The Inorganic Fluoride and Oxyfluoride Ferroelectrics

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(Received 20 June 1996, accepted 12 November 1996)

PACS 77 80.-e – Ferroelectricity and antiferroelectricity

Abstract. — The ferroelectric fluorides belong to six families of type $(\text{NH}_4)_2\text{BeF}_4$, BaMnF_4 , SrAlF_5 , $\text{Na}_2\text{MgAlF}_7$, $\text{K}_3\text{Fe}_5\text{F}_{15}$ or $\text{Pb}_5\text{Cr}_3\text{F}_{19}$. The oxyfluorides can be separated in two groups: i) the true oxyfluorides with a relatively high F/O value ($\text{K}_3\text{MoO}_3\text{F}_3$, $\text{Na}_5\text{W}_3\text{O}_9\text{F}_5$, $\text{Pb}_5\text{W}_3\text{O}_9\text{F}_{10}$, $\text{Bi}_2\text{TiO}_4\text{F}_2$, ...); ii) the compositions derived from ferroelectric oxides (perovskite, tetragonal tungsten bronze, pyrochlore, LiTaO_3 , ...) characterized by a continuous F-O substitution. The phase transitions and the physical properties are discussed. The origin of the spontaneous polarization is described structurally. The variations of the Curie temperature with the type of substitution are related to chemical bonding. The potential interest of these materials for applications is briefly given.

Résumé. — Les ferroélectriques fluorés appartiennent à six familles de type $(\text{NH}_4)_2\text{BeF}_4$, BaMnF_4 , SrAlF_5 , $\text{Na}_2\text{MgAlF}_7$, $\text{K}_3\text{Fe}_5\text{F}_{15}$ ou $\text{Pb}_5\text{Cr}_3\text{F}_{19}$. Les oxyfluorures peuvent être séparés en deux groupes : i) les oxyfluorures “vrais” comportant un rapport F/O relativement élevé ($\text{K}_3\text{MoO}_3\text{F}_3$, $\text{Na}_5\text{W}_3\text{O}_9\text{F}_5$, $\text{Pb}_5\text{W}_3\text{O}_9\text{F}_{10}$, $\text{Bi}_2\text{TiO}_4\text{F}_2$, . . .), ii) les compositions dérivées des oxydes ferroélectriques (perovskite, bronze quadratique de tungstène, pyrochlore, LiTaO_3 , ...) et caractérisées par une substitution F-O continue. Les transitions de phases et les propriétés physiques sont analysées. L'origine de la polarisation est précisée sur le plan structural. Les variations de la température de Curie avec le type de substitution sont reliées à des considérations de liaison chimique. L'intérêt potentiel de ces matériaux pour les applications est brièvement abordé.

1. Introduction

Inorganic ferroelectrics are mainly oxides (families KDP, perovskite, tetragonal tungsten bronzes, LiNbO_3 , pyrochlore, boracite, Aurivillius phases, ...). Ferroelectric fluorides are much less numerous; one of the causes is that although stable up to about 400 K, the high temperature preparation of crystals and ceramics requires particular care to prevent hydrolysis. Some compounds are declared as ferroelectrics from theoretical studies (HF , PbF_2 , NaCaF_3 , ...) [1, 2]. Nevertheless the proofs of ferroelectric properties have been demonstrated only for the six following families: $(\text{NH}_4)_2\text{BeF}_4$, BaMnF_4 , SrAlF_5 , $\text{Na}_2\text{MgAlF}_7$, $\text{K}_3\text{Fe}_5\text{F}_{15}$ and $\text{Pb}_5\text{Cr}_3\text{F}_{19}$.

The ferroelectric oxyfluorides form a bridge between the fluoride and oxide families; the corresponding research has been on the increase for about forty years:

Number of publications on oxyfluoride ferroelectrics			
1957-1966	1967-1976	1977-1986	1987-1996
5	16	39	59...

