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Up-conversion emission phosphors based on doped silica glass ceramics prepared by sol–gel methods: control of silica glass ceramics containing anatase and rutile crystallites

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Using sol–gel methods novel silica based glass ceramics containing TiO_2, Er^{3+} and Yb^{3+} ions have been prepared. Anatase and rutile crystallites composed of TiO_2, Er^{3+} and Yb^{3+} ions that segregate in the glasses have been shown to be new yellow emitting up-converting materials. It is demonstrated that by annealing SiO_2 glasses containing TiO_2, Er^{3+} and Yb^{3+} ions, crystals of either the anatase or rutile phases can be grown in the glass (dependent on annealing temperature). Laser Raman spectroscopy is shown to be a useful technique to characterise the crystallographic phases in the pure state, and in these new ceramics. Furthermore, their emission can be excited at a wavelength of 632.8 nm, and the up-converted luminescence in the visible region can be detected and monitored using a Raman spectrometer.

Introduction

Rare earth element fluoride lattices are thought to be amongst the best matrices for up-conversion luminescence.[1] For efficient optical applications it has been shown that fluoride glasses are suitable hosts. The drawbacks are that they are toxic, expensive to manufacture, corrosive, unstable and must be processed in a dry oxygen-free atmosphere.[2] Oxide glasses do not have these drawbacks, they are durable, chemically stable and can be processed entirely in air. However they are thought to be more unsuitable than fluorides for optical uses as they have high phonon energies and hence poor luminescence efficiencies compared to those required for optical materials.[2]

It is known that the incorporation of small quantities of fluoride ions can significantly influence the optical properties of rare earth element (REE) containing glass matrices.[3] Developments, which may lead to new applications of REE doped materials, with the capability of emitting light in the visible region, have included investigations of their potential for three colour volumetric (*i.e.* three dimensional, 3D) displays[4] using bulk ZrF_4 based fluoride glasses.[5] Within such low phonon energy environments of halide host lattices, the REE ions (Pr^{3+}, Er^{3+}, Tm^{3+}) can absorb two photons of different frequencies, and then efficiently generate red, green and blue radiation which is bright enough to be observed with the naked eye in ambient room light.[6–8] Up-conversion into the visible region stems from the stepwise absorption of two infrared photons of different wavelengths. As emission occurs only at the point of intersection of two crossed pump beams, then rastering them results in the formation of real 3D images.[4]

It is also known that crystalline ionic materials have better properties as hosts for *anti*-Stokes luminescence processes than covalent glasses.[9] Oxyfluoride glass ceramics have been developed which combine the luminescence efficiency of a fluoride crystalline material with the chemical stability of an oxide glass.[2,10]

Oxide glasses containing microscopic crystals (*ca.* 10–30 nm in diameter) have been developed (based on early work[11]), and currently these are being evaluated as matrices for 3D imaging.[5] The choice of these systems originates in the ease of processability of oxide glasses and their enhanced physical characteristics (both thermal and mechanical), arising from the presence of the crystallites. In the last eight years oxide glasses containing $Pb_xCd_{1-x}F_2$ crystallites have been prepared in two investigations.[10,12] In both of these studies the REE ions were found to be preferentially located in the crystallites rather than the glass matrix. Enhanced intensities of the light output were observed due to reduced radiationless deactivation owing to the lower phonon energies of the fluoride host.[10,12] Recently a number of articles have appeared on REE containing glass ceramics which have been reviewed by Dejneka.[2]

The synthesis of fluoride glasses using sol–gel methods has been described by several authors.[13,14] Generally the methods involve the synthesis of an amorphous oxide matrix based on the correct stoichiometry of the cations required for the glass. Control of the order of addition enables these cations to be mixed homogeneously. After the resulting gel has been dried it is fired in a dry fluoride atmosphere to produce a fluoride glass at a temperature above the glass transition point of the glass. The advantage of this method is that the cations involved are mixed homogeneously at the molecular level. The main disadvantage is that the samples are full of hydroxyl ions, water and other species that reduce the efficiency of any optical processes that they are intended for. Even careful elimination of water and oxygen in the firing processes cannot always guarantee loss of these species.

