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SYNTHESIS, CRYSTAL STRUCTURE AND CHARACTERIZATION OF A NEW FLUORIDE ZIRCONATE HYBRID, $(C_8H_{12}N)_4 \bullet Zr_2F_{12}$

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ABSTRACT: Solvothermal preparation, characterization by IR absorption, DTA-TG analysis, X-ray thermodiffraction and crystal structure determination are reported for a new fluoride zirconate $(C_8H_{12}N)_4 \bullet Zr_2F_{12}$. The cell is monoclinic ($P2_1/a$; Z = 2) with a = 14.407(2)Å ; b = 7.727(3) Å ; c = 17.37(4) Å and β = 94.83(6)°. The structure solution is refined to R = 0.025 and Rw = 0.079 using 2789 independent reflections. The 3D arrangement consists of (001) layers of Zr_2F_{12} dimers and phenylethylammonium cations in which organic cations are linked to fluoride ions by N-H…F hydrogen bonds. The interlayer Van der Waals interactions are weak and the thermal stability of the structure is poor. Thermal analysis and X-ray thermodiffraction reveal a phase transition at $T \approx 100°C$ before the decomposition starts at $T \approx 120°C$ and ends at $T \approx 350°C$ to give ZrF_4.

Keywords: Solvothermal, XRD, crystal structure, hybrid.

RESUME : Un nouveau fluorozirconate hybride $(C_8H_{12}N)_4 \bullet Zr_2F_{12}$ est synthétisé par voie solvothermale et caractérisé par absorption IR, analyses thermiques (ATD-ATG) et diffraction de rayons X (DRX) . Ce composé cristallise dans une maille monoclinique (groupe d'espace $P2_1/a$; Z = 2) avec les paramètres : a = 14.407(2)Å ; b = 7.727(3) Å ; c = 17.37(4) Å et β = 94.83(6)°. Sa structure est résolue et affinée jusqu'aux facteurs de reliabilité R = 0.025 and Rw = 0.079 en utilisant 2789 réflexions indépendantes. L'arrangement tridimensionnel 3D est constitué par des couches (001) formées par des dimères Zr_2F_{12} et des cations phenylethylammonium connectés aux ions fluorures par des liaisons hydrogène N-H…F. Les interactions entre les couches sont faibles de type Van der Waals indiquant une structure fragile pour ce composé. L'analyse thermique et la DRX en fonction de la température montrent une transition de phase vers $T \approx 100°C$. Elle est suivie d'une décomposition du solide qui s'étend de $T \approx 120°C$ jusqu'à $T \approx 350°C$ pour donner ZrF_4.

Mots clés : Solvothermale, DRX, structure, hybride.

INTRODUCTION

Microporous materials are of great interest because of their diverse properties. The expected applications range from petroleum chemistry to catalysis or gas storage–separation [1,2]. The solvothermal synthesis is the leading technique to obtain new organic-inorganic hybrid materials which have inorganic frameworks with variable dimensionalities [3,4,5,6]. Despite this intense activity, the search of purely fluoride inorganic frameworks is still weak and few 3D microporous fluorides are known [7].

In this paper, we report on the chemical preparation and the structure determination of a new hybrid fluoride zirconate: $(C_8H_{12}N)_4 \bullet Zr_2F_{12}$. This compound is also characterized by infrared absorption, thermal analyses (DTA-TGA) and X ray thermodiffraction.

EXPERIMENTAL

Parallelepipedic crystals of $(C_8H_{12}N)_4 \bullet Zr_2F_{12}$ were prepared by solvothermal synthesis during the investigation of the ZrO_2 – $C_6H_5(CH_2)_2NH_2$ – $HF_{aq.}$ system. This preparation method has proved to be effective for the synthesis of hybrid fluorides [8-9]. 5 ml of ethanol were added to $ZrO_2/C_6H_5(CH_2)_2NH_2/HF_{aq.}$ in molar proportions 13.3/13.3/73.4 respectively. The mixture was inserted in a

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Teflon container (filling rate 50%) and enclosed in a stainless steel autoclave. After heating at 190°C for 48 h, the product was recovered by vacuum filtration and air drying.

