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Synthesis, crystal structure, and preliminary study of luminescent properties of $\text{InTbGe}_2\text{O}_7$

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Abstract

A new indium terbium germanate $\text{InTbGe}_2\text{O}_7$, which is a member of the thortveitite family, was prepared as a polycrystalline powder material by high-temperature solid-state reaction. This new compound crystallizes in the monoclinic system, space group $C2/c$ (No. 15), with unit cell parameters $a = 6.8818(2) \text{ \AA}$, $b = 8.8774(3) \text{ \AA}$, $c = 9.7892(4) \text{ \AA}$, $\beta = 101.401(1)^\circ$, $V = 586.25(4) \text{ \AA}^3$ and $Z = 4$. Its structure was characterized by Rietveld refinement of powder laboratory X-ray diffraction data. It consists of octahedral sheets that are held together by sheets of isolated Ge_2O_7 diorthogroups composed of two tetrahedra sharing a common vertex. It contains only one octahedral site occupied by In^{3+} and Tb^{3+} cations. The characteristic mirror plane in the thortveitite ($\text{Sc}_2\text{Si}_2\text{O}_7$) space group ($C2/m$, No. 12) is not present in this new compound. Besides, in $\text{InTbGe}_2\text{O}_7$, the Ge–O–Ge angle bridging two diorthogroups is $156.8(2)^\circ$ as compared to the one in thortveitite, which is 180° . On the other hand, luminescent properties were observed when it is excited with 376.5 nm wavelength. The luminescence spectrum shows typical transitions from the $^5\text{D}_4$ multiplet belonging to the trivalent terbium ion.

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Keywords: Indium terbium germanate; Crystal structure; Rietveld refinement; Terbium luminescence

1. Introduction

The association of a transition metal oxide with covalent elements such as silicon or germanium in oxides generates different opened structures. Recently, compounds with the thortveitite-type structure ($\text{Sc}_2\text{Si}_2\text{O}_7$ [1]) have received a lot of attention due to their laminate shape. This shape is the result of a combination of alternate layers of octahedral and tetrahedral sites. Research has been directed toward the inclusion of different cations into the octahedral and tetrahedral sites in order to find specific interesting optical, electrical or magnetic properties.

Recently, the crystal structure of the iron indium germanate $\text{FeInGe}_2\text{O}_7$ [2] has been reported to belong to the monoclinic germanates with stoichiometric formula $M\text{RGe}_2\text{O}_7$ (where $M = \text{Al}^{3+}$, Ga^{3+} or Fe^{3+} and

$R = \text{rare earth ion}$). These kinds of compounds are of large interest in laser crystal physics; for instance, the incorporation of R^{3+} activators into single-centered hosts up to full substitution of all cations gives the possibility of obtaining the so-called self-activated crystals. The spectroscopic study of a series of such compounds supplies much valuable information for the crystal field theory of R^{3+} ions and for understanding numerous applied optical effects. For the indium pyrogermanate $\text{In}_2\text{Ge}_2\text{O}_7$ and pyrosilicate $\text{In}_2\text{Si}_2\text{O}_7$, luminescent properties below 160 and 200 K, respectively, have been reported. It was shown that the luminescence is due to the presence of In^{3+} having the $4d^{10}$ electronic configuration [3]. Detailed studies on the absorption, luminescence and stimulated emission, have also been carried out in the $\text{AlNdGe}_2\text{O}_7$ compound [4], which crystallizes in the monoclinic crystal system with space group $P2_1/c$ (No. 14) and $Z = 4$. In order to study and understand the physical properties of Tb^{3+} in this monoclinic laminar compound, in the present work,

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we present the crystal structure refinement of the new compound $\text{InTbGe}_2\text{O}_7$ and a preliminary study on its luminescent properties.

2. Experimental

2.1. Sample preparation

The compound $\text{InTbGe}_2\text{O}_7$ was prepared as polycrystalline powder material by solid-state reaction from a stoichiometric mixture of analytical grade Tb_4O_7 , GeO_2 and In_2O_3 in the molar ratios $\text{Tb}:\text{In}:\text{Ge} = 1:1:4$. The sample was ground and heated in air at 1150°C for 5 days with intermediate grindings. The standard powder X-ray diffraction analysis indicated that the final sample was well crystallized and appeared completely free of secondary crystalline phases.

