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Recent progress in tetravalent terbium chemistry

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Abstract

The stability of the tetravalent state in Ln compounds has been the subject of numerous investigations. If tetravalent cerium compounds are among the most stable and can be handled with minor risk of decomposition, the existence of tetravalent praseodymium fluorides is of no doubt, but they cannot give rise to reliable experimental data. With regard to the terbium, it has now been established that the tetravalent oxidation state may be stabilized under certain circumstances. However, the terbium tetrafluoride itself exhibits a domain of thermal instability which has turned out to synthesize mixed-valence terbium fluorides, such as Tb_4F_{15} or KTb_3F_{12}. Up to now, there were no available crystallographic data from single-crystal works for the Tb^{4+} ion. Obtaining single-crystals of Li_2TbF_6, $KTbF_5$, $CsTbF_5$, Li_2CaTbF_8, KTb_3F_{12}, both α and β-$BaTbF_6$, represents a quantum leap in the capability of crystal structure determination and refinement. These results have brought a revival of the search for new Tb^{IV} compounds which has lead to the discovery of a large family of $LiLnTbF_8$ fluorides, the structural relationships of which, with $LiNaY_2F_8$ and BaY_2F_8, are discussed.

Keywords: Tetravalent terbium; Fluorides; Crystal structure; Lanthanides

1. General trends on the thermal behaviour of terbium tetrafluoride and the synthesis of mixed-valence terbium fluorides

The first synthesis of terbium tetrafluoride reported in the literature [1] dates back about half a century, and the first fluorinated combination, namely Cs_3TbF_7 [2], more than 35 years. It was necessary to wait until 1994 for success in growing single crystals of a fluorinated tetravalent terbium compound [3]. Meanwhile a number of phases containing tetravalent terbium were synthesized [4–6].

The difficulty in growing single crystals of tetravalent terbium fluorides arises from the thermal instability of TbF_4 itself [7–9]. Indeed, it is well known that TbF_4 undergoes a thermal decomposition in the temperature range 540–680°C [7] with elimination of fluorine, even under a fluorine atmosphere at pressure close to the ambient pressure. It has also been ascertained that the resulting TbF_3 formed during the thermal decomposition of TbF_4 is capable of reacting with the remaining part of the TbF_4 to yield intermediate combinations [7], provided they are more stable from a thermodynamic point of view. Thus, the $TbF_{3.75}$ compound, which is better represented by the $Tb^{III}Tb_3^{IV}F_{15}$ formula has been mentioned by Nikulin et al. [7], then obtained by Brechovskich et al. [10], and later by Popov et al. [11], who reported this compound as being isostructural with $BiZr_3F_{15}$ [12]. We confirmed this result by our own experimental results, except for the cationic repartition (see discussion of 6-coordination below), but we observed a strong departure from the cell parameters reported by Popov et al. [11]. This probably results from the experimental conditions, essentially the reaction temperature, but might also mean that a narrow homogeneity domain around the 1–3 theoretical composition could exist. Let us also mention that heating an initially pure TbF_4 sample or a Tb_4F_{15} composition under pure fluorine gas flow at a temperature up to 750°C still results in pure TbF_4. This means that terbium tetrafluoride is again re-formed at high temperature, above its instability temperature range around 700°C, and is stable on cooling under routine conditions. More precisely, on heating under fluorine gas flow, TbF_4 undergoes a thermal decomposition between 650 and 750°C, yielding Tb_4F_{15} as mentioned above. When obtained in such a way, Tb_4F_{15} is always stable on cooling under fluorine gas flow. In turn, Tb_4F_{15} decomposes on heating above 750°C, leading to orthorhombic terbium trifluoride. This result has already been reported by Brechovskich et al., who carried out an investigation on the thermal stability of $LnTb_3F_{15}$ phases [10]. Thus, if the sample is maintained under fluorine gas flow and the temperature raised up to 750°C, the trivalent terbium present under the form of terbium trifluoride is oxidized into tetravalent terbium under the form of monoclinic terbium tetrafluoride of β-ZrF_4 type

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[13]. On cooling that sample in a routine way, from 750°C, Tb_4F_{15} does not form: it has not been identified by X-ray diffraction even though it is itself stable under those cooling conditions.

