

Gadolinium ytterbium trifluoride,  
 $\text{Gd}_{0.81}\text{Yb}_{0.19}\text{F}_3$ Valentyn Vasyliiev,<sup>a\*</sup> Encarnacion G. Villora,<sup>a</sup> Masaru Nakamura,<sup>a</sup> Akira Sato<sup>b</sup> and Kiyoshi Shimamura<sup>a</sup><sup>a</sup>Frequency Conversion Group, Optronics Center, National Institute for Materials Science, 1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan, and <sup>b</sup>Materials Analysis Station, Department of Materials Infrastructure, National Institute for Materials Science, 1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan  
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A new gadolinium ytterbium trifluoride has been grown for the first time by the Czochralski technique. Although  $\text{GdF}_3$  and  $\text{YbF}_3$  both present a high-temperature phase transition, the mixed compound  $\text{Gd}_{0.81}\text{Yb}_{0.19}\text{F}_3$  maintains its crystallographic structure upon cooling to room temperature. Taking into account that both  $\text{Gd}^{3+}$  and  $\text{Yb}^{3+}$  ions are distributed randomly on a single site (Wyckoff position 4c), this is attributed to a mean cationic radius coincident with that of the  $\text{Tb}^{3+}$  ion, so that the stability of the crystal structure resembles that of  $\text{TbF}_3$ . The grown crystal melts noncongruently at  $\sim 1413$  K, it is transparent and colourless, and it has a high density.

## Comment

Rare earth trifluorides ( $\text{REF}_3$ ) have long been studied as hosts for scintillation applications (Kobayashi *et al.*, 2003). These crystals present a series of important characteristics, such as easy doping by isovalent  $\text{Ce}^{3+}$  substitution, high density and high visible transparency. Among the near-UV-visible transparent  $\text{REF}_3$  (RE = La, Ce, Gd, Yb and Lu), only the well known  $\text{LaF}_3$  and  $\text{CeF}_3$  do not present a phase transition upon cooling.

Initial studies of the synthesis of  $\text{REF}_3$  identified a structural dimorphism along this series of compounds, which can crystallize in the tysonite hexagonal form and/or in the orthorhombic  $\beta\text{-YF}_3$  form (Zalkin & Templeton, 1953; Thoma & Brunton, 1966). Later authors have concluded that  $\text{REF}_3$  possess three different crystal structures. Depending on the occurrence or absence of a phase transition,  $\text{REF}_3$  are classified into four morphotropic series as a function of decreasing lanthanide ionic radius (Fedorov & Sobolev, 1995; Spedding *et al.*, 1974; Sobolev *et al.*, 1976; Greis & Cader, 1985; Petzel & Rathjen, 1994):

(1)  $\text{LaF}_3$  to  $\text{NdF}_3$  (trigonal  $\text{LaF}_3$ -type,  $P\bar{3}c1$ ),

(2)  $\text{SmF}_3$  to  $\text{GdF}_3$  (hexagonal Schlyter type,  $P6_3/mmc$ ; trigonal  $\text{LaF}_3$ -type,  $P\bar{3}c1$ ; and orthorhombic  $\beta\text{-YF}_3$ -type,  $Pnma$ ),

(3)  $\text{TbF}_3$  to  $\text{HoF}_3$  (orthorhombic  $\beta\text{-YF}_3$ -type,  $Pnma$ ) and

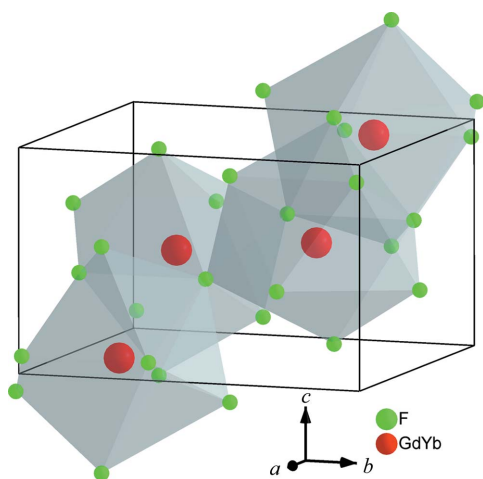
(4)  $\text{ErF}_3$  to  $\text{LuF}_3$  (trigonal  $\alpha\text{-UO}_3$ -type,  $P\bar{3}m1$ ; and orthorhombic  $\beta\text{-YF}_3$ -type,  $Pnma$ ).