Infrared spectra were recorded on a Bomen Michelson MB 120 spectrophotometer using grinded crystals

Thermal analyses were carried out with a DTA-TGA 2960 TA Instrument under argon flow in the temperature range 25-400° C and the heating rate of 5° C/min.

Table I: Crystallographic data of $[C_8H_{12}N]_4\bullet(Zr_2F_{12})$.

Empirical formula	$Zr_2F_{12}N_4C_{32}H_{24}$
Formula weight (g mol^{-1})	898.32
Crystal system	monoclinic
Space group	$P2_1/a$ (14)
a (Å)	14.407(2)
b (Å); β (°)	7.727(3); 94.83(6)
c (Å)	17.37(4)
V (Å^3), Z	1926.9(40), 2
Four circle diffractometer / radiation	Siemens AED2 / MoKα
Crystal size (mm^3)	0.70 × 0.24 × 0.35
μ(MoKα) (mm^{-1})	0.63
$\rho_{calc.}$ (g cm^{-3})	1.55
$\rho_{exp.}$ (g cm^{-3})	1.53(2)
Temperature (K)	298
2θ range (°)	2 - 50
(hkl) limits	$\lvert h \rvert \leq 16, 0 \leq k \leq 9, 0 \leq l \leq 20$
R_{int}/R_{sigma}	0/0.0092
Scan mode	ω - 2θ
Absorption correction	Gaussian
T_{min}/T_{max}	0.729 / 0.906
Reflexions measured/unique/($F_0>4\sigma(F_0)$)	3368/3098/2789
Number of refined parameters (on F^2)	262
$^aR/R_w$	0.025/0.079
^{b}Goodness of fit	1.059
Weighting scheme ($P = [F_0^2+2F_c^2]/3$)	$1/[\sigma^2(F_0^2)+(0.0449P)^2+2.01P]$
Difference Fourier residues (e Å^{-3})	0.48, -0.29

^{a} $R = \Sigma||F_{obs.}-F_{calc.}||/\Sigma|F_{obs.}|$ $R_w = \Sigma[w(|F_{obs.}|^2-|F_{calc.}|^2)^2/\Sigma w|F_{obs.}|^4]^{1/2}$

^{b}Goof = $S = \{\Sigma[w(|F_{obs.}|^2-|F_{calc.}|^2)^2]/(n-p)\}^{1/2}$

Structure determination

The X-ray diffraction intensities from a single crystal were collected with a Siemens-Stoe AED2 diffractometer using MoKα radiation ($\lambda = 0.71073$ Å). The unit cell parameters were refined using 32 reflections at 2θ ≈ 30°. One set of 3368 (hkl) intensities was collected with ω scan method in the theta range : $1 < \theta < 25°$ and one independent set of 3098 unique reflections and 2789 $|F_0| > 4\sigma|F_0|$ was considered in the structure analysis. The Gaussian absorption correction method using SHELX-76 program was applied [10]. Analysis of the systematic absences was consistent with $P2_1/a$ space group. The starting structure solution was found (Patterson method) using SHELXS-97 [11] and refined by SHELXL-97 program [12]. One zirconium atom and three fluorine atoms were first obtained and subsequent Fourier difference syntheses allowed for the location of all carbon, nitrogen and fluorine atoms which were distinguished from distance criteria [13]. The refinement of zirconium, carbon and fluorine positions with anisotropic thermal parameters led to R = 0.040. Hydrogen atoms were located from Fourier difference maps and their positions were geometrically constrained. The final reliability ratios converged to R = 0.025 and R_w = 0.079.

Crystallographic data and several experimental details are summarized in Table I. The fractional atomic coordinates are reported in Table II. Selected bond distances and angles are given in Table III.

RESULTS AND DISCUSSION

1. Description of the structure

The basic building unit of $[C_8H_{12}N]_4•(Zr_2F_{12})$, given in Figure 1, consists of one ZrF_6 polyhedron and two $[C_8H_{12}N]^+$ cations. The atomic arrangement, illustrated by the [100] projection in figure 2, consists of a succession of (001) layers of anionic Zr_2F_{12} dimers and of phenethylammonium cations. Within the layers, the organic and inorganic entities are linked by N-H…F hydrogen bonds. Interlayer bonds are ensured by weak Van der Waals interactions. Successive inorganic sheets are separated by the c parameter (17.37 Å).

