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Electronic structures and chemical bonding of $\text{Bi}_{2-x}\text{Pb}_x\text{Sr}_3\text{Co}_2\text{O}_9$ ($x = 0.0$ and 0.5)

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Abstract

Electronic structures and chemical bonding in $[\text{Co}_{10}\text{O}_{11}]^{8+}$ and $[\text{Co}_{10}\text{O}_{11}]^{10.5+}$ clusters have been studied by ab initio molecular-orbital calculations using discrete-variational $X\alpha$ cluster method in order to investigate the relationship between thermoelectric natures and electronic structures in $\text{Bi}_{2-x}\text{Pb}_x\text{Sr}_3\text{Co}_2\text{O}_9$ ($x = 0.0$ and 0.5). The most significant features are that O $2p$ band is hybridized with Co $3d$ orbital in the energy range of 5 to -15 eV. This result indicates the strong correlation between the thermoelectric performance in $\text{Bi}_{2-x}\text{Pb}_x\text{Sr}_3\text{Co}_2\text{O}_9$ and Co $3d$ -O $2p$ hybridization near Fermi level. Therefore, Pb^{2+} -substitution for Bi^{3+} yields high conductive materials by increasing the amount of ligand holes in t_{2g} bands and the thermoelectric nature in $\text{Bi}_{2-x}\text{Pb}_x\text{Sr}_3\text{Co}_2\text{O}_9$ is sensitive to Co $3d$ -O $2p$ hybridization near the Fermi level. © 2002 Elsevier Science B.V. All rights reserved.

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Thermoelectric (TE) materials have recently attracted a renewed interest as an application to a clean energy-conversion system [1]. The conversion efficiency of a TE material is characterized by the figure of merit $Z = S^2/\rho\kappa$, where S , ρ and κ are thermopower, resistivity and thermal conductivity. A good TE material then involves high thermopower, low resistivity and low thermal conductivity. However, a high value of Z is difficult to realize, because these parameters do not change independently. Despite such a difficulty, recent research on TE oxides is accelerated by the global need for utilizing the waste heat of high temperature.

With respect to new transition metal oxides which have high potential for TE materials, NaCo_2O_4 , one of layered cobalt oxides, surely shows promising TE properties, i.e., large S of $100 \mu\text{V}/\text{K}$ and low ρ of $200 \mu\Omega \text{ cm}$ at room temperature [2]. Very recently, Ando et al. [3] have found that the electron specific-heat coefficient of NaCo_2O_4 is as large as $48 \text{ mJ}/\text{mol K}^2$, which is substantially enhanced from the free-electron value, possibly owing to the strong electron-electron correlation due to narrow $3d$ metal bands. Because of this, other transition metal oxides with narrow $3d$ metal bands could also be candidates for good TE materials. The most attractive candidate for TE materials at the moment is $\text{Bi}_{2-x}\text{Pb}_x\text{Sr}_3\text{Co}_2\text{O}_9$, one of layered Co-oxides [4,5]. This material is a good reference material for NaCo_2O_4 because resistivity, ρ , decreases monotonically by one order with increasing x , and thermopower, S , is nearly

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independent of x , i.e., $S_100 \mu\text{V}/\text{K}$ at room temperature. This fact clearly indicates that the carriers are doped by Pb^{2+} -substitution for Bi^{3+} , whereas thermopower is independent of the carrier density if some conditions are satisfied.

$\text{Bi}_{2-x}\text{Pb}_x\text{Sr}_3\text{Co}_2\text{O}_9$ has the crystal structure isomorphic to that of $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$ (BSCCO) superconductors, although chemical analysis of this material shows that the Sr content is lower than the stoichiometric value [6]. The experimental magnetic susceptibility on $\text{Bi}_2\text{Sr}_3\text{Co}_2\text{O}_9$ yields $S = 0$ [7], where S is the effective spin value. Almost all Co^{3+} are then in the low-spin state (t_{2g}^6). $\text{Bi}_{2-x}\text{Pb}_x\text{Sr}_3\text{Co}_2\text{O}_9$ has double Bi–O layers separated by alternating rocksalt Sr–O layers and a two-dimensional structure with pseudosquare CoO_2 plane. The primitive cell with the lattice parameters of $a \sim b$ 5.0 [8] and c 30 [9,10] is smaller than that of BSCCO superconductors, which must be mainly due to the ionic radius of the low-spin Co^{3+} [11].