In this paper we report the synthesis of silica based ceramics containing fluoride and rare earth element ions using sol–gel techniques. To modify the properties of these materials, aluminium and titanium ions were also added. The addition of titanium to silica based materials increases the refractive index.[15] Conversely, the incorporation of fluoride ions into these matrices reduces the refractive index,[16,17] and it is hoped the presence of titanium may well counteract this effect of the fluoride ions. The addition of titanium also improves the chemical durability of the material and increases the glass transition temperature (T_g).[18] It has been proposed that the addition of aluminium to a rare earth doped glass material reduces clustering of the REE ions.[19] Sol–gel synthetic methods have several advantages over other methods of glass synth-

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esis.[20] These include greater homogeneity due to the mixing of components in solution, and lower firing temperatures. It has been found due to the nature of sol–gel synthesis, the addition of fluoride ions to a silica system containing rare earth ions will generally cause the precipitation of soluble rare earth fluorides.[2] In this study we found that under controlled circumstances transparent glass ceramic samples containing both REE and F^- ions can be produced. Titanium dioxide samples doped with erbium were also synthesised and the up-conversion luminescence from these samples was compared with the emission from the titanium doped silica glass ceramic materials.

Experimental

Glass samples were synthesised in three stages.

(1) Mixing of cation solutions in a suitable solvent, with the addition of a catalyst (hydrochloric acid), water, and hydrofluoric acid. In some cases, titanium and aluminium alkoxides were also added.

(2) Gelation and drying of the samples (typical time is two weeks).

(3) Firing of these samples at temperatures in the range 600–1000 °C.

Stage 1: mixing of the precursors

The most suitable solvent for this work was found to be 2-methoxyethanol and it was used whilst taking suitable precautions. Tetraethylorthosilicate was prehydrolysed with an equivalent volume of water. To this the required amounts of rare earth element acetates dissolved in 2-methoxyethanol were added followed by hydrochloric acid as catalyst. Finally the hydrofluoric acid was added. This was made up from a 48% solution (supplied by Aldrich) and diluted with water so that amounts up to 6 mol% (with respect to the silicon content) could be pipetted into the mixture. Teflon beakers and plastic pipettes were used throughout this synthesis and all gels were mixed at room temperature.

Titanium propoxide and aluminium tri-*sec*-isobutoxide were added to the mixture prior to the addition of hydrofluoric acid. Concentrations of 2 and 10 mol% of the overall cation amount of aluminium and titanium were used which produced transparent samples upon firing.

It was necessary to add the hydrochloric acid prior to the fluoride solution otherwise precipitation occurred very quickly. A range of samples was synthesised with variations in REE and fluoride concentrations. The concentration ranges which produced transparent final samples were found in the range of 2 mol% fluoride and 10 mol% REE up to 6 mol% fluoride and 2 mol% REE. The effect of titanium in these glasses was also investigated. Aluminium has been shown to aid dissolution of the fluorine, and the titanium was initially added to raise the refractive index whereas aluminium lowers it.

Stages 2 and 3: gelation, drying and firing of the samples

After mixing, the samples were poured into plastic petri-dishes, covered, and placed in an oven at 40 °C for two weeks. During this time the samples gelled and dried to leave amorphous transparent glass-like products. These samples were then fired in a temperature-programmable muffle furnace. The starting temperature was set to room temperature and a ramp of $2\,^{\circ}\mathrm{C\,min^{-1}}$ was set to reach a final temperature between 600 and 1100 °C. When no annealing was carried out the samples were removed as soon as the final temperature was reached. Where annealing followed directly from the firing at high temperature, the temperature was lowered using a ramp of $10\,^{\circ}\mathrm{C\,min^{-1}}$ until the annealing temperature was reached. All firings were carried out in a Carbolite furnace fitted with a Eurotherm 92 controller.