These materials may be separated in two sub-groups:

- the "true" ferroelectric oxyfluorides with a relatively F/O ratio and belonging to families in which fluorides and oxides are not necessarily ferroelectrics; as an example $\text{Na}_5\text{W}_3\text{O}_9\text{F}_5$ is ferroelectric although $\text{Ca}_5\text{Te}_3\text{O}_{15}$ and $\text{Na}_5\text{Al}_3\text{F}_{14}$ are not;
- oxyfluorides derived from ferroelectric oxides by a generally progressive and weak fluorine-oxygen substitution.

Table I gives the list of main fluoride and "true" fluoride families known at the present time.

2. The Ferroelectric Fluorides

2.1. $(\text{NH}_4)_2\text{BeF}_4$. — Ammonium fluoroberyllate is the longest known ferroelectric fluoride [3]. Its crystalline network is composed of distorted $(\text{BeF}_4)^{2-}$ tetraedra. Although of close structure, however it is not isomorphous of the ferroelectric sulfate $(\text{NH}_4)_2\text{SO}_4$ [19].

2.2. FAMILY BaMF_4 ($\text{M} = \text{Mg}, \text{Mn}, \text{Fe}, \text{Co}, \text{Ni}, \text{Zn}$). — The BaMF_4 fluorides are ferroelectric up to their melting temperature [4]. The value of the spontaneous polarization is close to $10 \mu\text{C cm}^{-2}$ at 300 K. The inversion of the polarization corresponds to a shift of the Ba^{2+} cation along the c -polar axis of the orthorhombic crystalline unit cell ($\text{mm}2$ point group); it goes with the rotation of octahedra linked by corners leading to layers separated by the Ba^{2+} cations (Fig. 1).

These fluorides are bidimensional ferroelectrics.

2.3. FAMILY ABF_5 ($\text{A} = \text{Sr}; \text{B} = \text{Al}, \text{Cr}, \text{Ga}$ AND $\text{A} = \text{Ba}; \text{B} = \text{Ti}, \text{V}, \text{Fe}$). — It is an analysis of the crystalline structure which made it possible to predict the ferroelectric properties of displacive type in SrAlF_5 ($T_C \sim 700 \text{ K}$). Physical studies on crystal have shown the existence of piezoelectric and second harmonic generation properties. Two solid solutions of $\text{BaFe}_{1-x}\text{In}_x\text{F}_5$ and $\text{Ba}_{1-x}\text{Sr}_x\text{FeF}_5$ compositions have shown that the value of T_C decreases with the size increase of the cation in 6 C.N. and with the size decrease of the alkaline-earth cation [6]. A similar result was obtained for perovskite phases derived from BaTiO_3 (for example $\text{BaTi}_{1-x}\text{Zr}_x\text{O}_3$ and $\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$): this result is correlated with steric and bond covalency effects [20].

2.4. FAMILY $\text{Na}_2\text{MgAlF}_7$. — Second harmonic generation studies performed at 300 K made it possible to confirm the polar point group 4mm for $\text{Na}_2\text{MgAlF}_7$ and Na_2NiMF_7 ($\text{M} = \text{Al}, \text{Fe}$). The phase transition temperature varies with composition; it takes place at $T > 725 \text{ K}$ [7].

2.5. FAMILY $\text{K}_3\text{Fe}_5\text{F}_{15}$. — Coupled ferroelectric and ferroelastic properties were predicted from atomic positions of $\text{K}_3\text{Fe}_5\text{F}_{15}$. The crystalline network of "tetragonal tungsten bronze" type shows an orthorhombic distortion at 300 K. The Curie temperature ($T_C \sim 490 \text{ K}$) was determined by calorimetric and dielectric measurements, and also by the disappearance of the ferroelastic domain structure under polarized light microscope [8]. The composition $\text{K}_3\text{Fe}_5\text{F}_{15}$

