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Raman and X-ray diffraction studies of terbium trichloride: phase characterization and temperature relationship

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Abstract

We have used phonon Raman spectrophotometry as a rapid and convenient tool, complimentary to X-ray diffraction, for investigating the polymorphism of $TbCl_3$. In the literature one finds references to the polymorphism of $TbCl_3$, but there is some confusion regarding the structural identity and temperature relationship of the different phases reported. In the present work $TbCl_3$ was prepared via reaction of Tb_4O_7 and anhydrous HCl gas. Its Raman spectrum was acquired at room temperature and pressure (RTP) and correlated with the results of X-ray diffraction analysis to confirm the $PuBr_3$-type orthorhombic structure. This $TbCl_3$ structure was then monitored as a function of temperature, including after being quenched from the molten state. From our Raman and X-ray results, a phase transition occurred at about 510°C to a tentatively assigned tetragonal structure, which appeared stable up to the melting point (582°C). Additional annealing studies down to about 250°C resulted in the observation of only the RTP form. No evidence for a UCl_3-type hexagonal or $AlCl_3$-type monoclinic structure was found in this work, though they are common forms of other lanthanide trichlorides.

Keywords: Chemical synthesis; X-ray diffraction; Optical properties; Phase transitions; Inelastic light scattering

1. Introduction

Polymorphism is common for several lanthanide trichlorides, and interconversion between the crystal structures has been achieved with the application of temperature and/or pressure [1–3]. In early work it was reported that $TbCl_3$ exhibits the $PuBr_3$-type orthorhombic structure at room temperature and pressure (RTP) [4]. It has been reported more recently that $TbCl_3$ at high temperature also exhibits the $AlCl_3$-type monoclinic structure [5,6] and the UCl_3-type hexagonal structure [7]. Other researchers have concluded that $TbCl_3$ may be trimorphic, exhibiting the UCl_3-type hexagonal structure at ambient temperature, the $PuBr_3$-type orthorhombic structure between 360 and 509°C, and a tetragonal structure related to that of natural rutile above 509°C [8–10]. It was our purpose in this work to examine the phase relationships with temperature in $TbCl_3$ and to record a Raman spectrum characteristic of each phase.

Raman spectroscopy is a useful tool for identifying the crystal structure of solid-state compounds. The Raman bands of an ionic crystalline solid are due to phonon vibrations in the crystal lattice and are specific to its crystal type. Compared to angle-dispersive X-ray powder diffraction using film techniques, Raman spectroscopy can offer advantages in that it can provide evidence of a sample's crystal structure in a relatively short period of time. Therefore, we chose to use Raman spectroscopy to monitor crystallographic changes in $TbCl_3$ as a function of temperature. Correlation of Raman spectra with crystal structure was carried out by X-ray powder diffraction analysis of the same sample and/or using a database developed earlier in this laboratory [11].

2. Experimental

About 100 mg of Tb_4O_7 was used in the preparation of anhydrous terbium trichloride (m.p. 582°C). The Tb_4O_7, contained in a fused silica capillary, was treated with anhydrous $HCl_{(g)}$ at 450–500°C for 25 min. The sample was allowed to cool and then the capillary was evacuated to 10^{-6} torr, followed by readmission of fresh HCl. This

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process was repeated several times until the sample melted completely and congruently [12]. The capillary was then evacuated to ≤550 Torr of residual HCl and flame sealed for X-ray and spectroscopic examination of the $TbCl_3$. Sample quenching was accomplished by quickly removing the sample from the furnace at temperature, followed by dousing the sample-containing capillary with RT water.

The Raman spectrometer used was a Ramanor Model HG-2S (Jobin-Yvon Instruments SA) that uses a double monochromator with curved holographic gratings, a cooled photomultiplier detector, an amplifier, and pulse counting electronics. A Nicolet Model 1170 signal averager was used to collect the spectra from multiple scans. An argon-ion laser Model Innova 90-5 from Coherent Radiation was the excitation source ($\lambda_{ex} = 488$ nm).

