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High temperature phase segregation of a new host for Er^{3+} upconversion: $Cs_3Tl_2Cl_9$

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$Cs_3Tl_2Cl_9$ is one of the few air stable low-phonon host lattices of interest to Er^{3+} upconversion. Solution growth at ambient temperature demonstrated that water and a number of other molecular liquids do not yield Er^{3+} doped crystals. Optical and differential scanning calorimetry measurements revealed a phase segregation at 310 °C which is reversible in the presence of 1 atm Cl_2. Growth from molten salt solutions or gas phase deposition techniques is hence restricted to a deposition temperature of less than 300 °C. Preliminary results show that molten $ZnCl_2$ may be used as a flux to obtain lanthanide doped single crystals or epitaxial layers.

Introduction

High optical storage density devices and displaying applications demand compact and efficient laser sources in the visible spectral range. One implementation may be resonant conversion of infrared to visible light by solid state devices, so-called upconversion (UC).[1] For UC to take place, appropriate host lattices are doped with different lanthanide ions, mainly Er, Tm, Pr or Ho. Recent investigations mainly used fluoride and oxide crystals as well as heavy metal glasses as host materials.[2] As the reduction of the phonon energies of the host significantly slows down non-radiative multiphonon relaxation[3,4] and thus increases UC efficiencies, there is considerable interest in low-phonon UC materials. Because lowering phonon energies can be achieved by introducing heavier ligands, chloride and bromide compounds have been investigated, showing pronounced UC efficiencies.[5,6] Due to the high sensitivity of most of these materials to air and moisture, applications such as those mentioned before are chemically demanding. We have found $Cs_3Tl_2Cl_9$ to be one of the only low-phonon UC hosts which is really stable in air and can be doped with, for example, Er^{3+}.[6] $Cs_3Tl_2Cl_9$ crystallizes in the rhombohedral space group $R\bar{3}c$ featuring two face-sharing distorted octahedra (Fig. 1).[7] Tl^{3+} ions are situated in the centre of the octahedra, leading to short Tl^{3+}–Tl^{3+} distances within a dimer ($d \approx 4$ Å) and facilitating energy transfer in the case of erbium. Furthermore, the site symmetry for the dopant is $3m$, a non-centrosymmetric site being a requirement for a high absorption cross section.

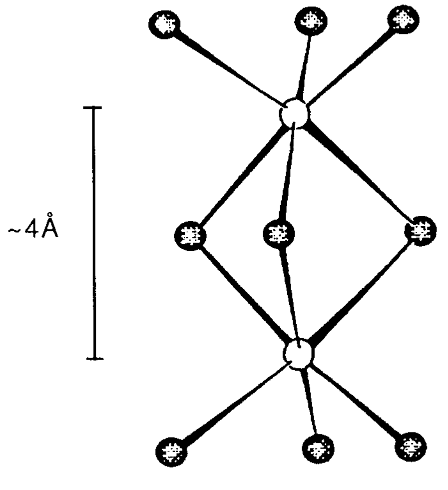

Fig. 1 Dimeric structure of $[Tl_2Cl_9]^{3-}$ (ref. 7)

Single crystals of $Cs_3Tl_2Cl_9$ have been obtained from aqueous solution.[7] However, lanthanide ions strongly coordinate to the oxygen of water molecules. It was therefore not possible to grow Er^{3+} doped $Cs_3Tl_2Cl_9$ crystals from H_2O solutions near 300 K. The ultimate alternative is high temperature growth either from a flux or from the vapour. Both routes need knowledge on the thermal stability field of $Cs_3Tl_2Cl_9$.

Solid state UC devices demonstrated so far are single crystals or waveguiding glass fibers grown at high temperatures.[2] In particular, single crystalline waveguides allow the combination of the advantages of bulk crystals (narrow bands leading to high gain coefficients) with those of the fiber geometry (high pump intensities along the whole absorption length). High quality waveguiding layers are most effectively grown by liquid phase epitaxy (LPE),[8] pulsed laser deposition[9] or high energy ion implantation.[10] A first fluoride LPE-grown UC waveguide has been reported recently.[11] A waveguide of $Cs_3Tl_2Cl_9$ may be achieved by growing a lanthanide doped epitaxial layer on a $Cs_3Tl_2Cl_9$ substrate. Here, too, knowledge of the thermal behaviour of this potential host or substrate material is basic to any further improvement.

