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Abstracts of forthcoming articles

Etudes par spectroscopie Raman et par RMN des verres du systeme B_2O_3–SiO_2–Li_2O. J. C. BRETHOUS, A. LEVASSEUR, G. VILLENEUVE, P. ECHEGUT, P. HAGENMULLER,* AND M. COUZI, Laboratoire de Chimie du Solide du CNRS, Université de Bordeaux I, 351 cours de la Libération, 33405 Talence Cédex, France. A structural approach by Raman spectroscopy of glasses belonging to the B_2O_3–SiO_2–Li_2O system has been carried out. A complementary study of the boron environment by RMN was also realized. The glasses are formed by two separate phases containing respectively a borate and a silicate framework. This phenomenon has been confirmed by some SEM investigations. No presence of borosilicate chains has been established.

X-Ray Photoelectron Spectra and Electronic Structure of Rare-Earth Orthovanadates. M. V. RYZHKOV,* S. P. KOSTIKOV, I. K. IVANOV, AND V. A. GUBANOV, Institute of Chemistry, Ural Science Center, Academy of Sciences, Sverdlovsk, USSR. Photoelectron spectra of 4*d* and valence states in RVO_4 (R = Y, Nd, Eu, Gd, Tb, Dy, Yb) have been investigated. The experimental spectra are interpreted using the results of $X\alpha$ discrete variational method calculations for orthovanadates. Transformations of electronic structure and covalency in the RVO_4 series are discussed. It is shown that lanthanide 4*f* orbitals significantly mix with the O 2*p* AOs and hybridize with the rare-earth 5*p* AOs. The 5*p* levels spin-orbital splitting in orthovanadates has been evaluted.

Alkali Metal Intercalated Transition Metal Disulfides: A Thermodynamic Model. A. S. NAGELBERG* AND W. L. WORRELL, Exploratory Chemistry Division I, Sandia National Laboratories, Livermore, California 94550. In the lithium intercalated disulfides, Li_xMS_2, where M = Ti, Ta, a nearly linear compositional variation of the lithium chemical potential is observed throughout the composition range $0 < x < 1.0$. For most sodium intercalated disulfides, chemical potential plateaus are observed between regions exhibiting linear variations of sodium chemical potential. Our thermodynamic model indicates that the two most important factors which determine the compositional variation of the alkali metal chemical potential are the interaction energy between intercalated alkali metal atoms and the compositional variation of the electron chemical potential. Although these two factors determine the compositional variation of chemical potential in single-phase regions. the existence of two-phase regions in the concentration range x = 0–0.15 are influenced by the energy required to expand the interlayer gap and the configurational entropy.

The Electrical Conductivity and Thermoelectric Power of Mn_3O_4 at High Temperatures. R. METSELAAR,* R. E. J. VAN TOL, AND P. PIERCY, Laboratory of Physical Chemistry, Eindhoven University of Technology, Eindhoven, The Netherlands. The electrical resistivity and the Seebeck coefficients of Mn_3O_4, in the temperature range 1100–1700 K, have been measured under oxygen partial pressures of 1–10^{-6} atm. The resistivity is thermally activated with an activation energy of 1.3 eV for the tetragonal (low temperature) phase and 0.65 eV for the cubic (high temperature) phase. The thermoelectric power shows p-type behavior with an activation energy of 1.1 eV for the tetragonal phase and 0.3 eV for the cubic phase. The data can be explained satisfactorily in terms of small-polaron hopping.