2.2. Chemical analysis

The elemental composition was determined by Rutherford backscattering spectrometry (RBS) [5]. The sample was previously well powdered, pressed in a small pellet, and then irradiated in a Pelletron NEC accelerator in vacuum using a 3.05 MeV α -particle beam (1 mm diameter, current intensity 5–10 nA). With this energy, it is possible to improve the oxygen quantity measurements because there is a resonance $^{16}\text{O}(\alpha, \alpha)^{16}\text{O}$ in the RBS spectrum at 3.05 MeV [6]. A Canberra passivated implanted planar silicon (PIPS) detector was placed at 168° from the beam direction to collect backscattered particles. Rump code [7,8] was used to simulate RBS spectrum in order to determine the elemental composition.

2.3. X-ray diffraction analysis

The powder X-ray diffraction pattern (XRD) was recorded at room temperature in a Siemens D5000 diffractometer with a vertical goniometer, fixed diffracted beam graphite monochromator and scintillation counter. A $\text{CuK}\alpha$ anode operating at 35 kV and 25 mA was used. The 2θ -range was $14\text{--}90^\circ$ with 0.02° step size and 10 s counting time. Silicon ($a = 5.43088(4) \text{ \AA}$) was used as internal standard. The powder diffraction pattern was indexed using the TREOR program [9]. The higher figure-of-merit solution $M_{20} = 46.0$ and $F_{20} = 55.0$ [10] showed a monoclinic cell with $a \approx 6.8770 \text{ \AA}$, $b \approx 8.8712 \text{ \AA}$, $c \approx 4.8910 \text{ \AA}$, $\beta \approx 101.403^\circ$ and $V \approx 292.50 \text{ \AA}^3$. This unit cell and the ratios between their lattice parameters were compatible with the unit cell exhibited by the thortveitite structure [1,11] and others like InYGe_2O_7 [12]. A detailed search in the inorganic crystal structure database (ICSD) [13] showed that $\text{Sc}_2\text{Si}_2\text{O}_7$ (thortveitite) with space group $C2/m$ and

$\text{CaZrSi}_2\text{O}_7$ (gittinsite [14]) with space group $C2$ were among the possible isostructural compounds. The structure of $\text{InTbGe}_2\text{O}_7$ was refined by Rietveld analysis, with program FULLPROF [15], using these structures as starting models. Two profile functions were attempted, pseudo-Voigt (pV) and Thompson–Cox–Hastings pseudo-Voigt (TCH). The following parameters were refined: zero point, scale factor, unit cell dimensions, half-width, pV or TCH and asymmetry parameters for the peak shape; positional, thermal isotropic (of all atoms) and occupancy factors (of In^{3+} and Tb^{3+}). The strategy for refinement was as follows: first a Le Bail refinement was performed, using linear interpolation between 23 fixed points for the background, in order to refine cell and profile parameters. After convergence, the structural model was incorporated and refinement continued in the following sequence: atomic positions of $\text{In}^{3+}/\text{Tb}^{3+}$, Ge^{4+} and O^{2-} , position in intensity of the 32 background points and isotropic temperature factors of $\text{In}^{3+}/\text{Tb}^{3+}$, Ge^{4+} and O^{2-} . The isotropic temperature factors of all O^{2-} were constrained to be all at the same value, otherwise some went to a negative value. After convergence, refinement of In^{3+} and Tb^{3+} occupancy factors were allowed to be refined.

2.4. Luminescence characterization

Luminescence measurements were carried out at room temperature (300 K); a Perkin-Elmer model 650–10S fluorescence spectrophotometer was used. The spectrum was corrected using a Perkin-Elmer DCSU, the resolution being $\approx 2 \text{ nm}$. At low temperature (20 K), for emission spectrum, the resolution was 1 nm.

Light emission from the sample was dispersed by an MS257 Oriel monochromator and the detection was made using appropriate photon counting and amplification techniques.