1.1. Synthesis and crystal structure of KTb_3F_{12}

The thermal instability of the terbium tetrafluoride mentioned above turned out to account for synthesizing an unprecedented mixed-valence terbium fluoride with the formula $KTb^{III}Tb_2^{IV}F_{12}$.

This compound has been obtained by heating a $1KCl+3TbF_3$ stoichiometric mixture under pure fluorine gas flow at 750°C for 12 h. It crystallizes in the tetragonal system with unit cell parameters: $a=7.716(1)$ Å and $c=7.528(1)$ Å and space group I4/m, $Z=2$. Its crystal structure (Fig. 1a,b), determined from single-crystal X-ray diffraction, may be regarded as being built of chains of edge-shared $(Tb^{IV}F_8)^{4-}$ dodecahedra lying in staggered rows and further joined together by isolated $(Tb^{III}F_8)^{5-}$ slightly distorted cubes by sharing corners. The $(Tb^{III}F_8)^{5-}$ cubes alternate along the *c* direction with cavities encompassing the potassium ions. These K^+ ions are coordinated by 12 F^- ions.

Let us mention that attempts to synthesize homologous compounds $KLn^{III}Zr_2^{IV}F_{12}$ of tetravalent zirconium were successful and led to a family of $KLn^{III}Zr_2^{IV}F_{12}$ phases that decompose in the solid state at relatively low temperature.

1.2. Limits of this synthesis procedure

By heating the stoichiometric mixture $1KCl+2TbF_3$ with the same starting components under pure fluorine gas flow at various temperatures, ranging from 500 to 750°C, the KTb_2F_9 fluoride already mentioned [4] has been obtained. This result is understandable if one remembers that KTb_2F_9 is the last stable intermediate compound that occurs on the rich TbF_4 side of the KF-TbF_4 system [4], whereas for the 1KF–$3TbF_4$ composition a diphasic domain involving KTb_2F_9 and TbF_4 is observed when the fluorination reaction is carried out at 500°C.

Therefore, by heating such a 1–3 composition at temperatures ranging between 500 and 750°C, the unreacted TbF_4 (in excess) undergoes a thermal decomposition yielding the TbF_3 necessary to form the stable KTb_3F_{12} compound. Thus it can be inferred from both $Tb^{III}Tb_3^{IV}F_{15}$ and $KTb^{III}Tb_2^{IV}F_{12}$ examples that mixed-valence terbium fluorides may be obtained by heating, under pure fluorine gas flow at ambient pressure and at temperature higher than 500°C, mixtures containing only terbium tetrafluoride. This synthesis procedure is based upon the formation in situ of terbium trifluoride, resulting from the thermal decomposition of terbium tetrafluoride and on the relative stabilities of the mixed-valence phases belonging to the system under investigation. This could be achieved in two distinct steps. The first one consists of using the high oxidizing power of the fluorine to reach the IV oxidation state, and allows to use oxide, trifluoride, chloride, nitrate and many other salts as the starting terbium source. The second step being to induce the thermal decomposition of a part of that terbium tetrafluoride by raising the temperature to at least 550°C. This may open a new route for the synthesis of new mixed-valence terbium fluorides with interesting optical and magnetic properties.