The carrier density of NaCo_2O_4 is larger in magnitude than conventional TE materials ($\sim 10^{19} \text{ cm}^{-3}$) by two orders [2]. Hall coefficient in $\text{Bi}_{2-x}\text{Pb}_x\text{Sr}_3\text{Co}_2\text{O}_9$ at room temperature ($\sim 2.0 \times 10^{-2} \text{ cm}^3/\text{C}$) estimates the carrier density which is larger than conventional TE materials but smaller than NaCo_2O_4 by about one order [9]. The theoretical formula for S indicates that the carrier density larger than the optimum value for conventional TE materials decreases thermopower [12]. Nevertheless, $\text{Bi}_{2-x}\text{Pb}_x\text{Sr}_3\text{Co}_2\text{O}_9$ includes a good thermoelectric performance. This is difficult to understand within the framework of a conventional one-electron picture based on band theories. Therefore, the strong electron–electron correlation due to narrow $3d$ metal bands must play an important role in the thermoelectric performance of $\text{Bi}_{2-x}\text{Pb}_x\text{Sr}_3\text{Co}_2\text{O}_9$ as well as NaCo_2O_4 .

The primary aim of the present study is to investigate the relationship between a thermoelectric performance and electronic structures in $\text{Bi}_{2-x}\text{Pb}_x\text{Sr}_3\text{Co}_2\text{O}_9$ crystals. Electronic structures are usually obtained by an ab initio molecular–orbital (MO) calculation based on local-density approximation (LDA) of density-functional theory (DFT). DV-X α method [13,14], based on self-consistent-field Hartree–Fock–Slater (HFS) one-electron model [15] and self-consistent-charge procedure [16], is one of the

most useful techniques for an approximate solution to HFS equation. This method is one of cluster methods using a local one-electron effective potential to approximate both the electron–correlation effect and the spin–correlation effect. In local-spin-density approximation (LSDA) approach [17], the effective Slater X α exchange–correlation potential is given by $-3\alpha[3/8\pi\rho_{\uparrow\downarrow}]^{1/3}$, where $\rho_{\uparrow\downarrow}$ is the local spin density, and the exchange–scaling parameter, α , is fixed at 0.7 throughout the calculation. In the present study, thus, we calculate electronic structures in $\text{Bi}_{2-x}\text{Pb}_x\text{Sr}_3\text{Co}_2\text{O}_9$ within first-principles MO calculation using a discrete-variational (DV)-X α cluster method [13,14], which accounts very well for electronic structures in VO_2 , Ti_2O_3 and $\text{LaCo}_{1-x}\text{Ti}_x\text{O}_3$ [18–20]. In the present calculation, we use a program code SCAT of DV-X α cluster method.

The MO wave function is expressed by a linear combination of atomic orbital (LCAO). As the basis function, we use numerical atomic orbital obtained by solving the radial part of the Schrödinger equation for individual atoms in a cluster. Furthermore, 235 numerical atomic basis functions, i.e., Co (18 numerical atomic basis functions ($1s$, $2s$, $2p$, $3s$, $3p$, $3d$, $4s$ and $4p$)) and O (5 numerical atomic basis functions ($1s$, $2s$ and $2p$)), are used to expand MO of $[\text{Co}_{10}\text{O}_{11}]^{8+}$ and $[\text{Co}_{10}\text{O}_{11}]^{10.5+}$ clusters. These basis functions are the Slater-type orbital basis sets obtained from short Herman–Skillman programs [21]. In order to evaluate charge transfer and chemical bonding of the cluster, Mulliken’s population analyses [22] is employed.