3. Results and discussion

3.1. Structural characterization

Refinements in space group $C2/m$ (using thortveitite as the iso-structural model) led invariably to higher R values than those obtained with space group $C2$; besides, with $C2/m$, some isotropic temperature factors were negative. For space group $C2$ (gittinsite as iso-structural model), R values were lower; however, the isotropic temperature factor of one of the two $\text{In}\backslash\text{Tb}$ sites was abnormally low. In order to overcome this problem, we attempted using a cell with a doubled c value. This model corresponds to the structure of $\text{Cu}_2\text{P}_2\text{O}_7$ [16,17] with space group $C2/c$. Besides the doubled c value and the presence of a glide plane, the

main difference with the other models is that there is only one site for In/Tb and that this site is a general position (8f) instead of a special position (2b in $C2$ or 4g in $C2/m$) as in the other two models. R values obtained with this model were lower than in the other cases and all isotropic temperature factors were reasonable (Table 1). Experimental calculated and difference X-ray diffraction powder pattern for $\text{InTbGe}_2\text{O}_7$ refined in $C2/c$, according to the strategy detailed in the experimental section, are shown in Fig. 1. The final refined positional and thermal parameters are given in Table 2, and Table 3 gives the main interatomic distances and angles. At the end of the refinement, occupancy factors of In^{3+} and Tb^{3+} were refined. Within the standard deviations,

they remained to be 0.50(1) each, confirming the chemical composition.

The $\text{InTbGe}_2\text{O}_7$ structure type contains only one octahedral site occupied by In^{3+} and Tb^{3+} cations denoted here as $(\text{In}\backslash\text{Tb})\text{O}_6$. In Fig. 2, the octahedral sites for $(\text{In}\backslash\text{Tb})\text{O}_6$ are represented by gray octahedra. It can be seen that the arrangement for $(\text{In}\backslash\text{Tb})\text{O}_6$ octahedra is such that, for each cation, there is a chain of alternate octahedra sharing edges along the a -axis. $(\text{In}\backslash\text{Tb})\text{O}_6$ octahedra share edges forming a honeycomb-like arrangement on the ab planes (Fig. 2). In this figure, we can visualize the glide plane characteristic of the space group $C2/c$ (No. 15). This glide plane replaces the characteristic mirror plane in the thortveitite ($\text{Sc}_2\text{Si}_2\text{O}_7$) space group ($C2/m$, No. 12).

The GeO_4 polyhedron has the usual tetrahedral coordination observed for Ge. These tetrahedra are grouped in pairs sharing a common vertex (O1) forming isolated Ge_2O_7 diorthogroups (Fig. 3). The $(\text{In}\backslash\text{Tb})\text{O}_6$ octahedral layers are held together by these isolated Ge_2O_7 diorthogroups (Fig. 3).

In comparison with the case of thortveitite structure ($\text{Sc}_2\text{Si}_2\text{O}_7$) in which the common vertex (O1) of the Si_2O_7 diorthogroups lies on a mirror plane m (space group $C2/m$) along the a -axis, the symmetry of this new thortveitite-like structure ($\text{InTbGe}_2\text{O}_7$, space group $C2/c$) allows the O1 oxygen to present a degree of freedom along the b -axis. This degree of freedom allows the angle Ge–O1–Ge to change from 180° (which is its value in thortveitite) to $156.8(2)$ in $\text{InTbGe}_2\text{O}_7$.

A reason for the change in space group ($C2/m$ in thortveitite to $C2/c$) is the increase of the distortion of the polyhedra, which allows a larger degree of freedom. This deformation generates the glide plane instead of the mirror plane and it provokes the doubling of the unit cell along the c -axis.

From Table 3, it can be seen that $\text{In}\backslash\text{Tb}\text{--O}$ interatomic distances have values from 2.12 to 2.41 Å (2.24 Å mean value). If the values of 0.8, 0.923 and 1.35 Å are used for the ionic radii of In^{3+} , Tb^{3+} and O^{2-} , respectively [18] then, it is possible to confirm that these distances are close to the sum of the corresponding ionic radii. The same distances can be found in indium and terbium oxides [19,20] and germanates [2,3,4,12,21,22]. The Ge–O distances given in the table range from 1.65 to 1.80 Å (1.72 Å mean value) which are in agreement with the values found in other pyrogermanates [2,3,4,12,21,22].

