

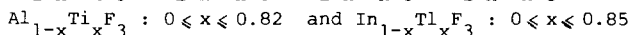
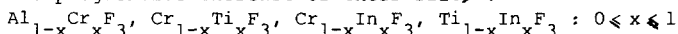
FERROELASTIC AF₃ AND A_{1-x}A'_xF₃ FLUORIDES WITH A VF₃-RELATED STRUCTURE

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Some trifluorides AF₃ (A = Al, Sc, Ti, V, Cr, Fe, Co, Ga, In) crystallize at room temperature with a rhombohedral VF₃ structure derived from the ReO₃ cubic-type.

By direct synthesis in sealed gold tubes or by fluorinating mixtures of AF₃ and Tl₂O₃, various solid solutions A_{1-x}A'_xF₃ have been characterized (the A³⁺ and A'³⁺ cations have been chosen in connection with the progressive increase of their size) :



They crystallize also with a rhombohedral symmetry. A phase transition has been detected for each composition by micro-DTA, microcalorimetry, optical measurements and thermal evolution study of the X-ray spectrum. The high-temperature form is cubic (Fm3m).

The ferroelastic domain structure and its disappearance above the transition temperature allowed us to predict this transition to be of ferroelastic type. The room temperature spontaneous strain e_s and the Curie temperature T_C (610 K < T_C < 1224K) have been correlated to the size of the various cations. The values of e_s (300K) and T_C increase as $r_{A^{3+}}$ decreases in a same family, for example for the 3d-transition metal fluorides AF₃ (A = Ti, V, Cr, Fe). The smallest A³⁺ cations allow a larger rotation of the fluorine atoms around the three-fold axis of the octahedron which is responsible for the strain of the crystal network.

When two different cations A³⁺ and A'³⁺ fill the cationic six-fold coordinated sites (for the composition A_{0.5}A'_{0.5}F₃) the variation of e_s and T_C has also been discussed with regards to the size of A³⁺ and A'³⁺ cations.