The anionic Zr_2F_{12} dimers result from the connection of two pentagonal ZrF_7 bipyramids; both zirconium polyhedra are related by the inversion center located at the middle of one common edge.

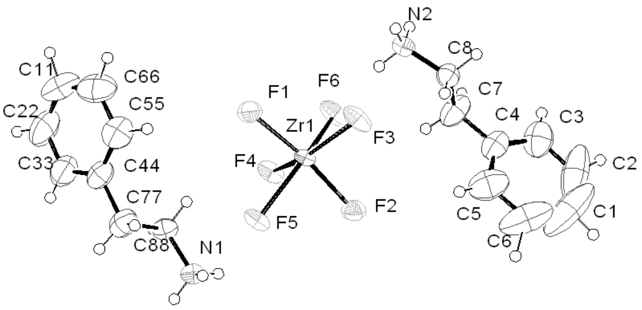

Figure 1: ORTEP drawing of the asymmetric unit of $[C_8H_{12}N]_4•(Zr_2F_{12})$. (Thermal ellipsoids are shown at 50% probability)

The ZrF_7 unit exhibits seven different Zr-F bond lengths varying from 1.995(4) Å to 2.175(2) Å with an average value of 2.06 Å. The longest distances, 2.161(2) and 2.175(2) Å, correspond to the bridging fluorine atoms F(5) and F(5)$_{\$i}$. Such geometrical characteristics are observed in comparable hybrid structures [14,15 ,16].

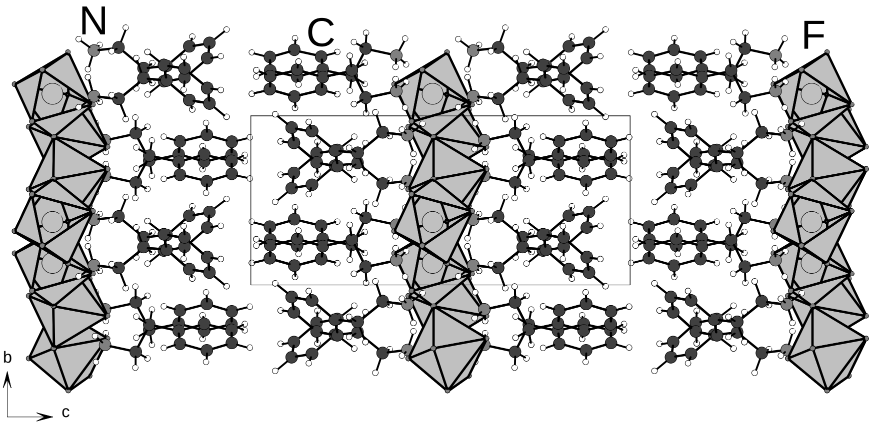

Figure 2: Projection of the structure of $[C_8H_{12}N]_4•(Zr_2F_{12})$ along [100].

The organic sheets are generated from two crystallographically independent phenethylammonium cations (Figure 2). The hexagonal rings, are nearly coplanar with the C-C-C angles ranging from 117° to 123°.

The ammonium groups of organic cations are linked to fluorine atoms of the Zr_2F_{12} dimers by N-H…F hydrogen bonds in the distance interval d(H…F) $\leq$ 2.2 Å (Table IV). F(1), F(2), F(3) and

F(6) are involved in one N-H…F bond, F(4) is linked by two hydrogen bonds while F(5) is not involved. This result is in good agreement with the bond valence sums $\Sigma s_{F\text{-}Zr}$ [13] for fluorine atoms: the lowest value is calculated for F(4) and the unique value close to 1 is found for F(5) (Table II). The Zr_2F_{12} unit is connected to twelve organic entities while the $[C_8H_{12}N]^+$ cations establish three hydrogen bonds with three different dimers (Figure 3).

Table II: Atomic coordinates and equivalent isotropic displacement parameters and bond valence calculation in $[C_8H_{12}N]_4 \bullet (Zr_2F_{12})$.