In order to confirm the validity of the structural refinement and to check the oxidation state of all the elements in this structure, bond valence calculations were performed according to the Brown model [23]. This model gives a phenomenological relationship between the formal valence of a bond and the corresponding bond lengths. In perfect non-strained structures, the bond valence sum (BVS) rule states that the valence (V)

Table 1
Lattice parameters and discrepancy factors for $\text{InTbGe}_2\text{O}_7$, space group $C2/c$ (No. 15), $Z = 4$

	$\text{InTbGe}_2\text{O}_7^a$
<i>Lattice parameters</i>	
a (Å)	6.8818(2)
b (Å)	8.8774(3)
c (Å)	9.7892(4)
β (deg)	101.401(1)
V (Å ³)	586.25(4)
<i>Reliability factors (%)</i>	
R_p	5.78
R_{exp}	5.18
χ^2	2.38
R_{Bragg}	2.15
R_{fcrys}	1.64
R_{w}	7.99

^a From laboratory X-ray diffraction data at room temperature.

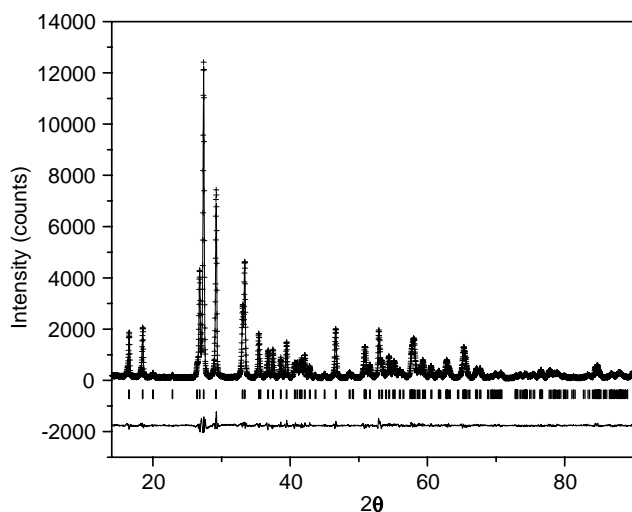


Fig. 1. Observed (\times), calculated ($—$), and difference (at the bottom) X-ray powder diffraction profile for $\text{InTbGe}_2\text{O}_7$ at room temperature. Vertical marks correspond to the position of the allowed Bragg reflections.

Table 2

Final refined positions and isotropic thermal parameters for InTbGe₂O₇ at room temperature

	Wyckoff position	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>B</i> (Å ²)	Occupancy factors
In/Tb	8 <i>f</i>	0.0016(8)	0.3027(1)	0.5020(5)	0.63(4)	0.50(1)/0.50(1)
Ge	8 <i>f</i>	0.2291(2)	−0.006(1)	0.2077(2)	0.62(6)	1.0
O(1)	4 <i>e</i>	0.0	0.035(2)	0.25	1.8(1)	0.5
O(2)	8 <i>f</i>	0.390(1)	0.006(4)	0.3635(7)	1.8(1)	1.0
O(3)	8 <i>f</i>	0.251(3)	0.165(2)	0.113(2)	1.8(1)	1.0
O(4)	8 <i>f</i>	0.217(3)	−0.158(2)	0.109(2)	1.8(1)	1.0

Table 3

Main interatomic distances (Å) and angles (°) in InTbGe₂O₇

In/Tb–O(2)	2.35(2)	In/Tb–O(2')	2.14(2)	Ge–O(1)	1.740(4)
In/Tb–O(3)	2.22(2)	In/Tb–O(3')	2.23(2)	Ge–O(2)	1.697(8)
In/Tb–O(4)	2.12(2)	In/Tb–O(4')	2.41(2)	Ge–O(3)	1.80(2)
⟨In/Tb–O⟩	2.24(2)			Ge–O(4)	1.65(2)
				⟨Ge–O⟩	1.72(2)
				Ge–Ge ^a	3.48(8)
O(2)–In/Tb–O(2')	77.8(7)	O(2')–In/Tb–O(4')	85.9(11)	O(1)–Ge–O(2)	102.7(5)
O(2)–In/Tb–O(3)	90.4(13)	O(3)–In/Tb–O(3')	74.4(12)	O(1)–Ge–O(3)	96.8(13)
O(2)–In/Tb–O(3')	90.0(11)	O(3)–In/Tb–O(4)	109.0(15)	O(1)–Ge–O(4)	112.1(15)
O(2)–In/Tb–O(4)	153.7(15)	O(3)–In/Tb–O(4')	117.8(15)	O(2)–Ge–O(3)	105.0(14)
O(2)–In/Tb–O(4')	79.7(10)	O(3')–In/Tb–O(4)	111.8(16)	O(2)–Ge–O(4)	124.0(17)
O(2')–In/Tb–O(3)	151.4(15)	O(3')–In/Tb–O(4')	163.7(17)	O(3)–Ge–O(4)	112.5(19)
O(2')–In/Tb–O(3')	79.6(11)	O(4)–In/Tb–O(4')	75.6(12)	Ge–O(1)–Ge ^a	156.8(2)
O(2')–In/Tb–O(4)	91.5(14)				

