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Journal of Solid State Chemistry 177 (2004) 2916–2919
JOURNAL OF SOLID STATE CHEMISTRY
http://elsevier.com/locate/jssc

High-energy-resolution electron energy-loss spectroscopy study of the electronic structure of Cu- and Mg-Si-doped β-rhombohedral boron crystals

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Received 4 December 2003; received in revised form 16 April 2004; accepted 25 April 2004

Abstract

Electronic structures of Cu and Mg-Si-doped β-rhombohedral boron (β-r-B) crystals were studied by using a high-energy-resolution electron energy-loss spectroscopy microscope. Boron 1s electron excitation spectra, which show the density of states of the conduction bands, of the crystals were obtained from single crystalline areas of 100 nm in diameter. The spectrum of Cu-doped β-r-B showed a chemical shift to a lower binding energy side. It means an electron transfers from the doped Cu atoms to B atoms. The intensity distributions of the spectrum was almost the same as that of the non-doped β-r-B, which suggests that all of the doped electrons occupy the intrinsic acceptor level just above the valence bands. The spectrum of Mg-Si-doped β-r-B showed not only a chemical shift to a lower binding energy side but also a sharp intensity increase at the onset with a width of an energy resolution of the experiment. The sharp onset may be assigned to a Fermi edge. It indicates that the doped electrons fill up the acceptor level and occupy the conduction bands forming the Fermi edge, a metallization of β-r-B by the Mg-Si-doping.

Keywords: β-rhombohedral boron; Cu dope; Mg dope; Metal transition; Fermi edge; Electron energy-loss spectroscopy; Density of states of the conduction bands

1. Introduction

β-rhombohedral boron (β-r-B) consists of 105 boron atoms (B_{105}), which contain B_{12} icosahedral clusters, in a rhombohedral unit cell. There are three different types of doping sites, which are called A_1, D and E sites, in the unit cell [1]. It was reported from crystal structure analyses of various elemental doped β-r-B crystals that the occupancies of the three doping sites are different for different doping atoms [2–6]. Since B_{12} clusters lack two electrons to fill up intra-molecular bonding orbitals, the clusters are deformed by the Jahn–Teller effect. As a result, an intrinsic acceptor level, which is separated by 0.2 eV from the top of the valence band, is formed. It is believed that doped electrons due to a metal doping occupy the intrinsic acceptor level. It has been reported that Li-doped β-r-B (Li_xB_{105}) showed an increase in electrical conductivity for $x<5.7$ but a decrease for $x>5.7$ [2]. The change in the conductivity was explained by electron doping to the intrinsic acceptor level. A high-energy-resolution electron energy-loss spectroscopy (EELS) study of Li-doped β-r-B (Li_xB_{105}) reported that boron 1 s electron excitation spectra showed a chemical shift to a lower binding energy side indicating an electron doping to β-r-B [7]. However, the Fermi edge was not observed in the spectrum suggesting that all of the doped electrons occupy the intrinsic acceptor level. These results were consistent with the conductivity measurements of the material. Metallizations of B_{12}-cluster solids (α- and β-r-B) by the electron doping have been reported targeting a superconductivity of B_{12}-cluster materials [8–10].

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doi:10.1016/j.jssc.2004.04.044

In the present study, boron 1s electron excitation spectra of Cu- and Mg-Si-doped β-r-B were measured by using a high-energy-resolution EELS microscope. Chemical shifts and changes in the intensity distribution of the spectra were examined. A sign of metallization, the Fermi edge, was observed for Mg-Si-doped β-r-B specimen. An origin of the changes for the density of states (DOS) of the conduction bands was discussed.

2. Experiment

Cu-doped β-r-B crystals were prepared by an arc discharge melt of a mixed material of Cu and B powders and a succeeding thermal annealing at a temperature of 900°C for 48 h under an Ar atmosphere [2]. The composition of the material was assigned to be $Cu_{4.2}B_{105}$ by an inductive plasma analysis (ICP). Mg-Si-doped β-r-B single crystalline particles were prepared by a reaction of Mg vapor with polycrystalline β-r-B in a Ta- or BN-tube put in an evacuated silica glass tube [9]. Compositions of the produced materials were examined by Rietveld analyses of the X-ray powder diffraction data and ICP analysis. The two specimens with different compositions of $Mg_{3.2}Si_{0.93}B_{105}$ and $Mg_{4.0}Si_{0.44}B_{105}$ were examined by EELS measurements. Si atoms were accidentally doped due to a reduction of the silica glass tube by the Mg vapor.

Electron diffraction patterns of the specimens examined showed high-quality single crystals. EELS were obtained from specimen areas of 100 nm in diameter with a thickness of about 100 nm with an energy resolution of 0.26 eV by using the high-energy-resolution EELS electron microscope [11]. An accelerating voltage of the EELS microscope was 60 kV. A collection semi-angle of the EELS measurements was 5 mrad. These experimental conditions mean that the spectra were measured under the condition of dipole transition. Thus, intensity profiles of boron 1s excitation spectra show the partial DOS of the conduction bands with *p*-character.