Atome	x(σ)	y(σ)	z(σ)	Beq ($Å^2$)	$\sum s^*_{cal.}$	$\sum s_{expected}$
Zr	0.89475(1)	0.37107(3)	0.47864(2)	1.957(9)	4.07	4
F(1)	0.8616(1)	0.4342(2)	0.58426(9)	3.42(3)	0.68	1
F(2)	0.9461(1)	0.3158(2)	0.37774(9)	3.38(3)	0.66	1
F(3)	0.8028(1)	0.5353(2)	0.4237(1)	3.60(3)	0.64	1
F(4)	0.9257(1)	0.1263(2)	0.5188(1)	3.27(3)	0.58	1
F(5)	1.0406(1)	0.3745(2)	0.5194(1)	2.84(3)	0.84	1
F(6)	0.7787(1)	0.2295(2)	0.4513(1)	4.20(4)	0.63	1
C(1)	0.781(1)	0.345(1)	0.0497(5)	13.9(5)		
C(2)	0.7001(9)	0.2670(1)	0.0508(3)	11.4(3)		
C(3)	0.6623(4)	0.2295(6)	0.1221(3)	6.7(1)		
C(4)	0.714(3)	0.2719(5)	0.1896(2)	4.67(7)		
C(5)	0.7999(4)	0.3477(7)	0.1864(4)	7.2(1)		
C(6)	0.8348(7)	0.3874(9)	0.1157(6)	11.1(3)		
C(7)	0.6780(3)	0.2358(5)	0.2665(2)	5.53(9)		
C(8)	0.6396(2)	0.3942(4)	0.3028(2)	3.40(6)		
C(11)	0.9386(4)	0.1626(8)	0.8857(3)	7.4(1)		
C(22)	1.0198(5)	0.0716(8)	0.8919(3)	7.7(1)		
C(33)	1.0838(4)	0.0918(6)	0.8385(2)	5.96(1)		
C(44)	1.0693(3)	0.2063(5)	0.7780(2)	4.36(7)		
C(55)	0.9868(3)	0.2984(5)	0.7711(3)	5.61(9)		
C(66)	0.9225(4)	0.2773(7)	0.8256(4)	7.1(1)		
C(77)	1.1379(3)	0.2194(5)	0.7177(2)	4.90(8)		
C(88)	1.1105(2)	0.0986(4)	0.6524(2)	3.27(5)		
N2	1.1698(2)	0.1154(3)	0.5871(1)	2.86(4)		
N1	0.6167(2)	0.3552(3)	0.3832(1)	2.93(4)		

$^*s_{ij} = \exp[(R_{ij}-d_{ij}) / b]$ where b = 0.37 [13]

Table III : Selected inter-atomic distances (Å) in $[C_8H_{12}N]_4 \bullet (Zr_2F_{12})$.

Zr-F(1)	1.995(4)	C(1)-C(2)	1.31(1)	C(11)-C(22)	1.361(8)
Zr-F(2)	2.005(4)	C(1)-C(6)	1.37(2)	C(11)-C(66)	1.374(8)
Zr-F(3)	2.016(2)	C(2)-C(3)	1.42(1)	C(22)-C(33)	1.371(7)
Zr-F(6)	2.021(2)	C(3)-C(4)	1.374(6)	C(33)-C(44)	1.377(6)
Zr-F(4)	2.052(2)	C(4)-C(5)	1.376(7)	C(44)-C(55)	1.382(6)
Zr-F(5)	2.161(2)	C(4)-C(7)	1.500(6)	C(44)-C(77)	1.502(5)
Zr-F(5)$i	2.175(2)	C(5)-C(6)	1.400(1)	C(55)-C(66)	1.389(7)
<Zr-F>	2.060	C(7)-C(8)	1.503(5)	C(77)-C(88)	1.496(5)
		C(8)-N(1)	1.493(5)	C(88)-N(2)	1.482(4)

$i : inversion symmetry operation : 0.5-x, -y, 0.5-z

Table IV : Hydrogen bond distances (Å) and N-H…F angles (°) in $[C_8H_{12}N]_4$•(Zr_2F_{12}).

