

## Abstracts of forthcoming articles

*Crystal Structure and Fast Ionic Conduction of  $TlZrF_5$ .* D. AVIGNANT, I. MANSOURI, R. CHEVALIER, AND J. C. COUSSEINS,\* Groupe de Cristallographie et de Chimie des Solides, Université de Clermont-Ferrand II, B.P. 45, 63170 Aubiere, France.  $TlZrF_5$  crystallizes in the monoclinic system with unit-cell dimensions  $a = 8.112(1) \text{ \AA}$ ,  $b = 7.927(3) \text{ \AA}$ ,  $c = 7.929(1) \text{ \AA}$ ,  $\beta = 123.99(1)^\circ$ , and space group  $P2_1/c$  (No. 14);  $Z = 4$ . The structure was solved by conventional Patterson and Fourier methods and refined by full-matrix least squares to a conventional  $R$  of 0.057 ( $R_w = 0.063$ ). The structure consists of sheets  $(ZrF_5)^-$  that may be described as edge-shared and corner-shared bicapped trigonal prism  $(ZrF_6)$ . The sheets run parallel to the  $\gamma\theta z$  plane and are bonded together by the Tl ions which are surrounded by 12  $F^-$  atoms. The ionic conductivity of  $TlZrF_5$  and  $TlHfF_5$  has been investigated by complex impedance measurements and the relationships between structure and fast ionic conduction are discussed.

*Oxidation in the  $\gamma$  Phase of Spinel's Containing Iron. II. Influence of Defects on the Oxidation Kinetics and Electrical Properties.* B. GILLOT,\* F. CHASSAGNEUX, AND A. ROUSSET, Laboratoire de Recherches sur la Réactivité des Solides, Faculté des Sciences Mirande, B.P. 138, 21004 Dijon Cédex, France. After a review of the distribution of vacancies in defect phases resulting from  $\gamma\text{-Fe}_2\text{O}_3$ , the authors give several examples drawn from oxidation kinetics and electrical properties where the vacancies play a basic part due to their concentration as well as their location. The decrease in chemical diffusion coefficient with increase in vacancy content and the variation of the exponent from the pressure law with the extent of association are dependent on concentration while the nature of the electron hopping between  $Fe^{2+}$  and  $Fe^{3+}$  ions is governed by the location of vacancies in the two types of sites in the spinel lattice.

*Isothermal Decomposition of Ternary Oxide  $A_xB_yO_z$  on Isobar Stability of Perovskite  $ABO_3$  ( $A = La, Sm, Dy$ ;  $B = Mn, Fe$ ) in Reducing Atmosphere.* T. NAKAMURA, Research Laboratory of Engineering Materials, Tokyo Institute of Technology, 4259 Nagatsuta-cho, Yokohama 227, Japan. The isothermal decomposition of any ternary oxide  $A_xB_yO_z$  on liberation of  $n$  moles of oxygen at a constant pressure is found to be driven by the mixing entropy  $\Delta S_m = -nR \ln P_{O_2}$  of the total entropy change  $\Delta S = \Delta S^\circ + \Delta S_m$ . The stability of  $A_xB_yO_z$  toward isothermal decomposition into a biphasic solid mixture is derived from the equilibrium condition  $\Delta G^* = 0$  as functions of standard changes  $\Delta H^\circ$  and  $\Delta S^\circ$ . Assuming  $\Delta S^\circ = 44n$  and calculating  $\Delta H^\circ$  in terms of lattice energies  $U(ABO_3)$  and  $U(A_2O_3)$ , the stability of perovskites  $St(ABO_3) = -\log P_{O_2}^*$  ( $A = La, Sm, Dy$ ;  $B = Mn, Fe$ ) is given as a function of the ionic radius of the  $A^{3+}$  ion. The calculated stability agrees with the observed. The effect of electronic entropy change  $\Delta S_e$  on  $\Delta S^\circ$  is demonstrated for  $AFeO_3$  ( $A = La, Sm, Dy$ ).

*Neutron Powder Diffraction on  $\alpha\text{-Ti}_4\text{CrI}_8$  and  $\beta\text{-Ti}_4\text{CrI}_8$ .* H. W. ZANDBERGEN, Gorlaeus Laboratories, University of Leiden, P.O. Box 9502, 2300 RA Leiden, The Netherlands.  $\alpha\text{-Ti}_4\text{CrI}_8$  ( $a = 9.132(1)$ ,  $c = 9.667(1) \text{ \AA}$ ,  $Z = 2$ ,  $P4/mnc$  at 293 K) adopts a distorted  $Tl_4HgBr_8$  structure. In  $\alpha\text{-Ti}_4\text{CrI}_8$  a random distribution of Jahn Teller distorted octahedra occurs, which are elongated perpendicular to the  $c$  axis. Between 77 and 4.2 K a phase transition occurs. In  $\beta\text{-Ti}_4\text{CrI}_8$  ( $a = 12.941(3) \text{ \AA}$ ,  $b = 12.596(3) \text{ \AA}$ ,  $c = 9.602(2) \text{ \AA}$ ,  $Z = 4$ ,  $Cccm$  at 4.2 K) the directions of elongation of the octahedra are ordered. The structure is very much related to that of  $\alpha\text{-Ti}_4\text{CrI}_8$ . A three-dimensional magnetic ordering takes place at 2.7(2) K. The magnetic space group at 1.2 K is  $C_122'2'$ . The magnetic moments ( $3.48(6) \mu_B$ ) are parallel to (001) and have an angle of  $41(9)^\circ$  with the  $a$  axis. Four magnetic sublattices are present forming two independent magnetic lattices which have no interaction due to the antiparallel ordering.

Note: Asterisks indicate author to be addressed.