When the dopant cation is tetravalent, the defect on the one hand of the fluorite-cell size finite octahedral ones, involving the association microscopy.

By H. Brigitte Krause and Steven Gollmar, compound is: the M barium ferrite. The refined chemical formula of the crystal structure of the barium exchanged compound has been determined. 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 850°C. It is isotypic with the M barium ferrite. The refined chemical formula of the compound is: Ba₃⁺Zn₁₋ₓFeₓ₂O₄₋ₓ. The easy magnetization direction is along the c axis for this compound. The magnetocrystalline anisotropy field has been determined.

The crystal structure can be regarded as an ordered arrangement of independent, either columnar ones, built up with the linear association of independent, either putting one of the following structures in the "spinel blocks":

- finite octahedral ones, involving the association around a cuboctahedral cavity of six corner-sharing Mg square antiprisms, as for instance in the Na₅Zr₂F₁₀, the K₂Ga₂O₄, the K₂Zr₂F₁₀ and the Na₂Zr₂F₁₀ series of superstructures observed in the M(V) systems;

- infinite columnar ones, built up with the linear association of independent, either Mg square antiprisms (Pb₃ZrF₁₀, Pb₃ZrF₁₀, MgReF₅ phases) or Mg monosubstituted trigonal prisms (A¹MgF₇, Pb₂ZrF₇ 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 Na₅Zr₂F₁₀ and MgReF₅ phases. For the CaF₂-based solid solution involving Sr⁺ and heavy rare-earths (La₂₋ₓYₓ), mainly F⁺ (1/2, u, w with u = 0.40) interstitials, characteristic of octahedral square antiprism-based clusters have been evidenced, whereas mainly F⁺ (x, u, v with v = 0.40) interstitials, characteristic of isolated MgF₄ or Mg₄F₁₀ polyhedra, are present in system involving Mg⁺, Th⁺ or light rare earths. For the Ba₂⁺, Pb₂⁺ or Sr₂⁺-based solid solutions, the interpretation of experimental data is not so evident.

- When the dopant cation is trivalent, the aggregation of allivalent cations, interstitial anions and anion vacancies within cuboctahedral clusters is favoured except for solid solutions as close as Sr₁₋ₓLaₓF₂₋ₓ⁺. The defect structure probably the same as homologous CaF₂-La₃⁺ one.

- When the dopant cation is tetravalent, the defect structure seems to be different and its evolution with increasing dopant concentration and MgF₄ cluster formation is different. The highly magnified Mg⁺ or Mg₄F₁₀ polyhedra-based clusters, which can be considered as precursors for the fully organized finite clusters observed in the Pb₂ZrF₁₀ superstructure. All these results emphasize the major influence on the one hand of the Mg⁺ or Mg₄F₁₀ cluster formation and 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.