The capillary containing the $TbCl_3$ was attached to a quartz rod, which was then lowered into a test tube and held in a centered position. A thermocouple (Chromel-Alumel) was placed near the sample to monitor the temperature. This apparatus was then lowered into a furnace, the power to which was controlled by two variable transformers in series. The sample was allowed to equilibrate for 10 min at each temperature (variable temperature intervals were used) prior to recording the Raman spectrum at that temperature.

A Phillips Electronics Model XRG 3100 generator, equipped with a 2 kW fine focus Mo target, was used to obtain X-ray powder diffraction patterns from the $TbCl_3$ samples. A 114.6 mm diameter Debye–Scherrer camera was used with Straumanis-type mounting of the Kodak Scientific Imaging film. All exposures were made at room temperature for about 2 h. Films were read on a Phillips-Norelco reader to ±0.05 mm precision. No film shrinkage corrections were made. Crystal structures were identified by comparison of the experimental data with that given in the JCPDS Powder Diffraction File [13] or in the literature [9].

3. Results and discussion

The relationship between crystallographic structures was determined by monitoring changes in the Raman spectrum with increasing and decreasing temperature. In the case of lanthanide trichlorides, observing reversibility of phase transformations is important, as these compounds are susceptible to oxychloride formation at high temperature. Reversibility is an indication that the sample remained $TbCl_3$.

$TbCl_3$ samples cooled from the melt by turning off the power to the furnace and leaving the sample in the furnace until it reached nearly RT (~30 min) always exhibited the $PuBr_3$-type orthorhombic structure. Selected Raman spectra from such a sample, recorded as the sample was heated in a stepwise fashion from 23 to 515°C, are given in Fig. 1. The spectrum at 509°C indicates that the sample had undergone a phase change to a new form, distinct from the known $LnCl_3$ hexagonal, orthorhombic, and monoclinic structures [11]. This crystallographic change is indicated by the decrease in intensity of the 248 cm^{-1} peak, characteristic of the orthorhombic form, and the simultaneous appearance of an intense peak at 85 cm^{-1}. The lowering of the energy of the most intense Raman band in

