SYNTHESIS AND CRYSTAL STRUCTURE OF PSEUDO-BINARY: (1-X) TlNbO$_3$ -xBi$_2$O$_3$ 0≤x≤ 1

Ghizlane El bahari, Abdeslam Chagraoui, BrahimOrayech, Abdelmjid Tairi, Omar Ait Sidi Ahmed

a- *Laboratoire de Physico-Chimie des Matériaux Appliqués (LPCMA); Faculté des Sciences Ben M'Sik ; Université Hassan II-Mohammédia Casablanca (Morocco).*

b- *Departamento de Fisica de la Materia Condensada, UniversidaddelPais,E-48080, Bilbao, Spain.*

E-mail: ghizlan.elbahari@gmail.com

Abstract

Different compositions of pseudo-binary (1-x)NbTlO$_3$ -xBi$_2$O$_3$ were prepared with0≤x≤1. New defect pyrochlore oxide (1-x)NbTlO$_3$ -xBi$_2$O$_3$ where x=0.091Tl$_{0.909}$Nb$_{0.909}$Bi$_{0.182}$O$_3$ has been isolated as polycrystalline powder giving X-ray diffraction patterns characteristic of defect pyrochlore, space group Fd-3m (n°227), with lattice parameter: a=10.6368(2)Å,(Z=8). Rietveld refinements of X-ray powder diffraction data indicate that the atomics positions are: Tl (32e), Bi and Nb in 16c. O occupied the sites 48fand 8b respectively. The reliability factors are: R$_F$=6.59%,R$_{wp}$= 8.62%, R$_B$=5.40%.For 0.091≤x <0.8 we noted mixture of phases situated in ternary system and for 0.8≤ x <1 we have stabilised δBi$_2$O$_3$.

Résumé

Diverses compositions au sein de la droite (1-x)NbTlO$_3$ -xBi$_2$O$_3$ avec 0≤x≤ 1 ont été préparées par réaction solide, dans laquelle nous avons mis en évidence deux nouvelle phases : phase de type pyrochlore Tl$_{0.909}$Nb$_{0.909}$Bi$_{0.182}$O$_3$ pour x=0.091avec groupe d'espace Fd-3m (n ° 227), avec paramètre de maille: a = 10,6368 (2) Å, (Z = 8).
L'étude structurale a été menée par analyse du profile des diagrammes de diffraction X de poudre Fullprofindiquent que les positions atomiques sont les suivantes: Tl (32e), Bi et Nb dans 16c. O occupaient les sites 48f et 8b respectivement. Les facteurs de reliabilité sont les suivants: R$_F$ = 6,59%, R$_{wp}$ = 8.62%, R$_B$ = 5,40%.

Mots clés : Diffraction X, Fullprof, pyrochlore, reliabilité.

1- INTRODUCTION

Pyrochlores oxides have received much attention for several decades due to their diverse physical properties, which allow for a broad range of applications, such as high permittivity dielectrics [1,2] solid electrolytes [3] host materials for the immobilization of fission products [4,5] catalysis [6]and thermal barrier coatings[7–9]. Ideal stoichiometric pyrochlores A$_2$B$_2$O$_7$ are cubic with space group Fd-3m and often described as two interpenetrating networks of B$_2$O$_6$ octahedral and A$_2$O tetrahedral [10,11]. The structure pyrchlore ideal A$_2$B$_2$X$_6$X'is the term n = 8 in the series of phases M$_n$X$_{2n-2}$-type anion-deficient fluorite[12].It derives from the fluorite structure by creation of gaps in the anionic sub network, one anion per eight; localizes along <111> is absent (chemical formula; A$_2$B$_2$X$_7$□). In ordinary pyrochlore oxides with the chemical formula A$_2$B$_2$O$_6$O', the A cation, which is a large, rare-earth alkali metal, alkaline earth metal or post-transition metal cation, lies in a distorted (6O+2O') coordination, while the B cation, which is a small transition metal cation, forms a slightly distorted BO$_6$ octahedron. In the space group Fd-3m with the origin chosen at the B site, the A, B, O and O' atoms occupy

the 16d, 16c, 48f and 8b Wyckoff positions respectively [13,14].The structural stability of $A_2B_2O_7$ pyrochlore depends on the ratio of cation radii, rA/rB (rA/rB$\geq$1.2[15]. The typical A, B cation radiiis around 1, 0.6 Å, but compounds with variations of up to0.2 Å for both cations are stabilized [10].

Recent attention has focused on bismuth based pyrochlore, where the Bi^{3+} cation resides in the Asite for their potential use in capacitor and high-frequency filter applications [16-18].Similarly many compounds containing both a monovalent cation of large size (Cs, Rb, K or Tl), bismuth trivalent cation and a pentavalent B as Nb, Ta, Sb or a combination of suitable elements are known [19-23].

We report in this paper the synthesis and crystal structures determined by X-ray powder diffraction of polycrystalline$Nb_{1-x}Tl_{1-x}Bi_{2x}O_3$ (x=0.091)in order to confirm the structural model of pyrochlore type and determine the nature and occupancy of various sites in the oxide occupied using different models.

