

Conductivity and Infrared Absorption of $\text{La}_{1-x}\text{Ba}_x\text{CoO}_3$ Conductive Ceramics

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In the present paper, the conductivity and infrared absorption of $\text{La}_{1-x}\text{Ba}_x\text{CoO}_3$ conductive ceramics have been investigated. Results show that with increasing x , the resistivity decreases, undergoes a minimum at $x = 0.5$, and then increases with further increases of x . The conductive ceramic with the largest infrared absorption peak corresponds to the smallest resistivity. Meanwhile the conducting mechanism of $\text{La}_{1-x}\text{Ba}_x\text{CoO}_3$ conductive ceramics have been investigated. © 1998 Academic Press

1. INTRODUCTION

Conductive ceramics have recently been developed as a new kind of functional material. Since they are prepared using conventional ceramic processes, their microstructure possesses ceramic structural characters. Conductive ceramics are superior to many other materials such as metals in some macroscopic performances, especially in antioxidation and anticorrosion properties and mechanical strength, which enable them to find wide potential applications. Perovskite ABO_3 -type $\text{La}_{1-x}\text{Ba}_x\text{CoO}_3$ conductive ceramics have been widely used in chemically sensitive materials, conductors, electric rods of dry cells, and permanent resistance materials (1). In the present work, conductivity and infrared absorption have been investigated for $\text{La}_{1-x}\text{Ba}_x\text{CoO}_3$ compounds with $x = 0.1$ – 0.9 . The conductive mechanism has been analyzed, considering the effects of lattice defect structure, which provides novel useful information for the research and application of conductive ceramics.

2. EXPERIMENT

Samples have been prepared using conventional ceramic processes. Chemically pure BaCO_3 , La_2O_3 , and Co_2O_3 were mixed with the composition $\text{La}_{1-x}\text{Ba}_x\text{CoO}_3$ ($x = 0.1$ – 0.9). The mixed powders were ball milled for 48 h. After drying and adding adhesive, the powders were pressed into disks under 1000 kg/cm^2 . Then the samples were sintered at 1400°C for 3 h. The resistivity of samples was measured by the four-electrode method. The infrared absorption spectra were measured in the wavenumber range 4000 – 200 cm^{-1} using an FT-IR-20SX infrared spectrometer made by Nicolet Company.

3. RESULTS AND DISCUSSION

3.1. Composition x Dependence of Resistivity ρ_r in $\text{La}_{1-x}\text{Ba}_x\text{CoO}_3$

Figure 1 shows the composition x dependence of resistivity ρ_r at room temperature in $\text{La}_{1-x}\text{Ba}_x\text{CoO}_3$ conductive ceramics. It can be seen that with increasing x , the resistivity ρ_r decreases, undergoes a minimum at $x = 0.5$, and then increases with further increase of x ($x > 0.5$). At $x = 0.9$ and 0.1 , the extent of variation of resistivity of ceramics is larger. The curve $\rho_r - x$ is of U-shape. The resistance ρ_r at $x = 0.5$ ($\text{La}_{0.5}\text{Ba}_{0.5}\text{CoO}_3$) is $10^{-3} \Omega \text{ cm}$, which enter the conductivity region of the conducting metal.

3.2. Analysis of Infrared Optical Spectra

Figure 2 shows the infrared optical spectra of $\text{La}_{1-x}\text{Ba}_x\text{CoO}_3$ conductive ceramics. It can be seen that from

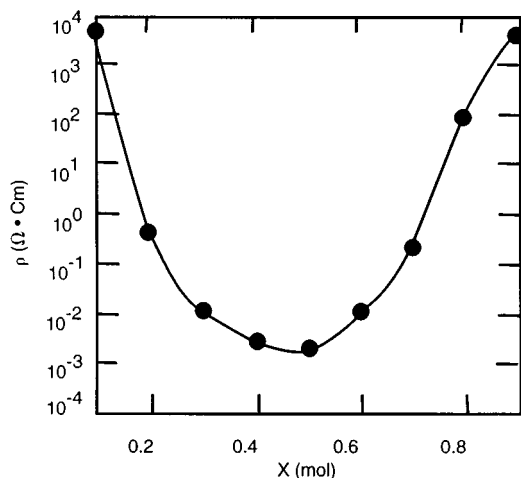


FIG. 1. The composition x dependence of resistivity at room temperature for $\text{La}_{1-x}\text{Ba}_x\text{CoO}_3$ conductive ceramics.

