

*Mössbauer Spectroscopic Study of  $\gamma$ -Ray-Irradiated Potassium Borate Glasses.* TETSUAKI NISHIDA, YOSHIMASA TAKASHIMA, AND YUSUKE NAKAYAMA. Department of Chemistry, Faculty of Science, Kyushu University 33, Hakozaki, Higashiku, Fukuoka, 812 Japan.

Potassium borate glasses denoted by the formula  $x\text{K}_2\text{O} \cdot (100-x)\text{B}_2\text{O}_3 \cdot 7\text{Fe}_2\text{O}_3$  were irradiated with  $^{60}\text{Co}$   $\gamma$ -rays at room temperature. Mössbauer parameters for the irradiated glasses containing alkali equal to or higher than 20 mole% showed that the  $s$ -electron density at the iron nucleus increased without any change of the steric configuration of oxygen atoms around the iron nucleus. The increase of  $s$ -electron density was ascribed to electron transfer from the nonbridging oxygen to the iron nucleus. The presence of the nonbridging oxygen was also confirmed by the irradiation effect of the borate glass ( $x = 30$ ) prepared using the enriched isotope of  $^{57}\text{Fe}_2\text{O}_3$ . Mössbauer parameters for the irradiated glass suggest that the newly observed  $\text{Fe}^{2+}$  ions are in tetrahedral symmetry.

*Solid State Decomposition Studies on Fluoroperoxo Species of Transition Metals. IV. Photodecomposition of  $\text{K}_3\text{Zr}_2(\text{O}_2)_2\text{F}_7 \cdot 2\text{H}_2\text{O}$ .* G. V. JERE AND S. M. KAUSHIK. Department of Chemistry, Indian Institute of Technology, New Delhi-110029, India.

The kinetics of photodecomposition of solid  $\text{K}_3\text{Zr}_2(\text{O}_2)_2\text{F}_7 \cdot 2\text{H}_2\text{O}$  has been studied under vacuum as a function of intensity and temperature by measuring the evolved oxygen with the help of a McLeod gauge. Pressure-time curves are parabolic in nature and the data fit the empirical equation  $p = kt^{1/2}$ . The rate of photodecomposition is a linear function of intensity. The activation energy determined from an Arrhenius plot, in the temperature range 15–55°C, of the title compound is 2.15 kcal mole $^{-1}$  (9.00 kJ mole $^{-1}$ ).

*High-Pressure/High-Temperature Phase Relations and Vibrational Spectra of  $\text{CsSbF}_6$ .* W. H. J. DE BEER, ANTON M. HEYNS, P. W. RICHTER, AND J. B. CLARK. National Physical Research Laboratory, P.O. Box 395, Pretoria, South Africa.

$\text{CsSbF}_6(\text{II})$  under ambient conditions is trigonal, space group  $D_{3d}^5-R\bar{3}m$ . At 187.8°C it undergoes a phase transition with an enthalpy change of  $5.267 \pm 0.316$  kJ mole $^{-1}$ , to phase  $\text{CsSbF}_6(\text{I})$ .  $\text{CsSbF}_6$  decomposes with loss of fluorine at atmospheric pressure at high temperatures, but under pressure the decomposition is prevented and a melting point of 310°C at atmospheric pressure can be inferred. The II/I phase boundary and melting curve were studied as functions of pressure. The infrared and Raman spectra of  $\text{CsSbF}_6(\text{II})$  were studied in the temperature range –256 to 20°C, at ambient pressure. The crystal chemistry of the  $\text{CsSbF}_6$  and its relationship with other related compounds are discussed.

*Silver  $\beta$ "-Alumina.* A. KAHN, PH. COLOMBAN, AND J. P. BOILOT. Laboratoire de Chimie Appliquée de l'Etat Solide, 11, rue P. et M. Curie 74231 Paris Cedex 05, France.

The "mean" structure of silver  $\beta$ "-alumina, stabilized by  $\text{MgO}$ , is refined with an  $R$  value of 0.037, on single crystals prepared by a self-crucible-heating method. Evidence is given for  $\text{Ag}^+$  ion static disorder in a wide temperature range.

*Untersuchung von Alkaliantimonaten des Typs  $\text{Me}^1\text{Sb}^{\text{V}}\text{O}_3 \cdot 1/6\text{Me}^1\text{F}$  mittels Dielektrischer Spektroskopie.* U. STAUDT UND G. SCHÖN. Universität Essen GHS, Fachbereich 8 Chemie, Teilbereich Anorganische und Allgemeine Chemie, D-4300 Essen, Germany.

Compounds of the type  $\text{Me}^1\text{Sb}^{\text{V}}\text{O}_3 \cdot 1/6\text{Me}^1\text{F}$  ( $\text{Me}^1 = \text{Li}, \text{Na}, \text{K}, \text{Rb}, \text{and Cs}$ ) were tested for their dielectric properties with a new dielectric spectrometer in the frequency range from 100 Hz to 10 MHz and in the temperature range from 238 to 147 K. The results show a high ionic conductivity for some of these compounds. A discussion of the structural properties of these substances suggests a model for a cooperative movement of the monovalent  $\text{Me}^+$  cations, which are responsible for the ionic conductivity.

*A New Alkali-Metal Titanotantalate,  $\text{KTi}_2\text{Ta}_5\text{O}_{17}$ —A Compound That Exhibits the "Chemically Twinned" Rutile Structure.* B. M. GATEHOUSE AND M. C. NESBITT. Chemistry Department, Monash University, Clayton, Victoria, 3168 Australia.