2- EXPERIMENTAL

Various compositions in the pseudo-binary $TlNbO_3$-Bi_2O_3 were prepared by solid-state reaction. Commercial products starting Tl_2CO_3, Nb_2O_5 and Bi_2O_3 purity greater than 99% were weighed from stoichiometric mixtures. The samples were ground, placed in alumina nacelles and heated in air at 300°C (24h) and then at 550°C (12h) to allow the decomposition of carbonates by the reaction:

(1-x)/2 Nb_2O_5 + xBi_2O_3+ (1-x) /2 Tl_2CO_3 →$Nb_{1-x}Tl_{1-x}Bi_{2x}O_3$+ (1-x)/2 CO_2
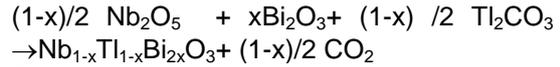
The grinding operation was renewed heating at higher temperatures (750 to 900°C see Table1) for a complete reaction and followed by quenching. X-ray diffraction patterns were obtained by using an automatic diffractometer type SiemensD5000, using the CuKα radiation(λ=1.5406 Å).The study of the structure is conducted by analyzing the profile of X-ray diffraction diagrams of powder with the program Fullprof [24] using the pseudo-Voight function.

Table1:Conditions of preparing different compositions (1-x) $NbTlO_3$ -xBi_2O_3
0$\leq$x$\leq$ 1.

Compositions	Temperature synthesis	Color	Phases identified in the annealed sample	ICPDS Cards
$Tl_{0.2}Nb_{0.2}Bi_{1.6}O_3$ (Compound D x=0.8)	800°C (24h)	Yellow	δ Bi_2O_3	77-2008
$Tl_{0.4}Nb_{0.4}Bi_{1.2}O_3$ (Compound B x=0.6)	800°C (24h)	Yellow	$Bi_3 Nb O_7$ $Bi_5 Nb_3O_{15}$ $BiNbO_4$ D	86-0875 50-0087 51-1752 71-1518
$Tl_{0.8}Nb_{0.8}Bi_{0.4}O_3$ (Compound A x=0.2)	800°C (24h)	Orange	B+ E $Bi_3Nb_{17}O_{47}$	72-0718
$Tl_{0.909}Nb_{0.909}Bi_{0.182}O_3$ (Compound E x=0.091)	900°C (24h)	Orange	Pyrochlore	
$TlNbO_3$ (Compound Cx=0)	900°C (24h)	Yellow	$TlNbO_3$	24-1303

3- RESULTS AND DISCUSSIONS

Crystallography analysis of $TlNbO_3$-Bi_2O_3 pseudo-binary (Fig.1) allowed isolating:
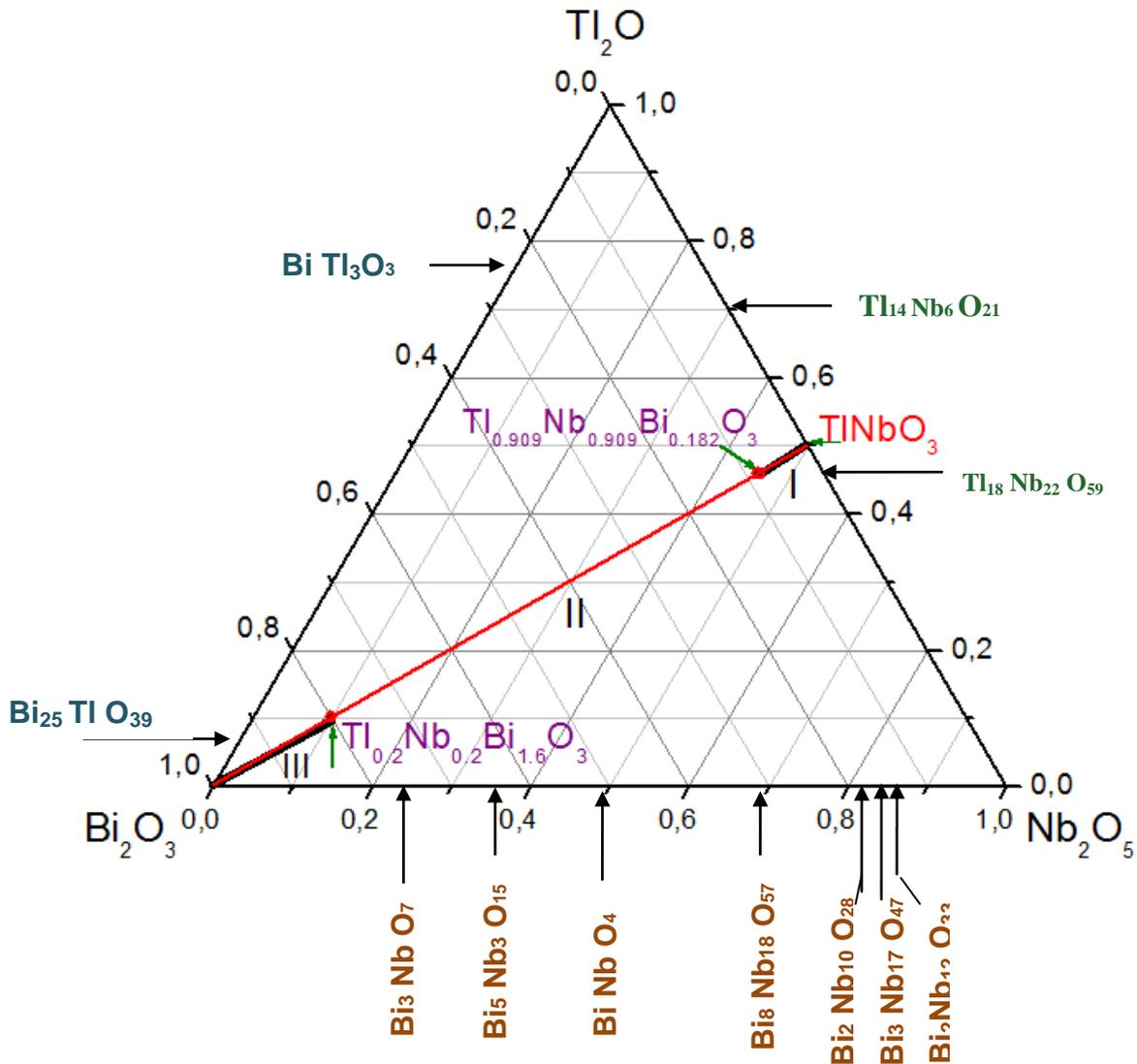
Fig.1: Localization of pyrochlore (I) and fluorine (III) phases in system Bi_2O_3-Nb_2O_5-Tl_2O.