A-H…F	d (H...F) (Å)	A-H…F (°)	d (A...F) (Å)
N2-H1A...F4	2.02	164.5	2.887(4)
N2-H1B...F1	1.98	150.1	2.794(3)
N2-H1C...F3	1.88	159.0	2.737(3)
N1-H2A...F2	1.91	167.1	2.784(3)
N1-H2B...F4	1.92	165.0	2.798(4)
N1-H2C...F6	1.82	168.0	2.706(3)

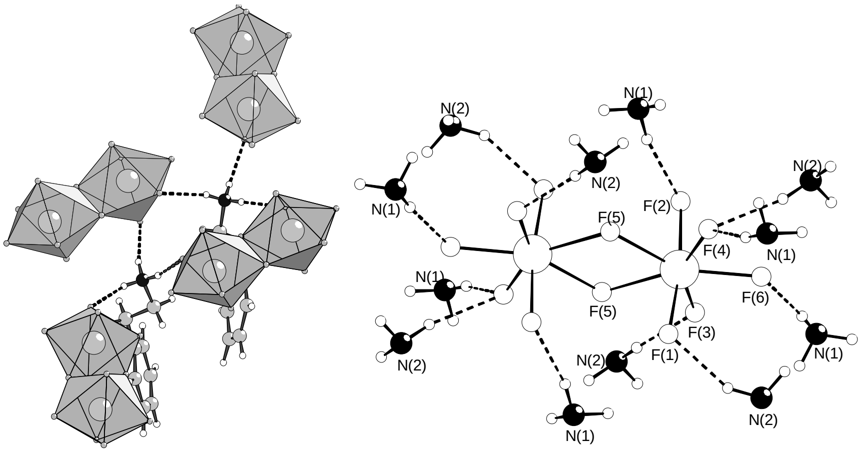

Figure 3: Environments of $C_8H_{12}N^+$ cations (left) and Zr_2F_{12} dimers (right) in $[C_8H_{12}N]_4$•(Zr_2F_{12}).

Though, the organic cations are linked by hydrogen bonds via their polar ammonium groups, their hydrophobic parts (phenyl group) interact only with weak Van der Waals forces. This feature explains the high thermal motion parameters of C_1, C_2, C_6, C_{11}, C_{22}, C_{66} carbon atoms (Fig.1). A similar situation was previously encountered in the hybrid copper chloride $[C_8H_{12}N]_2$•$CuCl_4$ [17]. It is also expected that the thermal stability of $[C_8H_{12}N]_4$•(Zr_2F_{12}) is poor.

2. IR spectroscopy results

The IR spectra of $C_6H_5CH_2CH_2NH_2$ (a) and $(C_8H_{11}N)_4Zr_2F_{12}$ (b) are depicted in fig.4. The presence of intense peaks in the range 3400-3200 cm^{-1} (spectrum a) is related to primary amine. Their maximum wavenumbers, observed at 3366 and 3284 cm^{-1}, are assigned to N-H vibrations. In the title compound (spectrum b), these bands appear larger with a decrease of their wavenumbers maxima to 3054 and 3024 cm^{-1}. This result indicates well the presence of strong hydrogen bonds involving the nitrogen atom [18].

3. Thermal behavior

The DTA and TGA thermograms are given in Figure 5. Above $T \approx 120°C$, a continuous weight loss occurs until a slope change is noted at $T \approx 240°C$ ($\Delta m/m = 0.109$) and a plateau is reached at $T \approx 340°C$ (total $\Delta m/m = 0.624$). These variations are related to the decomposition of $[C_8H_{12}N]_4$•(Zr_2F_{12}) with the successive loss of 4HF ($\Delta m/m_{th} = 0.089$) and of the organic amine (total $\Delta m/m_{th} = 0.627$) to give the final residue ZrF_4. The overall reaction is:

$$[C_8H_{12}N]_4\bullet(Zr_2F_{12}) \rightarrow 4\,C_8H_{11}N + 4\,HF + 2\,ZrF_4 \qquad (\mathbf{R})$$

