Luminescence of γ-radiation-induced defects in α-quartz

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Abstract
Optical transitions associated with γ-radiation-induced defects in crystalline α-quartz were investigated by photoluminescence excited by both pulsed synchrotron radiation and steady-state light. After a 10 MGy γ-dose we observed two emissions at 4.9 eV (ultraviolet band) and 2.7 eV (blue band) excitable in the range of the induced absorption band at 7.6 eV. These two luminescence bands show a different temperature dependence: the ultraviolet band becomes bright below 80 K; the blue band increases below 180 K, but drops down below 80 K. Both emissions decay in a timescale of a few ns under pulsed excitation, however the blue band could also be observed in slow recombination processes and it afterglows in about 100 s at the end of steady-state excitation. The origin of the observed luminescence bands and the comparison with optical features of oxygen-deficient centres in silica glass are discussed in the framework of different models proposed in the literature.

1. Introduction

Optical transitions of point defects play a crucial role in applications of silicon dioxide (SiO_2). In fact, just in consideration of technological aspects, the attention of many researchers was drawn to the amorphous form of SiO_2 (silica). This has led to the outlining of a composite picture of several optical bands (absorption and luminescence) which have been associated, never unambiguously, to different types of defects in silica (see review papers by Griscom [1] and Skuja [2], and references therein). On the other hand, the most common form among the SiO_2 crystalline forms, α-quartz, has attracted interest mainly to speculate on defect

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models because α-quartz and silica have the same short range order of corner sharing SiO_4 tetrahedra. However, as critically outlined in [2], the glassy state, besides introducing isotropy and inhomogeneity, provides new structural degrees of freedom that allow the formation of defects peculiar to the amorphous form.

Observation of optical features only related to crystal-like defects has been until now difficult, because the heavy irradiation (neutrons, protons) that is required to induce defects in pure α-quartz produces amorphous micro-regions that could accommodate defects peculiar to silica [2]. In this framework, there is an open question regarding whether photoluminescence (PL) follows the optical absorption (OA) at 7.6 eV, also called the E-band [3], observed in both neutron irradiated α-quartz [4] and in irradiated or oxygen deficient silica [5, 6]. On the one hand, several experiments on silica samples have considered in detail the temperature dependence and the kinetics features of a fast emission band at 4.4 eV, the lifetime of $\sim$2 ns, associated with the E-band [7–11]. On the other hand, the little data available for the crystalline SiO_2 limit show that excitation at 7.6 eV of neutron-irradiated α-quartz produces an emission band centred around 4.7–4.9 eV [12, 13], also observed by cathodoluminescence (CL) measurements [14, 15], but a careful examination of this luminescence activity has not yet been achieved. This puzzling picture linking the absorption at 7.6 eV with the emissions in quartz and silica is further complicated by the fact that two different approaches exist for modelling the E-band attributed to an oxygen deficient centre of first type or ODC(I) [2]. One hypothesis ascribes the 7.6 eV transition to the neutral oxygen vacancy, $\equiv$Si–Si$\equiv$ (the $\equiv$ symbol indicates three bonds to oxygen atoms), a defect that can be present both in crystalline and in amorphous SiO_2 [16–20]. In a second approach, the OA at 7.6 eV is related to localized states in a cluster of a non-tetrahedrally coordinated network embedded in the structure of glass [21, 22].

In this paper, we deal with the experimental investigation of the optical features associated with defects in α-quartz induced by γ-ray irradiation. In fact, γ-rays are expected to be less effective than neutrons in causing heavy damage with the appearance of an amorphous phase island. Our experiments are mainly focused on the spectral and kinetic properties of the luminescence activity and their temperature dependence under vacuum-ultraviolet (UV) excitation, aiming to clarify the de-excitation processes following the 7.6 eV absorption.

2. Experiments

We investigated pure synthetic crystalline α-quartz specimens, supplied by Sawyer, both as grown and after γ-ray irradiation with a dose of 10 MGy (SiO_2). The samples have sizes $8 \times 6 \times 1$ mm^3 with the larger surfaces optically polished.