^aGe–Ge distance and Ge–O(1)–Ge angle in Ge₂O₇ diorthogroups.

of the cation (anion) is equal to the sum of the bond valences (v_{ij}) around this cation (anion). The departure from the BVS rule is a measure of the existing stress in the bonds and indicates the presence of covalent bonds. Bond valences are calculated with the formula: $v_{ij} = \exp[(R_{ij} - d_{ij})/0.37]$ [23–25]. Using R_{ij} values calculated according to the method proposed by O'Keefe and Brese [25], which does not need to assume the oxidation state of the elements (1.905, 2.050 and 1.780 for $R(\text{In}^{3+} - \text{O}^{2-})$, $R(\text{Tb}^{3+} - \text{O}^{2-})$ and $R(\text{Ge}^{4+} - \text{O}^{2-})$, respectively), we obtain for our structure 3.093 and 4.702 for the In/Tb and Ge sites, respectively. In order to explain the unusual high value obtained for Ge, we performed calculations using the same procedure for similar compounds tabulated in the ICSD, i.e., NdAlGe₂O₇ (ICSD # 35144), NdGaGe₂O₇ (ICSD # 30986) and GdGaGe₂O₇ (ICSD # 63357) and we obtained values ranging from 4.3 to 4.5, indicating that, at least with this kind of compounds, unusually high values are obtained for Ge, which must be attributed to the very large covalency of this bond.

3.2. Luminescence characterization

The room temperature excitation spectrum of Tb³⁺ ($\lambda_{\text{em}} = 550$ nm) is shown in Fig. 4a. A structured broad band was obtained between 330 and 385 nm. The main structure of this band is due to transitions from the

ground state ⁷F₆ to excited multiplets of the 4*f* configuration of Tb³⁺, namely ⁵D₃, ⁵L₁₀, ⁵G₆, ⁵D₂ in the order of increasing energy. The first of them is the most prominent and it shows a peak at 376.5 nm. Transition of mixed configuration 4*f*5*d* of Tb³⁺ was not detected in this region. On the other hand, taking advantage of the maximum at 376.5 nm, a low-temperature (20 K) emission spectrum of Tb³⁺ ions was obtained. The multiplet ⁵D₃ decays to ⁵D₄ from which the emission arises.

Fig. 4b shows four main groups, corresponding to the most significant transitions arising from the ⁵D₄-Stark multiplet of the 4*f* configuration of Tb³⁺. The following transitions can be recognized easily: the weak ⁵D₄ → ⁷F₆ transition at ≈ 500 nm, the higher intensity ⁵D₄ → ⁷F₅ transition centered at ≈ 551 nm, the ⁵D₄ → ⁷F₄ transition centered at about ≈ 590 nm and the ⁵D₄ → ⁷F₃ transition at ≈ 630 nm. All of them are structured; the splitting in each multiplet is about 200 cm^{−1}. Of these, the ⁵D₄ → ⁷F₅ transition is the most prominent, with an intensity and splitting of each multiplet comparable to the same transitions in other Tb³⁺ compounds [26–28].

The effect of the crystalline field on the Tb³⁺ ion in the new InTbGe₂O₇ compound and on the observed splitting into the Stark multiplets have been analyzed as a function of the temperature and the results will be published later.