Table I. — *List of the main fluoride and "true" oxyfluoride families.*

Type compound	T_C (K)	Point Group	Ferroelectricity type	Main other compositions	Ref.
$(\text{NH}_4)_2\text{BeF}_4$	175	mm2	order-disorder	BaMF_4 (M = Mg, Fe, Co, Ni, Zn) SrMF_5 (M = Cr, Ga), BaMF_5 (M = Ti, V, Fe) Na_2NiMF_7 (M = Al, Fe) $\text{K}_{3-x}\text{Fe}_5\text{F}_{15}$	[3]
BaMnF_4		mm2	displacive		[4]
SrAlF_5	700	4	displacive		[5, 6]
$\text{Na}_2\text{MgAlF}_7$	725	4mm			[7]
$\text{K}_3\text{Fe}_5\text{F}_{15}$	490	mm2	displacive and order-disorder		[8]
$\text{Pb}_5\text{Cr}_3\text{F}_{19}$	555	4mm	displacive	$\text{Pb}_5\text{M}_3\text{F}_{19}$ (M = Al, Ti, V, Fe, Ga)	[9]
$\text{K}_3\text{MoO}_3\text{F}_3$	328	3m	displacive	$\text{A}_3\text{MO}_3\text{F}_3$, $\text{A}_2\text{BMO}_3\text{F}_3$, $\text{A}_3\text{M}'\text{O}_2\text{F}_4$, A_3TiOF_5 , $\text{Na}_3\text{MO}_3\text{F}_3$ [A = K, Rb, Cs; M = Mo, W; M' = Nb, Ta]	[10-12]
$\text{Bi}_2\text{TiO}_4\text{F}_2$	285	mm2	displacive	$\text{Bi}_2\text{MO}_5\text{F}$ [M = Nb, Ta]	[13]
$\text{Na}_5\text{W}_3\text{O}_9\text{F}_5$	800	2	displacive	$\text{Na}_5\text{W}_2\text{MoO}_9\text{F}_5$, $\text{Na}_5\text{Ti}_3\text{O}_3\text{F}_{11}$, $(\text{Na}_4\text{Ln})(\text{WNB}_2)\text{O}_9\text{F}_5$ [Ln = Y, Eu, Gd, Dy, Lu], $(\text{Na}_{5-x}\text{A}_x)\text{W}_3\text{O}_9\text{F}_5$ [A = Li, K], $\text{Na}_5(\text{W}_{3-x}\text{M}_x)\text{O}_{9-x}\text{F}_{5+x}$ [M = Nb, Ta]	[14, 15]
$\text{Pb}_5\text{W}_3\text{O}_9\text{F}_{10}$	785	4	displacive	$\text{Pb}_5\text{Mo}_3\text{O}_9\text{F}_{10}$, $\text{Pb}_5\text{Ti}_3\text{O}_3\text{F}_{16}$, $\text{A}_5\text{Nb}_3\text{OF}_{18}$ [A = K, Rb]	[16, 17]
$\text{Mg}_3\text{B}_7\text{O}_{13}\text{F}$	> 770	3m		$\text{A}_3\text{B}_7\text{O}_{13}\text{F}$ [A = Mn, Fe, Co, Zn]	[18]

Fig. 1. — Atomic arrangement for the two polarities of BaMF_4 .

implies the simultaneous presence of Fe^{2+} and Fe^{3+} cations. The spontaneous polarization origin is correlated with the displacements along the polar axis of Fe^{2+} and Fe^{3+} cations in their octahedral sites, these cations being ordered in the crystalline network. Above T_C , the iron atoms are localised at the octahedron center and Fe^{2+} and Fe^{3+} cations are disordered in some crystallographic sites [21]. This ferroelectric fluoride is thus both displacive and of the order-disorder type. So, it is different from oxides (for example $\text{Ba}_2\text{NaNb}_5\text{O}_{15}$, $\text{Pb}_2\text{Nb}_5\text{O}_{15}$) of displacive type for which it is not isomorphous. Moreover, as will be mentioned in the oxyfluoride section, a low rate of F-O substitution leads to the disappearance of the ferroelectric properties. The solid solution $\text{K}_{3-x}\text{Fe}_5\text{F}_{15}$ ($0 \leq x \leq 1$) also leads to the disappearance of the spontaneous polarization, the K^+ defect involves a change of the $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio which is not favourable to the creation of an order between the two cations [22].