[There is a controversy about the existence of the high-temperature hexagonal Schlyter-type phase (2). On the one hand, its appearance is claimed (Greis & Cader, 1985; Schlyter, 1953), while on the other it has been argued that it corresponds to twinned crystals in the space group  $P\bar{3}c1$  with balanced volume ratios (Maximov & Schulz, 1985).]

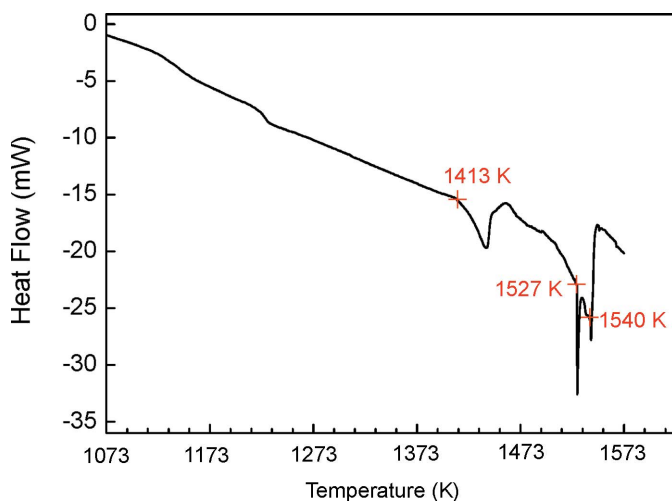
The transitions between these series are a consequence of their relative structural instabilities. According to previous studies regarding the stabilization of each structural type [see Sobolev *et al.* (1977), and references therein], the mean cationic radius is the geometric factor that plays a decisive role. In that particular paper, Sobolev deals with the stability of the orthorhombic  $\beta\text{-YF}_3$ -type in the phase diagrams of the  $\text{GdF}_3\text{-LnF}_3$  systems (with Ln = Tb, Ho, Er or Yb). Taking into account the ionic radii (Shannon, 1976), one can calculate the stability range of this phase, which extends from peritectic to eutectic composition. In all four diagrams, this range relates to a mean cationic radius which lies between the ionic radii of Tb and Ho, *i.e.* it matches the range (3) above where no phase transition is observed.

In the present work, we intended to synthesize a binary  $\text{REF}_3$  which was transparent and did not present any phase transitions. For this purpose, we chose  $\text{Gd}^{3+}$  and  $\text{Yb}^{3+}$  as cations and considered the  $\text{GdF}_3\text{-YbF}_3$  phase diagram (Sobolev *et al.*, 1977). Due to the noncongruent nature of mixed  $\text{Gd}_{1-x}\text{Yb}_x\text{F}_3$  compounds, the initial composition of the melt was chosen to be  $x = 0.30$ , so that, according to the phase diagram, a crystal with the approximate composition  $\text{Gd}_{0.91}\text{Yb}_{0.09}\text{F}_3$  should crystallize at a temperature of about 1443 K with an orthorhombic structure.

A transparent crack-free single crystal was grown by the Czochralski method. Chemical analysis carried out by the inductively coupled plasma technique indicated that the crystal composition was  $\text{Gd}_{0.81}\text{Yb}_{0.19}\text{F}_3$ . According to the phase diagram, this concentration of Yb should correspond to a starting melt value of  $x = 0.43$ , instead of the nominally used  $x = 0.3$ . X-ray diffraction measurements confirmed that the grown crystal has the expected  $\beta\text{-YF}_3$  structure, characterized by two anionic sites and a single cationic site. Consequently, both  $\text{Gd}^{3+}$  and  $\text{Yb}^{3+}$  occupy the same site randomly (Wyckoff position 4c), as shown in Fig. 1. Furthermore, as the two cations are very similar to each other, it is not possible to distinguish them by X-ray diffraction measurements. The lattice parameters obtained correspond precisely with those known for  $\text{TbF}_3$ . Considering Vegard's law (Vegard, 1921) and the ionic radii for coordination number 9 for the cationic site, we found that the average radius coincides with that of  $\text{Tb}_9^{3+}$ , namely 1.235 Å. Therefore, in agreement with previous observations about average ionic radius for the stabilization of the orthorhombic structure, our experiment reinforces the hypothesis that the  $\text{Tb}^{3+}$  ionic radius represents the maximum average limit.