Preparation of new erbium doped titanium dioxide up-converters

A solution of titanium(IV) ethoxide (5 g 0.02 M) and absolute ethanol (25 ml) was prepared. To this, solutions of ytterbium nitrate pentahydrate (1.8 g, 0.004 M) and erbium nitrate pentahydrate (0.18 g, 0.0004 M) in water were slowly added whilst stirring. A gel formed and stirring was ceased. This gel was dried in an oven at 100 °C. The resulting product was fired in a furnace at 750 °C for 2 hours in order to produce the anatase phase and 1150 °C for 2 hours to form the rutile phase. Spherical particles were obtained for the anatase and rutile phases with a particle diameter of 0.4–1.0 µm. Transmission electron microscopy (TEM) of the anatase phase shows particles composed of 50–100 nm crystallites. The rutile phase showed sintering between the particles that manifest as single crystals when ground and observed in the TEM showing that these had grown during the phase transformation.

Measurements

Luminescence and Raman spectra were obtained using a Labram Raman spectrometer equipped with a $1800\,\mathrm{g\,mm^{-1}}$ holographic grating, a holographic supernotch filter and a peltier cooled CCD detector. Samples were excited using a helium neon laser with an output of 8 mW of power at the sample on the 632.8 nm line, unless an attenuation filter was used. Luminescence observed using infrared excitation was detected using a Spex Triplemate Raman spectrometer equipped with an intensified photodiode array detector. A 3900 titanium sapphire laser, pumped by a Millenia intracavity frequency doubled Nd : YAG laser (Spectra Physics), provided the infrared excitation: the laser power varied between 20 mW and 50 mW at the sample, and the wavelength was 974 nm.

Transmission electron micrographs were obtained using a JEOL JEM 200CX microscope operating at 200 kV.

Results and discussion

No up-conversion emission was observed in the silica glass matrices in the absence of Ti^{4+} ions, even though many of the clear glasses contained small precipitated crystallites. In the presence of Ti^{4+} ions, glass ceramics were prepared which show some up-conversion emission. The structure of a typical slow-cooled ($10\,^{\circ}\mathrm{C\,min^{-1}}$) glass ceramic (before annealing) shows the presence of very small crystallites when studied by TEM (Fig. 1). The crystallite size was of the order of 5–6 nm in length along the longest edge. The up-conversion emission of this glass before annealing is presented as an inset in Fig. 2.

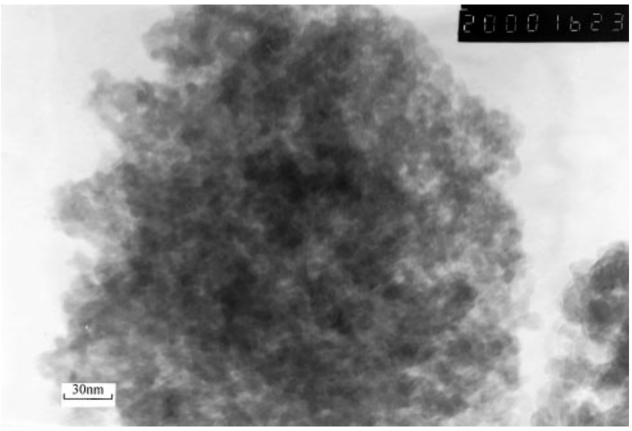

Fig. 1 TEM (magnification 50 000 ×) of TiO_2, Er^{3+}, Yb^{3+} anatase phase heated to 990 °C and not annealed. This shows the presence of only tiny crystallites having a maximum diameter of only 5–6 nm.

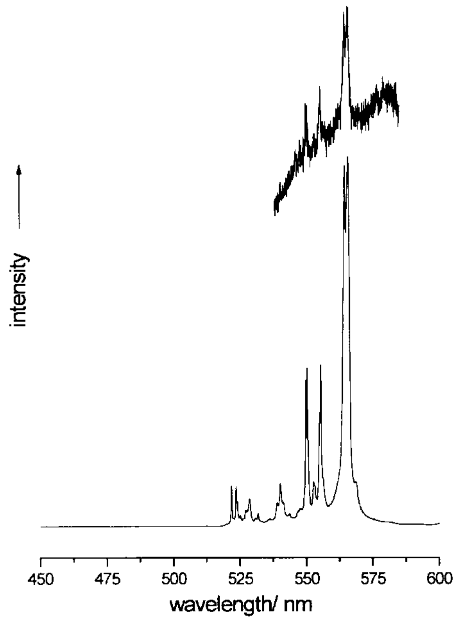

Fig. 2 Up-conversion emission from new material in glass (upper spectrum). Up-conversion emission spectrum of pure new material (TiO_2 anatase : Er^{3+}, Yb^{3+}) prepared in the absence of silica (lower spectrum).