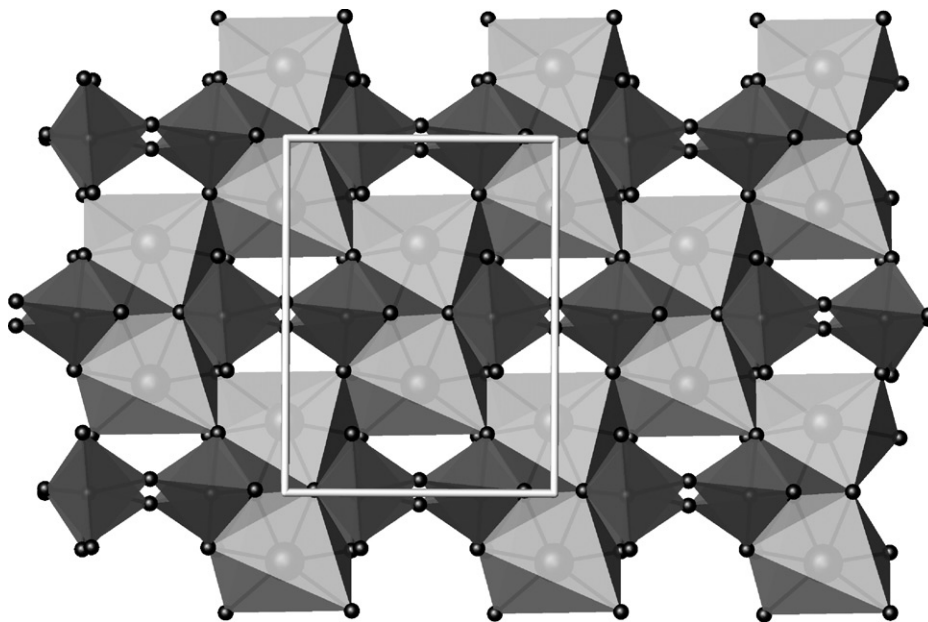


Fig. 2. Arrangements of chains RO_6 ($R = \text{Tb, In}$) forming octahedral layers on the ab planes. Dark and light gray octahedral represents the TbO_6 and InO_6 and polyhedral, respectively. It can be observed that the Ge_2O_7 diorthogroups are linked in hexagonal rings of octahedra.

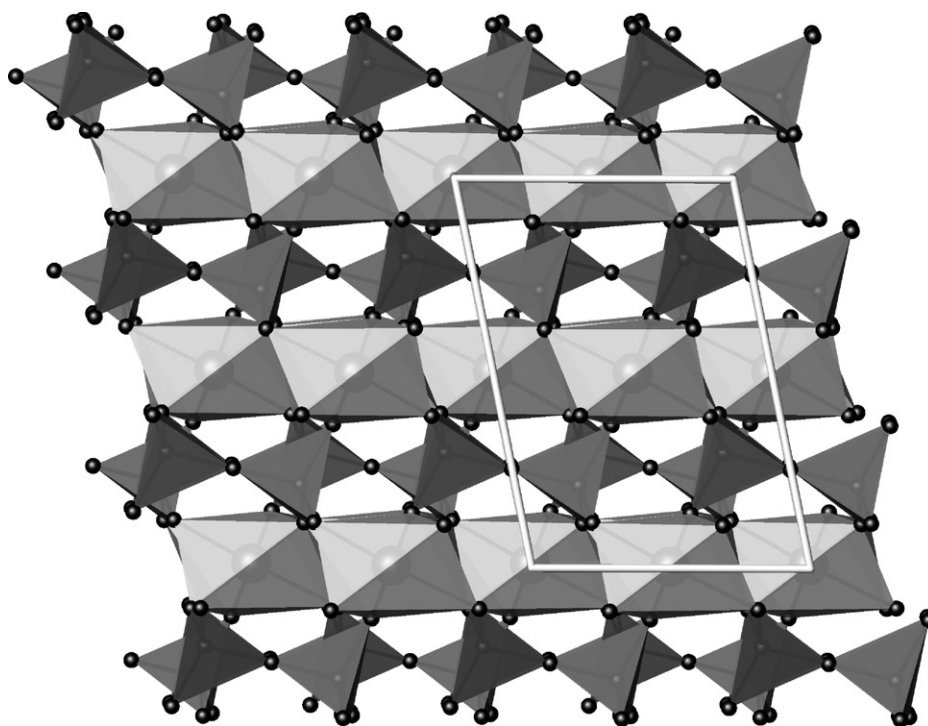


Fig. 3. RO_6 octahedra layers (in light and dark gray) where R represents indium or terbium are held together alternately along the c -axis by sheets of isolated Ge_2O_7 diorthogroups (in white).