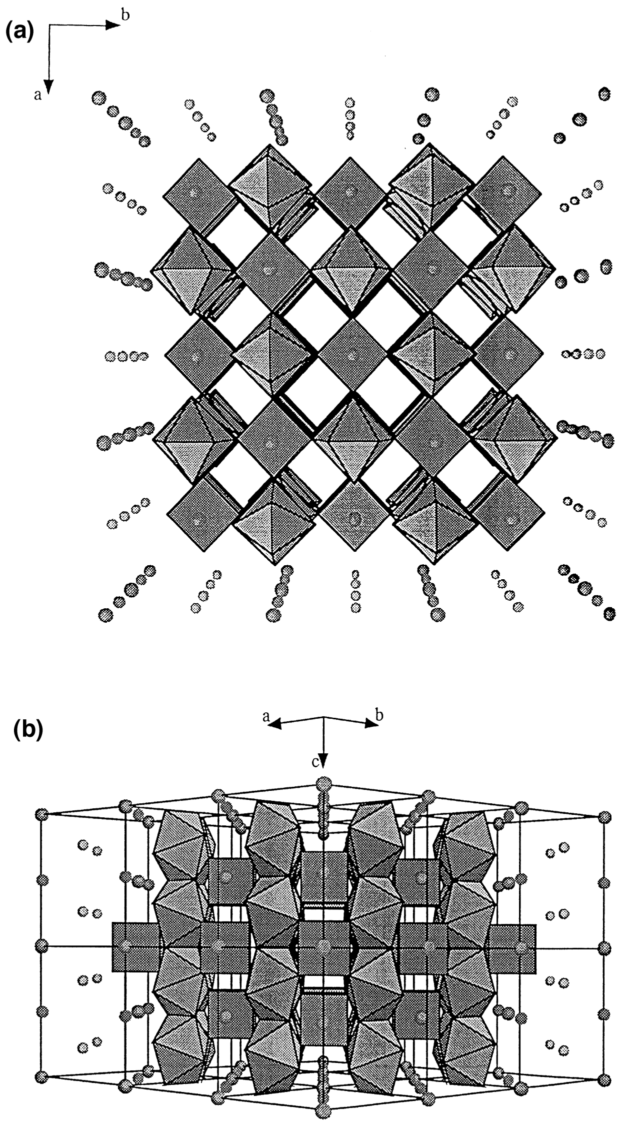

Fig. 1. (a) Projection of the structure of KTb_3F_{12} along [001]. The circles represent K atoms. (b) Perspective view of the polyhedral representation of the structure of KTb_3F_{12}.

2. Obtaining single-crystals of tetravalent terbium fluorides

To overcome the difficulty arising from the low thermal stability of TbF_4, which tends to decompose with elimination of fluorine at temperatures higher than 500°C, the 4+ oxidation state of the terbium was first stabilized by reacting the stoichiometric mixture of the starting fluorides at low temperature (typically around 400°C) under pure fluorine gas flow. Then single crystals of the same compositions could have been obtained through a heating step at higher temperature (about 700–750°C), as the terbium tetrafluoride is involved in a chemical combination which prevents its thermal decomposition. A heating period of a few hours was necessary to obtain single crystals suitable for structure determination. When raising the reaction temperature from 550 to 750°C, the samples must be put in a nickel boat because the use of an alumina container would yield aluminum trifluoride. By doing so, single-crystals of Li_2TbF_6, $KTbF_5$, $CsTbF_5$, Li_2CaTbF_8 were obtained. Their crystallographic characteristics are gathered in Table 1.

Another case of great interest is that of the $BaTbF_6$ compound, which is the first tetravalent terbium fluoride for which a polymorphism has been evidenced. This compound was first mentioned by Feldner and Hoppe [5]. At present it is well established that the variety of $BaTbF_6$ reported by these authors, the X-ray powder pattern of which is given in reference [5], is a low-temperature form called α-$BaTbF_6$. In fact its crystal structure has been determined from single-crystal diffraction data [14], whereas a high-temperature form β-$BaTbF_6$ has been evidenced, the structure of which has also been refined from single-crystal X-ray diffraction data [15]. This high temperature polymorph is isotypic with β-$BaZrF_6$ [16].

2.1. Some aspects of the crystal chemical properties of the Tb^{4+} ion

In a previous paper we reported the singular crystal chemical behaviour of Li_2TbF_6 within the series of the

Table 1
Crystallographic characteristics of single-crystals of tetravalent terbium fluorides