- **Domain I**: solid solution cubic pyrochlore type $Nb_{1-x}Tl_{1-x}Bi_{2x}O_3$ with $0 \leq x \leq 0.091$. All compositions gave single phase with X-ray patterns indexable in face-centred pyrochlore–type cubic structure. Lattice constant decreased linearly with increasing of bismuth concentration. It seems that the difference of the niobium $rNb^{5+}[6] = 0.64$Å and thallium $rTl^+[8] = 1.59$ Å ion radii larger than bismuth ionic $rBi^{3+}[6] = 1.03$Å. (The lattice parameter of $Tl_2Nb_2O_7$ is a=10.62 Å) [25].

- **Domain II** (0.091<x<0.8): In this domain three phases are observed: cubic phase isotypeδ-Bi_2O_3 [26], $BiNbO_4$ [27] and Bi_3NbO_7 [28]. In fact the stripes on the pyrochlore structure and reflect the structure of it compared to the fluorine intensity decreases with increasing content of Bi_2O_3 (Fig. 2).

- **Domain III** (0.8< x<1): solid solution fluorine type where with limit composition $Bi_{1.6}Tl_{0.2}Nb_{0.2}O_3$.
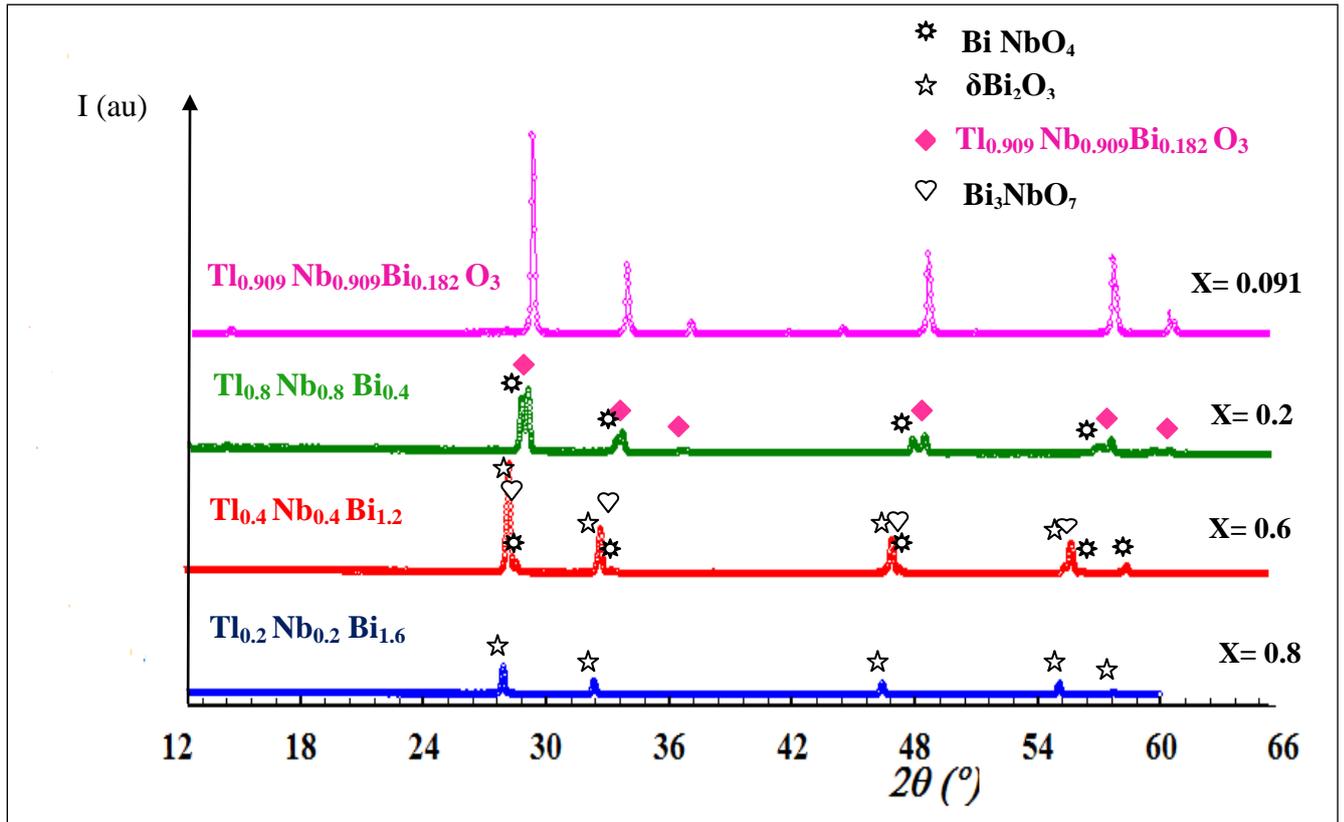
Fig.2: X-ray diffraction patterns of compositions (1-x)TlNbO₃ -xBi₂O₃ for (0 ≤x ≤1).