This glass contained 0.14 mol% Er^{3+}, 0.85 mol% Yb^{3+} and 7 mol% Ti^{4+} ions as well as 88 mol% SiO_2 and 4 mol% F^- ion. The precipitate detected in the TEM was not expected to contain fluoride. This is known because the main up-conversion peak was not in the same region as that expected for ErF_3 lattice up-conversion emitters. This is shown in Fig. 3, which shows up-conversion emission from a YF_3 matrix containing Er^{3+} and Yb^{3+} ions. However the main up-conversion peak was closer to the region expected for an oxide lattice, as can be seen from Fig. 4 which shows up-conversion emission from a Y_2O_3 matrix containing Er^{3+} and Yb^{3+} ions.

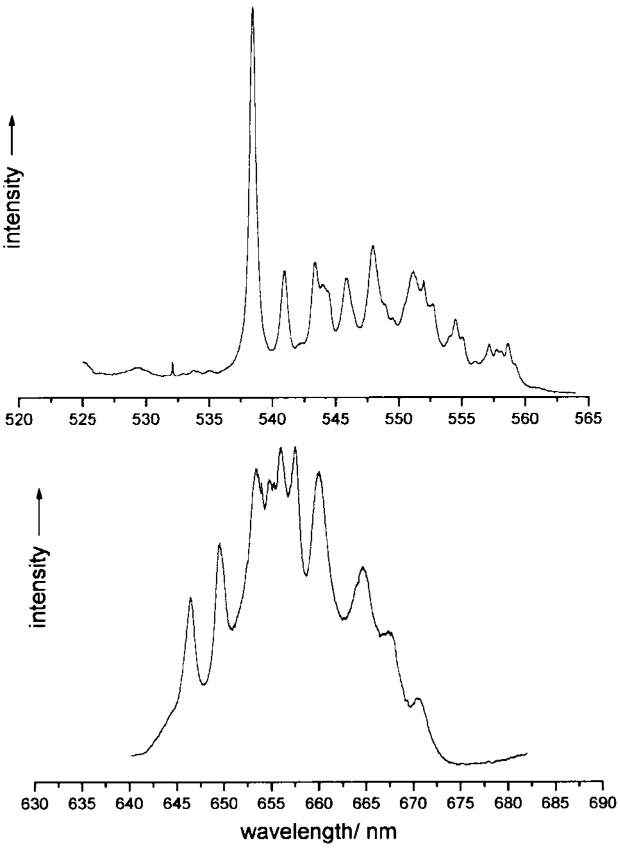

Fig. 3 Red (lower spectrum) and green (upper spectrum) up-conversion emission from Er^{3+} and Yb^{3+} co-doped YF_3 under infrared excitation ($\lambda = 974$ nm).

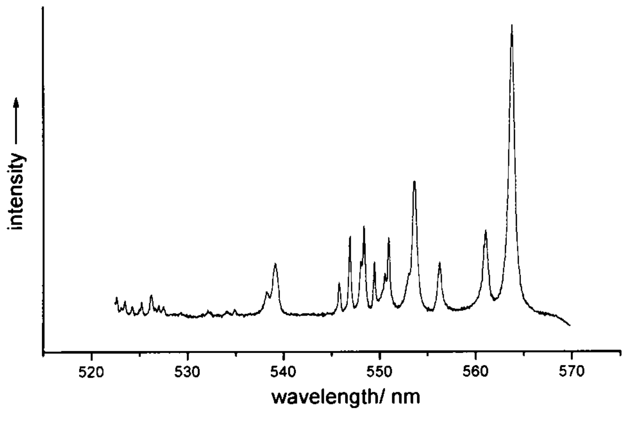

Fig. 4 Up-conversion emission from a Y_2O_3 matrix containing Er^{3+} and Yb^{3+} ions.