Vacuum-UV optical absorption spectra were performed at room temperature using a spectrophotometer (ACTON SP 150) fluxed with nitrogen gas (equipment in Palermo, Italy). The light source was provided by a deuterium lamp using a MgF_2 window and was selected with a monochromator equipped with a $Al + MgF_2$ coated grating with 1200 grooves mm^{-1} and 150 nm blaze. The transmitted light was detected by a photomultiplier (EMI 9635QB) with a bi-alkali cathode. To avoid collection of luminescence light from the sample, a second monochromator, working synchronously with the excitation one, was placed before the detection system.

Steady-state PL measurements were obtained with a double vacuum monochromator spectrometer under continuous excitation with a hydrogen discharge source and detection by a grating monochromator (MDR-23) and a photomultiplier (FEU-71) with silica glass window (equipment in Tartu, Estonia). The samples were kept in a helium cryostat which allowed changing the temperature from 10 up to 290 K. Time decay after continuous excitation
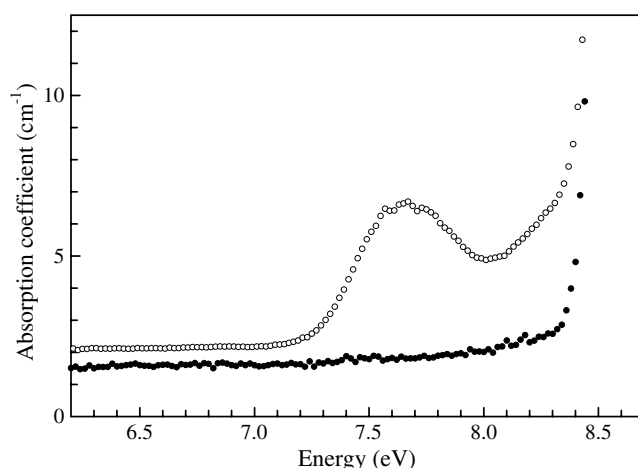
Figure 1. Vacuum-UV absorption spectra detected at $T = 290$ K in samples of crystalline α-quartz γ-irradiated with a dose of 10 MGy (empty symbol) and not irradiated (full symbol).

(afterglow) was recorded by measuring the PL signal, selected by optical band-pass filters, on increasing the delay, by steps from 0.2 to 150 s, after shutting down the source.

Time resolved PL was investigated with pulsed excitation light, in the range from 4.5 to 9.0 eV, using the synchrotron radiation (SR) at the SUPERLUMI station on the I-beamline of HASYLAB at DESY (Hamburg). The emitted light was analysed by a 0.5 m monochromator (Czerny–Turner mounting) and detected by a photomultiplier (Hamamatsu R2059) over a time window of 21 ns correlated with the arrival of SR pulses. The excitation spectra were corrected for the spectral efficiency of the source and excitation monochromator. The transient time decay was measured by using 1024 channels for scanning the time interval of 192 ns between adjacent pulses, with a pulse width of 130 ps. The temperature could be varied from 10 up to 290 K using a sample chamber with a continuous helium-flow cryostat.

3. Results

Figure 1 shows the OA spectra detected in the as grown and in the 10 MGy γ-irradiated quartz samples. The comparison between the two spectra evidences a band centred around 7.6 eV with amplitude of $\sim$3 cm^{-1}, induced by γ-rays. It is worth noting that the peak nearly coincides with that reported for the E-band in silica [5, 23] and in neutron irradiated quartz [4].

The PL signal excited within the E band could be detected only in the low temperature range. The luminescence excited by SR photons at 7.6 eV is shown in figure 2 as detected at $T = 17.5$ K. The emission spectrum consists of two bands whose profiles are well described by Gaussian line shapes: one centred at 4.93 ± 0.01 eV with full width at half maximum (FWHM) = 0.48 ± 0.02 eV (UV-band), the other peaked at 2.71 ± 0.02 eV with FWHM = 0.46 ± 0.03 eV (blue-band). Both PL bands have a common excitation profile peaked at 7.60 ± 0.01 eV, slightly asymmetric with FWHM = 0.28 ± 0.02 eV.