3.1- Indexation

The structural formula of this compound can be presented as $Tl_2Bi_{0.4}Nb_2O_6O'_{0.6}$while the empirical chemical formula can be written as: $Nb_{0.909}Tl_{0.909}Bi_{0.182}O_3$.The diffraction peaks were indexed in the cubic system (Fd-3m) (Table 2).

3.2- Refinement of the structure

Rietveld refinement results obtained for pyrochlore-type $Tl_2Bi_{0.4}Nb_2O_6O'_{0.6}$using four different models (Table3).

<u>Model 1</u> corresponds to the ideal pyrochlore structure; (Bi,Tl) in 16d Nb in 16c O (48f) (x 1/81/8) (x=0.31) O'(8b) (3/8 3/8 3/8), the anomalously large thermal parameter obtained for Bi site. <u>In model 2</u>based on the previously work [23] the authors were able to locate the atoms of thallium, bismuth and niobium phases as : $TlBi_2Nb_5O_{16}$: Tl32e

(xxx) (x=0.42), Bi 96g(x xz)(x=0.48, z=0.52)Nb in 16c (000) O and O' respectively in (48f) and (8b); we have applied these results to our product, we foundfactors reliability remain too high and a thermal agitation thallium too important. In <u>Model 3</u>according to L.L Fourquet and al [29] on phase $TlNbO_{6+x}$, the presence 442, 446, 842 … corresponding hkl with h=2n ; k=2n and l=2n are present in the pattern of these lines indicates that heavy atoms are localized in different positions 32e , 96g, 96h or 192i observation. Previous studies on the neighbouring retain the Bi and Tl cations displace together to 96g and 32*e* sites respectively very near to (½ ½ ½), the thermal parameter is negative for bismuth too. These results are poor location of atoms of bismuth. As seen in the fit statistics obtained for <u>Model 4</u> returns a better thermal

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parameter and best factors reliability which atoms are localized Tl in 32e, Nb 16c. Fourier-difference analysis revealed the remains of electronic density around the position (000) corresponding to bismuth atoms. The size of thallium is much higher than that of niobium and its electronic structure different from that of the latter make their existence very unlikely. The parameters were refined by correlating those of niobium and bismuth on site 16c.

Successive refinement of cations positions and isotropy thermal coefficient ofatoms led to reliability R_F=6.59%, R_{wp}=8.62%, R_B=5.72%. The X-ray diffraction diagrams of observed, calculated and difference are given in Fig. 3. Experimental details, crystallographic data and atomic coordinates, thermal coefficients of agitation and occupancy refinement are given respectively in Tables (4, 5).

Table 2: Indexed powder X-ray diffraction of $Tl_2Bi_{0.4}Nb_2O_6O'_{0.6}$

Hkl	dhklobs.	dhklcal.	I/Io
111	6.1407	6.1408	3
220	3.7604	3.7605	<1
311	3.2069	3.2069	2
222	3.0704	3.0704	100
400	2.6590	2.6590	37
331	2.4401	2.4401	6
422	2.1711	2.1711	<1
333	2.0470	2.0469	<1
440	1.8803	1.8802	45
531	1.7978	1.7979	<1
442	1.7727	1.7727	<1
620	1.6817	1.6817	<1
533	1.6220	1.6220	<1
622	1.6035	1.6034	47
444	1.5352	1.5352	13
711	1.4894	1.4894	<1
642	1.4213	1.4213	<1
553	1.3847	1.3847	<1
800	1.3295	1.3295	48

Table 3: Rietveld refinement results of different models.