The up-conversion emission spectrum was obtained using a Raman spectrometer. Raman bands at 144, 392, 512 and 636 cm^{-1} (see Fig. 5) in the same spectrum also indicated the presence of crystalline anatase in the glass. The anatase phase arose from the presence of the Ti^{4+} ions in the original sol–gel solution. A recent literature report also refers to the formation of the anatase phase in the sol–gel process.[21]

The interpretation of these results suggested that preparation of a pure TiO_2 anatase material containing Er^{3+} and Yb^{3+} ions would confirm the origin of the up-conversion emission spectrum obtained from the ceramic. The anatase phase of TiO_2 co-doped with Er^{3+} and Yb^{3+} ions was prepared and identified from the positions of the Raman bands (see Fig. 6). The up-conversion emission spectrum of this material is shown in Fig. 2, and confirms that it is responsible for the up-conversion emission from the ceramic. This up-conversion emission is yellow and about one-seventh as intense as that obtained from YF_3 co-doped with Er^{3+} and Yb^{3+} ions. Converting this material by heating it to 1150 °C produced the rutile phase, evident from its Raman spectrum (see Fig. 7). The up-conversion emission from this phase was still in the yellow region, but more than two orders of magnitude weaker in intensity than that of the anatase phase (see Fig. 8).

The anatase phase also gave Stokes emission (see Fig. 6) in the same wavelength region as the Stokes emission of $YF_3 : Er^{3+}$, Yb^{3+} and $Y_2O_3 : Er^{3+}$, Yb^{3+} phosphors (see Fig. 3). The Stokes emission from the rutile phase was observed

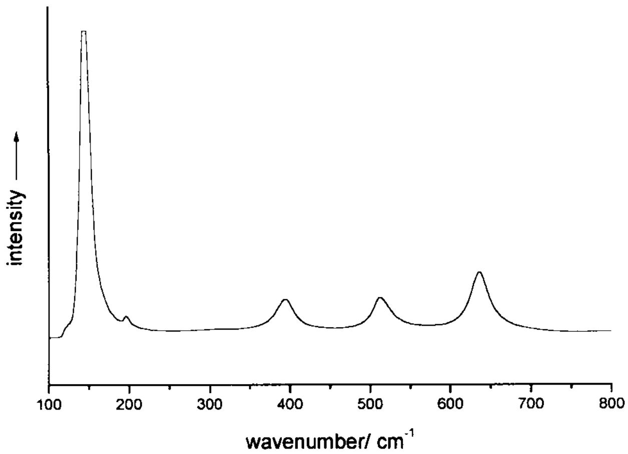

Fig. 5 Raman spectrum obtained from new material in silica glass (see Fig. 2 and text) showing bands indicative of the presence of anatase.

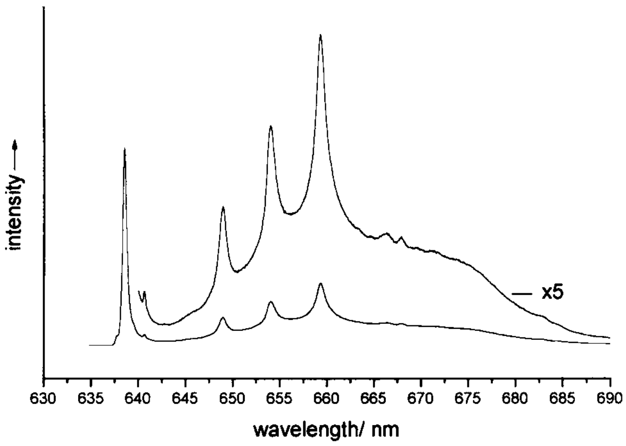

Fig. 6 Raman spectrum obtained from the pure $TiO_2:Er^{3+}$, Yb^{3+} anatase material showing the Raman bands due to anatase. The upper trace is a × 5 ordinate expansion showing the presence of an underlying Stokes emission.

as structured luminescence in the 640–700 nm region (see Fig. 7). The two intense *anti*-Stokes Raman bands at -447 and $-610\ cm^{-1}$ confirm that the titanium dioxide is in the rutile phase (see inset of Fig. 7). This Stokes emission was observed to be approximately ten times more intense than the Stokes emission from the anatase phase.