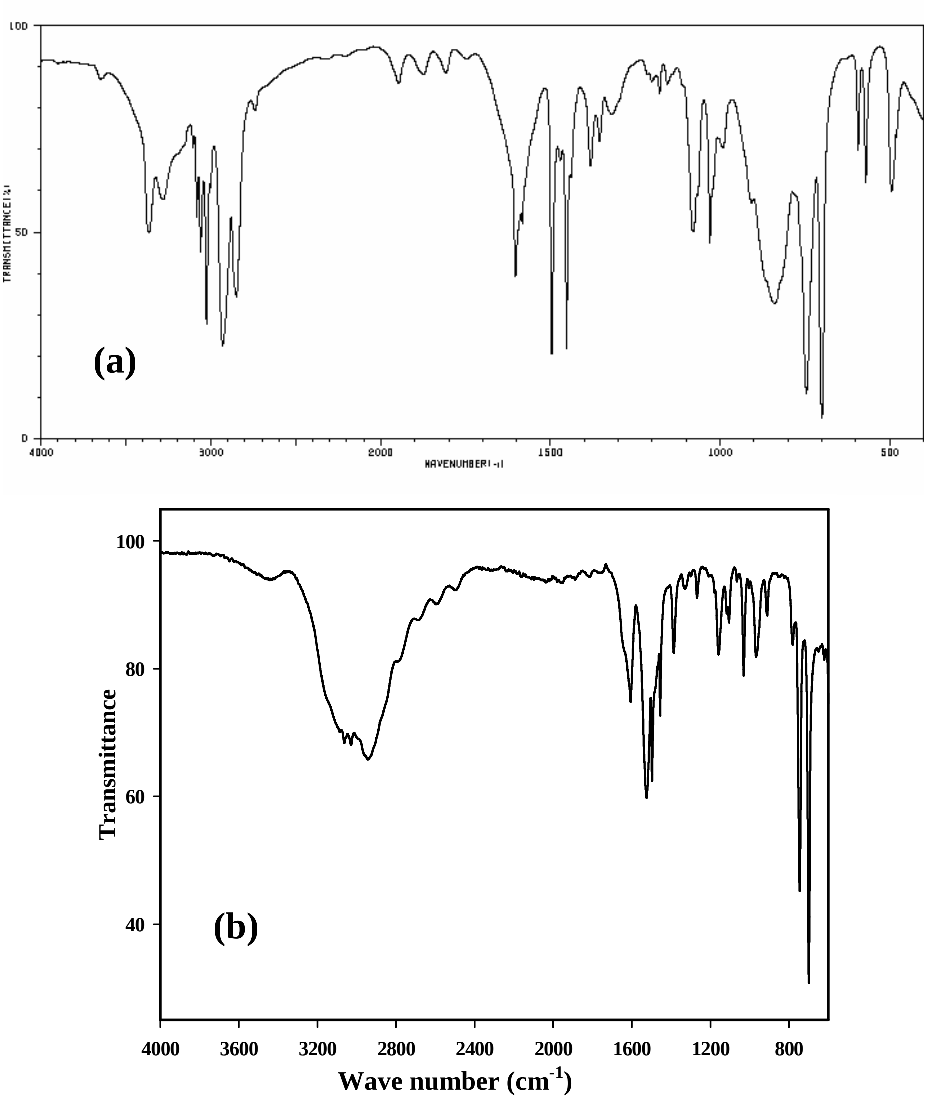

Figure 4: Infrared spectra of $C_6H_5CH_2CH_2NH_2$ (a) and $[C_8H_{12}N]_4Zr_2F_{12}$(b)

The DTA curve shows four endothermic events at 95°C, 181°C, 235°C and 325°C. The last three events are correlated with a weight change. A thermodiffraction study was undertaken in order to examine the structural transformations that occur on heating.

The X ray diffraction diagram of the post TGA residue is clearly assigned to zirconium tetrafluorides ZrF_4 in accordance with the decomposition reaction (**R**).

The DTA thermogram exhibits two peaks without weigh loss at ca 95°C and 181°C. The last is probably due to the melting of the organic molecule. In fact, an experience realized on banc Kofler shows that the compound sample presents a viscous aspect at ca 170°C. The first endothermic peak at 95°C can be related to a possible phase transition which may occur at a such low temperature. This result is in accordance with the structural study concerning the weak phenyl group interactions.

The plot of the powder diffraction patterns collected at different temperatures (Fig.6) shows the thermal evolution of $[C_8H_{12}N]_4$•(Zr_2F_{12}).

Thermodiffraction (fig.6) confirms that the compound undergoes a crystallized phase transition in the range : 85°C - 125°C. The pattern recorded at 125°C with a weak rate indicates well the formation of a new unknown phase.

