

S₃₀

SILVER-SODIUM SUBSTITUTION IN FERROELASTIC-FERROELECTRIC OXYFLUORIDES WITH THE CHIOLITE-TYPE

J. Grannec*, A. Yacoubi and J. Ravez

Laboratoire de Chimie du Solide du CNRS, Université de Bordeaux I, 33405 Talence Cédex (France)

New silver oxyfluorides with a chiolite-type structure have been prepared by solid state reactions in sealed gold tubes from AgF and TiOF₂ or WO₃ : Ag₅Ti₃O₃F₁₁ and Ag₅W₃O₉F₅. Both crystallize with the tetragonal prototype symmetry 4/mmm.

A great number of studies have been previously performed on ferroelectric oxyfluorides containing sodium (e.g. Na₅W₃O₉F₅, Ferroelectrics, 38,777,1981). These compounds crystallize with a monoclinic distortion. The disappearance of the domain structure and the change of crystalline system (monoclinic + tetragonal) at the transition temperature T_C implies also ferroelastic properties for T < T_C.

The influence of silver-sodium substitution on ferroelastic-ferroelectric properties has been studied in the system containing tungsten. Two solid solutions have been isolated : Na_{5-x}Ag_xW₃O₉F₅ (0 < x < 1 ; 2 < x < 5). The evolution of the cell parameters has been related to the size of the monovalent cation. For compositions close to Na₅W₃O₉F₅, the phase is still ferroelectric with a decrease of the spontaneous strain and of the transition temperature from e_s = 67x10⁻⁴, T_C = 800 ± 10K (x=0) to e_s = 49x10⁻⁴, T_C = 680 ± 20K (x=1). The temperature of the two other transitions which occur in the ferroelectric region decreases simultaneously. For high silver content (x > 2), the monoclinic distortion appears only in the temperature range 4 K < T < 80 K.

The following table gives symmetry, spontaneous strain e_s and transition temperature T_C for the four titanium and tungsten oxyfluorides.

Symmetry	10 ⁴ x e _s (300 K) ^S	T _C (300 ^C K)	Refer. (K)	
Na ₅ Ti ₃ O ₃ F ₁₁	monocl.	65	760	*
Ag ₅ Ti ₃ O ₃ F ₁₁	tetrag.	0		*
Na ₅ W ₃ O ₉ F ₅	monocl.	67	800	
Ag ₅ W ₃ O ₉ F ₅	tetrag.	0		*

* Present work