Fig. 2 that the infrared absorption peak of $\text{La}_{0.5}\text{Ba}_{0.5}\text{CoO}_3$ ($x = 0.5$) is very strong. In contrast, the infrared absorption peak is relative weak. There is a relationship between infrared optical spectra and $\rho_r - x$ curve. The conductive ceramic with largest infrared absorption peak has the smallest resistivity, and the largest absorption frequency moves in the direction of low wave number (see Fig. 1 and Fig. 2). The absorption peak with largest frequency has been indicated by rows in Fig. 2 (a) $x = 0.2$ and (c) $x = 0.5$, respectively. For $x = 0.8$ shown in Fig. 2c, the corresponding absorption peak is not so clear.

When infrared light goes through the sample, there is a jump from low energy bands to adjacent high energy bands; thus an absorption peak occurs in infrared optical spectra. The infrared spectra reflect the structure of the crystal. The absorption peak in infrared spectra accords with the vibration of the ions. The higher the absorption peak, the larger the amplitude of vibration. Each ion of the lattice has its specific range of infrared absorption. From Fig. 2, it is evident that the wave number of the highest absorption peak in infrared spectra is 560 cm^{-1} . Thus the resonance frequency of the largest absorption peak is $1.68 \times 10^{13} \text{ Hz}$, which stand in the range of vibration frequencies ($10^{12} - 10^{14} \text{ Hz}$).

From the analysis of infrared spectra, the conducting ceramic $\text{La}_{0.5}\text{Ba}_{0.5}\text{CoO}_3$ has an evident absorption peak of infrared spectra, which show the crystal structure of this conducting ceramic has relative more oxygen vacancy. These oxygen vacancies easily induce the weakly bonded electron, which play the role of the screening on the center of positive ions and thus decreases the strength of interaction among ions. This results in the shift of the absorption peak to the low frequency.

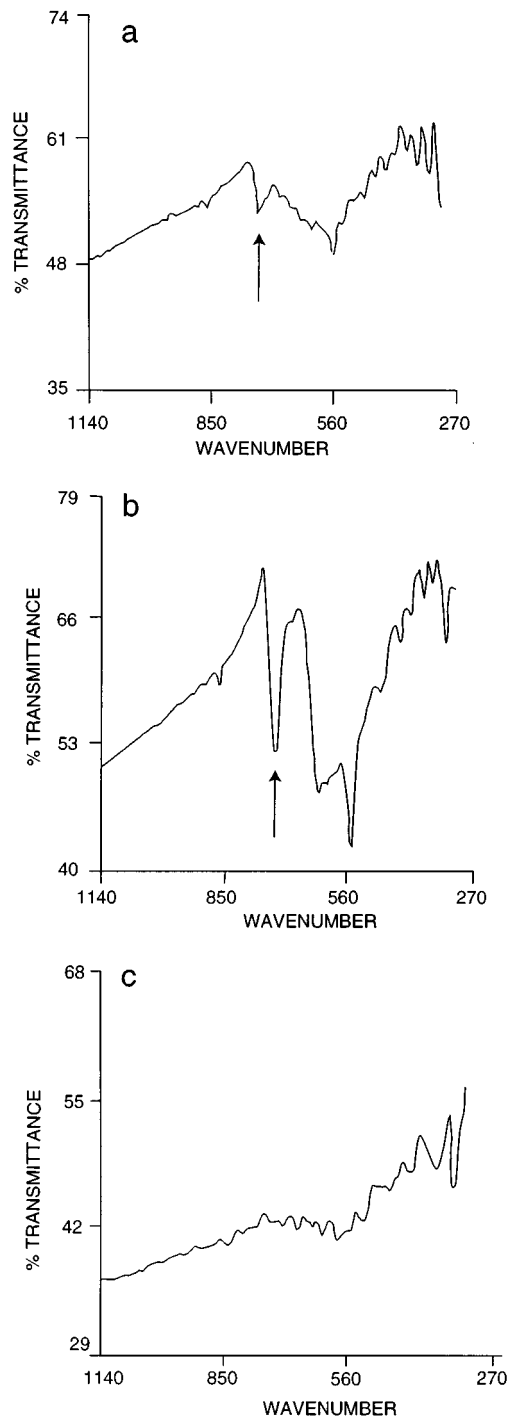


FIG. 2. The infrared optical spectra of $\text{La}_{1-x}\text{Ba}_x\text{CoO}_3$ conductive ceramics with (a) $x = 0.2$, (b) $x = 0.5$, and (c) $x = 0.8$.