Polaron Interaction Energies in Reduced Tungsten Trioxide. E. IGUCHI, E. SALJE, AND R. J. D. TILLEY, * School of Materials Science, University of Bradford, Bradford BD7 IDP, West Yorkshire, United Kingdom. Consideration of the properties of reduced tungsten trioxide suggest that the mobile charge carriers are polarons. As it is uncertain how the presence of polarons will influence the microstructures of the crystallographic shear (*CS*) planes present in reduced tungsten trioxide we have calculated both the polaron–*CS* plane and polaron–polaron interaction energy for a variety of circumstances. Three *CS* plane geometries were considered, {102}, {103}, and {001} *CS* plane arrays, and the nominal compositions of the crystals ranged from $WO_{2.70}$ to $WO_{3.0}$. The polarons

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were assumed to have radii from 0.6 to 1.0 nm and the polaron–*CS* plane electrostatic interaction was assumed to be screened. The results suggest that for the most part the total interaction energy is small and is unlikely to be of major importance in controlling the microstructures found in *CS* planes. However, at very high polaron densities the interaction energy could be appreciable and may have some influence on the existence range of *CS* phases.

Subsolidus Phase Relations in the Systems CeO_2–Re_2O_3 *(*RE_2O_3 *= C-Type Rare Earth Sesquioxide).* J. G. PEPIN,* E. R. VANCE, AND G. J. MCCARTHY, Materials Research Laboratory, The Pennsylvania State University, University Park, Pennsylvania 16802. The systems CeO_2–RE_2O_3 (RE_2O_3 = *C*-type rare earth sesquioxide) were studied to (1) investigate the claims of several workers for the existence of a complete solid solution series between CeO_2 and RE_2O_3 and (2) to characterize the weak *C*-type X-ray diffraction peaks reported by others from samples in the single-phase fluorite solid solution region. It is shown that a complete solid solution series does not exist, and an explanation for the observations of others reporting such is tendered. It is also shown that the observation of *C*-type reflections in the supposed single-phase fluorite field can be attributed to the partial reduction of Ce^{4+} to Ce^{3+} at the firing temperature, resulting in movement of the bulk composition into a two-phase field of the CeO_2–RE_2O_3–Ce_2O_3 phase diagram, rather than formation of a domain structure due to ordering.

Evolution structurale de monoxydes non-stoechiometriques du type Wüstite. Simulations et relations entre parametres structuraux. J.-R. GAVARRI AND C. CAREL,* Laboratoire de Cristallochimie, Avenue du Marechal Leclerc, 35042 Rennes Cedex, France. For nonstoichiometric monoxides $M_{1-z}O$ (or MO_x) of the wüstite type, it is possible to forecast the trend of the experimental graphs representing the parameters a of the cubic cell or the temperature factor B vs temperature θ or composition z (or x). A criterion for the experimental accuracy allows us to justify the existence or not of a curvature on the graphs. The parameter a is calculated a priori for wüstite (M = Fe) vs z. A model gives the law of variation of a vs some ionic species and the ratio $\rho = (z + t)/t$; t is the rate of interstitials. The law is $a = a_0[1 - \frac{1}{3}\beta^* z]$. The calculated value obtained for β^* agrees well with the experimental mean value $\langle\beta\rangle = 0.28$. This model applies to the monoxide $Mn_{1-z}O$ for which the calculated value of β^* is close to $\langle\beta\rangle = 0.29$. In a second model, the cell volume is defined as being the weighted mean of the volumes of distorted and undistorted cells. With knowledge of β^* and ρ, it is possible to evaluate the mean radius of a vacancy for each oxide. The factor B is the sum of two contributions $B_{Th}(\theta)$ and $B_{St}(z)$. This latter varies linearly with z. The coefficient $p = (\partial B/\partial z)_\theta$ can be calculated a priori from simulations of the shifts resulting from clusters of point defects. Knowing β^*, p may be located between 3 and 10 Å^2 according to the assumptions. The experimental value for the wüstite under equilibrium conditions is p = 4.2 Å^2. An empirical relation between $B_{Th}(\theta)$ is discussed from the point of view of Grüneisen's law. When the molar heat C_v is known, it is possible to evaluate the mean force constant D = 0.78 mdyn/Å for the bonds in $Fe_{1-z}O$. The compressibility coefficient χ_D is then obtained. It can be compared with the measured value from the literature, at 25°C under zero pressure.