**Figure 1**  
A view of the unit cell of  $\text{Gd}_{0.81}\text{Yb}_{0.19}\text{F}_3$  in a polyhedral representation.



**Figure 2**  
Differential scanning calorimetry curve of  $\text{Gd}_{0.81}\text{Yb}_{0.19}\text{F}_3$  under a  $\text{CF}_4$  atmosphere.

The thermal behaviour of the as-grown crystal was investigated by differential scanning calorimetry and is shown in Fig. 2. Similar to the  $\text{GdF}_3$ – $\text{YbF}_3$  phase diagram, three transitions at high temperature can be clearly distinguished. The first one, at 1413 K, corresponds to the nucleation temperature, the second, at 1527 K, with the peritectic temperature and the highest, at 1540 K, with the completely liquid phase. These values are shifted from those indicated in the phase diagram for the measured crystal composition ( $x = 0.19$ ), namely 1398, 1453 and 1466 K for the nucleation temperature, eutectic phase and total melting, respectively.

In summary, we have presented the first report of the growth of a single crystal of  $\text{Gd}_{0.81}\text{Yb}_{0.19}\text{F}_3$  by the Czochralski technique. Due to its noncongruent nature, the growth of large crystals will require nonstandard techniques to counteract the continuous shift of the melt composition during growth. On the other hand, this growth behaviour could be an advantage

for the synthesis of core–shell nanoparticles based on  $\text{REF}_3$  luminescent ions, which have specific applications in the fields of biology and optoelectronics (see *e.g.* Wang *et al.*, 2006). Crystalline  $\text{Gd}_{0.81}\text{Yb}_{0.19}\text{F}_3$  is transparent and colourless, it crystallizes in the orthorhombic  $\beta$ - $\text{YF}_3$  structure and it does not present any phase transition upon cooling. Furthermore, the density is as high as  $7.25 \text{ Mg m}^{-3}$ . Therefore,  $\text{Gd}_{0.81}\text{Yb}_{0.19}\text{F}_3$  represents a new  $\text{REF}_3$  with attractive properties for scintillation and core–shell nanoparticle applications.

## Experimental

A single crystal of the title compound was grown by the Czochralski (Cz) technique under a high-purity  $\text{CF}_4$  (99.999%) atmosphere. Commercial  $\text{GdF}_3$  (99.99%) and  $\text{YbF}_3$  (99.99%) powders were mixed with a nominal composition of  $\text{Gd}_{0.7}\text{Yb}_{0.3}\text{F}_3$ , and loaded into a Pt crucible. This was surrounded by refractory carbons and heated inductively using a 30 kW generator. Using a Pt wire as a seed, a single crystal was pulled up at a speed of  $2 \text{ mm h}^{-1}$  and a rotation of  $10 \text{ r min}^{-1}$ .

The chemical composition of the grown crystal was determined by inductively coupled plasma (ICP) atomic emission spectroscopy using an IRIS Advantage from Nippon Jarrell–AshCo. Thermal analysis of the crystal was performed by differential scanning calorimetry (DSC) using a DSC Rigaku Thermoplus 8270. The heating rate was set at  $10 \text{ K min}^{-1}$  and the measurements were carried out under a  $200 \text{ ml min}^{-1}$  flow of  $\text{CF}_4$  in order to prevent sample oxidation.

### Crystal data

$\text{Gd}_{0.81}\text{Yb}_{0.19}\text{F}_3$	$V = 198.82 (6) \text{ \AA}^3$
$M_r = 217.24$	$Z = 4$
Orthorhombic, $Pnma$	Mo $K\alpha$ radiation
$a = 6.518 (1) \text{ \AA}$	$\mu = 35.83 \text{ mm}^{-1}$
$b = 6.950 (1) \text{ \AA}$	$T = 293 \text{ K}$
$c = 4.389 (1) \text{ \AA}$	$0.16 \times 0.16 \times 0.1 \text{ mm}$

### Data collection

Bruker SMART APEX CCD area-detector diffractometer	4098 measured reflections
Absorption correction: empirical (using intensity measurements) ( <i>SADABS</i> ; Sheldrick, 1996)	656 independent reflections
$T_{\min} = 0.023$ , $T_{\max} = 0.086$	646 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.035$

### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.020$	23 parameters
$wR(F^2) = 0.052$	$\Delta\rho_{\max} = 2.34 \text{ e \AA}^{-3}$
$S = 1.23$	$\Delta\rho_{\min} = -1.69 \text{ e \AA}^{-3}$
656 reflections	

**Table 1**

Selected bond lengths ( $\text{\AA}$ ).