The thermal behaviour of powdered $Cs_3Tl_2Cl_9$ samples in open and closed systems has been investigated by Richter.[12] Following this analysis, $Cs_3Tl_2Cl_9$ undergoes phase segregation at 301 °C, *i.e.* it decomposes into $Cs_2Tl^{I}Tl^{III}Cl_6 + CsCl + Cl_2$ with an intermediate product identified as $Cs_{11}Tl_6Cl_{29}$ (see ref. 12, p. 59). A weight loss of 6.2% has been found by thermogravimetry on unsealed samples. Compared to $Cs_3Tl_2Cl_9$, a significantly simpler powder diffraction pattern was measured at temperatures above 301 °C. The $Fm3m$ symmetry was attributed to $Cs_2Tl^{I}Tl^{III}Cl_6$. Raman spectroscopy demonstrated a reversible phase segregation.

In this work we present a thermal analysis relying on single crystals of $Cs_3Tl_2Cl_9$ being kept under Cl_2 (*ca.* 1 atm) in closed glass capillaries. Experimental conditions for the phase segregation study have been chosen as close as possible to parameters needed for high temperature single crystal and epitaxial growth of $Cs_3Tl_2Cl_9$ to follow.

Experimental

Due to the toxicity of thallium compounds, care had to be taken. When handling powders or samples at elevated temperatures, they were kept in a special dry box (used for Tl compounds only) or in sealed ampoules, respectively.

Synthesis of $Cs_3Tl_2Cl_9$ (ref. 13)

Wet $TlCl_3$ (4 g; hygroscopic) and 5 g CsCl were dissolved separately in 10 ml distilled H_2O, poured together and stirred. A white, finely spread precipitate was immediately obtained. CsCl was added in excess to bring all $TlCl_3$ to reaction. The precipitate was recrystallised by addition of 70 ml distilled H_2O, heating to 60 °C and slow cooling in a previously heated dewar. Transparent, needle shaped crystals were finally obtained which could be filtered off and dried at 80 °C under vacuum for several hours.

Single crystal growth

Single crystals (Fig. 2) were grown using the ΔT method.[14] An excess of $Cs_3Tl_2Cl_9$(s) and a saturated aqueous $Cs_3Tl_2Cl_9$ solution were filled into a specially designed tube. The tube was inclined at an angle of 30° to the horizontal. A ΔT of 1.5 °C was sufficient to induce constant convection, transporting saturated solution to the upper part of the tube where cooling led to supersaturation and subsequent nucleation. Nucleation could be promoted, *i.e.* controlled by use of a Peltier cooling element which was placed in the upper part of the tube.[15] δT pulses allowed the supersaturation to be increased for a short time of 20–30 s.

By X-ray diffraction we determined the growth direction to be the *c*-axis of the $R\bar{3}c$ system. The lattice constants are $c = 18.27$ Å and $a = 12.82$ Å.[7]

Differential scanning calorimetry

DSC measurements were carried out using a Mettler Toledo DSC 25. The heating/cooling rates were 2 °C min^{-1}. Crystals of *ca.* 10 mg were placed into sealed aluminium crucibles under N_2.

Gandolfi X-ray photographs

These were taken using an UB/71 Officine Elettrotecnica Di Tenno instrument. A typical exposure time for single crystals was 4 h at 900 W Cu-Kα_1 radiation. Photographs at elevated temperatures were obtained by heating crystals sealed in Lindemann type capillaries (normal or quartz glass) under *ca.* 800 mbar of Cl_2 by means of a heated air flow. The exposure time for rotated samples was typically 9 h at 900 W Cu-Kα_1. Additional photographs of single or polycrystalline samples were taken with the Gandolfi camera without rotating the sample, with sample exposure for 2 h.

Orthoscopic investigation

Orthoscopic investigations were performed using a Linkham THMS 600 heatable microscope table and a Leitz Orthoplan microscope with tenfold magnification. The samples were mounted in small Pyrex ampoules under N_2 or Cl_2 atmosphere. The ampoules were glued to a thin glass plate with silver paste in order to improve the thermal contact.

