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Laser-induced time-resolved luminescence of rare-earth elements in scheelite

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ABSTRACT

Natural and synthetic scheelite are investigated by time-resolved laser-induced luminescence to detect and ascribe various luminescence lines to a variety of *REE*. The selectivity of detection is possible by using different time delays after excitation, different gate widths and different excitation wavenumbers and allowed to detect *REE* in samples where they are hidden by intrinsic luminescence and not visible in the steady-state spectra as well as by cathodoluminescence. Luminescence of Pr^{3+}, Er^{3+} and Tm^{3+} are detected even with low concentrations and in the presence of Tb^{3+}, Dy^{3+} and Sm^{3+}. Luminescence of Ho^{3+} and Yb^{3+} is firstly detected in natural scheelites and luminescence of Eu^{2+} and Ce^{3+} is preliminary suggested.

KEYWORDS: scheelite, time-resolved luminescence, *REE*.

Introduction

SCHEELITE, is a calcium tungstate, $CaWO_4$, with a tetragonal structure ($I4_1/a$) consisting of irregular tetrahedra WO_4 in which edges are shared with CaO_8 polyedra. In nature, *REE* can easily substitute for Ca, becoming luminescent centres in such a crystallographic environment. The method of luminescent spectroscopy is widely used to study the rare-earth element distributions in natural scheelites. Nevertheless in many cases its possibilities are limited because scheelite is characterized by broad luminescent bands of intrinsic WO_4-groups and impurity MoO_4-groups (Taraschan, 1978; Gaft, 1989). Such strong bands prevent in many cases the detection of lines of rare-earth elements, especially Tm, Er and Ho, which have weak luminescence in the corresponding spectral range.

The thermal X-ray excited luminescence enables a solution for this problem to be found in certain cases, using the fact that while the intensity of broad-band luminescence quickly decreases with increasing temperature, the intensities of the *REE* lines remains nearly constant (Uspensky, 1998). Nevertheless, besides the fact that it is preferential to study unchanged samples, the lines of certain *REE* may be hidden by the stronger luminescence of others. For example, luminescence of Pr^{3+} is difficult to detect because its radioactive transitions are hidden by the lines of Sm^{3+}, Dy^{3+} and Nd^{3+}; the luminescence of Tm^{3+} is concealed by Tb^{3+} and so on.

The purpose of this work is to examine scheelite by laser-induced time-resolved luminescence which allows differentiation between luminescence centres with emission spectra in the same spectral range but with different decay times. The method involves recording the intensity in a specific time gate at a given delay after the excitation pulse where both the delay and the gate-width have to be carefully chosen. Such a method proved to be extremely effective for the investigation of natural apatite luminescence (Gaft *et al.*, 1997). We selected the scheelites with dominant broad-band luminescence under steady-state excitation (photons or electrons) where *REE* are not detected. Time-resolved spectroscopy allows the detection of previously unseen centres hidden under broad-band luminescence and the differentiation of separate rare-earth elements.

Experimental methods

Spectroscopy

The luminescence spectra were investigated under excimer UV (308 nm), nitrogen (337 nm) and dye-pulsed lasers (357, 460 and 570 nm) excitations which deliver pulses of 10 ns duration and 0.1 cm^{-1} spectral width. The pulse energy has been maintained to about 80 and 10 mJ for excimer and dye lasers, respectively. The spectra observed at the geometry of 90° were analysed by INSTASPEC equipment enabling time-resolving spectra acquisition with the following facilities: delay times and strobe pulse duration 20 ns–9 ms, spectral detection range 300–900 nm (1200 channels, spectral resolution 0.5–1 nm, gratings with 300 and 600 lines/mm), detector type — intensified CCD matrix. The system is combined with an optical microscope enabling spectra acquisition on a micrometer scale.

Such manipulation permits recording of the emission during specific gates (delay and gate-width) corresponding to short, intermediate and long decay luminescence and thus avoiding the overlapping of the emission produced from different centres without any pick deconvolution.

The steady-state luminescence in the range of 900–1600 nm was detected by a Ge-detector. The steady-state cathodoluminescence spectra were recorded with a CL spectrometer on a Jeol JSM-840 scanning electron microscope. The recording system consists of a parabolic mirror, a silica window allowing the passage of UV emission, a Jobin-Yvon H-10 spectrometer and a Hamamtsu R636 photomultiplier, which allows detection from 200 to 900 nm.

The spectra were corrected according to the spectral functions of the equipment.

Natural specimens

Two natural samples were selected from two different types of tungstate occurrences, pegmatitic and lode deposits.

Scheelite ZRK1 of yellow and greenish-yellow colour (Zeriken, Transbaikalia, Russia) is situated in granites of molybdenum pegmatitic deposit and forms irregular occurrences (0.5 × 0.5–3.0 × 3.0 cm). Sometimes the plates of molybdenite are situated inside scheelite. It contains 10–12 wt.% Mo and is characterized by visual luminescence of a yellow colour under UV-lamp excitation.