3. Cu-doped β-r-b

Fig. 1 shows boron 1s excitation spectrum obtained from a single crystalline specimen area of $Cu_{4.2}B_{105}$. The spectrum of the non-doped β-r-B is also shown for comparison. Onsets of the spectra, which are assigned by vertical lines, correspond to the bottom of the conduction bands.

It is clearly seen that the peak indicated by an arrow in the spectrum of $Cu_{4.2}B_{105}$ is shifted to lower-energy side by 0.2 eV compared to that of the non-doped β-r-B. The shift is the sign of electron doping to β-r-B. The value of the chemical shift of 0.2 eV is about one-half of that observed for $Li_{7.9}B_{105}$ [7]. It may be reasonable because an amount of electron doping of $Cu_{4.2}B_{105}$ is expected to be about one-half of that of $Li_{7.9}B_{105}$.

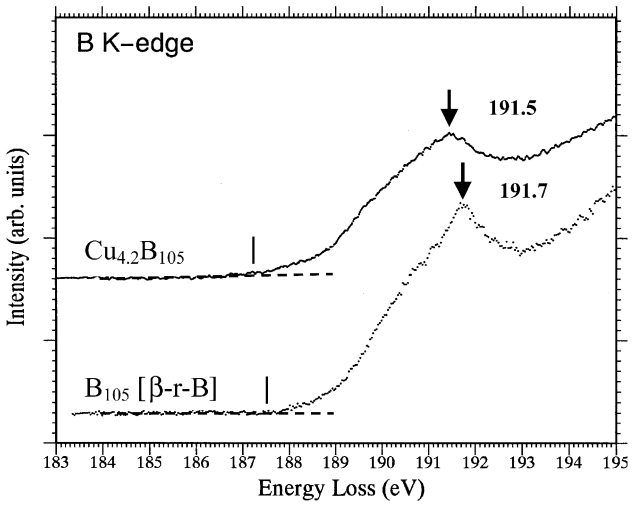

Fig. 1. Boron 1s excitation spectrum obtained from a single crystalline specimen area of $Cu_{4.2}B_{105}$. The spectrum of the non-doped β-r-B is also shown for comparison. Spectrum onsets indicated by vertical lines correspond to the bottom of the conduction bands.

The intensity profile of $Cu_{4.2}B_{105}$ is almost similar to that of non-doped specimen. This indicates that all of the doped electrons occupy the intrinsic acceptor level above the valence bands and do not form a Fermi edge in the conduction bands. A similar intensity profile also indicates that there is little mixing of electron orbitals between Cu and B atoms. It was reported that the doped Cu atoms mainly occupy the E and D doping sites. It contrasts with the case of V-doped β-r-B, in which the doped V atoms were reported to mainly occupy the A_1 site [12]. In that case, an effect of the mixing of electron orbitals of V and B atoms was observed in a boron 1s excitation spectrum obtained by a high-energy-resolution EELS measurement [7].

4. Mg-Si-doped β-r-b

Fig. 2 shows boron 1s excitation spectra obtained from single crystalline specimen areas of $Mg_{3.2}Si_{0.93}B_{105}$ and $Mg_{4.0}Si_{0.44}B_{105}$. The spectrum of the non-doped β-r-B is also shown for comparison. It should be noted that the spectra of Mg-Si-doped β-r-B show step-like onsets at 188.5 eV for $Mg_{3.2}Si_{0.93}B_{105}$ and 188.8 eV for $Mg_{4.0}Si_{0.44}B_{105}$ as indicated by arrows. The width of each intensity increase is about 0.3 eV, which is almost the same with an energy resolution of 0.26 eV of the measurement. Thus, the step-like onsets can be assigned to a Fermi edge. It indicates that the doped electrons fill up the acceptor level and occupy the conduction bands forming the Fermi edge. It means a metallization of β-r-B by the Mg-Si-doping.