3.3. Analysis of Conducting Mechanism and Infrared Absorption Behavior of $\text{La}_{0.5}\text{Ba}_{0.5}\text{CoO}_3$ Conducting Ceramic

The X-ray pattern of $\text{La}_{0.5}\text{Ba}_{0.5}\text{CoO}_3$ conducting ceramic is shown in Fig. 3. It is evident that the sample is of

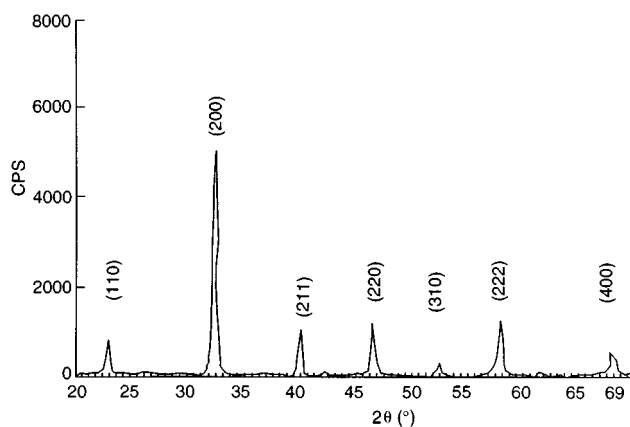


FIG. 3. X-ray pattern of La_{0.5}Ba_{0.5}CoO₃ conducting ceramic.

ABO₃ perovskite structure. Since the La⁺³ ionic radius (0.132 nm) is similar to the Ba⁺² ionic radius (0.139 nm) but considerably different from the Co⁺⁴ ionic radius (0.057 nm), La⁺³ and Ba⁺² occupy the A site, and since their atomic valences are different, variation of crystal structure may occur in order to satisfy the electrical neutrality condition. The most possible variation of structure is the formation of the oxygen vacancy La_{0.5}³⁺Ba_{0.5}²⁺Co_{1-δ}⁴⁺Co_δ³⁺O₃²⁻ + (1 + 2δ)/4V_O (2); here δ ≪ 1 and V_O is a positive bivalence oxygen vacancy. Therefore, the lattice defect structure expression is O_o^x → 1/2 O₂(g) + V_O + 2e⁻, where O_o^x represents an electrically neutral oxygen atom, O₂(g) is an oxygen molecule and e⁻ is a conducting electron.

The bivalence oxygen vacancy V_O can act as a semiconductive donor impurity, which induces the formation of weakly bonded electrons or conducting electrons. On the other hand, the appearance of bivalence oxygen may result in the reduction of Co⁺⁴ at the B site in the ABO₃ structure (3) and the formation of Co⁺³ ionic cluster. The Co⁺³ ion weakly bonds one conduction electron. These weakly bonded electrons change from the local state to the itinerant state like electrons in metal.

With change in the x addition, the number of oxygen vacancies also change; meanwhile a number of electrons change from the local state to the itinerant state, resulting in a change of resistivity. Since the change in number of oxygen vacancies induce variation of the crystal lattice, the vibrational state of ions and the weakly bonded electrons around ions should vary. In other words, variation of the vibrational energy bands occurs and the infrared absorption can reflect this variation. With further increasing x addition (x > 0.5), the crystal structure changes into a multiphase structure (1); accordingly the behavior of oxygen vacancies also changes, which may result in increased resistivity.

REFERENCES

1. Chengjian Wang *et al.*, *J. Chine. Rare Earth Soc.* **15**, 281 (1997).
2. T. Pskeele, R. E. Newnhan, and L. E. Cross, *J. Am. Ceram. Soc. C* **71**, 963 (1963).
3. Yuanqiang Li, Tai Qiu, Xuchu He, *et al.*, *J. Funct. Mater.* **26**, 537 (1995). [In Chinese]