substance: MnO
property: lattice defects

defect equilibria

the predominant defects are Mn vacancies in pure MnO, for which the following equilibria hold

$1/2\ O_2 \leftrightarrow V_{Mn} + O_O$;	$[V_{Mn}]/p_{O2}^{1/2} = K_x = K_{x0} \exp(-\Delta g_v/kT)$	67H1,
$V_{Mn} \leftrightarrow V'_{Mn} + e^+$;	$p\cdot[V_{Mn}']/[V_{Mn}] = K_1 = K_{10} \exp(-E_1/kT)$	67H2,
$V'_{Mn} \leftrightarrow V''_{Mn} + e^+$;	$p\cdot[V_{Mn}'']/[V_{Mn}'] = K_2 = K_{20} \exp(-E_2/kT)$	70O

where Δg_v is the Gibbs energy of formation of a neutral cation vacancy and E_1 and E_2 are the ionization energies of the vacancy. For the defects, standard Kröger-Vink notation is used throughout.

Because the mobility of the conduction band electrons is so much greater than that of the holes, intrinsic conduction at high temperatures gives an additional significant contribution to the conductivity. As shown in Fig. 1, three regions can be distinguished:

region A:	$[V_{Mn}''] >> [V_{Mn}'], [V_{Mn}]$	$\mu_n n >> \mu_p p$
region B:	$[V_{Mn}''] >> [V_{Mn}'], [V_{Mn}]$	$\mu_n n << \mu_p p$
region C:	$[V_{Mn}'] >> [V_{Mn}'']$	$\mu_n n << \mu_p p$.

MnO is unusual in that it can be doped both p-type and n-type [81P, 71K, 70O], the latter by addition of Ti, Sb, Cr.

defect formation energy

$\Delta g_v + E_1 + E_2$	1.41 eV	$T > 1375$ K		67H2
$d(\ln x)/d(kT^{-1})$	0.94 eV		x is deviation from stoichiometry	67H2
	1.26(5) eV		in $Mn_{1-x}O$	72B

In lithium-doped samples, intrinsic effects are very much reduced. The main equilibrium is

$$1/2\ O_2 + 2\ MnO + Li_2O \leftrightarrow 2\ Li_{Mn}' + 4\ O_O + 2\ Mn_{Mn}.$$

and a dielectric process corresponding to the holes on $Mn_{Mn}^{\cdot}$ hopping around Li_{Mn}' has been identified [68C] with a relaxation energy of 0.29 eV (Fig. 2) [70C].

The trapping energy of the $Li_{Mn}' - Mn_{Mn}^{\cdot}$ site is 0.4 eV [70C] on the basis of an activated mobility or 0.64eV [68A) if the mobility is unactivated. The extent of compensation in Li-doped MnO is controversal, being regarded as slight [70C, 68A] or extensive [76K].

Equilibrium constants for the reactions

$$2\ MnO + 1/2\ O_2 \leftrightarrow 2\ Mn_{Mn}^{\cdot} + V_{Mn}^{''} + 3\ O_O : K_{ox}$$
$$Cr_2O_3 \leftrightarrow 2\ Cr_{Mn}^{\cdot} + V_{Mn}'' + 3\ O_O : K_{Cr}$$

are shown in Fig. 3.

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81P Pai, M., Honig, J. M.: J. Solid State Chem. 40 (1981) 59.

Fig. 1.

MnO. Conductance vs. CO_2/CO pressure ratio of ambient atmosphere during measurement for single crystals. The regions A, B and C delineate regions of differing behaviour (see tables) and the numbers refer to the different exponents n as $1/R \propto p_{O_2}^{1/n}$ [67H2].

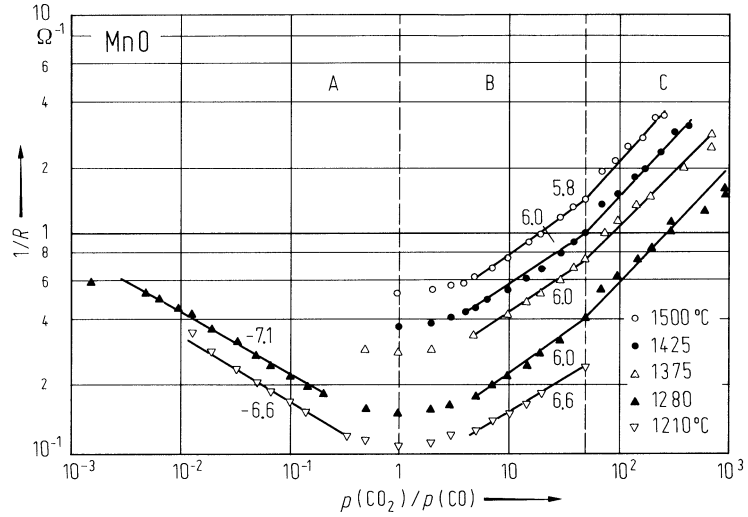

Fig. 2.

MnO:Li. Relaxation time vs. reciprocal temperature for local hole-hopping in Li-doped MnO and CoO [70C]. Li content x = 10^{-3}.

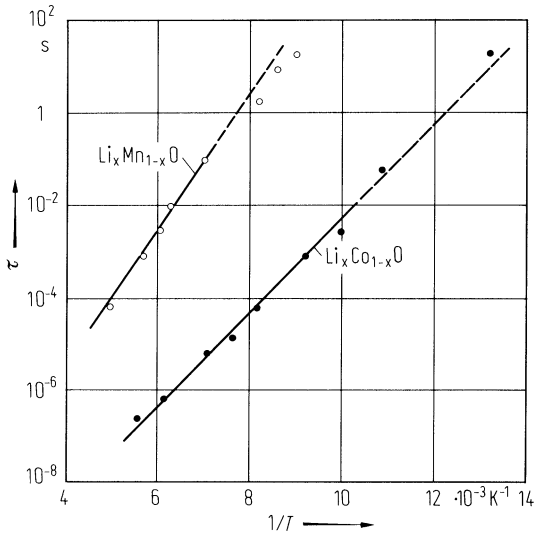

Fig. 3.

MnO. Hole mobility (in $cm^2\ V^{-1}\ s^{-1}$) and constants K_{ox} (in $atm^{1/2}$) and K_{Cr} vs. reciprocal temperature [70O].