2.6. FAMILY $\text{Pb}_5\text{Cr}_3\text{F}_{19}$. — Examination of the atomic positions of the polar crystalline network (4mm point group) of $\text{Pb}_5\text{Cr}_3\text{F}_{19}$ shows the Cr^{3+} cation to be off center from its octahedral site [9]. The ferroelectric-paraelectric transition at $T_C = 555$ K is of first order type, in particular the birefringence sign changes abruptly at T_C (Fig. 2) [23]. The value of T_C varies with the M^{3+} cation size in the series of isomorphous compounds $\text{Pb}_5\text{M}_3\text{F}_{19}$ ($\text{M} = \text{Al}, \text{Ti}, \text{V}, \text{Cr}, \text{Fe}, \text{Ga}$) of displacive type [24]. The $\text{Pb}_5\text{Al}_3\text{F}_{19}$ compound shows a transition sequence very rich in ferroic properties [25]:

Fig. 2. — Temperature dependence of the birefringence for a $\text{Pb}_5\text{Cr}_3\text{F}_{19}$ crystal.

A pyroelectric current and a piezoelectric resonance have been shown in phase V [26]. Ferroelastic domains have been observed for phase III; the spontaneous strain appears abruptly on heating at the IV-III transition; it decreases then progressively and cancels at the III-II transition [27]. Figures 3 and 4 show a projection of the unit cell on xOy plane and the shift of Al^{3+} cations in the octahedra forming chains which develop along the polar axis.

The various distortions which appear in $\text{Pb}_5\text{Al}_3\text{F}_{19}$ result from the association of both the $6(\text{sp})^2$ lone pair of Pb^{2+} cation and the small size of the Al^{3+} ion.

3. "True" Ferroelectric Oxyfluorides

3.1. FAMILY $\text{K}_3\text{MoO}_3\text{F}_3$. — Numerous $\text{A}_2\text{BMO}_3\text{F}_3$ ($\text{A}, \text{B} = \text{K}, \text{Rb}, \text{Cs}$ with $r_{\text{A}^+} > r_{\text{B}^+}$ and $\text{M} = \text{Mo}, \text{W}$) show a crystallographic distortion of the prototype cubic phase ($m\bar{3}m$) of $(\text{NH}_4)_3\text{FeF}_6$ type. The ferroelectric properties which appear below T_C are coupled with ferroelastic properties. Physical studies on a $\text{K}_3\text{MoO}_3\text{F}_3$ crystal make it possible to visualize ferroelastic domains and to obtain both a P-E hysteresis loop and a pyroelectric current [28]. The value of T_C decreases when Mo is replaced by W, but is much more sensitive to the B^+ cation nature in the 6 C.N. site: the order which appears when B^+ is smaller than A^+ localized in the 12 C.N. site, leads to a decrease in both the octahedron distortion and the

Fig. 3. — Crystallographic unit cell projection of the phase V of $\text{Pb}_5\text{Al}_3\text{F}_{19}$ along $[001]$.

phase V	phase IV (2V)	phase III	phase II

Fig. 4. — Schematic shift of Al^{3+} cations along the (001) axis for the $\text{Pb}_5\text{Al}_3\text{F}_{19}$ various phases.

value of T_C (as an example, $T_C(\text{Rb}_3\text{MoO}_3\text{F}_3) = 538 \text{ K}$ and $T_C(\text{Rb}_2\text{KMoO}_3\text{F}_3) = 328 \text{ K}$) [10, 11, 29]. All ions of the ferroelectric phase are displaced from their ideal positions in the prototype phase. Amplitudes and directions of atomic displacements show the crystal to be a tridimensional ferroelectric. Such a result is in good agreement with the small value of the spontaneous polarization ($0.1 \leq P_s \leq 3 \mu\text{C cm}^{-2}$). A F-O substitution leads to a decrease in T_C [30]. Nine other compounds belong to this family, having the compositions A_3TiOF_5 and $\text{A}_3\text{MO}_2\text{F}_4$ ($\text{A} = \text{K, Rb, Cs}$; $\text{M} = \text{Nb, Ta}$). They are also ferroelectric-ferroelastic and generate second harmonics [31]. Recent studies also showed ferroelectric properties for the compounds $\text{Na}_3\text{MO}_3\text{F}_3$ ($\text{M} = \text{Mo, W}$) ($T_C \sim 805 \text{ K}$); the harmonic yield in nonlinear optics is here relatively strong ($R_h/R_h(\text{quartz}) \sim 40$ at room temperature) [12, 32].