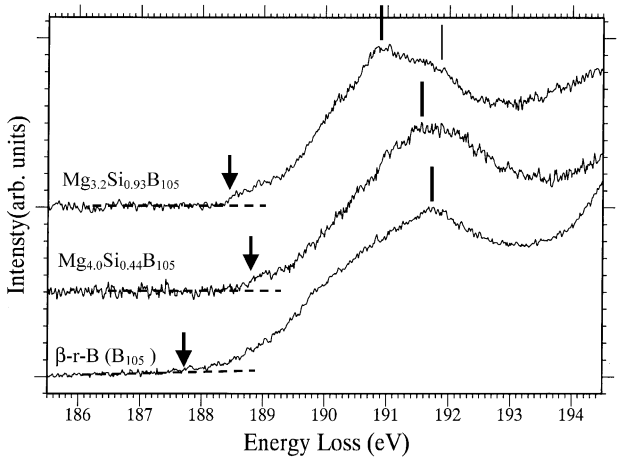

Fig. 2. Boron 1s excitation spectra obtained from single crystalline specimen areas of $Mg_{3.2}Si_{0.93}B_{105}$ and $Mg_{4.0}Si_{0.44}B_{105}$ together with a spectrum of the non-doped β-r-B for comparison. The spectra of Mg-Si-doped β-r-B specimens show a step-like intensity increases at 188.5 eV for $Mg_{3.2}Si_{0.93}B_{105}$ and at 188.8 eV for $Mg_{4.0}Si_{0.44}B_{105}$ as indicated by arrows. The width of each intensity increase is almost the same with an energy resolution. Thus, the step-like onsets can be assigned to a Fermi edge.

The spectrum of $Mg_{3.2}Si_{0.93}B_{105}$ shows a peak at 190.9 eV with a shoulder at about 191.9 eV, which are assigned by thick and thin vertical lines, respectively. The peak energy is 0.8 eV smaller than that of non-doped β-r-B. A shift amount of 0.8 eV cannot be assigned to the chemical shift only due to the electron doping, because the intensity distribution of the spectrum has changed by the doping. This contrasts with the case of $Cu_{4.2}B_{105}$; a possible origin of the change is the accidental doping of Si atoms. It was revealed from a Rietveld analysis that the doped Si atoms mainly occupy the intra-cluster B_1 site and the remaining Si atoms occupy the inter-cluster A_1 sites [9]. Si atoms at the intra-cluster B_1 site, which is an atom position of a B_{12} cluster, should form covalent bondings with surrounding boron atoms and may change the profile of the DOS of the conduction bands. The B_1 site doping may be a reason of the changes of the DOS of the conduction bands of the doped β-r-B. It is reasonable because the spectrum of $Mg_{4.0}Si_{0.44}B_{105}$, which has a smaller amount of Si doping, shows a smaller peak shift and a smaller shoulder intensity compared to those of $Mg_{3.2}Si_{0.93}B_{105}$. A_1 and B_1 sites are seen in Fig. 3, which show an apex region of the rhombohedral unit cell of β-r-B.

Mg atoms, which occupy the inter-cluster doping sites, can give two electrons per Mg atom to β-r-B. Si atoms, which mainly occupy the intra-cluster B_1 site, may give one electron/atom under the same situation as the boron atom in the B_1 site because an Si atom has one more electron in the outermost shell than a boron atom. Thus, amounts of electron doping of $Mg_{3.2}Si_{0.93}B_{105}$ and

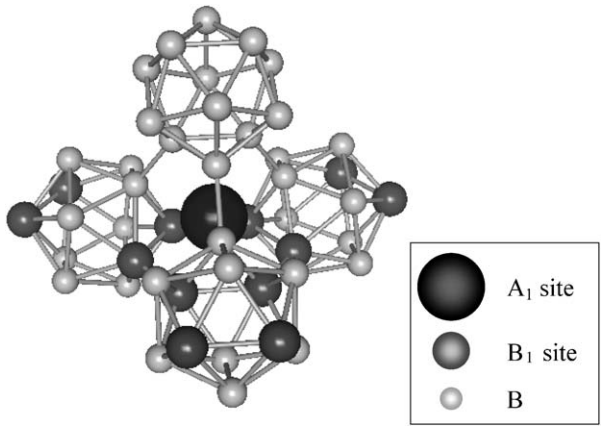

Fig. 3. A_1 and B_1 sites of an apex region of the rhombohedral unit cell of β-r-B.

$Mg_{4.0}Si_{0.44}B_{105}$ are estimated to be 8.5 and 9.1 electrons per unit cell. These doping amounts are larger than those expected for $Cu_{4.2}B_{105}$ and $Li_{7.9}B_{105}$. Therefore, a doping amount of more than eight electrons per unit cell is needed for the metallization of β-r-B.

5. Conclusion

Electron dopings to β-r-B were successfully confirmed by the presence of the chemical shifts in boron 1s excitation spectra using a high-energy-resolution EELS microscope. The doped electrons of Cu-doped β-r-B occupy only the intrinsic acceptor level. Boron 1s excitation spectrum of Mg-Si-doped β-r-B shows a presence of the Fermi edge in the conduction bands. It may be an evidence of the metallization of β-r-B. Present results indicate that the position of the Fermi level of β-r-B can be controlled by the electron doping. High-energy-resolution EELS based on microscopy becomes a key technique to evaluate pioneering materials.

Acknowledgments

The authors thank Mr. F. Sato for his skillful technical assistance. This work was partly supported by Grant-in Aid for Scientific Research from Ministry of Education, Science and Culture of Japan.

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