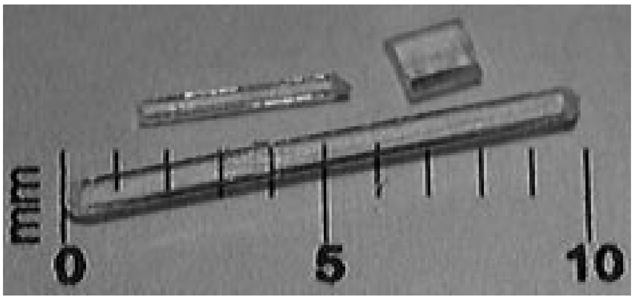

Fig. 2 Single crystals of $Cs_3Tl_2Cl_9$ grown from aqueous solution by the ΔT method[14]

Results and Discussion

While heating up to 330 °C DSC showed a strong endothermic peak around 310 °C (10.6 ± 0.65 kJ mol^{-1}) accompanied by several weaker endothermic signals in the range of 180–250 °C (Fig. 3). Crystals tempered above 200 °C under N_2 (48 h) did not show such spurious signals. In any case, there were no endothermic peaks around 100 °C, indicating that the crystals do not represent a hydrate or show water bubble inclusions. Upon cooling an exothermic peak around 280 °C was observed.

Interesting thermal features were observed by orthoscopy: sealed crystals were positioned under crossed polars to yield maximum extinction. Several bright spots indicated defects and strained areas [Fig. 4(a)]. On heating up to 180–250 °C these areas dimmed and some of them came to complete extinction. Upon further heating, the entire crystal volume lit up around 310 °C [Fig. 4(b) and (c)]. This phenomenon started

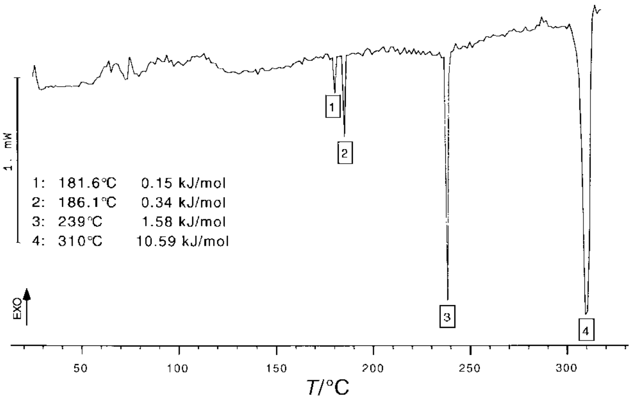

Fig. 3 DSC measurement of a $Cs_3Tl_2Cl_9$ single crystal from room temperature to 330 °C

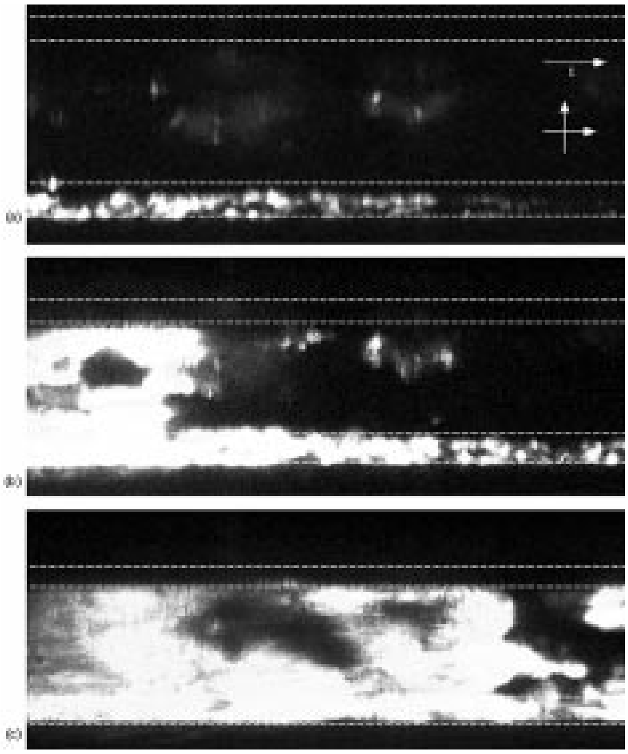

Fig. 4 Orthoscopy of the phase transition close to 310 °C (dashed lines indicate crystal edges). (a) $T < 310$ °C; (b) start of the phase segregation around 310 °C; (c) end of the phase segregation.

from crystal edges and defects, which did not come to complete extinction in the first phase of heating. From there, the illuminated sections spread over the entire crystal. No difference was noticed whether working under N_2 or Cl_2 atmosphere. Upon cooling and about 30 °C below the transformation temperature (heating cycle), crystals showed some increase of local extinction, albeit not complete.