Fig. 5. — Schematic view of the $\text{Na}_5\text{Al}_3\text{F}_{14}$ structure.

3.2. FAMILY $\text{Bi}_2\text{TiO}_4\text{F}_2$. — The three compounds $\text{Bi}_2\text{TiO}_4\text{F}_2$ and $\text{Bi}_2\text{MO}_5\text{F}$ ($\text{M} = \text{Nb}, \text{Ta}$) have only one perovskite layer in a crystalline network of “Aurivillius phase” type. They show a ferroelectric-paraelectric ($\text{mm}2-4/\text{mmm}$) transition [13]. A P-E hysteresis loop has been visualized. The close values of T_C ($283 \leq T_C \leq 303$ K) confirm that T_C is mainly influenced by the polarizability of A^{n+} cations and by the number of perovskite layers in the family of composition $\text{A}_{m-p+1}\text{Bi}_{p-2}\text{B}_m(\text{O}, \text{F})_{3m+1}$.

3.3. FAMILY $\text{Na}_5\text{W}_3\text{O}_9\text{F}_5$. — The compound $\text{Na}_5\text{W}_3\text{O}_9\text{F}_5$ with crystalline structure derived from that of the chiolite $\text{Na}_5\text{Al}_3\text{F}_{14}$ (Fig. 5) generates a second harmonic and shows coupled ferroelectric-ferroelastic properties [14,33]. Ferroelastic domains have been observed on crystal under polarized light microscope (Fig. 6). A detwinning of the crystal was obtained by application of an external mechanical stress leading to an increase in the pyroelectric coefficient as expected when the two ferroic properties are coupled. A strong maximum of the permittivity occurs at T_C (Fig. 7). The temperature dependence of the atomic positions showed the appearance of the spontaneous polarization, for $T < T_C$, to be related to rotations of $\text{W}(\text{O}, \text{F})_6$ octahedra around the a and b axes of the prototype tetragonal phase ($4/\text{mmm}$) [34]. Two other transitions occur in the ferroelectric region of $\text{Na}_5\text{W}_3\text{O}_9\text{F}_5$. Various substitutions ($\text{Mo}, \text{Ti}, \text{Nb}, \text{Ta}$ to W ; Li, K to Na ; fluorine-oxygen) lead to a very rich family [35]. The value of T_C varies with the size of the cations and with the bond M-X ($\text{X} = \text{O}, \text{F}$) covalency. The partial substitution of Li^+ to Na^+ made it possible to obtain crystals of very good optical quality and large size ($\sim 2 \text{ cm}^3$).

Fig. 6. — Ferroelastic domains of $\text{Na}_5\text{W}_3\text{O}_9\text{F}_5$.

Fig. 7 — Temperature dependence of the permittivity for a $\text{Na}_5\text{W}_3\text{O}_9\text{F}_5$ crystal

3.4. FAMILY $\text{Pb}_5\text{W}_3\text{O}_9\text{F}_{10}$. — Ferroelectric properties were predicted from the atomic arrangement of $\text{Pb}_5\text{W}_3\text{O}_9\text{F}_{10}$ which derives from that of $\text{Pb}_5\text{Cr}_3\text{F}_{19}$. The possibility of reversing the spontaneous polarization, characteristic dielectric properties and second harmonic generation led to confirming such an hypothesis [36]. The Curie temperature ($T_C = 785$ K) corresponds to a ferroelectric (I4)-paraelectric (I4) transition. Two isotypic phases have the same properties: $\text{Pb}_5\text{Mo}_3\text{O}_9\text{F}_{10}$ and $\text{Pb}_5\text{Ti}_3\text{O}_3\text{F}_{16}$ [16].