This establishes that the up-conversion emission was originating from TiO_2 based phases. Next it was decided to anneal the original glass ceramics to encourage crystal growth of these phases. Fig. 9a shows the emission from the glass ceramic which gave the emission shown in the inset of Fig. 2, after it had been annealed at 800 °C for 6 h. After this treatment the rutile phase should dominate (see TEM of the crystallites of this phase, 7–12 nm in diameter, shown in Fig. 10a). There is some residual anatase phase giving emission, which is more enhanced than that shown in the inset of Fig. 2, but the up-conversion emission originates predominantly from the rutile phase. It is noted that this up-conversion emission from the

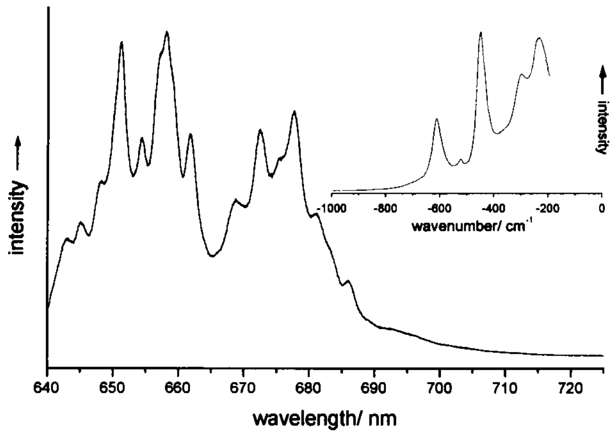

Fig. 7 Stokes emission and Raman bands of TiO_2 rutile : Er^{3+}, Yb^{3+}. The Raman spectrum in the *anti*-Stokes region is shown in the inset.

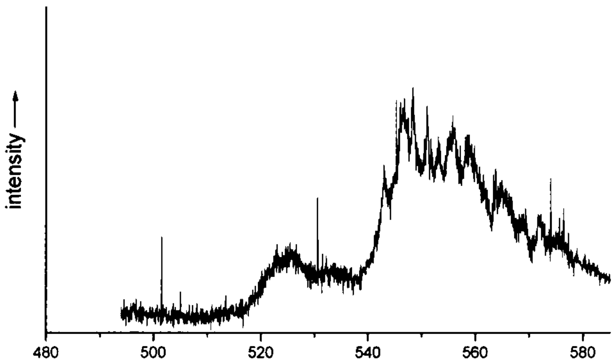

Fig. 8 Up-conversion emission from $TiO_2:Er^{3+}$, Yb^{3+} rutile. The emission intensity was less than 1/20 of that of the anatase phase.

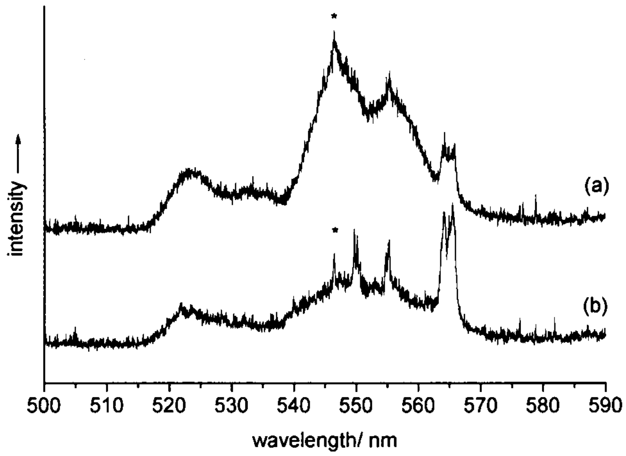

Fig. 9 Up-conversion emission from $TiO_2:Er^{3+}$, Yb^{3+} rutile/anatase. In (a) the sample was originally that which showed the up-conversion emission in the inset in Fig. 2. However for this spectrum (a) it was annealed at 800 °C for 6 h. In (b), the sample was from the same batch that formed (a), but in this case it was initially fired to 1100 °C (rather than 990 °C), then annealed at 400 °C for 12 h. The asterisks indicate the leakage of a mercury emission line from the room lights.