Scheelite FRS-16 of light brownish-yellow luminescent colour (Golden Chest mine, Vein Gold deposit, Idaho, USA) is situated in quartz veins with pyrite, arsenopyrite and free gold (lode deposit). It contains 0.07–0.1 wt.% Mo and is characterized by the blue colour of visual luminescence under UV-lamp excitation.

Synthetic samples

For the correct interpretation of all the lines of rare-earth elements, synthetic scheelite standards doped with individual REE^{3+} were prepared. Stoichiometric mixtures of $Na_2WO_4 \cdot 2H_2O$ and $CaCl_2$, together with the *REE* chloride of interest, were kept for 2 hours at 900°C in open quartz test-tubes filled with molten NaCl, and then were slowly cooled for 20 hours. After washing with distilled water, colourless crystals of scheelite were obtained, 0.01–0.5 mm in size.

Results

Figure 1 represents laser-induced luminescence spectra recorded from pure artificial scheelite activated by *REE* which have luminescent lines connected with electron transitions from the same excited level: $Dy^{3+}-{}^4F_{9/2}$, $Eu^{3+}-{}^5D_0$, $Ho^{3+}-{}^5S_2$, $Sm^{3+}-{}^4G_{5/2}$ (Table 1). Consequently, the spectra are not changed with delay time and excitation energy and all luminescence lines of Eu^{3+} are characterized by decay time of $\approx$ 600 μs, Sm^{3+} — 400 μs, Dy^{3+} — 100 μs and Ho^{3+} — 5 μs. Luminescent lines of Er^{3+} are connected with different excited levels, ${}^2P_{3/2}$ and ${}^4S_{3/2}$ (Table 1), but they have close decay times of $\approx$ 50 μs which is consistent with the temporal characteristics of Er^{3+} in other lattices (Reisfeld and Jorgensen, 1978). Furthermore, the broad emission of WO_4 is still present under the specific transition of Er^{3+}, Ho^{3+} and Tm^{3+} (Fig. 1).

Luminescence of Pr^{3+} was recorded with different delays (0 ns, 5 μs, 100 μs and 500 μs) under 337 nm excitation (Fig. 2). The spectra reveal that the emission lines have different decay times, namely, the lines at 490 and 650 nm have very short decay components (τ = 1 μs) while the line at 606 nm has a longer one (τ = 5 μs).

The same situation takes place in Tb^{3+} recorded after 0 ns, 1 ms, 2 ms and 4 ms under 337 nm

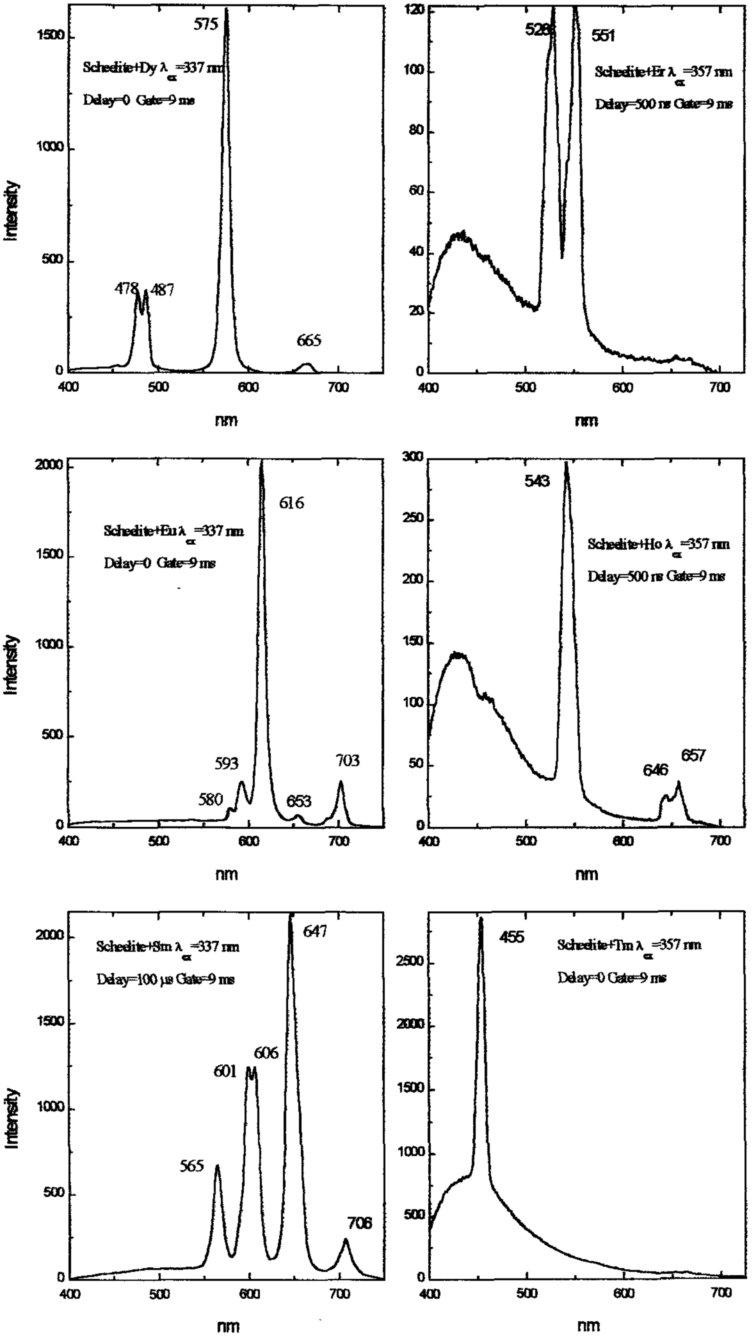

FIG. 1. Laser-induced time-resolved luminescence spectra of artificial scheelite activated by different *REE*.

excitation. The lines at 436 and 414 nm have τ = 375 µs whereas the lines at 546 and 489 nm are characterized by a very long time delay (τ = 2.4 ms; Fig. 3).