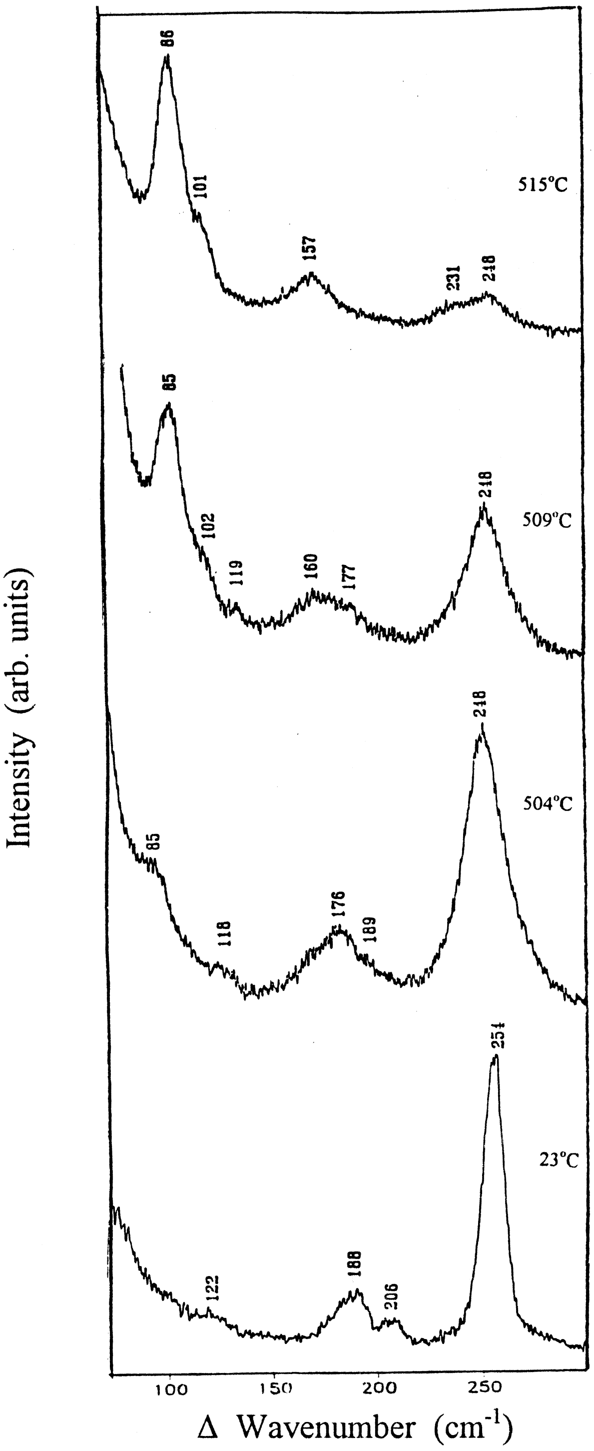

Fig. 1. Raman spectra of initially RTP $TbCl_3$ as a function of increasing temperature.

going from the orthorhombic form to the high temperature form is consistent with an increase in the symmetry of the high temperature form compared to that of the orthorhombic structure. The Raman spectrum recorded at 515°C indicates that the sample maintained this same high temperature form with characteristic peaks around 86, 101, 157, 231, and 248 cm^{-1}. Upon further thermal cycling studies of this sample, it was concluded that the apparent phase transformation was reversible at 510°C.

Identifying the high temperature form of $TbCl_3$ was our next challenge. This modification could only be obtained at RTP by quenching above 530°C up to, but not above, the melting point. Selected Raman spectra recorded from such a $TbCl_3$ sample which initially exhibited the high temperature form, as the sample was heated in a stepwise fashion from 18 to 564°C, are shown in Fig. 2. A phase transformation (high temperature form to orthorhombic form) occurred between 160 and 252°C. The spectrum obtained at 564°C confirms that the sample still exhibited the orthorhombic structure at this temperature. This same sample was then heated rapidly to ca. 630°C (well above the melting point) and then cooled to 585°C, where, upon solidification, the top spectrum in Fig. 3 was recorded. This spectrum is consistent with that expected for the high temperature form of $TbCl_3$. The sample was then cooled to 500°C, where the recorded spectrum (Fig. 3, bottom) is consistent with a phase transformation to the orthorhombic form having occurred at 510°C.

Thermodynamics and kinetics are the two factors which control phase transformations. When thermodynamically possible, the rate at which a reaction proceeds to completion is determined by kinetic effects. Based on our experimental observations, we conclude that between 252 and 509°C, the apparently stable form of $TbCl_3$ is the $PuBr_3$-type orthorhombic structure. Above 510°C and up to the melting point, $TbCl_3$ exhibits a high temperature form, which can only exist at RTP in a metastable state. Upon annealing at temperatures below 510°C, this modification transforms into the orthorhombic structure.

Gunsilius et al. [8,9] prepared $TbCl_3$ in the UCl_3-type hexagonal modification by a transport reaction with $AlCl_3$ below 307°C, while Mitra et al. [10] obtained the same hexagonal $TbCl_3$ via dehydration below 320°C. Both groups concluded that the hexagonal modification was the stable form of $TbCl_3$ at ambient temperature and that a phase change to the $PuBr_3$-type orthorhombic modification occurred around 370°C. They argued that the reformation of the UCl_3-type hexagonal modification upon cooling was kinetically hindered and does not occur. An attempt in this work to capture the hexagonal structure by heating orthorhombic $TbCl_3$ at 300°C for 2 weeks was unsuccessful; in fact, no evidence for the hexagonal form of $TbCl_3$ was seen in this work.