The present study has been carried out under the assumption that the crystal structure of $\text{Bi}_{2-x}\text{Pb}_x\text{Sr}_3\text{Co}_2\text{O}_9$ is similar to that of BSCCO superconductors and electronic structures in $[\text{Co}_{10}\text{O}_{11}]^{8+}$ and $[\text{Co}_{10}\text{O}_{11}]^{10.5+}$ clusters have been found to be reliable at least qualitatively in $\text{Bi}_2\text{Sr}_3\text{Co}_2\text{O}_9$ and $\text{Bi}_{1.5}\text{Pb}_{0.5}\text{Sr}_3\text{Co}_2\text{O}_9$, respectively. In addition, MO calculations using a minimal number of atomic orbital as basis functions are very useful for understanding the phenomena from the viewpoint of chemical bonding. This is the greatest advantage in exchange for the lack of precision in the present type of calculations.

Fig. 1 shows the structure of $[\text{Co}_{10}\text{O}_{11}]^{8+}$ or $[\text{Co}_{10}\text{O}_{11}]^{10.5+}$ cluster employed in the present calculation and coordinates of atoms along the x -, y - and z -axes in the cluster are presented in Table 1. The

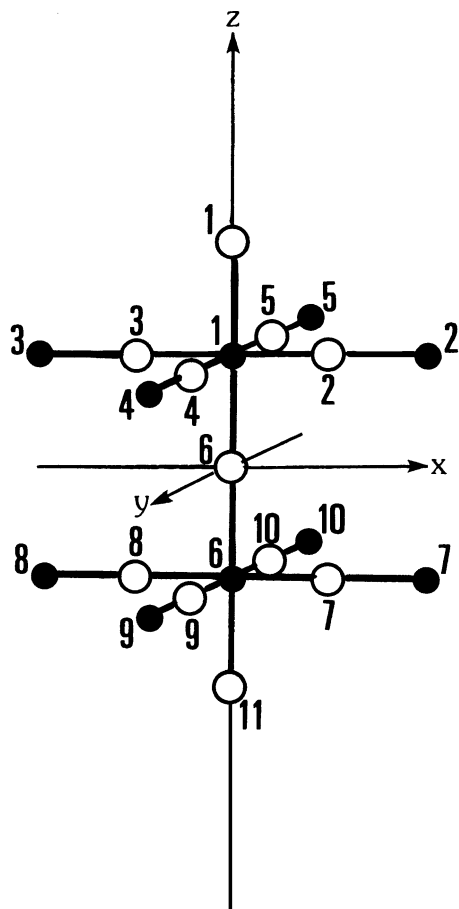


Fig. 1. Geometric structure of $[\text{Co}_{10}\text{O}_{11}]^{8+}$ or $[\text{Co}_{10}\text{O}_{11}]^{10.5+}$ cluster employed in DV- $X\alpha$ cluster method, where closed circles and open circles indicate Co and O atoms, respectively. Coordinates of atoms in the cluster are presented in Table 1.

unit cell ($\sqrt{2}\mathbf{a} \times \sqrt{2}\mathbf{b} \times \mathbf{c}$) employed in the calculation is composed of $\text{Bi}_{16-y}\text{Pb}_y\text{Sr}_{24}\text{Co}_{16}\text{O}_{72}$ ($y = 0$ for $x = 0.0$ and $y = 4$ for $x = 0.5$). As the crystallographic translational symmetry has to be taken into consideration, the calculation of Madelung potential requires a structure composed of $6 \times 6 \times 6$ unit cells, where $[\text{Co}_{10}\text{O}_{11}]^{8+}$ and $[\text{Co}_{10}\text{O}_{11}]^{10.5+}$ clusters are situated at the center in $6 \times 6 \times 6$ structure, and other Bi^{3+} , Pb^{2+} , Sr^{2+} , Co^{3+} , $\text{Co}^{3.25+}$ and O^{2-} are replaced by point charges, i.e., $+3.25e$ for $\text{Co}^{3.25+}$, $+3e$ for Bi^{3+} or Co^{3+} , $+2e$ for Pb^{2+} or Sr^{2+} and $-2e$ for O^{2-} , respectively.