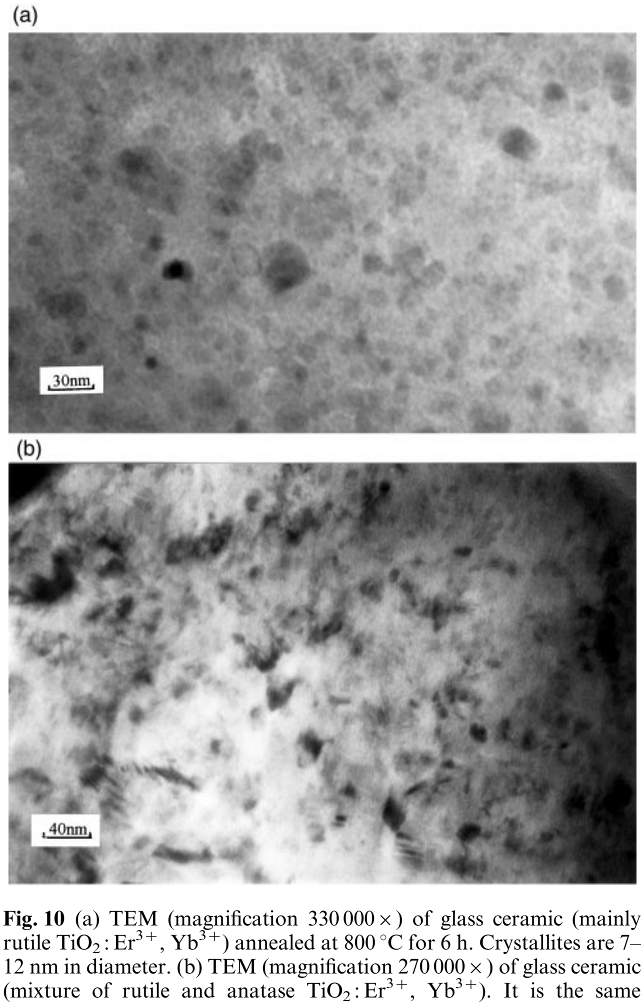

Fig. 10 (a) TEM (magnification 330 000 ×) of glass ceramic (mainly rutile $TiO_2:Er^{3+}$, Yb^{3+}) annealed at 800 °C for 6 h. Crystallites are 7–12 nm in diameter. (b) TEM (magnification 270 000 ×) of glass ceramic (mixture of rutile and anatase $TiO_2:Er^{3+}$, Yb^{3+}). It is the same material batch as that shown in (a), but fired to 1100 °C then annealed at 400 °C for 12 h. Crystallites are 8–11 nm in diameter.

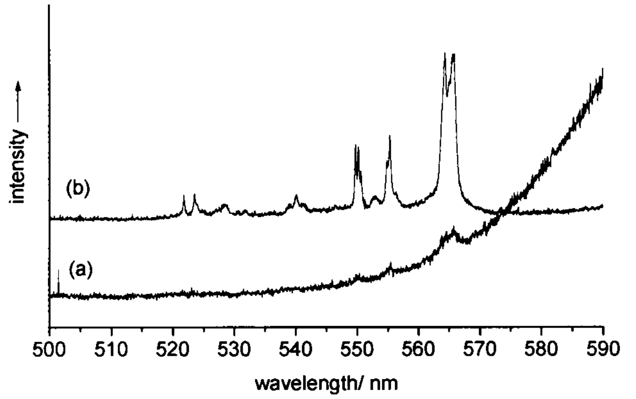

Fig. 11 Second glass ceramic containing $TiO_2:Er^{3+}$, Yb^{3+} anatase phase, (a) fired to 990 °C and (b) the same material annealed at 400 °C for 12 h. Both spectra have identical intensity scales.

