08.2-16 SYNTHESIS, CRYSTAL STRUCTURE, ELECTRON-MICROSCOPY ANALYSIS AND MAGNETIC PROPERTIES OF NEW ß"-ALUMINA-LIKE FERRITES : $(A,B)_{1+x}Zn_xFe_{11-x}O_{17}$ $(x \sim 0.9)$ WITH A, B = Li, Na, K, Ag, Ca, Sr, Ba, Pb. By <u>H. Vincent</u>*, A. Bekka*, M. Anne*, J.C. Joubert**, J. Gonzalez-Calbet***, *Laboratoire de Cristallographie, C.N.R.S., 166 X, 38042 Grenoble Cedex (France).**LMGP, ENSPG, BP 46, 38402 St Martin d'Hères (France). ***Instituto de Quimica Inorganica, CSIC, Madrid (Spain).

We have synthetized single crystals of a new rhombohedral ferrite using a flux method and carried out an X-ray crystal structure determination. The ferrite is isotypic with ß" alumina with a chemical formula $Na_{1.4}K_{0.5}Fe_{10.1}Zn_{0.9}O_{17}$. According to bond length-bond strength calculations, Zn^{2+} cations are positioned on the tetrahedral sites in the "spinel blocks". Ionic conductivity and magnetization measurements have been performed on single crystal. The (a, b) hexagonal plane is an easy magnetization plane ; magnetocristalline anisotropy constants have been determined.
A series of new compounds derived from this ß" ferrite has been obtained by ion exchange in molten salt. Li^+, Na^+, K^+, Ag^+, Ca^{2+}, Sr^{2+}, Ba^{2+}, Pb^{2+} cations have been completely or partially substituted for the large cations Na^+ and K^+. These new ferrites have magnetic properties different from the former. All these compounds have been characterized using X-ray diffraction and scanning or transmission electron-microscopy.
The crystal structure of the barium exchanged compound has been determined after annealing at 950°C. It is isotypic with the M barium ferrite. The refined chemical formula of the compound is : $Ba_{1.1}Zn_{0.1}Fe_{11.9}O_{19}$. The easy magnetization direction is along the c axis for this compound. The magnetocristalline anisotropy field has been determined.

08.2-17 ELECTRON MICROSCOPE AND X-RAY INVESTIGATIONS ON A (1.6) INTERGROWTH TUNGSTEN BRONZE. By <u>H. Brigitte Krause</u> and Steven Gollmar, Physics Department, Northern Illinois University, DeKalb, IL 60115, U.S.A.; and Roger Vincent and John W. Steeds, H.H. Wills Physics Laboratory, University of Bristol, Bristol BS8 1TL, U.K.

Extensive investigations on (1,n) intergrowth tungsten bronze (ITB) structures of Cs_xWO_3, Rb_xWO_3 and K_xWO_3 for $x < 0.10$ have previously been reported by Hussain and Kihlborg[1]. The structures can be regarded as an ordered intergrowth of slabs of hexagonal tungsten bronze (HTB) type structure with slabs of ReO_3 -(WO_3) type structure. The width of the WO_3 structure slabs in the (1,n) family of ITB structures is measured by n and thus increasing n – values require smaller alkali atom concentrations x. However, we found a segregation of (HTB) and (ITB) phases in K_xWO_3 for $x \leq 0.20$ starting at x = 0.20 with the sole value of n = 6. High resolution electron microscope images as well as single crystal x-ray photographs indicated uniform (1,6) ITB crystals. Convergent beam electron diffraction and high resolution electron microscope imaging techniques as well as x-ray diffraction techniques were used to determine the space group and atom parameters. Similarities and differences with the previous investigations will be discussed.

1. Intergrowth Tungsten Bronzes by Altaf Hussain and Lars Kihlborg Acta Cryst. (1976) A <u>32</u>, 551.

08.2-18 SHORT RANGE AND LONG RANGE-ORDER MODELS IN ANION-EXCESS FLUORITE-RELATED PHASES. By J.P. Laval and <u>B. Frit</u>, Laboratoire de Chimie Minérale Structurale, U.A.-C.N.R.S. n° 320, Université de Limoges, France.

If we except the vernier-structures, in the currently known MX_{2+y} fluorite-related superstructures, the excess of anions is accommodated by the formation within the fluorite matrix of fully ordered defect clusters. These clusters are of two kinds :
- finite octahedral ones, involving the association around a cubooctahedral cavity of six corner-sharing MX_8 square antiprisms, as for instance in the $Na_7Zr_6F_{31}$, the βU_4O_9, the KY_3F_{10} and the M_mF_{2m+5} series of superstructures observed in the CaF_2-LnF_3 systems.
- infinite columnar ones, built up with the linear association of independent, either MX_8 square antiprisms (Pb_3ZrF_{10} , Pb_5ZrF_{14} , K_2ReF_8 phases) or MX_7 monocapped trigonal prisms (K_2NbF_7 , Pb_2InF_7 phases).
On the basis of these long-range order clusters, short-range order models have been elaborated for the corresponding disordered solid solutions. They have been systematically checked by a neutron powder diffraction study of moderately and highly doped $M^{II}_{1-x}M^{III}_xF_{2+x}$ and $M^{II}_{1-x}M^{IV}_xF_{2+2x}$ phases (M^{II} = Ba, Ca, Pb, Sr ; M^{III} = Ln,Y; M^{IV} = Th, U, Zr).
For the CaF_2-based solid solution involving Zr^{4+} and heavy rare-earths (Lu-Yb), mainly F' (1/2, u,u with u = 0.40) interstitials, characteristic of octahedral square antiprism-based clusters have been evidenced, whereas mainly F" (v,v,v with v = 0.40) interstitials, characteristic of isolated MF_9 or MF_{10} polyhedra, are present in system involving U^{4+}, Th^{4+} or light rare earths.
For the BaF_2, PbF_2 or SrF_2-based solid solutions, the interpretation of experimental data is not so evident.

- When the dopant cation is trivalent , the aggregation of aliovalent cations, interstitial anions and anion vacancies within cuboctahedral clusters is favoured except for solid solutions associating cations of close size as $Sr_{1-x}La_xF_{2+x}$ e.g. whose defect structure is probably the same as homologous $CaF_2:La^{3+}$ one.
- When the dopant cation is tetravalent, the defect structure seems to be different and its evolution with increasing dopant cation concentration and fluorite-cell size, more complex : both F' and F" interstitials and even more dilute interstitial positions are observed. This behaviour has been interpreted as the result of a progressive extent with increasing dopant concentration of linear MF_8 or MF_9 polyhedra-based clusters, which can be considered as precursors for the fully organized infinite clusters observed in the Pb_3ZrF_{10} superstructure. All these results emphasize the major influence
- on the one hand of the fluorite-cell size
- on the other hand of the dopant cation charge and size
on the nature of the short-range order in anion-excess fluorite-related phases.