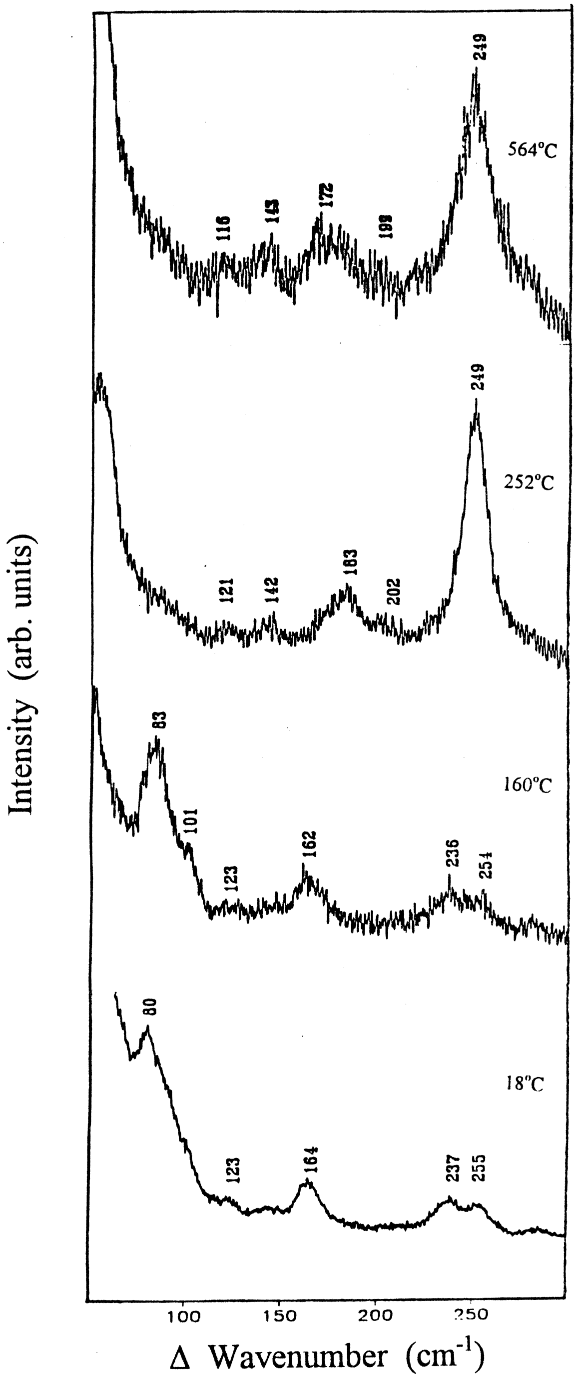

Fig. 2. Raman spectra of initially high temperature $TbCl_3$ (obtained at RTP by quenching from 550±20°C) as a function of increasing temperature.

Lyzlov and Nisel'son have claimed that $TbCl_3$ at high temperature exhibits the $AlCl_3$-type monoclinic structure, isostructural with the room temperature trichlorides of Dy to Lu [5]. This isotypic character was also used to explain the occurrence of the continuous mixed crystal series $(Dy,Tb)Cl_3$ and $(Lu,Tb)Cl_3$ [5]. Samples heated to, or quenched from, the melt in the present work showed no evidence for this monoclinic structure.

Gunsilius et al. have suggested that $TbCl_3$ exhibits a tetragonal structure (space group $P4_2/mnm$; ITC No. 136) as its high temperature form, with $a_0 = 6.42$ and $c_0 =$