	Model1	**Model2**	**Model3**	**Model4**
A-site	16d	32e	32e	32e
Occ	0.09530	0.07699	0.07031	0.07699
X	0.5	0.42	0.48181	0.51048
Y	0.5	0.42	0.48181	0.51048
Z	0.5	0.42	0.48181	0.51048
Uiso	0.87932	0.35563	3.87600	0.35563
Bsite	16c	16c	16c	16c
Occ	0.09530	0.07699	0.07031	0.07699
Uiso	0.87932	0.35563	3.87600	0.35563
Osite	48f	48f	48f	48f
Occ	0.25	0.25	0.25	0.25
X	0.32199	0.31	0.24522	0.31974
Uiso	0.3	0.3	0.3	0.3
O'site	8b	8b	8b	8b
Occ	-0.01197	0.00634	0.01302	0.00634
X	0.37500	0.37500	0.37500	0.37500
Y	0.37500	0.37500	0.37500	0.37500
Z	0.37500	0.37500	0.37500	0.37500
Uiso	0.3	0.3	0.3	0.3
Cell Parameter(Å)	10.6363	10.6363	10.6285	10.6363
Rbfactor	8.37	113.5	88.7	5.19
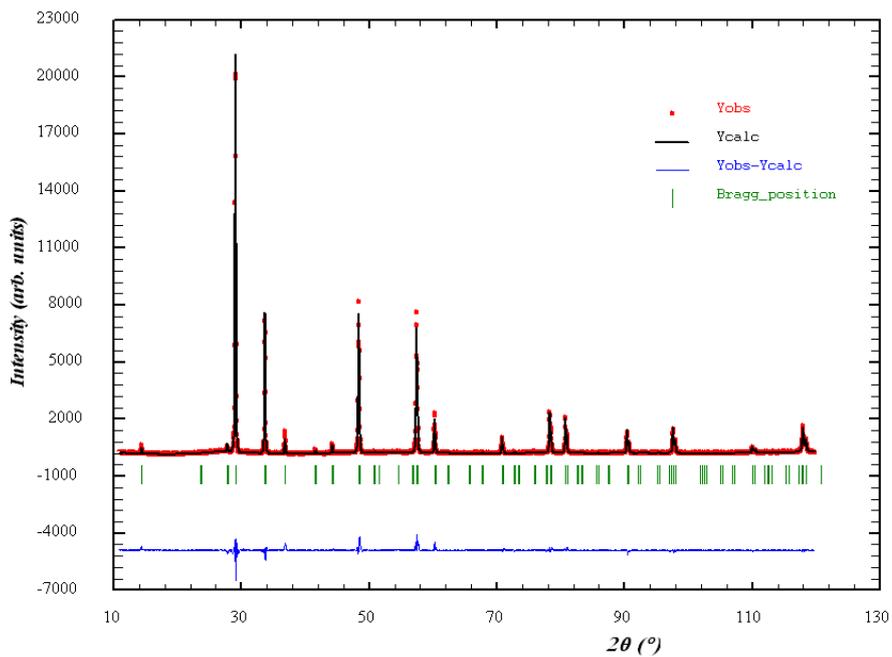
Fig.3: Experimental (crosses), theoretical (solid line), and difference powder XRD patterns for
$Tl_2Bi_{0.4}Nb_2O_6O'_{0.6}$*; reflection positions are marked by vertical bars.*

Table 4: Experimental details and crystallographic data for $Tl_2Bi_{0.4}Nb_2O_6O'_{0.6}$.

Crystal system	Cubic
Lattice parameter	10.6368(2) Å
Cell volume	1203,28(0.03)$Å^3$
Formula units per cell	8
Calculated density	8.62
Measured density	8.50
2θ scan range; step	10-120°; 0.04s
Parameters	64
Reliability factors	R_F= 6.59%, R_b= 5.40%, R_{wp}=8.62%

3.3-Discussion of the structure

A projection of $Tl_2Bi_{0.4}Nb_2O_6O'_{0.6}$ onto (1-10) is represented in Fig.4. The center of hexagon composed of corner shared six $(Nb/Bi)O_6$ octahedra contains overlapping projection of one Tl (16d) and two O(2) units. The $(Nb/Bi)_2O_6$ network is regarded as the rigid frame structure. Eight atoms of oxygen polyhedra around the thallium atom are occupied in the following way; six oxygen occupied (48)f an two oxygen O' (8b) in site. The structure is built from corner-sharing $(Nb,Bi)O_6$ octahedra which form the classical pyrochlore framework $(Nb,Bi)_2O_6$ (Fig.4). The $(Nb, Bi)O_6$ octahedron share their corners to form a three-dimensional network. The atom coordinate x of O (48f) is a unique parameter that determines the distortion of a $(Nb,Bi)O_6$ octahedra. According to Faucher and al [30], the form of coordination polyhedra change depending on the oxygen x parameter (x= 0.3199). This value lies between 0.3125 and 0.375 when the origin of coordinates is set at B sites. Coordination around B site becomes a regular octahedral for x= 0.3125 and the coordination around A site becomes a regular cube for x= 0.375.