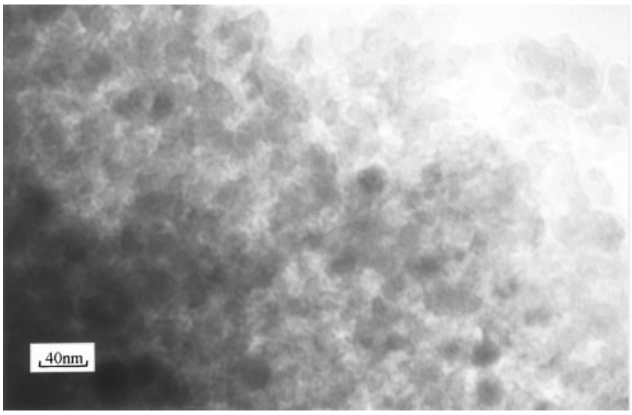

Fig. 12 TEM (magnification 270 000 ×) of a sample of the same material as used in Fig. 1, but first fired to 1100 °C then annealed at 400 °C for 12 h. The diameters of the crystallites are 9–12 nm.

rutile phase in the ceramic is of equivalent intensity to that of the parent material, but lacks some of the fine structure (see Fig. 8).

Fig. 9b shows the up-conversion spectrum of the glass ceramic prepared from the same batch that gave the emission shown in the inset of Fig. 2. This batch differs since it was fired to 1100 °C, then annealed at 400 °C for 12 h. The up-conversion emission spectrum shows the presence of some rutile phase (due to initial firing at 1100 °C), but the emission from the anatase phase is similar to that shown in Fig. 2. In Fig. 10b, the TEM of the ceramic which produced the emission shown in Fig. 9b shows that the crystallites are on average 8–11 nm in diameter. The positions of the Raman bands (in other parts of the spectrum) indicate that the phase giving the spectrum of Fig. 9b contains some anatase, whilst the emission shown in Fig. 9a was from the ceramic with residual anatase present.

Fig. 11 presents the up-conversion spectrum of the second glass ceramic containing 0.25 mol% Er^{3+}, 1.1 mol% Yb^{3+}, 4 mol% F^-, 10 mol% Ti^{4+} ions and 84.65 mol% SiO_2. Fig. 11a shows the up-conversion emission of the ceramic fired at 990 °C, but not annealed; the TEM of this uniform sample showed crystallites of 3–4 nm in diameter. Fig. 11b shows some of the material from this batch fired to 1100 °C, then annealed at 400 °C for 12 h. The up-conversion emission spectrum is now fully developed and the TEM (Fig. 1 and 12) shows that before the annealing process the crystallite diameter is 3–4 nm, whereas after annealing it is 9–12 nm. The Raman spectra of the ceramic before and after annealing only show evidence for the anatase phase.

Finally, it is noteworthy that the emission from the nanoparticles in the ceramics and the pure bulk ($TiO_2:Er^{3+}$, Yb^{3+}) anatase and rutile materials was identical.

Conclusions

In attempts to make SiO_2 up-converting glasses, ceramics were produced which contained anatase crystallites, doped with Er^{3+} and Yb^{3+} ions. The anatase material was prepared in the absence of the glass and found to be a new up-converting emitter in the yellow region of the spectrum. Surprisingly, converting this phase to the rutile phase almost destroyed the up-converting emission properties.

It was demonstrated that by controlling the annealing temperatures, ceramics could be prepared in which the desired phase, either anatase or rutile, could be increased. Moreover, ceramics containing both phases could be prepared. Furthermore it has been shown that the use of sol–gel techniques makes the production of these new ceramics facile.

To our knowledge, this is the first report of an up-converting emission phosphor which shows phase dependent emission.

The Raman spectroscopic technique is useful for rapidly identifying the crystallographic modification of titanium dioxide. Raman spectrometers can also be used in order to study up-conversion luminescence from glasses and ceramics and provide sensitive detection and good spectral resolution of visible light.

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