

Ionic Conductivity and Coulometric Titration of Copper Selenide. T. TAKAHASHI, O. YAMAMOTO, F. MATSUYAMA, AND Y. NODA. Department of Applied Chemistry, Nagoya University, Nagoya 464, Japan. The ionic conductivity of copper selenide was measured in the temperature range of 30–180°C by blocking the electronic current by the copper ion high conductivity solid electrolyte, $37\text{CuBr} \cdot 3[\text{C}_6\text{H}_{12}\text{N}_2 \cdot 2\text{CH}_3\text{Br}]$. It was found that the α -phase of $\text{Cu}_{2-\delta}\text{Se}$ has a high ionic conductivity; for example, $\text{Cu}_{1.75}\text{Se}$ exhibited an ionic conductivity of $3 \times 10^{-2} \text{ ohm}^{-1} \text{ cm}^{-1}$ at room temperature. The coulometric titration of copper selenide was carried out with the help of the cell, $\text{Au}/\text{Cu}_{2-\delta}\text{Se}/\text{solid electrolyte}/\text{Cu}$; from the temperature dependence of the cell voltage, the β - α transition temperatures of $\text{Cu}_{2-\delta}\text{Se}$ were determined as functions of δ .

A Study of the $\text{MgO}-\text{V}_2\text{O}_5$ System. G. M. CLARK AND R. MORLEY. Department of Applied Chemical and Biological Sciences, The Polytechnic, Huddersfield HD1 3DH, England. An investigation was made of solid–solid reactions in $\text{MgO}/\text{V}_2\text{O}_5$ mixtures of various stoichiometries. Three compounds were obtained: $\text{Mg}_3\text{V}_2\text{O}_8$, $\text{Mg}_2\text{V}_2\text{O}_7$, and MgV_2O_6 . No evidence was obtained to indicate formation of other $\text{MgO}-\text{V}_2\text{O}_5$ compounds reported in the literature. DTA data are listed for the three compounds and some observations are made on the mechanism of formation of the compounds. A new polymorph of $\text{Mg}_2\text{V}_2\text{O}_7$ was prepared and its space group and cell parameters were deduced from the X ray powder diffraction pattern. This polymorph undergoes a transition, reversible with difficulty, at 980–990°K.

Etude par Diffractions X et Neutronique d'un Monocristal de UCr_2O_6 Obtenu par Synthèse Hydrothermale sous Très Haute Pression. Détermination des Structures Cristallographique et Magnétique. A. COLLOMB, M. GONDRAND, M. S. LEHMANN, J. J. CAPPONI, AND J. C. JOUBERT. Laboratoire des Rayon X, C.N.R.S., B.P. 166, Centre de Tri, 38042 Grenoble Cedex, France. The structure of UCr_2O_6 , PbSb_2O_6 type compound, has been refined from X ray and neutron single crystal data. The symmetry is trigonal, space group $\text{P}\bar{3}1\text{m}$, with $a = 4.990$ (1) Å and $c = 4.622$ (1) Å. There is one molecule per unit cell. The uranium, chromium and oxygen atoms occupy the $1a$ (0, 0, 0), $2d(\frac{1}{3}, \frac{2}{3}, \frac{1}{2})$, $6k(x, 0, z)$ positions respectively with $x = 0.3405$ (3) and $z = 0.2647$ (2). The final R factors are 0.033 for the X ray data and 0.0294 for the neutron data. The anisotropic temperature factors have been introduced in the last stage of both refinements. The average cation–anion interatomic distances are $\text{U}-\text{O} = 2.094$ (1) Å, $\text{Cr}-\text{O} = 1.9726$ (8) Å. From these values it can be deduced that the uranium and chromium are hexavalent and trivalent, respectively. From powder diffraction diagrams at 298 and 4.2°K, it has been determined that the spins of the Cr^{3+} are located in the basal plane with an antiferromagnetic type arrangement. The value of the magnetic moment is 2.6 μB .

The Electrical Conductivity and Thermodynamic Behavior of SrO-Doped Nonstoichiometric Cerium Dioxide. R. N. BLUMENTHAL AND J. E. GARNIER. Metallurgy and Materials Science, College of Engineering, Marquette University, Milwaukee, Wisconsin 53233. Electrical conductivity and thermogravimetric measurements were made on SrO-doped nonstoichiometric cerium dioxide (i.e., $\text{Ce}_{1-y}\text{Sr}_y\text{O}_{2-y-x}$) as a function of temperature ($\sim 700^\circ$ to 1500°C) and oxygen partial pressure (~ 1 to 10^{-21} atm). Assuming limiting case defect models the ionic σ_i , and electronic, σ_e conductivities were calculated from this data. In the region where $y \gg x$ (i.e. at low temperatures and high oxygen pressures) the conductivity is independent of P_{O_2} and up to approximately 3 mole% SrO it is proportional to mole% SrO. The equation for ionic conductivity, $\sigma_i \approx [4.5 \pm 0.5][m/o\text{SrO}]\exp(-0.58/kT)$, was obtained by fitting the conductivity data in this region to an expression derived on the basis of an oxygen vacancy model. In the composition region between approximately $x = 10^{-3}$ and $x = 10^{-2}$, both the thermodynamic behavior and the electrical conductivity were shown to be consistent with a defect model involving randomly distributed doubly ionized oxygen vacancies and electrons localized on normal cerium sites. In this region, the electronic conductivity varies linearly with x and the electronic mobility decreases with increasing SrO content.