

EXAFS and XANES Study of Thermistor Oxides

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Introduction

Complex nickel-copper-cobalt-manganese oxides with spinel structure exhibit semiconducting behavior and are utilized in industry for negative temperature coefficient (NTC) thermistors. The electrical conduction is known to proceed via electron hopping between Mn^{4+} and Mn^{3+} cations located in the octahedral sites of the lattice. In these devices, increased room-temperature resistivity due to prolonged thermal stress (aging) is a serious technological problem that has yet to be resolved. It is suggested that aging might be caused by the structural changes within the lattice.^{1,2} Unfortunately, very little data are available on the coordination and local environment of cations in thermistor spinels. For the first time, the structure of the thermistor oxides was studied using synchrotron radiation.

Materials and Methods

Typical thermistor oxide with composition $Ni_{0.48}Co_{0.24}Cu_{0.6}Mn_{1.68}O_4$ was prepared via low-temperature metalorganic decomposition (MOD) technique.³ Samples were annealed at temperatures between 500 and 800°C. Electrical measurements revealed a strong dependence of resistivity on annealing temperature (Fig. 1). X-ray absorption spectra at the Mn, Ni, Co, and Cu K-edges were obtained from powder specimens. Coordinations of different cations were found using EXAFS (Fig. 2). Experiments were conducted at the 20ID-B/PNC-CAT beamline at the Advanced Photon Source. Oxidation states of the elements were obtained using XANES, XPS, and EELS.

Results and Discussion

It was previously thought that the resistivity increase with elevated annealing temperatures was a consequence of redistribution of the cations between tetrahedral (A) and octahedral (B) sites of the spinel lattice AB_2O_4 .^{1,2} No evidence of this was seen. The cation coordination was not found to be significantly different during the course of annealing. The experimental data obtained instead suggests that an alternative mechanism, in which the redox reaction shown below depletes the original concentration of the Mn^{4+} , might be responsible for the observed change in resistivity.



In this situation, a conversion of Mn^{4+} to Mn^{3+} increases the distortion of the manganese octahedral environment and increases the Jahn-Teller polaron activation energy. This increase was confirmed by electrical measurements.

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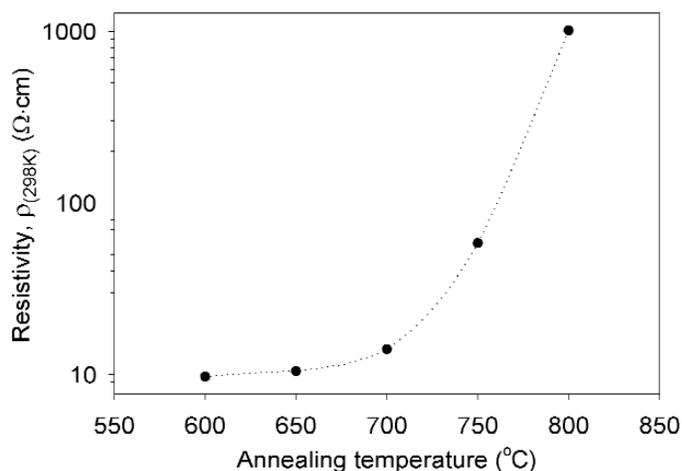


FIG. 1. Dependence of the room temperature resistivity, $\rho_{(298K)}$, of the $Ni_{0.48}Co_{0.24}Cu_{0.6}Mn_{1.68}O_4$ thermistor on the annealing temperature.

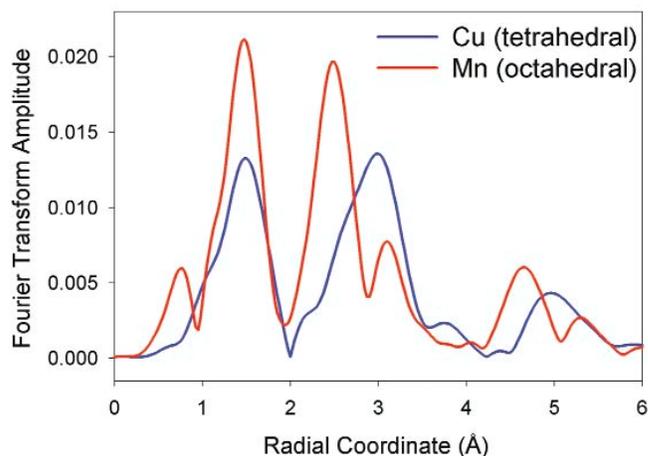


FIG. 2. Typical Fourier transformed EXAFS data from Mn and Cu edges. The transforms were obtained using k^2 weighting. Here, manganese cations occupy predominantly octahedral sites, and copper cations occupy tetrahedral sites of the spinel lattice.

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