Crystals of size $1.5 \times 1.5 \times 5$ mm³, of composition $\text{A}_5\text{Nb}_3\text{OF}_{18}$ (A = K, Rb) and of crystalline structure close to that of $\text{Pb}_5\text{W}_3\text{O}_9\text{F}_{10}$ were obtained by slow cooling after dissolving in a HF solution. A piezoelectric resonance and a pyroelectric current were observed between 300 and 500 K [17].

4. Oxyfluorides Derived from Ferroelectric Oxides

4.1. PEROVSKITE, TETRAGONAL TUNGSTEN BRONZE AND PYROCHLORE TYPES. — Oxygenated phases of perovskite, tetragonal tungsten bronze and pyrochlore type have ferroelectric properties. Their crystalline network shows octahedra linked by corners. The fluorine-oxygen substitution associated with a cationic substitution to ensure electric neutrality gives rise to a decrease in the Curie temperature, the spontaneous polarization and the harmonic yield in nonlinear optics. The decrease in T_C may be very abrupt even for low substitution rates. Figure 8 shows, as an example, that the replacement of only one oxygen on 60 (0.25/15) leads to a decreasing in T_C of about 600 K. Figure 9 shows clearly the decrease in T_C for such materials compared to true oxyfluoride ferroelectric [37]. The distortion of the MX_6 (X = O, F) octahedra related to the displacement of the M^{n+} cation out of the octahedron center is responsible for ferroelectricity. When fluorine replaces oxygen, the M-X bonds become less covalent, and the anisotropy decreases. So the increase in temperature up to T_C leading to more isotropic bonds (paraelectric phase) decreases.

When other transitions exist in the ferroelectric region, their temperature does not necessarily decrease when the amount of fluorine increases. Figure 10 shows the case of the solid solution $\text{Ba}(\text{Ti}_{1-x}\text{Li}_x)\text{O}_{3-3x}\text{F}_{3x}$ for which T_1 (orthorhombic-tetragonal transition) decreases and T_2 (rhombohedral-orthorhombic transition) increases. This system is very attractive. In fact, for composition $0 \leq x \lesssim 0.03$, the behavior is of classical ferroelectric type as for BaTiO_3 . On the contrary for $0.03 < x \lesssim 0.15$, it is of relaxor type: when the frequency increases, the temperature T_m of ϵ_r'' (max) increases, the value of ϵ_r' decreases progressively and ϵ_r'' remains relatively constant, its value being relatively strong ($\epsilon_r'' \sim 100$ at 10^4 Hz) for $T < T_m$ [38, 39]. In addition, they show a microwave relaxation whose origin is related to 6 C.N. cation motions, along correlation chain in a double well potential model [40].

4.2. LiTaO_3 TYPE. — Oxyfluorides of the LiTaO_3 type have been obtained in LiNbO_3 -LiF-NbO₂F, LiTaO_3 -LiF-TaO₂F and LiMO_3 -“ LiMgF_3 ” (M = Nb, Ta) systems. The crystalline network is composed of octahedra linked by faces in the polar direction and by edges in other directions. The variation of T_C is correlated to the variation of the covalency degree of the M-X (X = O, F) bonds, and to the cationic non stoichiometry [41, 42]. The fluoride MgLiF_3 used as sintering additive is of great interest for densifying LiTaO_3 ceramics at low temperature (Fig. 10) [43].

4.3. $\text{Pb}_5\text{Ge}_3\text{O}_{11}$ TYPE. — The replacement of oxygen by fluorine goes with the creation of defects in the site of Pb^{2+} : $(\text{Pb}_{1-x/2}\square_{x/2})_5\text{Ge}_3\text{O}_{11-5x}\text{F}_{5x}$ ($0 \leq x < 0.10$). The Curie temperature decreases with x from 453 to 355 K [44].