The effects of varying the temperature on these two emissions were investigated by SR and steady-state measurements. In figure 3, we show the PL spectra acquired at different temperatures under SR excitation at 7.6 eV. The UV-emission quenches on increasing the temperature up to $\sim$80 K; in this temperature interval its shape can be fitted by a Gaussian function whose peak shifts from 4.93 ± 0.01 to 4.89 ± 0.02 eV and whose FWHM increases
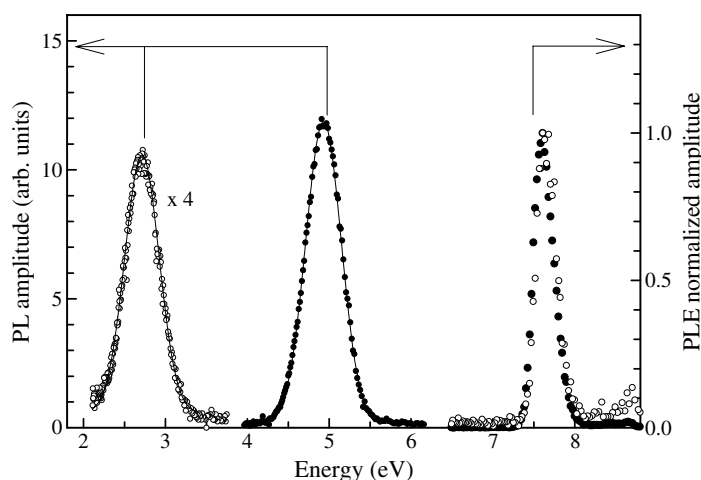
Figure 2. PL activity detected under synchrotron radiation excitation at $T = 17.5$ K in the γ-irradiated α-quartz. The emissions peaked at $\sim$2.7 eV (empty symbol) and $\sim$4.9 eV (full symbol) are shown together with the corresponding excitation profiles normalized to their maximum amplitude. Solid lines plot the Gaussian curves that best fit the two emission bands.

from 0.48 ± 0.02 to 0.51 ± 0.03 eV. As regards the blue-band, its quenching requires higher temperatures, larger than $\sim$80 K, while its profile keeps the Gaussian shape, always centred at 2.71 ± 0.01 eV with a FWHM increasing from 0.46 ± 0.03 up to 0.64 ± 0.04 eV.

In figure 4(a) we compare the temperature dependence of the amplitudes of the 4.9 and 2.7 eV emission bands detected under continuous excitation at 7.6 eV. Whereas the former drops down monotonically above $\sim$30 K, the second exhibits a composite behaviour, it rises up to $\sim$80 K and then it decreases. To quantify the thermal quenching of the two PL bands, in figure 4(b) their amplitudes with temperature are plotted in accordance with the law [24]:

$$I(T) = \frac{I_0}{1 + A \exp(-E/kT)} \tag{1}$$

where I_0 is the maximum amplitude while A and E represent the pre-exponential factor and the activation energy in the Arrhenius function accounting for the non-radiative processes which lower the luminescence quantum yield. The decrease of the 4.9 eV emission is analysed in the range 40–120 K and, from the slope of the curve, we get the activation energy $E = 28 \pm 2$ meV. At variance, the quenching of the 2.7 eV mainly occurs over a higher temperature range, 85–190 K, with $E = 68 \pm 4$ meV.

The time decay features of these two PL bands are reported in figure 5 as detected at $T = 17.5$ K under SR pulsed excitation at 7.6 eV. The two curves, referred to the amplitude of the emissions at 4.9 and 2.7 eV, respectively, are well described by an exponential decay over almost two orders of magnitude, occurring in a timescale of a few nanoseconds. By a best fit procedure with the function $\exp(-t/\tau)$, we get the lifetime $\tau = 1.0 \pm 0.1$ ns for the 4.9 eV PL and $\tau = 3.6 \pm 0.1$ ns for the 2.7 eV emission.

