JOURNAL OF SOLID STATE CHEMISTRY 38, 406–407 (1981)

Abstracts of Forthcoming Articles

XPS Study on Valence Band Structures of Transition-Metal Trisulfides, TiS_3, NbS_3, and TaS_3. K. Endo,* H. Ihara, K. Watanabe, and S. Gonda, Electrotechnical Laboratory, 1-1-4, Umezono, Sakura-mura, Ibaraki 305, Japan. Transition-metal trisulfides TiS_3, NbS_3, and TaS_3 with a quasi-one-dimensional structure are investigated by X-ray photoelectron spectroscopic (XPS) measurements to obtain information on the valence band structures. The band structures at the Fermi level of these compounds correspond well to their transport properties. A shoulder is observed at the top of the valence band in NbS_3 and TaS_3, suggesting that this band is made up of the metal d_{z^2} electrons. The d_{z^2} band is occupied in NbS_3 and TaS_3 and empty in TiS_3. The characteristic features at the top of the valence band in NbS_3 imply the occurrence of d_{z^2} band separation, leading to a semiconducting nature.

On the Luminescence of Titanium-Activated Stannates. G. Blasse,* G. A. M. Dalhoeven, J. Choisnet, and F. Studer, Physical Laboratory, State University, P.O. Box 80.000, 3508 TA Utrecht, The Netherlands. The luminescence of the following systems is reported: $Li_{1.6}Zn_{1.6}(Sn_{1-x}Ti_x)_{2.8}O_8$ and $Zn_2Sn_{1-x}Ti_xO_4$. The luminescence properties are independent of x and cannot be due to the titanium ions. The emission transitions are ascribed to centers with energy levels within the forbidden energy gap.

Crystallization and Phase Transformation of Sodium Orthoferrites. S. Okamoto, Technological University of Nagaoka; Nagaoka; Niigaka-ken, 949-54, Japan. On heating mixtures of α-Fe_2O_3 powder in sodium hydroxide melts at around 200°C, unstable β-$NaFeO_2$ crystallizes in the first reaction stage and transforms spontaneously to stable α-$NaFeO_2$. The process is typical of the Ostwald Step Rule. When γ-Fe_2O_3 is used as the starting material, instead of α-Fe_2O_3, stable α-$NaFeO_2$ always crystallizes out. It was clearly observed that even though the reactions are of the dissolution and recrystallization type, three-dimensional structural relations can be preserved between the reactant and the product crystals. The nucleation mechanism is discussed on the basis of topotaxy.

La spectroscopie de photoelectrons induits par rayons X et la repartition des ions cuivre Cu^+ et Cu^{2+} dans les ferrites de cuivre. A. D'Huysser, B. Lerebours-Hannoyer, M. Lenglet, et J. P. Bonnelle,* Laboratoire de Catalyse Hétérogène et Homogène, Université des Sciences et Techniques de Lille, 59655 Villeneuve D'Ascq Cedex, France. XPS study of copper ferrite oxide spinels $Cu_{1-x}Fe_{2+x}O_4$ with $0 < x \leq 0.5$ gives information about valence states and cationic distribution of copper in the spinel matrix. It appears that copper is monovalent and divalent and that Cu^{2+} and Cu^+ cations are found in the tetrahedral and octahedral O^{2-} anion environments. X-Ray irradiation induces reduction of tetrahedral Cu^{2+} into tetrahedral Cu^+. The different copper types give shifted Cu $2p_{3/2}$ lines, the intensity ratios of which can be used to evaluate the relative proportions of one type on each site. There is satisfactory agreement between our results, Mössbauer spectroscopy studies, and statistical calculations of cationic distribution. The transformation under X-ray irradiation is attributed to displacement of the redox equilibrium $Cu^{2+}_{Tetra} + Fe^{2+}_{Octa} \rightleftarrows Cu^{+}_{Tetra} + Fe^{3+}_{Octa}$ in the sites.

Phase Diagrams of Systems SrF_2–$(Y, Ln)F_3$. II. Fusibility of Systems and Thermal Behavior of Phases. B. P. Sobolev* and K. B. Seiranian, Institute of Crystallography, USSR Academy of Sciences, Moscow, USSR. The phase diagrams of 14 SrF_2–$(Y, Ln)F_3$ systems are given, where Ln represents all the lanthanides except Pm and Eu. The diagrams have been constructed for temperature intervals from 850°C to the melting points according to the thermal and X-ray analysis. The fusibility diagrams for 12 systems have been obtained for the first time. The oxygen content in the specimens before and after thermal treatment was checked. The thermal behavior of the three types of solid solutions has been studied: (1) with the fluorite-type defect structure and its derivatives; (2) with the defect structure of lanthanum fluoride, and (3) α-YF_3 (α-UO_3) types. Maxima reflecting a noticeable effect of thermal stabilization on the fluorite-type structure by the heterovalent isomorphous substitution have been found for the majority of systems (with Ln = La–Ho). The $Sr_{1-x}Ln_xF_{2+x}$

Note. Asterisks indicate author to be addressed.

0022-4596/81/090406-02$02.00/0

nonstoichiometric fluorite phases are formed in all the systems. Similar maxima corresponding generally to irrational compositions are present on the fusibility curves of the $Ln_{1-y}Sr_yF_{3-y}$ nonstoichiometric phases with the LaF_3-type structure (tysonite). Tysonite solid solutions are in all the systems, too. Nonstoichiometric phases with the α-YF_3-type structure are formed in the systems with *Ln* = Er–Lu. They are decomposed in the process of cooling and are the most unstable. The structure of the phase diagrams in the regions adjacent to lanthanide trifluorides are determined by polymorphism and morphotropy of the above-named compounds. Changes in the thermal stability of the nonstoichiometric phases and double chemical compounds in the series of lanthanides have been observed. The SrF_2–$(Y,Ln)F_3$ systems studied give examples of the formation of phases with the highest concentrations of point defects among all the known binary fluoride systems (up to 50 at%). The thermal stabilization effect of the nonstoichiometric phases with the fluorite structure results in the fact that the series of the two-component compositions is melted at considerably higher temperatures as compared with scandium fluoride, the most refractory single-component fluoride compound. This effect leads to formation of tysonite-type solid solutions with melting points exceeding 1500°C (mp of LaF_3—the most refractory fluoride material with tysonite-type structure).