MO calculations have obtained the discrete MO energy levels which are broadened by Gaussian functions of 0.5 eV full width at half maximum (FWHM) for easy visualization of the density of states (DOS). We assume that discrete MO energy levels obtained here form continuous energy bands, and that Fermi level is at the highest occupied molecular orbital (HOMO). The energy scale is shifted to take Fermi level as zero. In this first-principles real-space calculation, molecular orbitals are constructed by linear combinations of numerical atomic orbitals that are optimized by solving the radial part of Schrödinger equation for each atom in a given environment.

We have found that the fully ionic picture cannot describe the bonding natures in $\text{Bi}_{2-x}\text{Pb}_x\text{Sr}_3\text{Co}_2\text{O}_9$ using the Mulliken's population analysis [22]. The average net charges evaluated for $[\text{Co}_{10}\text{O}_{11}]^{8+}$ and $[\text{Co}_{10}\text{O}_{11}]^{10.5+}$ clusters at $x = 0.0$ and 0.5 are $+2.378e$ and $+2.629e$ for Co and $-1.434e$ and $-1.436e$ for O, respectively. There must be a small covalent component in the bonding between Co and O. Thus, the investigation on Pb-substitution effects requires an electronic structure calculation in Bi_2Sr_3

Table 1

Coordinates of atoms in $[\text{Co}_{10}\text{O}_{11}]^{8+}$ or $[\text{Co}_{10}\text{O}_{11}]^{10.5+}$ cluster of $\text{Bi}_{1.5}\text{Pb}_{0.5}\text{Sr}_3\text{Co}_2\text{O}_9$ ($x = 0.0$ or 0.5) along the x -, y - and z -axes

Atoms	x/a	y/b	z/c
Co(1)	0.00000	0.00000	0.07143
Co(2)	0.70710	0.00000	0.07143
Co(3)	-0.70710	0.00000	0.07143
Co(4)	0.00000	0.70710	0.07143
Co(5)	0.00000	-0.70710	0.07143
Co(6)	0.00000	0.00000	-0.07143
Co(7)	0.70710	0.00000	-0.07143
Co(8)	-0.70710	0.00000	-0.07143
Co(9)	0.00000	0.70710	-0.07143
Co(10)	0.00000	-0.70710	-0.07143
O(1)	0.00000	0.00000	0.14286
O(2)	0.35355	0.00000	0.07143
O(3)	-0.35355	0.00000	0.07143
O(4)	0.00000	0.35355	0.07143
O(5)	0.00000	-0.35355	0.07143
O(6)	0.00000	0.00000	0.00000
O(7)	0.35355	0.00000	-0.07143
O(8)	-0.35355	0.00000	-0.07143
O(9)	0.00000	0.35355	-0.07143
O(10)	0.00000	-0.35355	-0.07143
O(11)	0.00000	0.00000	-0.14286

Co_2O_9 by DV-X α cluster method, along with the calculation in $\text{Bi}_{1.5}\text{Pb}_{0.5}\text{Sr}_3\text{Co}_2\text{O}_9$.

Fig. 2 displays the total and partial DOS calculated for $[\text{Co}_{10}\text{O}_{11}]^{8+}$ cluster in $\text{Bi}_2\text{Sr}_3\text{Co}_2\text{O}_9$. In the energy range of 5 to -15 eV, the predominant atomic basis functions in each MO are Co ($3d$) and O ($2p$). This indicates that electronic structures around Fermi level consists of Co $3d$ and O $2p$ orbital which are hybridized with each other. All of these curves are constructed by broadening discrete MO energy eigenvalues by Gaussian functions of 0.5 eV FWHM. The most significant feature in Fig. 2 is that O $2p$ bands (5 to -15 eV) include some contribution from Co $3d$ orbital.