Optical inspection carried out in addition to orthoscopy monitored an increasing absorption (yellow colour) above 200 °C. Around 300 °C, the crystal sharply turned yellow–brown.

Preliminary Gandolfi measurements were acquired without rotation of the crystal, showing a typical single crystalline pattern at $T < 310$ °C replaced by a powder pattern above 310 °C. Diffraction of rotated samples taken above the transition temperature produced photographs showing only a few lines (Table 1). Samples cooled to room temperature recovered lines typical of $Cs_3Tl_2Cl_9$.

Taking into account all the observations mentioned above, the endothermic peak and the loss of birefringence around 310 °C can be attributed to a segregation reaction, transforming single crystalline $Cs_3Tl_2Cl_9$ into a composite of one or more new crystalline phases, at least one of them being yellow. On cooling, $Cs_3Tl_2Cl_9$ is recovered in form of a polycrystalline, opaque material. However, this phase segregation was found to be reversible only if carried out in a closed system of either a small volume (under N_2) or under Cl_2 (*ca.* 1 atm). It may be that Cl_2 gas is released in the course of this reaction. Note that the recovery of the $Cs_3Tl_2Cl_9$ phase required non-reactive vessels, such as Pyrex or quartz glass. In the case of normal Lindemann capillaries a completely different and also unknown diffraction pattern was obtained.

As the high temperature diffraction data revealed only a few lines, we conclude that predominantly one solid phase is formed, other minor contributions being below the detection limit. The small number of lines in the high temperature diffraction pattern indicate a new phase of high symmetry. The present pattern could not be attributed to either $Cs_2Tl^ITl^{III}Cl_6$, $Cs_{11}Tl_6Cl_{29}$ or CsCl, proposed by Richter (the products of phase segregation of powder samples).[12]

The release of Cl_2 at the phase change complicates the DSC measurements on cooling, because Cl_2 may react with the aluminium pan. However, at 280 °C an exothermic peak supports reversibility of the transition under Cl_2.

Thermodynamical calculations[16] applied to TlCl(s) and $TlCl_3$(s) show the preferred formation of Tl^+ at high temperatures, thus indicating the presence of at least one Tl^+ containing compound after the phase segregation. The sharp colour change to yellow around 310 °C may therefore be attributed to the formation of a mixed valence compound containing Tl^{3+} and Tl^+.

Finally, strain as a source of defects mentioned in the paragraph on orthoscopy can be excluded, as relaxation of strain would lead to exothermic peaks in the DSC. The observed relaxation temperatures varied with the crystals examined. We assume that these areas act as nucleation centres for the phase segregation behaviour observed by optical means.

Compared to the transition temperature reported for powdered samples of $Cs_3Tl_2Cl_9$,[12] the single crystal transition temperature is shifted by about 10 °C. This can be explained by the presence of fewer defects and a smaller surface.

Conclusions and preliminary results on solvent systems

Single crystals of $Cs_3Tl_2Cl_9$ could be grown to optical quality and dimensions that allowed phase transition phenomena to be tracked, indicating significant deviations from results gained on powder data.[12]

Investigations on single crystals are indicative of phase segregation at 310 °C. At this temperature, an as yet unknown new phase is formed. However, there is strong evidence that Cl_2 and Tl^+ are involved in the reaction. Within experimental

Table 1 *d*-Values (Å) of the new and so far unknown high temperature phase, measured by a Gandolfi camera (further columns contain powder data of products reported by Richter;[12] there is no agreement between the data of the first column with *d*-values reported by Richter)