The PL kinetics was also measured after cut off of continuous excitation at 7.6 eV with the hydrogen discharge source. The decay of the 2.7 eV emission, detected at $T = 60$ K where its amplitude is close to the maximum, is reported in figure 6 and shows that this luminescence lasts for $\sim$100 s. The decay curve is characterized by a power law: the initial slope is $\sim(-2)$ which is consistent with bimolecular recombination processes of closest pairs, whereas the slope $\sim(-1)$ in the range 10–100 s may be related to tunnelling recombination of more distant
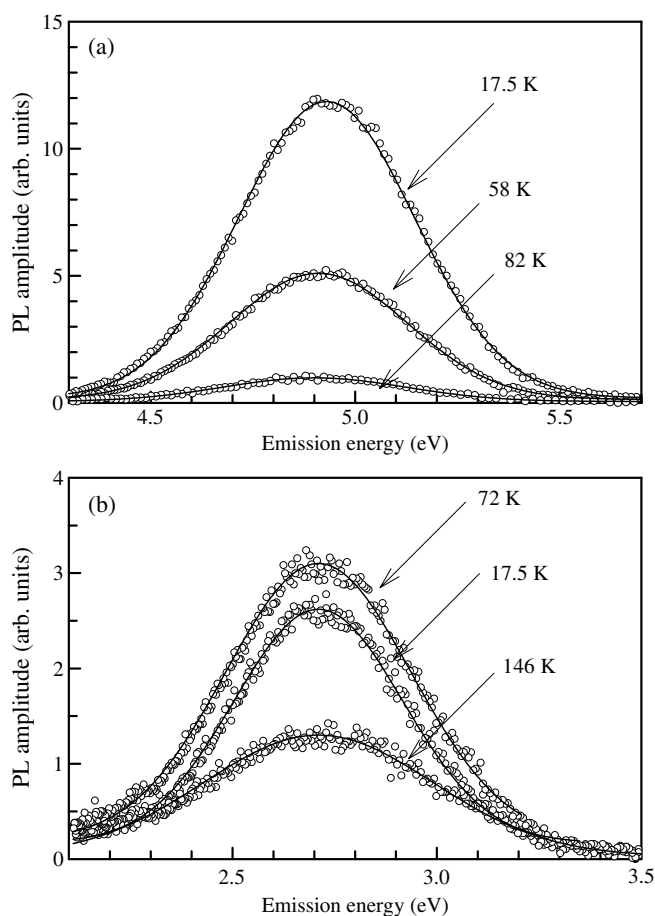
Figure 3. Emission spectra showing the UV (a) and Blue band (b) excited at 7.6 eV with synchrotron radiation at different temperatures. Solid lines plot the Gaussian curves that best fit the emission profiles.

pairs [21, 25]. At variance, as shown in the same figure, no luminescence at 4.9 eV could be observed in afterglow measurements.

4. Discussion

The optical properties of the investigated γ-ray irradiated α-quartz are characterized by two PL bands centred at 2.7 eV (blue) and at 4.9 eV (UV), both excited within the induced absorption band at 7.6 eV and decaying in a few nanoseconds. The comparison of these results with previous experimental and theoretical studies on the luminescence in crystalline and amorphous SiO$_2$ allows us to address the problem of the structure of the γ-induced luminescence defect in quartz.

Pacchioni and Ieranò [19], through *ab initio* calculations, found that an emission at 4.3 eV, with a lifetime of 3 ns, is associated with the inverse singlet to singlet transition of the 7.6 eV absorption at the neutral oxygen vacancy. Alternatively, the observation in silica of a PL emission at 4.4 eV excited at 7.6 eV has been associated with a conversion process of the
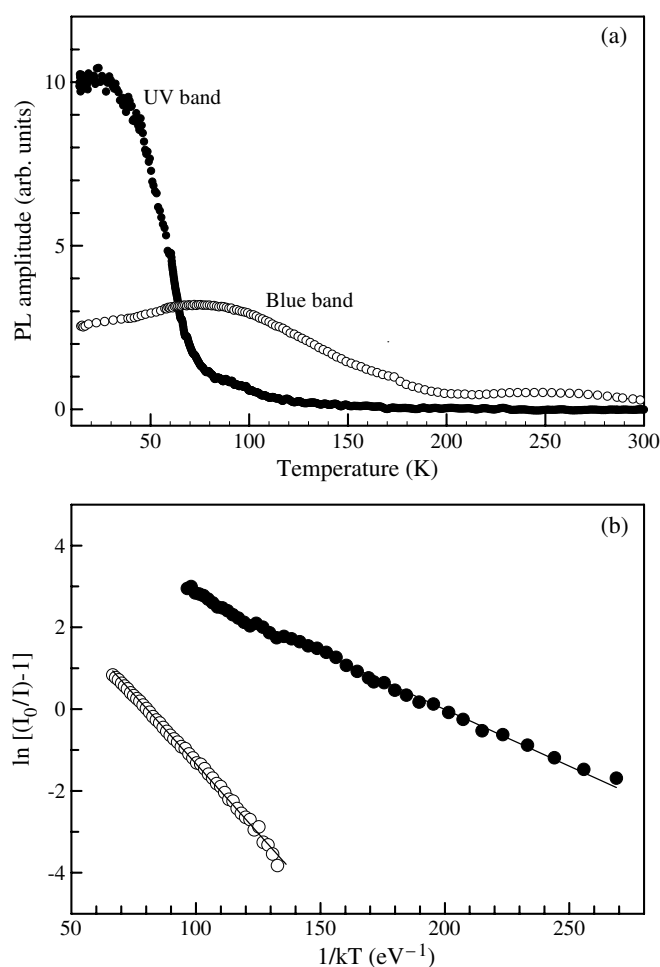
Figure 4. Temperature dependence of the intensity of UV (full symbol) and blue (empty symbol) luminescence bands detected in the γ-irradiated α-quartz under steady-state excitation at 7.6 eV (a). Plot of temperature dependences in term of the equation (1) in the text; solid lines represent the best fit functions whose slope gives the activation energy E (b).