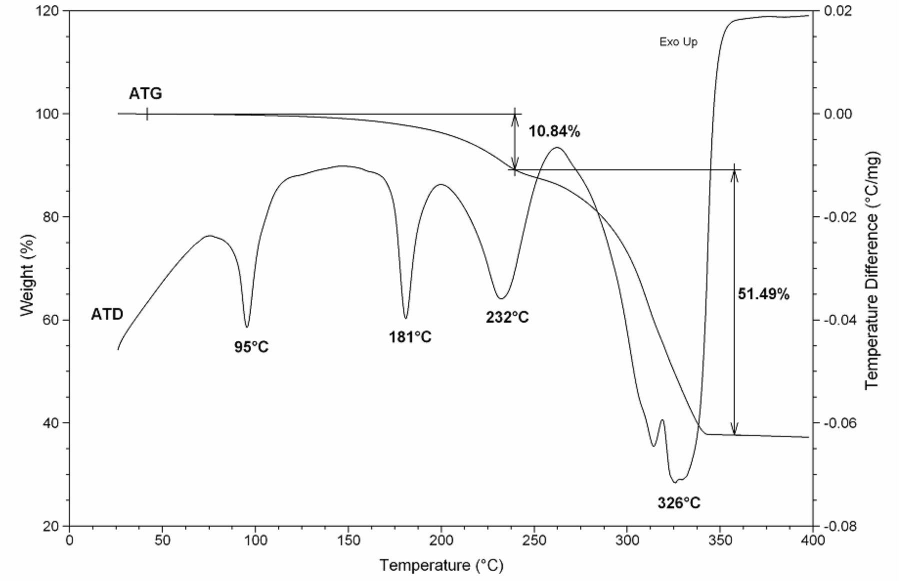

Figure 5: DTA and TGA curves of $[C_8H_{12}N]_4$•(Zr_2F_{12}).

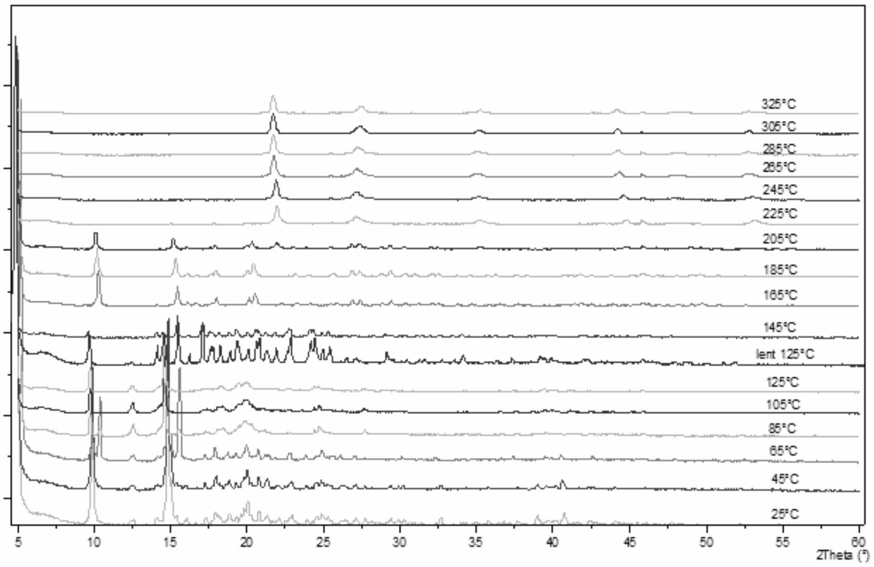

Figure 6: Thermodiffractometry analysis of $[C_8H_{12}N]_4$•(Zr_2F_{12}).

CONCLUSION

The new inorganic–organic hybrid material based on zirconium (IV) fluorine inorganic entities and phenylethylamine as organic template has been synthesized using sub-critical solvothermal method in ethanol as solvent. The structure can be described from inorganic sheets of Zr_2F_{12} dimmers formed by edge chairing between two ZrF_7 polyhedra. These dimmers establishe strong hydrogen bonds with phenylethylammonium cations.

Thermal analysis clearly shows a phas transition at T ≈ 100°C which is confirmed by X-ray thermodiffraction.

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