

9- or 8-fold coordination (trigonal prism with capped rectangular faces or cube). Ba-S distances are about 3.4 Å, Fe-S distances are 2.26 Å. In  $\text{Ba}_3\text{FeS}_5$ , single, isolated tetrahedra are present. In  $\text{Ba}_{15}\text{Fe}_7\text{S}_{25}$  there are eight isolated trinuclear units, formed by a central tetrahedron sharing one edge and one corner, respectively, with two terminal tetrahedra, and four isolated single tetrahedra in the unit cell. The  $\text{BaS}_6$  trigonal prisms form infinite columns by sharing the triangular faces. The columns share edges to form distorted hexagonal rings. Within the rings are additional S and Ba ions, and Fe in tetrahedral sites. The main difference between the two structures is the filling of the tetrahedral sites inside the hexagonal rings. The effective paramagnetic moment in  $\text{Ba}_{15}\text{Fe}_7\text{S}_{25}$  is  $5.5 \mu_B$  in good agreement with a value expected from 6  $\text{Fe}^{3+}$  and  $\text{Fe}^{2+}$  from the stoichiometry. The room temperature Mössbauer spectrum shows isomer shifts of 0.2 mm/sec. The data indicate that electron delocalization occurs across the edge-shared tetrahedra so that an effective charge distribution  $5\text{Fe}^{3+}$  and  $2\text{Fe}^{2.5}$  is present. The material has a room temperature electrical resistivity of  $10^5$  ohm/cm. The effective magnetic moment for  $\text{Ba}_3\text{FeS}_5$  is  $5.1 \mu_B$  as might be expected for  $\text{Fe}^{2+}$  or  $\text{Fe}^{4+}$ . One quadrupole-split Mössbauer spectrum is observed with an isomer shift of 0.2 mm/sec, a value usually observed for  $\text{Fe}^{3+}$ . The observations are reconciled by postulating the delocalization of an electron within the tetrahedral configuration. The room temperature electrical resistivity is  $10^5$  ohm/cm.

*Observation Directe par Microscopie Electronique a Haute Resolution de la Transformation des Hydroxycarbonates de Terres Rares (Type B) en Oxycarbonates (Type II).* H. DEXPERT, G. SCHIFFMACHER, AND P. CARO. Laboratoire des Terres Rares, 1, Place Aristide Briand, 92190 Meudon-Bellevue, France. Type B rare earth hydroxycarbonate  $(\text{LnOH})\text{CO}_3$  is a lamellar hexagonal structure isomorphous to bastnaesite ( $\text{LnFCO}_3$ ). Type II oxycarbonate  $(\text{LnO})_2\text{CO}_3$  is another hexagonal lamellar structure built on an  $(\text{LnO})_n^{n+}$  complex cation of ternary symmetry. Lattice images were obtained for both compounds directly exhibiting the lamellar character. The thermal decomposition of the hydroxycarbonate into the oxycarbonate was followed in the electron microscope. The transition is topotactic and the crystallographic orientations were determined. The two compounds may have their triad axes and the [110] (hydroxycarbonate) and [010] (oxycarbonate) axes in common, or the two triad axes may be parallel and the lamellar structures merge together. The oxycarbonate appears then in the form of bubbles in the hydroxycarbonate matrix, because of a slight deficiency (12 to 14) in the number of rare earth atom planes for the same distance along the triad axes for the oxycarbonate versus the hydroxycarbonate.

*Identification of Binary Compounds in the System  $\text{Ce}_2\text{O}_3$ - $\text{WO}_3$ .* M. YOSHIMURA, F. SIBIEUDE, A. ROUANET, AND M. FOEX. Laboratoire des Ultra-Refractaires, Odeillo, 66120 Font-Romeu, France. The system  $\text{CeO}_2$ - $\text{Ce}_2\text{O}_3$ - $\text{WO}_3$  and  $\text{Ce}_2\text{O}_3$ - $\text{WO}_3$ -W are studied at high temperature. Six compounds were found as stable phases in the system  $\text{Ce}_2\text{O}_3$ - $\text{WO}_3$ . The compound  $3\text{Ce}_2\text{O}_3 \cdot \text{WO}_3$  has a fluorite-like cubic structure of  $a_0 = 11.040$  Å and forms solid solutions with constituent oxides or  $\text{CeO}_2$ . The compound  $3\text{Ce}_2\text{O}_3 \cdot 2\text{WO}_3$ , which seems to be isostructural with  $3\text{La}_2\text{O}_3 \cdot 2\text{WO}_3$ , is stable only in the temperature range of  $1545 \sim 1730^\circ\text{C}$ . The compound  $\text{Ce}_2\text{O}_3 \cdot \text{WO}_3$ , which has a monoclinic structure, transforms reversibly at  $1360^\circ\text{C}$  to a tetragonal structure with the cell parameters  $a_0 = 5.469$  Å,  $c_0 = 8.790$  Å. The compound  $\text{Ce}_2\text{O}_3 \cdot 2\text{WO}_3$ , identified as monoclinic, also has a reversible transformation at  $1105^\circ\text{C}$ . Its high-temperature phase has a cubic cell with the cell parameter  $a = 7.046$  Å. As is well known,  $\text{Ce}_2\text{O}_3 \cdot 3\text{WO}_3$  appeared to have a high-temperature behavior similar to that of  $\text{La}_2\text{O}_3 \cdot 3\text{WO}_3$ . The compound  $2\text{Ce}_2\text{O}_3 \cdot 9\text{WO}_3$ , whose structure could not be analyzed, melts congruently at  $1026^\circ\text{C}$ .

*On the Formation of  $\text{FeSe}_2$  Single Crystals by Chemical Transport Reactions.* J. PICKARDT, B. REUTER, E. RIEDEL, AND J. SÖCHTIG. Institut für Anorganische und Analytische Chemie, Technische Universität Berlin, 1 Berlin 12, Germany. The formation of synthetic ferroselite single crystals,  $\text{FeSe}_2$ , during chemical transport experiments in the system Fe-Cr-Se was observed. The crystals are orthorhombic,  $a = 4.804(2)$ ,  $b = 5.784(3)$ , and  $c = 3.586(2)$  Å. They were characterized by X-ray structure analysis and refined atom parameters are reported.

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