4. Conclusions

It can be concluded that the introduction of terbium in the $\text{In}_2\text{Ge}_2\text{O}_7$ thortveitite-type structure is possible for the stoichiometric formula $\text{InTbGe}_2\text{O}_7$. The resulting structure is laminar with monoclinic symmetry as in

thortveitite but described in the space group $C2/c$ instead of $C2/m$. Unlike the case of thortveitite structure, in which the common vertex (O1) of the Si_2O_7 diorthogroups lies on a mirror plane m in the space group $C2/m$, in this structure, the O1 oxygen presents a degree of freedom along the b -axis. This

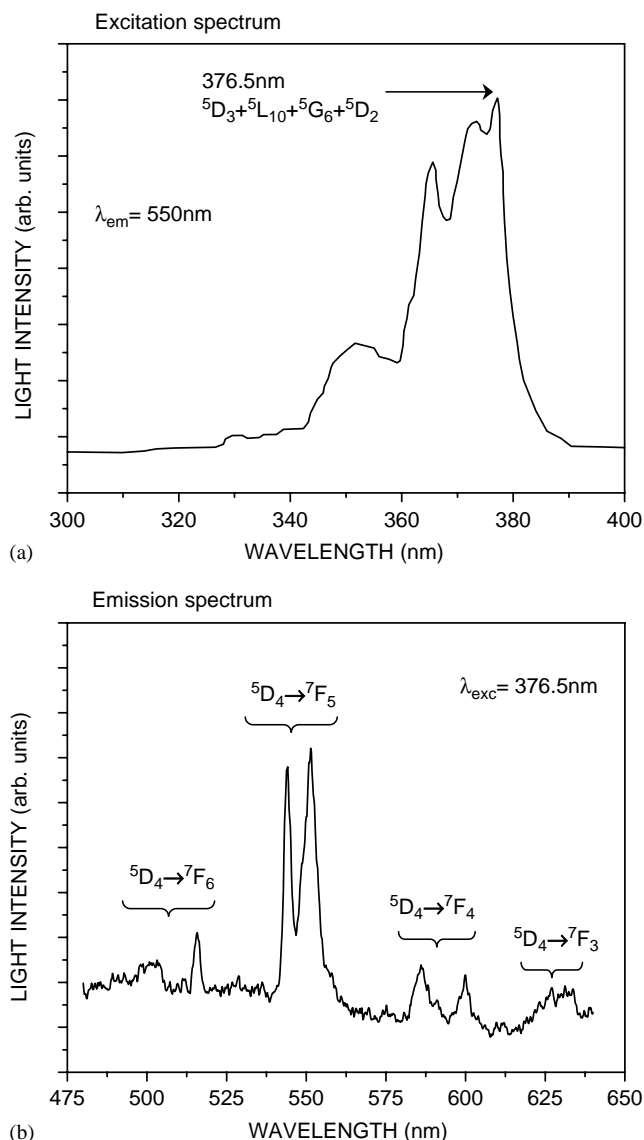


Fig. 4. (a) Room-temperature excitation spectrum of $\text{InTbGe}_2\text{O}_7$ ($\lambda_{\text{em}} = 550 \text{ nm}$); the spectrum shows the excitation maximum located at 376.5 nm ; (b) the emission spectrum ($\lambda_{\text{exc}} = 376.5 \text{ nm}$) at 20 K .

degree of freedom allows the angle Ge-O1-Ge to change from 180° (which is its value in thortveitite) to $156.8(2)$ in $\text{InTbGe}_2\text{O}_7$. A reason for the change in space group ($C2/m$ in thortveitite to $C2/c$) is the increase of the distortion of the polyhedra, which allows a larger degree of freedom. This deformation generates a glide plane instead of the mirror plane and it provokes the doubling of the unit cell along the c -axis. Taking into account that the ionic radii of In^{3+} and Tb^{3+} are quite similar to other trivalent ions such as luminescent and paramagnetic rare earth ions, the $\text{InTbGe}_2\text{O}_7$ compound is a good candidate as a crystalline host to synthesize new optomagnetic ceramics.

With respect to the preliminary study of luminescent properties, from the emission spectrum, it shows the four characteristics groups centered at 500 , 551 , 590 and

630 nm , that corroborate the presence of the trivalent terbium ion in an octahedral site.

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