Fig. 3 show DOS (total, per Co $3d$, Co $4sp$ and O $2p$, respectively) computed for $[\text{Co}_{10}\text{O}_{11}]^{10.5+}$ cluster in $\text{Bi}_{1.5}\text{Pb}_{0.5}\text{Sr}_3\text{Co}_2\text{O}_9$. Recently, Tsukada et al. examined the effects of Pb-substitution on $\text{Bi}_2\text{Sr}_3\text{Co}_2\text{O}_9$ bulk single crystals [10]. They reported large negative magnetoresistance at low temperatures together with ferromagnetic transition below 4.2 K in $\text{Bi}_{2-x}\text{Pb}_x\text{Sr}_3\text{Co}_2\text{O}_9$ [10]. However, this is difficult to explain because Co^{3+} in the parent $\text{Bi}_2\text{Sr}_3\text{Co}_2\text{O}_9$ are in low spin states [7]. As Pb-concentration increases, furthermore, the lattice lengthens monotonically along c -axis and the absolute value of the Hall coefficient decreases [9]. Referring to the results in Figs. 2 and 3, Pb^{2+} -substitution for Bi^{3+} must be

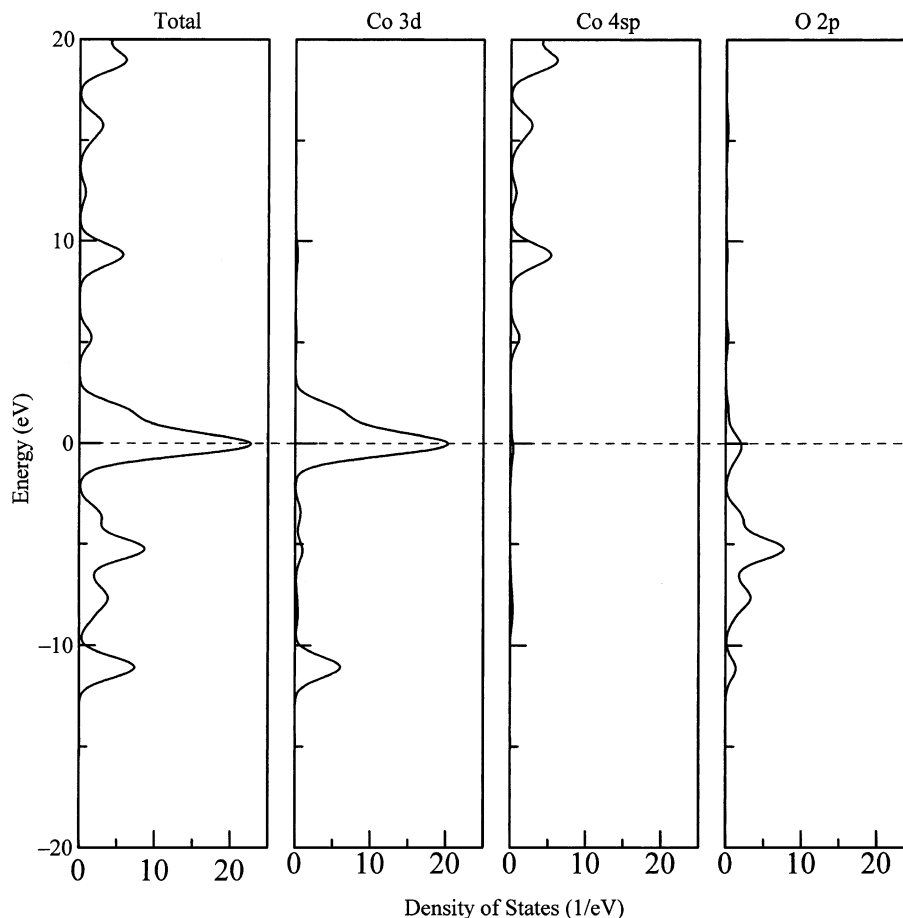


Fig. 2. DOS (total, per Co $3d$, Co $4sp$ and O $2p$, respectively) computed for $[\text{Co}_{10}\text{O}_{11}]^{8+}$ cluster in $\text{Bi}_2\text{Sr}_3\text{Co}_2\text{O}_9$ ($x = 0.0$) and constructed by broadening discrete MO energy eigenvalues by Gaussian functions of 0.5 eV FWHM.

