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DIELECTRIC AND THERMOCURRENT STUDIES OF SOME FLUORIDE AND OXIDE FLUORIDE COMPOUNDS WITH A $(NH_4)_3FeF_6$-RELATED STRUCTURE

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Dielectric and thermocurrent measurements have been carried out on $(NH_4)_3AlF_6$,$(NH_4)_3FeF_6$ and Rb_3FeF_6 ceramic samples. A maximum of permittivity is observed close to the transition temperature ($T_{tr}(NH_4)_3AlF_6$ = 217 K ; $T_{tr}(NH_4)_3FeF_6$ = 264 K ; $T_{tr}(Rb_3FeF_6)$ = 629 K) . This non cubic-cubic transition is of the ferroelastic type. The high Curie temperature of the rubidium iron fluoride causes large dielectric losses at the transition and thermocurrent measurements cannot be performed. On the contrary, in the low-temperature phase of the ammonium compounds a polarization current of about 10^{-9}A/cm^2 is obtained and can be reversed when the sign of the polarization field is changed This property could correspond to a ferroelectric behavior. However no pyroelectric current is detected when the temperature decreases from T_{tr}. Another hypothesis, based on the field-induced polarization, has been also considered.

In connection with the ferroelectric properties of $Rb_3MoO_3F_3$, the system $Rb_3MoO_3F_3$-Rb_3FeF_6 has been performed. Extended domains of solid solution with $Rb_3(Mo_{1-x}Fe_x)O_{3-3x}F_{3+3x}$ formula and having a $(NH_4)_3FeF_6$-related structure have been pointed out. The replacement of oxygen by fluorine leads to a strong decrease of the ferroelectric Curie temperature : $T_C(x=0)$ = 538 K , $T_C(x=0.4)$ < 80 K . This result is in good agreement with the lack of ferroelectricity in A_3MF_6 fluorides. In any case, the low-temperature phase is ferroelastic and is characterized by a remanent polarization.

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SOLID STATE REACTIONS OF HEXAFLUOROSILICATE WITH Al_2O_3

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Reaction of Na- und K-hexafluorosilicates with α - and γ-Al_2O_3 at temperatures above 500°C is discussed further. The differences between the Na- and K-systems consist in formation of $Na_5Al_3F_{14}$ respectively $KAlF_4$, the latter one has a low smelting point and causes sinter processes. At beginning reaction γ-Al_2O_3 has a lower reactivity than α-Al_2O_3. The reaction mechanism and the role of water will be discussed. $Al_2SiO_4F_2$ is an intermediate product. Final products are $NaAlSiO_4$ and an ultramarine like substance respectively $KAlSiO_4$ and other products with network structure besides fluoroaluminates.