neutral oxygen vacancy into a metastable Si lone pair centre [2, 11, 26, 27]. It is worth noting that this latter defect exists also in a stable configuration consisting in a Si atom bonded with two oxygen atoms, $=Si^{\bullet\bullet}$ [28], which, besides the 4.4 eV PL, emits a 2.7 eV band with lifetime of $\sim$10 ms [29], both excitable at 5.0 and 6.9 eV [29–31]. In the framework of this model, the suggestion that both the 4.9 and 2.7 eV bands arise from the corresponding defect in α-quartz is in disagreement with the following points:

 (i) lack of excitation bands around 5.0 and 6.9 eV associated with $=Si^{\bullet\bullet}$;
 (ii) significant difference in the decay time constant of the PL at 2.7 eV, from which it follows that the blue band in crystalline SiO_2 cannot be associated with the forbidden triplet to singlet transition occurring in silica [29].

The absence of correlation between our PL data with the Si lone pair centre is consistent with the hypothesis that this defect cannot exist in the crystal lattice of the quartz due to the steric
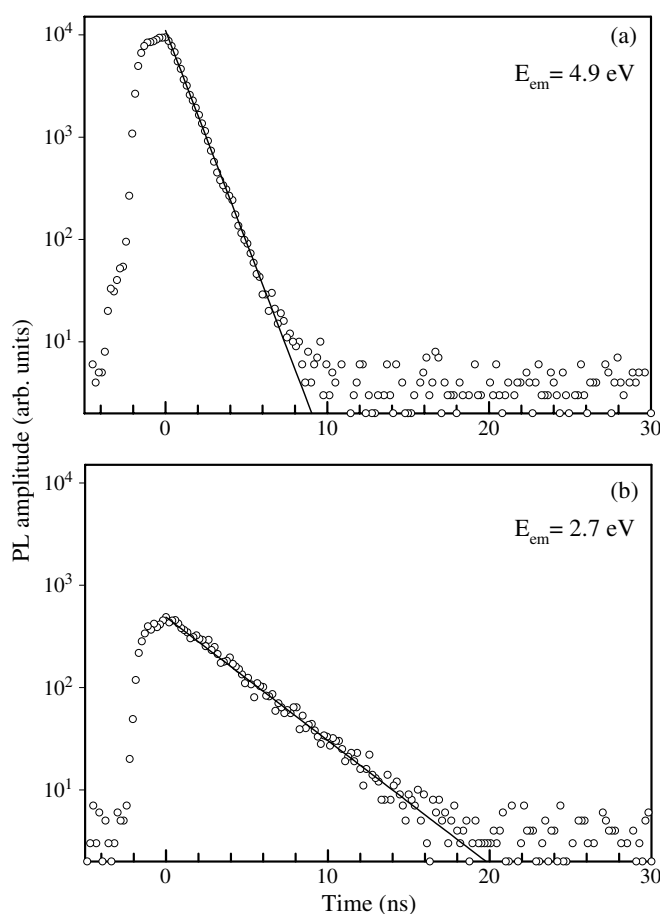
Figure 5. Decay of the PL emission at 4.9 eV (a) and 2.7 eV (b) detected at $T = 17.5$ K under excitation at 7.6 eV with SR pulsed light. Solid lines plot the exponential functions, $\exp(-t/\tau)$, with the time decay τ determined by best fitting.