The deviation from the special value of x= O.3125 for the ideal octahedron leads to a trigonal distortion with an equal distance (Nb,Bi)-O=2.022Å. The value of x= 0.3199 observed for is smaller than for others pyrochlore [13, 31-32]. So there is small distortion of the octahedron, with internal O-(Nb,Bi)-O angle (87-92)° and large O-(Nb,Bi)-O angle (179°) between neighbouring octahedral. The main interatomic distances and bond angles are given in Table 6.

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a)

b)
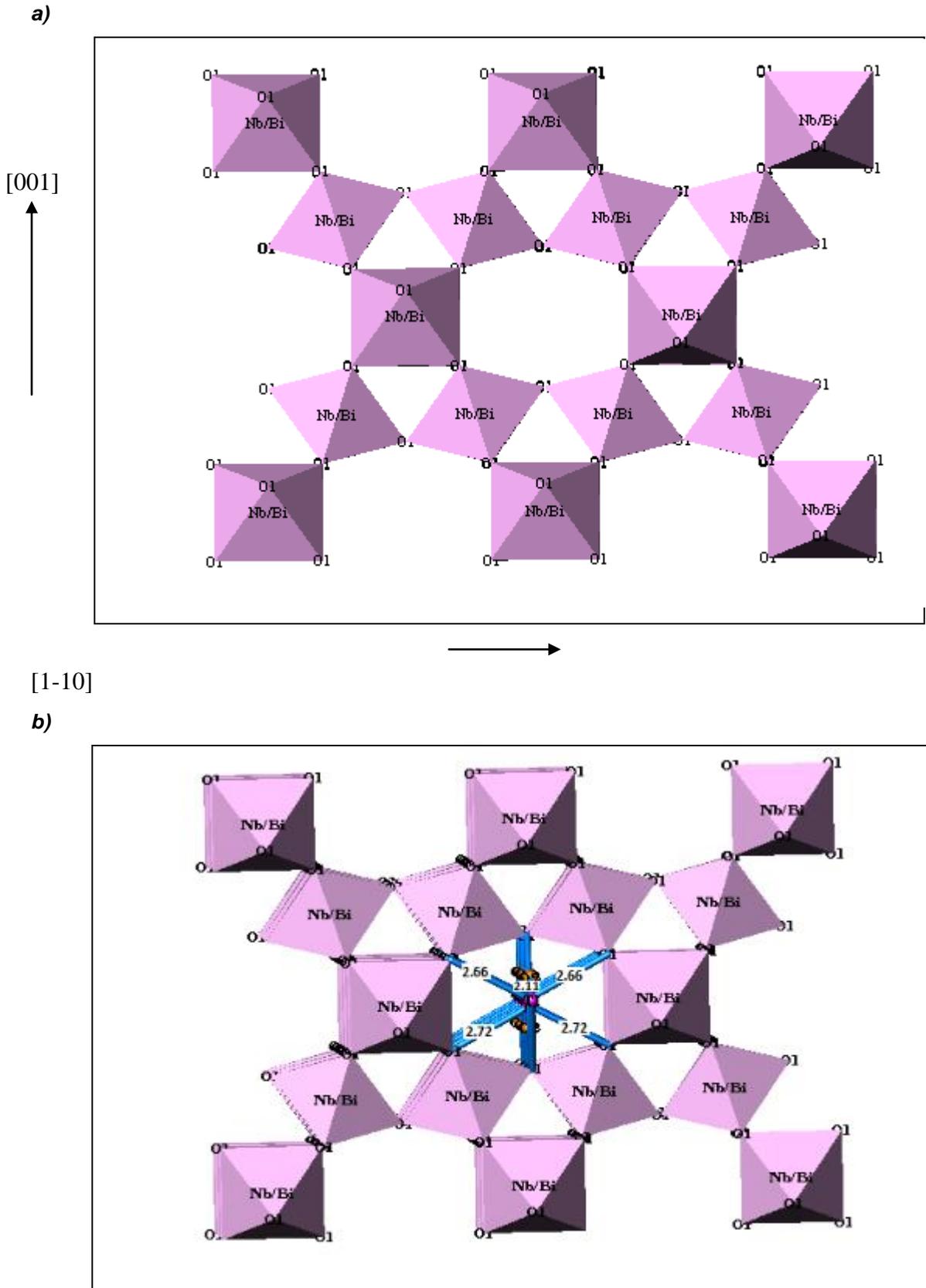
Fig.4:a) Projection of the pyrochlore structure along [1-10] showing tunnels in the (Nb,Bi)O$_6$framework

b) Interpenetrating networks of (Nb/Bi)$_2$O$_6$ and Tl$_2$O.

