

Cation defects and conductivity in transparent oxides

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Free carrier and polaron-based oxide conductors owe their unique properties to the presence of chemical and structural defect states that are a consequence of deposition or post-deposition processing. ZnO and trivalent cation doped ZnO is rendered n-type conducting when prepared in a slightly reduced form. Under these conditions, the normally weak E_1 LO Raman mode near 580 cm^{-1} significantly increases in intensity with respect to the strongly allowed E_2 TO mode at 438 cm^{-1} . In cyclic voltammetry studies where Raman spectra are simultaneously acquired from a ZnO electrode, the LO mode intensity correlates directly with conductivity. Film conductivity also increases upon hydrogen reduction at elevated temperature but is diminished when films become oxidized in air. The time dependent physical response of such films is related to the nature and stability of these defects.

In contrast to free carrier-based conducting oxides, mixed transition metal spinel oxides also are found to exhibit significant electrical conductivity [1], [2]. Resistivities on the order of milliohm-cm have been observed in p-type NiCo_2O_4 where a polaron hopping mechanism drives conductivity. While such materials exhibit diminished charge mobility due to the bound nature of the polaron, their inherent large concentration promotes conductivity. Transition metal spinel oxides show optical absorption in the visible region of the spectrum due to interband d-electron transitions. However, such materials are indeed transparent in the infrared to wavelengths as long as $16\text{ }\mu\text{m}$. This is in contrast to free carrier oxide conductors where, strong absorption at wavelengths beyond $1\text{ }\mu\text{m}$ always is evident. In p-type NiCo_2O_4 , a highly oxidized state of the material stabilizes the trivalent state of nickel [3]. The polaron nature of the conductivity has been confirmed by means of Seebeck measurements, XPS, XRD, temperature dependent infrared and Raman spectroscopy, and resistivity measurements. A cation-disordered state exists in these materials where both the nature of the cation and its charge are randomly distributed among available lattice sites [4]. Consequently, activation energies for conduction are about 0.05 eV. Far infrared absorption measurements that probe localized cation site vibrations indicate the presence of mixed oxidation states on both tetrahedral and octahedral lattice sites. The breadth of these resonances and their behavior as nickel is progressively substituted for cobalt in the structure offers compelling evidence for this disordered state. A combinatorial PVD approach allows preparation of multiple composition films in a single coating run from which correlations between film resistivity, transparency, composition, and cation site disorder have been discerned. The unusually high conductivity of this material is thought to arise from the strong covalent interaction between nickel and oxygen that is associated with the polaron. Electronic structure modeling studies confirm localization of nickel on octahedral sites in the lattice; related modeling studies suggest that resident cation disorder leads to lower hopping activation energies.

[1] C.F. Windisch, Jr., G.J. Exarhos, and R.R. Owings. *J. Appl. Phys.* 95(10):5435 (2004).

[2] C.F. Windisch, Jr., G.J. Exarhos, and S.K. Sharma, *Magnetic Transparent Conducting Oxide Film and Method of Making*, U.S. Patent 6,761,985. (July 13, 2004).

[3] R.R. Owings, P.H. Holloway, G.J. Exarhos, and C.F. Windisch, Jr., *Surf. and Interface Anal.* 37(4), pp. 424 (2005).

[4] R.R. Owings, C.F. Windisch, Jr., P.H. Holloway, and G.J. Exarhos, *Thin Solid Films* 483(1-2):175 (2005).