	Symmetry, space groups and unit cell parameters	Mean ⟨Tb–F⟩ distance (Å)	Coordination		Tb–F distances (Å)			Ref.
			Number	Polyhedra				
Li_2TbF_6	Monoclinic, C2/c a=11.471(1) Å b=4.960(1) Å c=7.572(1) Å β=112.20(1)°	2.170	8	D	2.066(5)–2.173(3) 2.075(4)–2.173(3) 2.109(4)–2.327(3) 2.109(4)–2.327(3)			[3]
$KTbF_5$	Triclinic, $P\bar{1}$ a=7.446(1) Å b=8.567(1) Å c=10.834(3) Å α=76.02(2)° β=72.51(2)° γ=67.03(2)°	⟨Tb(1)–F⟩ 2.164 ⟨Tb(2)–F⟩ 2.170 ⟨Tb(3)–F⟩ 2.168	8 8 8	A A B T P D	Tb(1)–F 2.018(8) 2.034(7) 2.175(5) 2.184(5) 2.208(6) 2.224(6) 2.226(6) 2.247(5)	Tb(2)-F 2.034(9) 2.036(8) 2.186(5) 2.194(6) 2.201(6) 2.219(5) 2.235(6) 2.259(6)	Tb(3)-F 2.018(8) 2.028(8) 2.122(5) 2.124(6) 2.124(6) 2.248(5) 2.291(6) 2.293(5)	[25]
$CsTbF_5$	Orthorhombic, Cmca a=14.067(1) Å b=8.163(2) Å c=8.161(2)	2.168	8	D	2.059(3)×2–2.224(2)×2 2.135(5) 2.254(5) 2.137(4) 2.255(4)			[24]
Li_2CaTbF_8	Tetragonal, $1\bar{4}$ a=5.143(1) Å c=10.671(2) Å	2.170	8	D	2.143(3)×4 2.196(2)×4			E. Largeau, pers. commun.
KTb_3F_{12}	Tetragonal, I4/m a=7.716(1) Å c=7.528(1) Å	2.170	8	D	2.107(2)×4 2.233(2)×4			[26]
α-$BaTbF_6$	Triclinic, $P\bar{1}$ a=7.344(1) Å b=8.448(1) Å c=8.677(1) Å α=101.63(8)° β=96.89(1)° γ=114.62(1)°	⟨Tb(1)–F⟩ 2.18 ⟨Tb(2)–F⟩ 2.18	8 8	D AA	Tb(1)–F 2.10(1) 2.10(1) 2.11(1) 2.15(2) 2.15(1) 2.17(1) 2.19(1) 2.45(1)	Tb(2)-F 2.10(1) 2.10(2) 2.13(1) 2.15(1) 2.16(1) 2.18(1) 2.28(1) 2.34(1)		[14]
β-$BaTbF_6$	Orthorhombic, Cmma a=7.761(1) Å b=11.513(3) Å c=5.523(1) Å	2.176	8	D	2.081(3)×4 2.271(2)×4			[15]

$Li_2M^{IV}F_6$ compounds [17]. Since then a single-crystal study confirmed the 8-coordination of the Tb^{4+} ion in this fluoride [3]. It is also worth noting that in all compounds mentioned in Table 1, the structures of which have been refined from single-crystals, the Tb^{4+} ions are always in 8-coordination with three kinds of polyhedra, namely the square antiprism or Archimedean antiprism (AA), the bicapped trigonal prism (BTP) or the dodecahedron (D), these polyhedra being defined according to the criteria given by Porai-Koshits and Aslanov [18].

Apart from the M_3TbF_7 (M=Rb, Cs) and Cs_2RbTbF_7, Rb_2CsTbF_7 and $CsRbKTbF_7$ [5] no other fluoride with Tb^{4+} ions in predictable 7-coordination, in the absence of structural data, has been reported.

There is no example of Tb^{4+} ion in 6-coordination in fluorides, apart from possibly the Tb_4F_{15} phase which has been reported as being isostructural with $BiZr_3F_{15}$ as mentioned above. Now, in this structural type one-third of the Zr^{4+} ions lie in octahedral 6-coordination (6a Wyckoff position), whereas the remaining Zr^{4+} cations are statistically distributed with the Bi^{3+} on the 18e site of the $R\bar{3}c$ space group [12]. However, a recent study of the MZr_3F_{15} phases (M=Y,In,Ln,Tl) takes into account different cationic distributions [19], namely a rigourous cationic ordering for M=In, with In^{3+} in an octahedral site in spite of an ionic radius greater than that of Zr^{4+}. So the cationic repartition in Tb_4F_{15} and $LnTb_3^{IV}F_{15}$ phases must be checked from single-crystal work or careful Rietveld refinement before concluding the existence of examples of 6-coordination for the Tb^{4+} ion in fluorides. Since their pioneering work on ionic radii determination in which Shannon and Prewitt [20] claimed that there were no available crystallographic data concerning tetravalent terbium, no report dealing with crystal structure of Tb(IV) compounds has appeared, especially in fluorinated medium. The data gathered in Table 1 are the first ones relative to single-crystal work. By using these values, the ionic radius of the Tb^{4+} ion in 8-coordination has been calculated to be equal to 1.01±0.01 Å, in good agreement with the value predicted by Shannon and Prewitt [20]. We also used these data to determine the R_{ij} parametral value used in the expression of the bond valence $V_{ij}=\exp[(R_{ij}-d_{ij})/b]$ [21]. Thus, this bond-valence parameter R_{ij} for the Tb^{IV}–F bond has been found to be equal to 1.905±0.006 Å.