3.3.1-Niobium and bismuth coordination polyhedra

The bismuth and niobium atoms are surrounded by six oxygen atoms at distance 2.021Å (Table 4).This distance is in perfect with the sum of radii as proposed by Shannon Nb-O=2.04 Å [33]. The (Nb, Bi)O_6 octahedron (Fig.5) is regular. BiO_6 and NbO_6 are distributed statically in network.
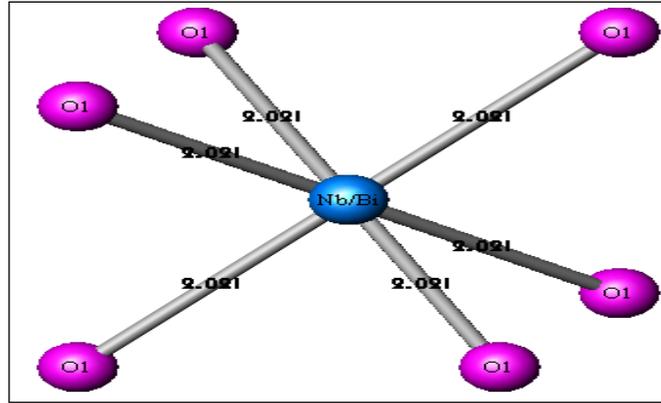
Fig.5: View of Nb/Bi anionic coordination.

Table 5: Main interatomic distances (Å), angles (°) and bond valences in $Tl_2Bi_{0.4}Nb_2O_6O'_{0.6}$

Polyhedra (Bi,Nb)O_6	O1(1)	O1(2)	O1(3)	O1(4)	O1(5)	O1(6)	Vij
O1(1)	**2.021(4)**	2.786(3)	2.928(3)	2.929(12)	4.042(6)	2.786(16)	0.74
O1(2)	87.1(3)	**2.021(8)**	4.042(11)	2.786(3)	2.928(3)	2.929(12)	0.74
O1(3)	92.9(3)	180.0(7)	**2.021(8)**	2.929(12)	2.786(3)	2.786(3)	0.74
O1(4)	92.9(5)	87.1(3)	92.9(5)	**2.021(4)**	2.786(16)	4.042(11)	0.74
O1(5)	180.0(4)	92.9(3)	87.1(3)	87.1(7)	**2.021(4)**	2.929(12)	0.74
O1(6)	87.1(7)	92.9(5)	87.1(3)	180.0(7)	92.9(5)	**2.021(8)**	0.74
							4.44

<Nb/Bi-O>= 2.021Å

The valence of (Nb,Bi) calculated using brown method [34] is estimated to 4.44. The electrostatic calculation of valence is not significant by taking account of the occupation site 16c by the niobium and bismuth together. However the valence of thallium calculation is higher than theoretical (1), it seems that thallium is ox dated at high temperature.

3.3.2-Oxygen O' (O2) coordination polyhedra

The oxygen O(2) is surround by four thallium atoms at 2.12Å distance. The oxygen atom is situated in center of regular tetrahedron formed by thallium atoms Fig. 6.

a)
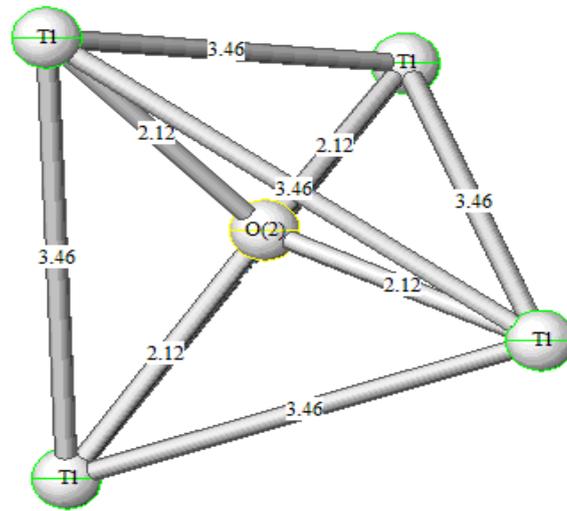
b)
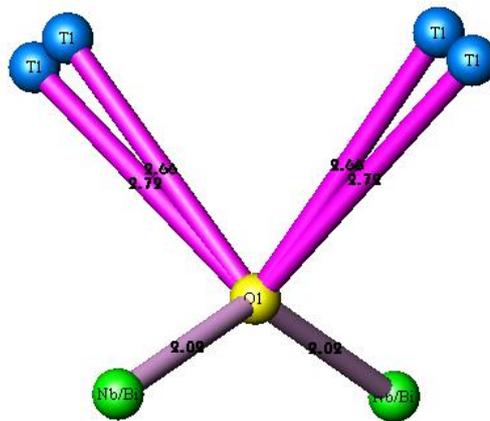
Fig.6: View of oxygen a) O2 and b)O1 cationic coordination.

3.3.3-Thallium coordination polyhedra

The thallium atom located in 32e between 8b and 16d (Fig. 7) is surrounded by eight oxygen atoms (2O' + 6O) at distances ranging 2.12- 2.72 Å with one short bond at 2.12 Å, another at 2.486Å tree at 2.661Å and 2.68Å and two shorter distances Tl-O at 2.30Å. The mean Tl-O distance is 2.585 Å. This small disparity reveals a weak streochemical activity of the lone pair of the thallium atom.

tree others at 2.72Å (Table7).This disparity reveals a stereochemical activity of the lone pair of the thallium. The short Tl-O' distance indicates a marked covalent interaction.

