\pi}{3}\left[N_i\alpha_i+\sum N_j\alpha_j\right]=A \qquad (1)$$

From equation (1) we can get

$$\varepsilon=n^2=\frac{2A+1}{1-A} \qquad (2)$$

Suppose a value B included B^{3+}, O^{2-} ions and electrons except Pb^{2+}ions

$$\frac{n'^2-1}{n'^2+2}=\frac{4\pi}{3}\sum N_j\alpha_j=B \qquad (3)$$

From equation (3) we can get

$$\varepsilon'=n'^2=\frac{2B+1}{1-B} \qquad (4)$$

Equation (1)-(3) is

$$\alpha_i=\frac{3(A-B)}{4\pi N_i} \qquad (5)$$

1) For the first peak the dielectric function $\varepsilon(\nu)$ decreases from ε_{Pb}=30.0 to ε_{Pb}'=25.0 at 1.4-1.7 THz.

$$A_1=\frac{\varepsilon_{Pb}-1}{\varepsilon_{Pb}+2}=\frac{29}{32}=0.906,$$

,

$$B_1=\frac{\varepsilon_{Pb}'-1}{\varepsilon_{Pb}'+2}=\frac{24}{27}=0.889$$

So the polarizability α_{Pb} of Pb^{2+}ion is

$$\alpha_{Pb}=\frac{3(A_1-B_1)}{4\pi N_{Pb}}=0.428\times10^{-24}cm^3$$

2 For the second peak the $\varepsilon(\nu)$ decreases from ε_O=25 to ε_O=22 at 1.7-2.5THz.

$$A_2=\frac{\varepsilon_O-1}{\varepsilon_O+2}=\frac{24}{27}=0.889, \qquad B_2=\frac{\varepsilon_O'-1}{\varepsilon_O'+2}=\frac{21}{24}=0.875$$

So the polarizability α_O of O^{2-}ion is

$$\alpha_O=\frac{3(A_2-B_2)}{4\pi N_O}=0.049\times10^{-24}cm^3$$

For the third peak the $\varepsilon(\nu)$ decreases from ε_1=22 at 2.5THz to ε_1=18 at 3.0THz. There is a gap in a range from 3THz to 149.9THz (2000nm) and the polarizability of B^{3+}-ion, α_B can not be calculated.

The polarizabilities α_k from electronic contribution of Pb^{2+} $B^{3+}$and O^{2-} ions was calculated by L. Pauling et al. [4] and Jacr R. Tessman et al. ($\alpha_{Pb}=4.9\times10^{-24}cm^3$ $\alpha_B=0.003\times10^{-24}cm^3$ and $\alpha_O=0.5\text{-}3.2\times10^{-24}cm^3$ respectively) [5]. The electronic dielectric function $\varepsilon_1(\lambda)$ is near a constant 6.0 from our experiment of the $R(\lambda)$ and the $T(\lambda)$curves in a range from 200nm to 2000nm. It is reasonable that electronic dielectric function is smaller than ionic and electronic dielectric function, $\varepsilon_1(\lambda)=6.0<18$ (at 3.0THz). We can detect the electronic polarizabilities α_{eO} of O^{2-} ion.

$$\frac{\varepsilon_e-1}{\varepsilon_e+2}=\frac{4\pi}{3}N(\alpha_{ePb}+4\alpha_{eB}+7\alpha_{eO})=A_e=0.625$$

So the polarizability α_{eO} of O^{2-}ion is $\alpha_{eO}=1.49\times10^{-24}cm^3$

IV. CONCLUSION

The polarizability of heavy element Pb^{2+} ion vanishing induces a decrease of the dielectric function $\varepsilon(\nu)$ with the frequency increasing. The polarizabilities of Pb^{2+} and O^{2-}ions are $0.428\times10^{-24}cm^3$ and $0.049\times10^{-24}cm^3$ respectively. The electronic polarizabilities $\alpha_{eO}=1.49\times10^{-24}cm^3$ from O^{2-} ion is detected

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