3. On a new series of $LiLn^{III}Tb^{IV}F_8$ phases (Ln=Eu→Lu,Y) and related compounds: structural relationships with $LiNaY_2F_8$ and BaY_2F_8

During the study of the phase relationships in the LiF–GdF_3–TbF_4 system a new fluoride with $LiGdTbF_8$ formula has been characterized. Homologous compounds have been found for the heavier rare earths, from Eu to Lu, and other representatives of this family have been evidenced for both Zr^{4+} and Hf^{4+}. Their structure consists of a three-dimensional network of edge- and corner-sharing MF_8 and $M'F_8$ polyhedra ($M=Ln^{3+}$, Y^{3+}; $M'=Tb^{4+}$, Zr^{4+}, Hf^{4+}) enclosing pseudo-hexagonal intersecting channels where the Li^+ ions are located (Fig. 2a). These phases present strong structural analogies with the $LiNaY_2F_8$ compound [22] and related $LiNaLn_2F_8$, in the sense that this last one is also built of edge- and corner-sharing $(YF_8)^{5-}$ polyhedra delimiting hexagonal intersecting tunnels, where both Li^+ and Na^+ cations lie (Fig. 2b). So it becomes obvious that a tetravalent cation can be substituted for half of the trivalent cations in the $LiNaY_2F_8$ skeleton, whereas the electroneutrality of the cationic

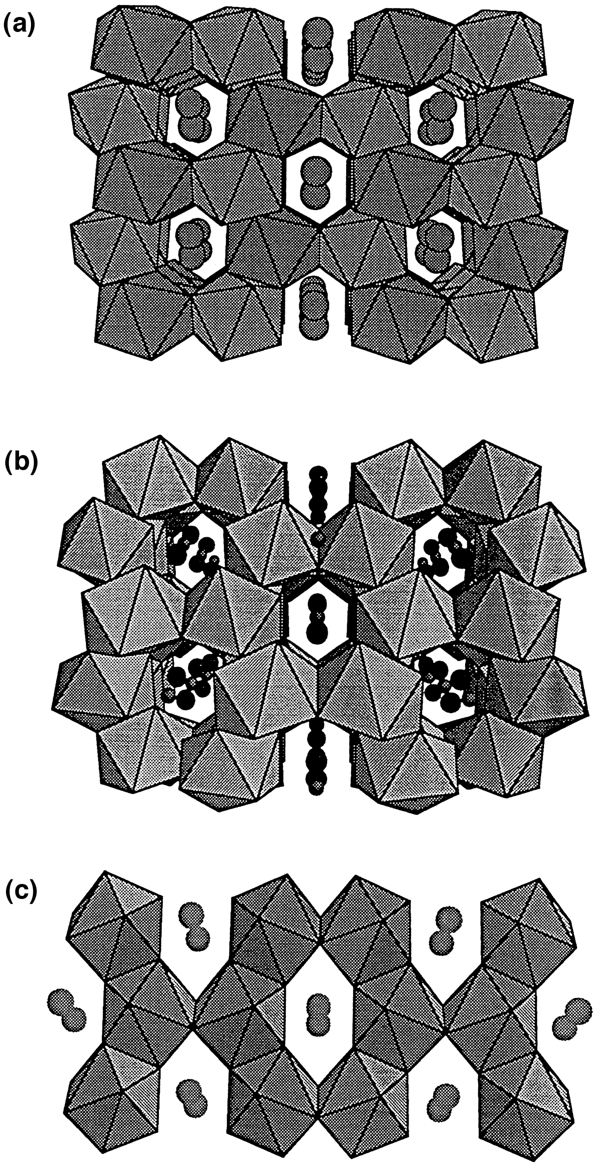

Fig. 2. (a) Projection of the structure of $LiGdTbF_8$ down [110] showing pseudo-hexagonal channels. (b) Projection of the structure of $LiNaY_2F_8$ down [111] showing pseudo-hexagonal channels. (c) Projection of the structure of BaY_2F_8 along [010] showing pseudo-hexagonal channels.

network may be preserved by removing a part of the alkaline cations, in this case the sodium ones. This polyhedral string is found once again in BaY_2F_8 fluoride [23] and related compounds (Fig. 2c).

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