As shown in figures there is two kinds of Tl interatomic distances, that is six Tl-O at The electrostatic calculation of valence is 3.38 its possible oxidation thallium atomic where 1 to 3. This result is confirmed by augmentation of weight

Table 6: Main interatomic distances (Å), angles (°) and bond valences in $Tl_2Bi_{0.4}Nb_2O_6O'_{0.6}$

Polyhedra TIO$_8$	O2(1)	O2(2)	O1(1)	O1(2)	O1(3)	O1(4)	O1(5)	O1(6)	Vij
O2(1)	**2.12(5)**	4.605(4)	3.806(18)	3.247(12)	3.247(12)	3.806(18)	3.247(5)	3.806(8)	**1.394**
O2(2)	179,96(19)	**2.493(5)**	3.806(8)	3.247(5)	3.806(8)	3.247(5)	3.247(5)	3.806(8)	**0.456**
O1(1)	95.1(3)	95.1(3)	**2.662(10)**	2.786(9)	2.786(16)	4.592(15)	4.592(12)	5.371(8)	**0.277**
O1(2)	84.9(2)	84.9(2)	62.3(3)	**2.662(8)**	4.592(5)	5.371(8)	2.786(3)	4.592(12)	**0.277**
O1(3)	76.9(2)	95.1(3)	62.3(4)	115.0(5)	**2.662(8)**	2.786(3)	5.371(12)	4.592(12)	**0.277**
O1(4)	103.1(4)	84.9(5)	119.2(2)	172.0(4)	62.3(3)	**2.722(9)**	4.592(12)	2.786(3)	**0.233**
O1(5)	76.9(2)	76.9(4)	119.2(5)	62.3(4)	172.0(4)	119.2(2)	**2.722(8)**	2.786(3)	**0.233**
O1(6)	103.1(4)	103.1(3)	172.0(4)	115.0(5)	115.0(5)	62.3(3)	62.3(3)	**2.722(8)**	**0.233**
									3.38
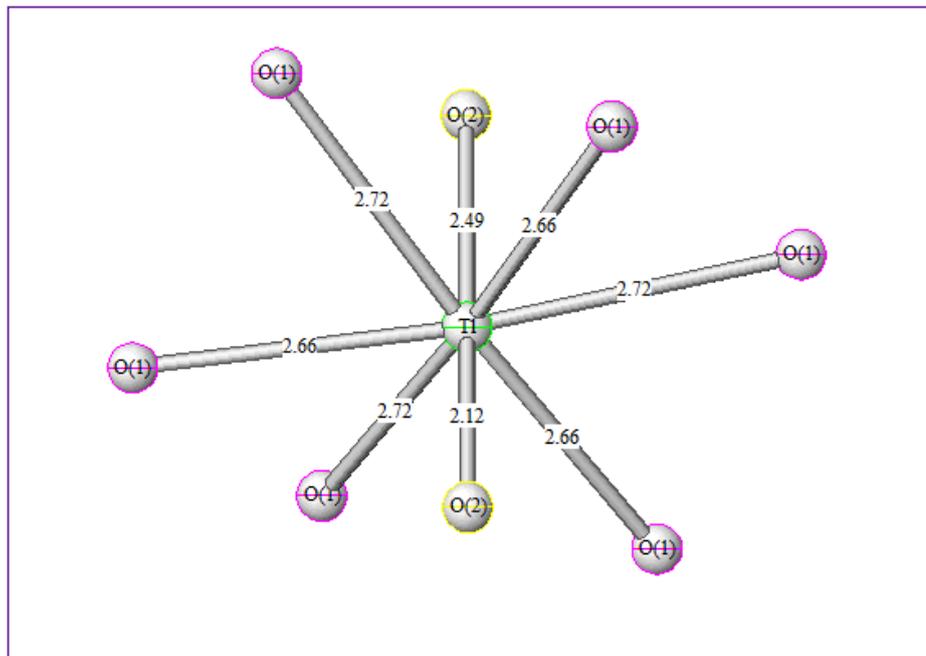
Fig.7: View of thallium anion coordination.

4- CONCLUSIONS

We have successfully synthesized polycrystalline samples in a range $Bi_{2x}Tl_{1-x}Nb_{1-x}O_3(1-x)$ $TlNbO_3$ $-xBi_2O_3$ $0\leq x\leq 1$ at high temperature synthesis and rapid cooling. The structural study by X-ray diffraction powder for the solid solution $Nb_{1-x}Tl_{1-x}Bi_{2x}O_3$ (x = 0.091) confirmed its membership in the defect pyrochlore structure. We have noted: a deficit of occupation sites 16c and 32e cationic, anionic (8b) and a statistical distribution of cations of bismuth and niobium on the 16c site. An ordered distribution of cations (Nb, Bi) and thallium respectively on sites 16c and 32e. The thallium ions are be distributed in 32e very near to (½ ½ ½), other than lying on the threefold axes. The gradual introduction of Bi^{3+} ions in the pyrochlore network of $Tl_2Nb_2O_6$ contributes to increase the cationic disorder and stabilize the fluorite type structure. This phase is obtained for x = 0.8.Its structure determination will be published after.

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