F1–Gd	2.325 (2)	Gd–F2 <sup>iv</sup>	2.325 (3)
F1–Gd <sup>i</sup>	2.329 (2)	Gd–F1 <sup>v</sup>	2.325 (2)
F1–Gd <sup>ii</sup>	2.341 (2)	Gd–F1 <sup>vi</sup>	2.329 (2)
F2–Gd <sup>iii</sup>	2.325 (3)	Gd–F1 <sup>vii</sup>	2.341 (2)
F2–Gd	2.349 (3)	Gd–F2 <sup>viii</sup>	2.498 (3)
F2–Gd <sup>ii</sup>	2.498 (3)		

Symmetry codes: (i)  $-x + \frac{1}{2}, -y, z - \frac{1}{2}$ ; (ii)  $x - \frac{1}{2}, y, -z + \frac{1}{2}$ ; (iii)  $x - \frac{1}{2}, y, -z + \frac{3}{2}$ ; (iv)  $x + \frac{1}{2}, y, -z + \frac{3}{2}$ ; (v)  $x, -y + \frac{1}{2}, z$ ; (vi)  $-x + \frac{1}{2}, -y, z + \frac{1}{2}$ ; (vii)  $x + \frac{1}{2}, -y + \frac{1}{2}, -z + \frac{1}{2}$ ; (viii)  $x + \frac{1}{2}, y, -z + \frac{1}{2}$ .

Data collection: *SMART* (Bruker, 2002); cell refinement: *SAINT-Plus* (Bruker, 2003); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg, 2000); software used to prepare material for publication: *SHELXL97*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: KU3037). Services for accessing these data are described at the back of the journal.

## References

- Brandenburg, K. (2000). *DIAMOND*. Crystal Impact GbR, Bonn, Germany.
- Bruker (2002). *SMART for Windows NT/2000*. Version 5.630. Bruker AXS Inc., Madison, Wisconsin, USA.
- Bruker (2003). *SAINT-Plus*. Version 6.45. Bruker AXS Inc., Madison, Wisconsin, USA.
- Fedorov, P. P. & Sobolev, B. P. (1995). *Crystallogr. Rep.* **40**, 284–290.
- Greis, O. & Cader, M. S. R. (1985). *Thermochim. Acta*, **87**, 145–150.
- Kobayashi, M., Nakamura, R., Ishii, M., Solovieva, N. & Nikl, M. (2003). *Jpn J. Appl. Phys.* **42**, 1648–1654.
- Maximov, B. & Schulz, H. (1985). *Acta Cryst.* **B41**, 88–91.
- Petzel, T. & Rathjen, H. (1994). Private communication. University of the Federal Armed Forces, Germany
- Schlyter, K. (1953). *Ark. Kemi*, **5**, 73–82.
- Shannon, R. D. (1976). *Acta Cryst.* **A32**, 751–767.
- Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Sobolev, B. P., Fedorov, P. P., Seiranian, K. B. & Tkachenko, N. L. (1976). *J. Solid State Chem.* **17**, 201–212.
- Sobolev, D. F., Sidorov, V. S., Fedorov, P. P. & Ikrami, D. D. (1977). *Sov. Phys. Crystallogr.* **22**, 574–577.
- Spedding, F. H., Beaudry, B. J., Henderson, D. C. & Moorman, I. (1974). *J. Chem. Phys.* **60**, 1578–1588.
- Thoma, R. E. & Brunton, G. D. (1966). *Inorg. Chem.* **5**, 1937–1939.
- Vegard, L. (1921). *Z. Phys.* **5**, 17–26.
- Wang, Z. L., Quan, Z. W., Jia, P. Y., Lin, C. K., Luo, Y., Chen, Y., Fang, J., Zhou, W., O'Connor, C. J. & Lin, J. (2006). *Chem. Mater.* **18**, 2030–2037.
- Zalkin, A. & Templeton, D. H. (1953). *J. Am. Chem. Soc.* **75**, 2453–2458.