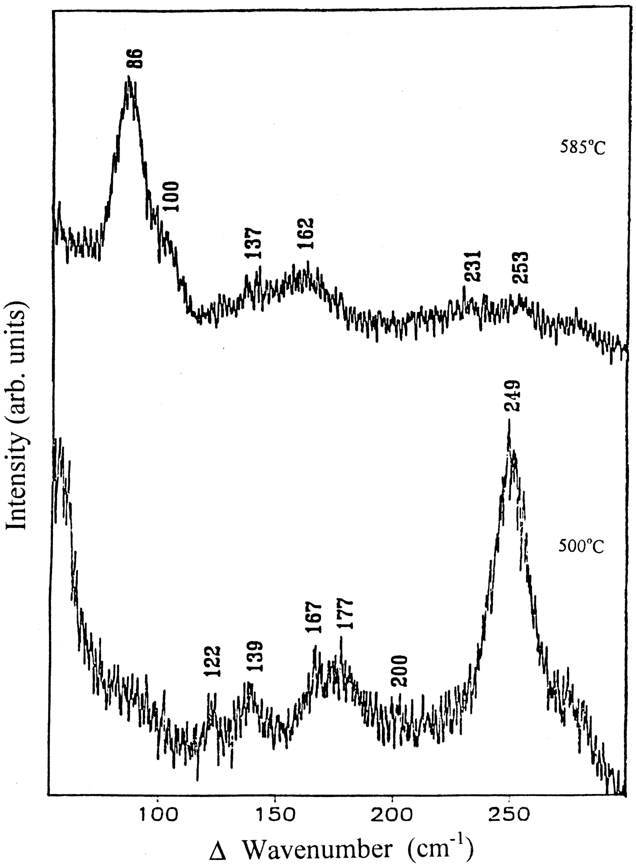

Fig. 3. Raman spectra of a $TbCl_3$ sample quenched from well above its melting point to 585°C and then upon slow cooling to 500°C.

Table 1
X-ray diffraction data from high temperature $TbCl_3$ analyzed at RTP

h	*k*	*l*	Intensity	*d* observed	*d* calculated
1	0	0	m	6.88	6.43
1	0	1	m	5.68	5.63
1	1	0	s	4.50	4.55
1	0	2	m	4.05	4.33
1	1	2	m	3.57	3.59
2	1	0	vw	2.87	2.87
2	0	2	vw	2.87	2.82
2	1	2	m	2.58	2.58
3	0	3	vw	1.89	1.88
1	0	6	vw	1.89	1.87
2	2	4	vw	1.79	1.79
3	2	0	vw	1.79	1.78
4	0	2	vw	1.55	1.55
4	0	4	vw	1.40	1.41
3	1	6	vw	1.40	1.41
2	1	8	vw	1.30	1.30
4	1	5	vw	1.30	1.30
4	0	6	vw	1.24	1.24
3	3	6	vw	1.19	1.20
5	2	0	vw	1.19	1.19
3	1	8	vw	1.19	1.19
4	4	2	vw	1.11	1.12
5	2	4	vw	1.11	1.11

11.77 Å at 555°C [9]. The more intense lines in a diffraction pattern of the high temperature form of $TbCl_3$ obtained in this work were indexed using a Hull–Davey chart for the tetragonal crystal system [14,15]. Listed in Table 1 are the assigned Miller indices, the observed *d* spacings, and the *d* spacings calculated by the LCR-2 least squares fitting program [16]. From these data the best fit lattice parameters (σ) at RTP were found [16] to be $a_0 = 6.43(1)$ and $c_0 = 11.70(4)$ Å, with a formula volume of 121 Å^3 assuming the number of formula units per unit cell is four, as suggested by others [9]. Although the lattice parameters found in this work are comparable to those of Gunsilius et al. [9], comparisons of the X-ray diffraction data based on both position and intensity revealed some discrepancies. It is noted also that the RTP formula volume of the high temperature form of $TbCl_3$ in this work is 26% greater than the RTP formula volume of the orthorhombic $TbCl_3$ (95.8 Å^3) reported by Forrester et al. [4], although no particular conclusion is drawn from this fact.

4. Summary and conclusions

$TbCl_3$ was prepared by reaction of Tb_4O_7 and anhydrous $HCl_{(g)}$. Its Raman spectrum was acquired at RTP and correlated with the results of X-ray diffraction analysis to confirm the $PuBr_3$-type orthorhombic structure. In the literature it is claimed that $TbCl_3$ is polymorphic; however, the correct crystal forms and their relationships with temperature are uncertain. The experimental evidence obtained in the present work suggests that a phase transition occurs at 510°C from the orthorhombic form to a tentatively assigned tetragonal structure related to that of natural rutile [9], which appears stable up to the melting point (582°C). The Raman spectra are consistent with a higher symmetry for this high temperature form over that of the orthorhombic form. Furthermore, this high temperature form was only obtained by quenching samples at temperatures between 530°C and up to, but not above, the melting point. Additional annealing studies down to about 250°C resulted in the observation of only the orthorhombic form. No evidence for a UCl_3-type hexagonal or $AlCl_3$-type monoclinic structure for $TbCl_3$ was found in this work, though their absence here may reflect only kinetic effects. Confirmation of the high temperature tetragonal structure is still of interest. An analysis of this structure via single crystal X-ray diffraction methods, or possibly by confirmatory X-ray diffraction studies at high temperature, would be desirable.

Acknowledgements

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