$\text{KTi}_2\text{Ta}_5\text{O}_{17}$  crystallizes in the orthorhombic system with unit-cell dimensions (from single-crystal data)  $a=6.672(4)$  Å,  $b=8.948(5)$  Å,  $c=21.403(9)$  Å and space group  $Cmcm$ ,  $Z=4$ . The structure was solved using three-dimensional Patterson and Fourier techniques. Of the 1034 reflections measured by counter techniques, 704 with  $I \geq 3 \sigma(I)$  were used in the least-squares refinement of the model to a conventional  $R$  of 0.041 ( $wR = 0.043$ ). The structure consists of edge- and corner-shared tantalum octahedra joined such that tunnels are formed in which the potassium ions are located. Slabs of octahedra are of the rutile ( $\text{TiO}_2$ ) type related to one another by mirror planes (in which the potassium ions are located), producing a structure that may be considered as a "chemical twin" of the rutile structure.

*An Experimental and Theoretical Study of Crystals of Calcium Fluoride Doped with Alkali Metal Cations.* P. W. M. JACOBS S. H. ONG, A. V. CHADWICK, AND V. M. CARR. Department of Chemistry, University of Western Ontario, London, Ontario N6A 5B7, Canada.

Experimental measurements of thermal depolarization in crystals of  $\text{CaF}_2$ , grown from the melt containing LiF, NaF, KF, or RbF, reveal a common relaxation (designated  $M_2$ ) with an activation energy of 0.51 eV. In addition, the  $\text{Li}^+$ - and  $\text{K}^+$ -doped crystals exhibit a relaxation ( $M_1$ ) with an activation energy of 0.34 eV. A similar relaxation has been found in  $\text{CaF}_2:\text{Rb}^+$  and in  $\text{CaF}_2:\text{Na}^+$ . Theoretical calculations on  $M^+$ -doped  $\text{CaF}_2$  (where  $M = \text{Li, Na, K, Rb}$ ) are in agreement with the hypothesis that the  $M_2$  relaxation is due to  $\text{Na}^+$  in all four systems studied and is associated with the jump of a nearest-neighbor (nn) anion vacancy ( $\text{F}_v^-$ ) around the substitutional  $\text{Na}^+$  ion ( $\text{Na}_s^+$ ). The assignment of  $M_1$  is less certain, but it appears to be associated with similar  $\text{Li}_s^+ - \text{F}_v^-$  dipoles resulting from  $\text{Li}^+$  impurity present because of the lower volatility of LiF compared to that of KF and RbF. When LiF dissolves in  $\text{CaF}_2$  the  $\text{Li}^+$  ion also forms quadrupoles consisting of a cation vacancy and two  $\text{Li}^+$  interstitials and the reorientation of these quadrupoles has also been studied theoretically.

*Defect Structures in the Brannerite-Type Vanadates. I. Preparation and Study of  $\text{Mn}_{1-x}\phi_x\text{V}_{2-2x}\text{Mo}_{2x}\text{O}_6$  ( $0 \leq x \leq 0.45$ ).* ROMAN KOZŁOWSKI, JACEK ZIOLKOWSKI, KRZYSZTOF MOCALA, AND JERZY HABER. Institute of Catalysis and Surface Chemistry, Polish Academy of Sciences, ul. Niezapominajek, 30-239 Krakow, Poland.

Phases of the formula  $\text{Mn}_{1-x}\phi_x\text{V}_{2-2x}\text{Mo}_{2x}\text{O}_6$  with the brannerite-type ( $\alpha$ ) structure, where  $\phi_x$  represents a vacancy at a Mn site, have been synthesized and characterized by X-ray diffraction and DTA. The X-ray data are listed for  $\text{MnV}_2\text{O}_6$  and solid solution with  $x = 0.40$ . They indicate random distribution of V and Mo over the original V sites and random distribution of Mn and vacancies over the original Mn sites. The monoclinic cell dilates with increasing  $x$ , primarily in the direction of the  $b$ -axis. The phase diagram of the pseudobinary  $\text{MnV}_2\text{O}_6\text{-MoO}_3$  system has been determined. The extent of the stability region for the investigated brannerite solid solution has been established ( $x_{\text{max}} = 0.45$  at  $580^\circ\text{C}$ ). Other features determined in this system were: (a) little solubility of  $\text{MoO}_3$  in the high-temperature ( $\beta$ ) modification of  $\text{MnV}_2\text{O}_6$ , (b) a two-phase area of  $\alpha$ - and  $\beta$ -type solid solution coexistence, (c) a eutectic point between  $\alpha$ -type solid solution and  $\text{MoO}_3$  at  $583^\circ\text{C}$  and 75 mole% of  $\text{MoO}_3$ , and (d) phase relationships at the liquidus.

*Electric Properties of Ferromagnetic  $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$  ( $0.5 \leq x \leq 0.9$ ).* H. TAGUCHI, M. SHIMADA, AND M. KOIZUMI. The Institute of Scientific and Industrial Research, Osaka University, Suita, Osaka 565, Japan. The electrical resistivity of ferromagnetic  $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$  ( $0.5 \leq x \leq 0.9$ ) was measured in the temperature range from 77 to 300 K. All cobaltites are good conductors and have a metallic coefficient. The magnetic transitions are independent of the electrical conductivity in this system. The logarithms of the specific electrical resistivities ( $\log \rho$ ) at 80 and 290 K monotonically increase with mole fraction  $x$ , and these increases are explained by the itinerant-electron model.