new high-temp. phase	$Cs_3Tl_2Cl_9$ (Ref. 18) (300 K)	$Cs_{11}Tl_6Cl_{29}$ (Ref. 19)	α-$Cs_2TlTlCl_6$ (Ref. 12) (low-temp.)/	β-$Cs_2TlTlCl_6$ (Ref. 12) (high-temp.)	CsCl (Ref. 20) (300 K)
		7.0562 (m)			
	6.4105 (m)		6.3551 (w)		
	4.4192 (m)	4.2322 (w)			4.120 (m)
	4.2305 (m)	3.9893 (s)			
		3.9414 (w)	3.8951 (s)	3.9468 (s)	
		3.7944 (m)	3.8659 (m)		
	3.7024 (s)	3.7522 (m)			
	3.5308 (w)	3.5364 (w)			
					2.917 (s)
		2.8934 (m)			
	2.8372 (s)	2.8158 (m)			
	2.7544 (s)	2.7925 (m)	2.7741 (m)	2.7914 (m)	
2.67 (m)		2.7066 (m)	2.7331 (m)		
2.59 (s)	2.5562 (w)	2.5695 (w)			
		2.5226 (m)			
2.29 (m)		2.3564 (m)			2.380 (w)
2.24 (s)	2.2525 (w)	2.2181 (m)	2.2534 (w)	2.2793 (m)	
	2.2096 (s)	2.2092 (m)	2.2367 (m)		
	2.1375 (m)	2.1402 (w)		2.1489 (w)	
		2.1205 (m)	2.1045 (w)		
		1.9952 (m)	1.9465 (w)	1.9738 (m)	2.062 (w)
	1.8972 (m)	1.8739 (m)			
	1.8510 (s)	1.8576 (m)			
1.65 (w)		1.8442 (m)			1.844 (w)
1.59 (s)	1.7171 (w)	1.7145 (w)	1.7514 (w)	1.7655 (w)	1.683 (m)
	1.6772 (w)	1.6643 (w)	1.7307 (w)		1.457 (w)
1.34 (w)		1.6469 (w)	1.6718 (w)		
1.32 (s)	1.5358 (w)	1.5496 (m)			
1.26 (w)	1.4190 (w)	1.5465 (w)	1.5412 (w)	1.4920 (w)	1.374 (w)

(s), (m), (w) denote strong, medium and weak, respectively.

error, the transition was reversible at *ca.* 1 atm Cl_2 pressure. These important new results imply that bulk and epitaxial growth of $Cs_3Tl_2Cl_9$ will have to be carried out at temperatures below $T \approx 300\,^{\circ}C$ and under Cl_2 atmosphere.

The evident approach to bulk and epitaxial growth would then be the use of a suitable low temperature solvent or high temperature flux under Cl_2 atmosphere. In the course of this work several solvents (DMSO, acetonitrile, liquid NH_3, *etc.*) were tested. All of them converted the $Cs_3Tl_2Cl_9$ single crystals into a white mush, probably due to the soft Tl^{3+} ion binding soft Lewis bases. Recrystallisation from liquid NH_3 yielded an unknown powder pattern. $Cs_3Tl_2Cl_9$ was insoluble in ethanol and methanol. Commonly used inorganic acids, HCl(l) and some other solvents (Cl_3PO) either yielded no significant solubility or led to redox reactions. We therefore turned to an exploration of several relatively low melting fluxes: rhodanides and nitrates were not suitable due to coordination to Tl^{3+}. $SnCl_2$ systems were oxidised to $SnCl_4$ under Cl_2 atmosphere. A mixture of $Cs_3Tl_2Cl_9$ and $ZnCl_2$ melting at 230 °C turned out to be a suitable system, showing sufficient solubility for both $Cs_3Tl_2Cl_9$ and $ErCl_3$. However, care has to be taken in order to avoid precipitation of $ZnCl_2 \cdot 2CsCl$.[17] Further investigations on the use of the $ZnCl_2$ flux in crystal growth experiments are in progress.

An alternative approach would be physical vapour deposition. In preliminary experiments, CsCl, $ErCl_3$ and $Cs_3Tl_2Cl_9$ were evaporated separately in a nitrogen flow, carried over a substrate crystal of $Cs_3Tl_2Cl_9$ held below 300 °C. Powder diffraction patterns of the materials deposited showed lines which were different from those of $Cs_3Tl_2Cl_9$, with the yellow colour indicating the presence of Tl^{+}. This could well be due to Cl_2 loss. In order to avoid reduction, the $Cs_3Tl_2Cl_9$ source should therefore be kept under a Cl_2 flow. Thermodynamical calculations using data given in ref. 16 and applied to $TlCl_3$ and TlCl show that the reduction of $TlCl_3$ to TlCl is exergonic at a sublimation temperature of about 400 °C in a N_2 atmosphere. In contrast, $TlCl_3$ is thermodynamically favoured under a Cl_2 atmosphere of about 5 atm to promote the formation of the $Cs_3Tl_2Cl_9$ phase.

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