Fig. 8. — Variation of T_C with x for ceramics of composition $Ba_{2-x}Na_xNb_5O_{15-x}F_x$

Fig. 9. — Variation of T_C with the rate of F-O substitution for a true oxyfluoride ferroelectric and for oxyfluorides derived from ferroelectric oxides

Fig. 10. — Variation of the transition temperature with x for ceramics with composition $\text{Ba}(\text{Ti}_{1-x}\text{Li}_x)\text{O}_{3-3x}\text{F}_{3x}$.

4.4. $(\text{NH}_4)_2\text{SO}_4$ TYPE. — The two solid solutions of compositions $(\text{NH}_4)_2(\text{SO}_4)_{1-x}(\text{BeF}_4)_x$ ($0 \leq x \leq 0.22$; $0.70 \leq x \leq 1$) derive from the two ferroelectric compounds $(\text{NH}_4)_2\text{SO}_4$ ($T_C = 223$ K) and $(\text{NH}_4)_2\text{BeF}_4$ ($T_C = 175$ K). The Curie temperature decreases when the composition deviates from one or the other of the limit phases [19].

4.5. BaAl_2O_4 TYPE. — Non-linear properties have been detected in crystals and ceramics of $(\text{Ba}_{1-x}\text{A}_x)(\text{Al}_{2-2x}\text{Li}_{2x})\text{O}_{4-4x}\text{F}_{4x}$ ($\text{A} = \text{Sr}, \text{Ba}, \text{Pb}$) ($0 \leq x \leq 0.30$) compositions. The Curie temperature varies from 240 to 426 K, the spontaneous polarization from 8 to $15 \mu\text{C cm}^{-2}$ and the coercive field from 5 to $2 \times 10^6 \text{ V m}^{-1}$. Although having a spontaneous polarization, these materials are in fact structurally ferroelectric [45–47].

4.6. SIMULTANEOUS FLUORINE-OXYGEN AND LEAD-ALKALINE EARTH SUBSTITUTIONS. — The F-O substitution generally leads to a decrease in T_C . Moreover, the $\text{Pb}^{2+} - \text{A}^{2+}$ ($\text{A} = \text{Sr}, \text{Ba}$) substitution in oxidized titanates, for an example, leads to an increase in T_C in correlation with the strong distortion created by the $6(\text{sp})^2$ lone pair of the Pb^{2+} cation. When F^- and Pb^{2+} ions are introduced together into the crystalline network, two competitive effects appear. The anionic substitution firstly causes a decrease in T_C followed by an increase in T_C , thus giving a minimum of T_C for a definite composition (Fig. 11 for example) [47].

Fig. 11. — Variation of T_C with x for ceramics with composition $Ba_{1-x}Pb_x(Al_{2-2x}Li_{12x})O_{4-4x}F_{4x}$.

5. Some Potential Applications

5.1. DIELECTRICS FOR TYPE I CAPACITORS. — The decrease in the Curie temperature by F-O substitutions may make it possible to situate the paraelectric phase in the usual temperature range for applications (250 to 350 K). In this temperature domain, the still high values of the permittivity ϵ'_r and its stability in frequency mean that such materials are of potential interest as dielectrics for type I capacitors. For example, let us consider the values of the following pyrochlore oxyfluoride $Pb_{1.80}Zn_{0.15}Na_{0.05}O_{6.95}F_{0.05}$ ($\epsilon'_r \sim 200$; $\tan \delta \sim 3 \times 10^{-4}$) [48]. Thick films have been prepared by serigraphy; the permittivity is very stable ($\epsilon'_r \sim 80$ from 10^3 to 10^6 Hz) and the dielectric losses are very low ($\tan \delta < 10^{-3}$) [49]. Thin films have also been obtained by cathodic sputtering, but the amorphous character of the films causes a decrease in permittivity ($\epsilon'_r \sim 30$) [50].

