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NON LINEAR OPTICS FERROELECTRIC–FERROELASTIC OXYFLUORIDES WITH COMPOSITION $K_3MO_2F_4$ (M = Nb, Ta)

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Polycrystalline $K_3MO_2F_4$ (M = Nb, Ta) are prepared by heating a mixture of thoroughly dried KF, MO_2F in a gold tube, sealed under dry oxygen to 650°C. Crystal growth tentatives by flux or Bridgman technics in platinum sealed tube lead to small and twinned crystals.

The room temperature X-ray spectrum presents both large lines characteristic of a pseudotetragonal subcell and small lines which imply either a much more large unit cell or a lower symmetry. Nevertheless Table I gives the pseudotetragonal parameters of both $K_3NbO_2F_4$ and $K_3TaO_2F_4$. The twins of the single crystals did not allow us to determine the real symmetry. Non linear optical tests on powder shows these phases to generate second harmonic and thus belonging to a non centrosymmetric point group.

A transition occurs, with endotherms on heating and exotherms on cooling (see ΔH and ΔS in Table I). A permittivity anomaly and a minimum of the dielectric losses tan δ occur at the same temperature. A Guinier Simon study shows this transition to correspond to the appearance of the cubic phase (m3m) for $T > T_c$. The value of T_c is given in Table I. A polarizing microscope study shows that the multidomain structure and the birefringence disappear at T_c. These results both with the change of crystalline system at $T = T_c$ reveal these crystals to be ferroelastic for $T < T_c$.

Dielectric anomalies, analogy of X-ray spectrum and physical properties with those of ferroelectric $K_3M'O_3F_3$ (M' = Mo, W) imply also probably ferroelectric properties for the $K_3MO_2F_4$ compounds (Table I). Moreover a continuous solid solution between $K_3NbO_2F_4$ and $K_3MoO_3F_3$ with gradual variation of unit cell parameters and transition temperature are in good agreement with this hypothesis. In any way, the transition temperature decreases with W-Mo or Ta-Nb substitution. This evolution is related to the covalency of the M-X bonds (X = O, F).

Table I

Pseudo cell parameters (300K), T_c, ΔH and ΔS at the transition temperature

	$\sqrt{2}$"a"$_{tetr.}$ (Å)	"c"$_{tetr.}$ (Å)	T_c (±10°C)	$\lvert\Delta H\rvert$ (J.mole^{-1})	$\lvert\Delta S\rvert$ (J.mole^{-1}K^{-1})
$K_3MoO_2F_3$	8.660	8.668	250	1980	3.80
$K_3WO_2F_3$	8.704	8.731	179	1930	4.30
$K_3NbO_2F_4$	8.728	8.805	145	1286	3.05
$K_3TaO_2F_4$	8.787	8.868	90	379	1.05