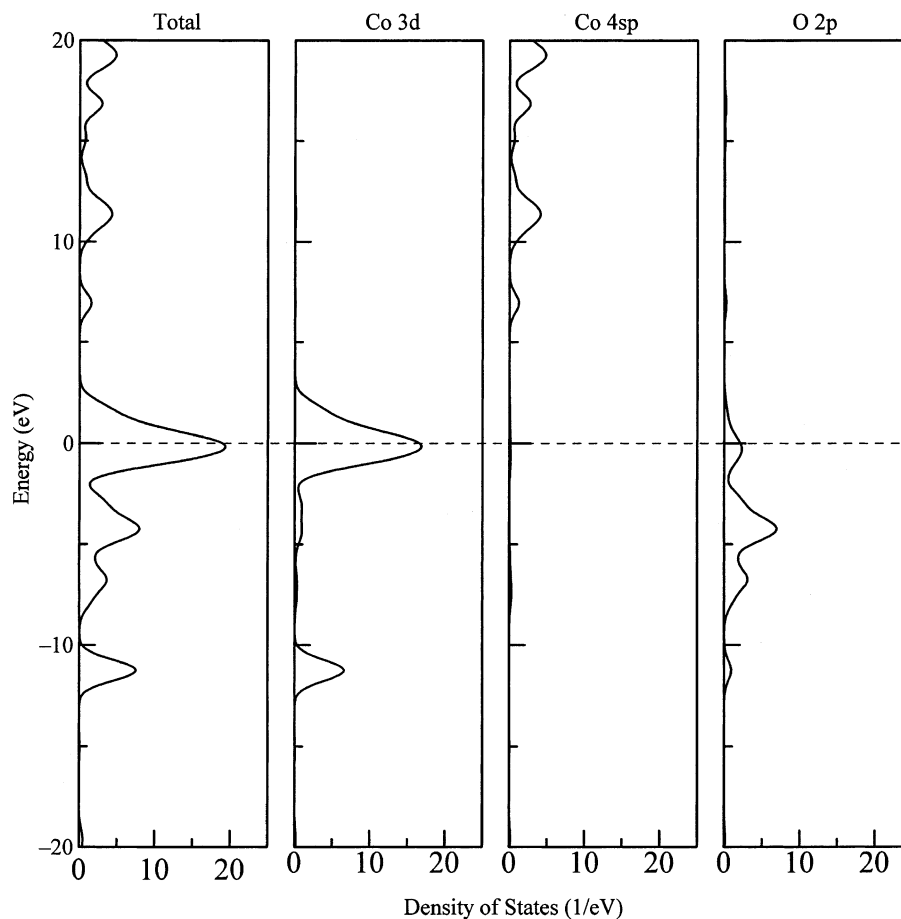


Fig. 3. DOS (total, per Co 3d, Co 4sp and O 2p, respectively) computed for $[\text{Co}_{10}\text{O}_{11}]^{10.5+}$ cluster in $\text{Bi}_{1.5}\text{Pb}_{0.5}\text{Sr}_3\text{Co}_2\text{O}_9$ ($x = 0.5$) and constructed by broadening discrete MO energy eigenvalues by Gaussian functions of 0.5 eV FWHM.

mainly responsible for some relevance to increase in the Co 3d–O 2p hybridization.

In summary, we have calculated electronic structures and chemical bonding in $[\text{Co}_{10}\text{O}_{11}]^{8+}$ and $[\text{Co}_{10}\text{O}_{11}]^{10.5+}$ clusters using DV- $X\alpha$ cluster method. The most significant points obtained in the present study are that Co 3d bands involve small components of O 2p orbital in the energy range of 5 to –15 eV. This result indicates the strong correlation between the thermoelectric performance in $\text{Bi}_{2-x}\text{Pb}_x\text{Sr}_3\text{Co}_2\text{O}_9$ and Co 3d–O 2p hybridization near Fermi level. Therefore, Pb^{2+} -substitution for Bi^{3+} yields high conductive materials by increasing the amount of ligand holes in Co–O hybridized t_{2g} bands near Fermi level.

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