limitations, but it is peculiar to the glassy state [2]. The lack of stable $=Si^{\bullet\bullet}$ in crystalline SiO_2 leads us to suppose that it appears upon 7.6 eV excitation as a metastable defect by a process analogous to that hypothesized for silica [2, 11, 26, 27]. So, the fast 4.9 eV emission in quartz would be the counterpart of the PL at 4.4 eV in silica. In this respect, the comparison of the present γ-irradiated quartz with a previously investigated silica sample [11] having an OA at 7.6 eV with an amplitude of $\sim$6 cm^{-1} shows that the quenching of the 4.4 eV emission in silica could be fitted by the equation (1) with an activation barrier $E \approx 29$ meV, in close agreement with the value here found for the 4.9 eV emission in quartz. However, under 7.6 eV excitation at $T = 17.5$ K, the relative yield of the 4.9 eV emission in α-quartz is higher by a factor $\sim$20 than the 4.4 eV emission in silica.

The models discussed above do not account for the blue luminescence, which shares the excitation at 7.6 eV with the UV emission, so that it cannot be associated with any transition occurring in the ODC of silica. We acknowledge that a fast PL band centred at $\sim$2.7 eV, decaying in a few nanoseconds, has been found in silica films consisting in buried oxide in Si prepared from the separation by implantation of oxygen (SIMOX) [32]. This PL
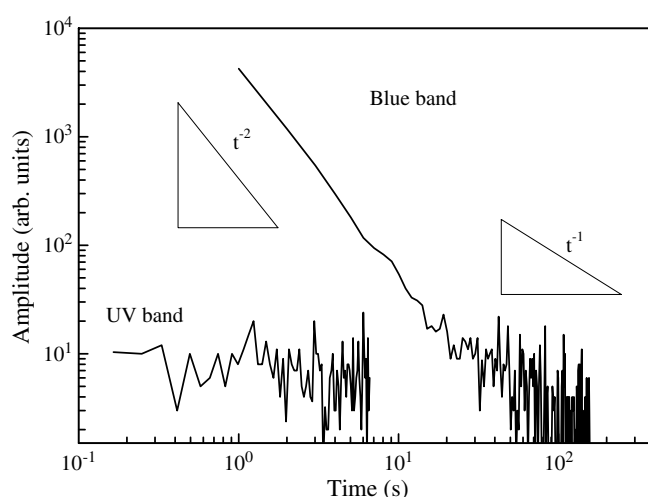
Figure 6. Afterglow of the blue and UV bands detected at $T = 60$ K at the end of continuous excitation with 7.6 eV photons. The slopes proportional to t^{-2} and t^{-1} are also indicated.

has an excitation profile peaked at 5.0 eV, different from that of the isoenergetic emission observed in irradiated α-quartz. Nevertheless, the mechanism proposed for the luminescence in SIMOX [32], involving defects at the interface between Si clusters and SiO_2, could apply to the irradiated α-quartz. In fact, analogously with particle irradiation [33], damaged regions may exist as an effect of γ-ray irradiation and their interfaces with the host crystalline matrix may accommodate defects. Under the hypothesis that these interface defects are distinct from the ODC absorbing at 7.6 eV, they could originate the fast blue luminescence by an excitation transfer. Also, these defects could play the role of traps which can be activated by 7.6 eV light and, by recombination, give rise to the afterglow blue luminescence.

5. Conclusions

The 10 MGy γ-irradiation of a pure synthetic crystalline α-quartz sample induces an absorption band at 7.6 eV. The photo-excitation in the range of this band at low temperature originates two luminescence bands at 2.7 eV (blue) and 4.9 eV (UV) that decay in the nanoseconds timescale. In analogy with silica glass, we relate the UV emission to oxygen deficiency induced by irradiation, the removal of oxygen being part of the radiation damage. The blue luminescence can be associated with structure peculiar to irradiated α-quartz as the interface between damaged and crystalline SiO_2 matrix.

Acknowledgments

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