5.2. DIELECTRICS FOR TYPE II CAPACITORS. — The replacement of palladium for electrodes by cheaper metals or alloys requires the use of dielectrics with a low sintering temperature. We give the two following examples:

- The addition of LiF or BaLiF₃ to BaTiO₃ has made it possible to decrease the sintering temperature from 1400 to 930 °C. The decrease of $T_C(\text{BaTiO}_3) = 393$ K to a temperature close to 300 K leads to very good electric performances ($\epsilon'_r(300 \text{ K}) = 8300$; $\tan \delta(300 \text{ K}) = 40 \times 10^{-4}$). Multilayer capacitors of $3.20 \times 2.40 \times 1.15 \text{ mm}^3$ dimensions have been made with such a dielectric: they reach a capacity of 162 nF with Ag-Pd electrodes with a high concentration in silver [51, 52].
- The addition of BaLiF₃ to $\text{Pb}(\text{Fe}_{1/2}\text{Nb}_{1/2})\text{O}_3$ has made it possible to decrease the Curie temperature of the latter ($T_C = 387$ K) to room temperature and to sinter ceramics at temperature lower than 900 °C. Figure 12 shows that the values of ϵ'_r are very strong; the thermal dependence of ϵ'_r means that such dielectrics may be put in the Z5U class [53].

Fig. 12. — Temperature dependence of ϵ'_r for an oxyfluoride ceramic derived from $\text{Pb}(\text{Fe}_{1/2}\text{Nb}_{1/2})\text{O}_3$.

The addition of both LiF and Li_2CO_3 makes it possible to sinter ceramics of $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ [PMN] at 850°C avoiding in addition the parasite formation of the pyrochlore phase [54].

5.3. CRYSTALS FOR ELECTRO-OPTIC APPLICATIONS. — Crystal growth studies are in progress on ferroelectric fluorides with a view to electro-optic applications due in particular to the good transparency of fluoride crystals.

6. Discussion – Conclusion

Fluoride and oxyfluoride ferroelectrics constitute a group of new materials. Although the metal-fluorine bonds lead to a strongly ionic character, their crystalline networks show distortions capable of leading to ferroelectrics of displacive or order-disorder type. The Curie temperature may be very high; for example, the phases of BaMF_4 type are ferroelectric up to their melting temperature. There are now large families in which the value of T_C may be related to the size and the electronic configuration of the various cations, and to the MX ($\text{X} = \text{O}, \text{F}$) bond covalency. Ferroelectricity in fluorides and oxyfluorides has been predicted from very precise structural studies [55].

The following results are to be noted. The $\text{Pb}_5\text{Al}_3\text{F}_{19}$ compound has a very rich transition sequence with various ferroic properties: ferroelectricity, antiferroelectricity, ferroelasticity. The fluorine $\text{K}_3\text{Fe}_5\text{F}_{15}$ of "bronze" type constitutes a very original example. In fact, the corresponding oxides are ferroelectric and a low F-O substitution rate ($\text{F/O} \sim 1/15$) generally causes the disappearance of the spontaneous polarization; the very distorted MO_6 octahedra leads to non-distorted $\text{M}(\text{O}, \text{F})_6$ ones, the M^{n+} cation being localized at the octahedron center.

In the case of the $K_3Fe_5F_{15}$ fluoride, it is the simultaneous presence of Fe^{2+} and Fe^{3+} which leads to an ordered arrangement giving rise to local dipolar moments in octahedra and thus to a spontaneous polarization. This material fully deserves its "bronzes" designation as is the case for the $K_{0.57}WO_3$ oxide type which also has tungsten in the two oxidized states +V and +VI. The oxyfluoride $Na_5W_3O_9F_5$ is the leading member of an important family of materials; their good quality and large crystals make them potential candidates for applications.

The progressive F-O substitution from ferroelectric oxides with octahedra linked by corners has the advantage for modulating the value of T_C , and thus the value of the permittivity at the desired temperature; in addition, it makes it possible to densify ceramics at low temperature. Moreover, the good transparency of fluorides means that the corresponding crystals have a potential value for electro-optic applications.

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