substance: chromium sesquioxide (Cr_2O_3)
property: transport mechanism, conductivity

Cr_2O_3 is a p-type semiconductor, but equilibrium with oxygen is only sluggishly established at temperatures below 1500 K, so thermogravimetric analysis has been unable to reveal the nature of the defect. Early work [51H] suggested: $Cr_{Cr} \rightarrow V_{Cr}''' + Cr_i^{2\cdot} + e^+$ with substantial mobility for the interstitial $Cr_i^{2\cdot}$ only found at high temperatures [61H]. More complex defect structures have been proposed to account for the oxygen pressure dependence [72M]. Ionic transport numbers remain less than 0.1% even at 1800 K [61H]; ionic diffusion coefficient of vacancies is ≈ $2\cdot10^{-7}$ cm^2 s^{-1} at 1500 K with an activation energy of 0.25 eV [72M].

conductivity

At high temperatures (1150...1400ºC), the conductivity becomes intrinsic and independent of p_{O2} [64C, 72M] (Fig. 1). In this region $\sigma \propto \sigma_0 \exp(-U/kT)$ with

U	1.63(1) eV	unoriented sample	64C
σ_0	1.48(10) 10^4 Ω^{-1} cm^{-1}		
U	1.68(1) eV	*a*-direction	
σ_0	1.96(16) 10^4 Ω^{-1} cm^{-1}		
U	1.59 (2) eV	*c*-direction	
σ_0	1.37(15) 10^4 Ω^{-1} cm^{-1}		

At low temperatures (T < 1100ºC), an extrinsic region is found with

conductivity activation energies

E_A	0.26 eV	T = 670...1370 K	see Fig. 2; hot pressed sample, $\sigma \propto CT^{-3/2} \exp(-0.26[eV]/kT)$	72M
	0.6 eV	T = 400...1000 K	ceramic, $\sigma = 3.8\cdot10^{-6}\, T^{-1} \cdot 2x(1-2x)\exp(-0.6[eV]/kT)$ [Ω^{-1} cm^{-1}] for Cr_2O_{3+x}	69C
	0.41 eV	T = 470...970 K	ceramic, from ac conductivity at 1 kHz	71R
	0.4 eV	RT		67V
	0.519 eV	T = 370 K	polycrystalline sample	74C

In the low T range the defects created at high temperatures, presumably [V_{Cr}'''], are "frozen in" and the thermopower is constant [72M], or varies only slightly [69C] with T and p_{O2} The variation of σ with p_{O2} is too small to be explained in terms of any simple defect equilibria. ac conductivity has an activation energy of 0.9 eV for T = 300ºC, f = 100...10^6 Hz [77R].

influence of non-stoichiometry: Fig. 3 (conductivity), Fig. 4 (Seebeck coefficient).

References:

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Fig. 1.

Cr_2O_3. Conductivity vs. (reciprocal) temperature for unoriented single crystal in the intrinsic region for two values of p_{O2} [64C].

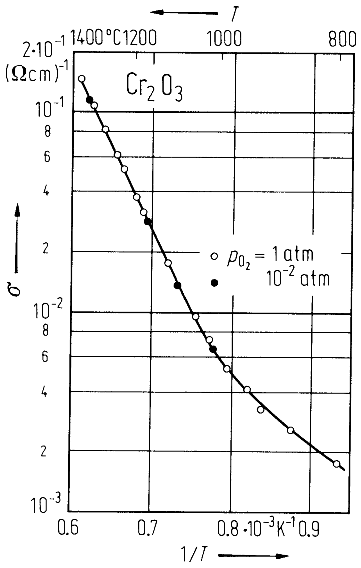

Fig. 2.

Cr_2O_3. Conductivity (times $T^{3/2}$) vs. (reciprocal) temperature for hot-pressed ceramic samples under oxygen and argon atmosphere, respectively [72M].

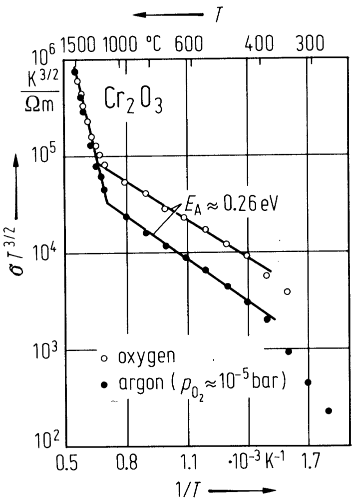

Fig. 3.

$Cr_2O_{3+\delta}$. Conductivity (times temperature) vs. reciprocal temperature for cold-pressed ceramic samples of different stoichiometry. $\delta = 0.06$ (A), 0.02 (B), 0.01 (C), 0.004 (D) [69C].

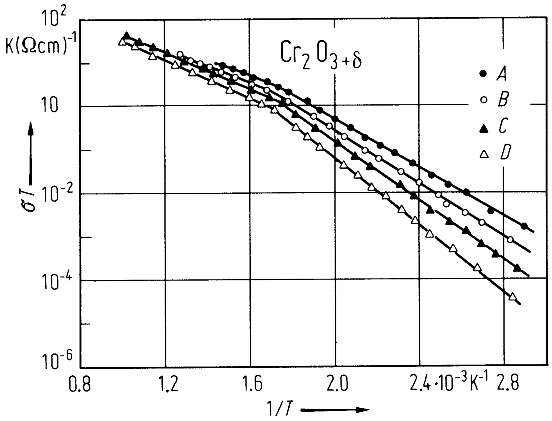

Fig. 4.

$Cr_2O_{3+\delta}$. Seebeck coefficient vs. temperature for the cold-pressed ceramic samples of Fig. 3 [69C].