Luminescence of Tm^{3+} recorded under two different excitation states (337 and 357 nm) without any delay, 50 µs and 25 µs respectively (Fig. 4). Without any delay the emission from a

TABLE 1. Characteristic lines of rare-earths in laser-induced luminescence of natural scheelite

Centre	λ_{lum}, nm	λ_{ex}, nm	τ, μs	Transition
Pr^{3+}	489	337	1	$^3P_0 \rightarrow {}^3H_4$
	606		5	$^1D_2 \rightarrow {}^3H_4$
	652		1	$^3P_0 \rightarrow {}^3F_2$
	1054		5	$^1D_2 \rightarrow {}^3F_4$
Nd^{3+}	894	337	175	$^4F_{3/2} \rightarrow {}^4I_{9/2}$
	1063		175	$^4F_{3/2} \rightarrow {}^4I_{11/2}$
	1335		175	$^4F_{3/2} \rightarrow {}^4I_{13/2}$
Sm^{3+}	565	337	400	$^4G_{5/2} \rightarrow {}^6H_{5/2}$
	601,606		400	$^4G_{5/2} \rightarrow {}^6H_{7/2}$
	647		400	$^4G_{5/2} \rightarrow {}^6H_{9/2}$
Eu^{3+}	616	308	600	$^5D_0 \rightarrow {}^7F_2$
Tb^{3+}	414	337	375	$^5D_3 \rightarrow {}^7F_5$
	436		375	$^5D_3 \rightarrow {}^7F_4$
	545		2400	$^5D_4 \rightarrow {}^7F_5$
Dy^{3+}	478, 487	337	100	$^4F_{9/2} \rightarrow {}^6H_{15/2}$
	575		100	$^4F_{9/2} \rightarrow {}^6H_{13/2}$
Ho^{3+}	543	357	5	$^5S_2 \rightarrow {}^5I_8$
Er^{3+}	528	357	50	$^2P_{3/2} \rightarrow {}^4I_{9/2}$
	551		50	$^4S_{3/2} \rightarrow {}^4I_{15/2}$
Tm^{3+}	455	357	5	$^1D_2 \rightarrow {}^3H_4$
	475	337	125	$^1G_4 \rightarrow {}^3H_6$
Yb^{3+}	1008	337	3000	$^2F_{5/2} \rightarrow {}^2F_{7/2}$

tungstate centre is present while after 25 μs it is not recorded any more. The line at 474 nm has τ = 125 μs, while the line at 455 nm is characterized by a much shorter τ of 5 μs.

The reason for these differing decay components (τ) is that the luminescent lines of Pr^{3+}, Tm^{3+} and Tb^{3+} are connected with electron transitions from different excited levels: Pr^{3+}–$^3P_0$ and $^1D_2$, Tm^{3+}–$^1D_2$ and $^1D_4$ and Tb^{3+}–$^5D_3$ and $^5D_4$ (Table 1). Different decay times from these levels are evidently connected with nonradioactive relaxation due to the presence of high frequency vibrations in the lattice (Reisfeld and Jorgensen, 1978).

We selected the natural scheelite ZRK1 with broad-band cathodoluminescence (Fig. 5*a*). In the spectra of natural samples with 337 nm excitation, the previously hidden lines at 414 and 436 nm permit identification of Tb^{3+} (Fig. 5*c*). The line at 575 nm belongs to Dy^{3+} and enables its confident identification. The doublet at 478 and 487 nm is also a characteristic of Dy^{3+} (Fig. 5*c*), and it remains after long delays when the luminescence of Dy^{3+} is already quenched. This is supported by the fact that the strongest line of Dy^{3+} at 575 nm is absent (Fig. 5*c,d*). The luminescence in this spectral region is also a characteristic of Tm^{3+}, Tb^{3+} and Pr^{3+} (Figs 2–4). The corresponding luminescence of Tm^{3+} and Pr^{3+} is short-lived and may not be responsible for the lines with long delay times. Thus the lines may be connected with Tb^{3+} when they have very long decay times.

The line at 607 nm is strong at short delay times whilst at longer times its relative intensity is reduced and a transformation to a doublet at 600 and 608 nm takes place (Fig. 5*b,d*). This line with a relatively short decay is characteristic of the luminescence spectrum of Pr^{3+} (Fig. 2) and may be used for its identification. The line at 648 nm, the doublet at 600 and 608 nm and the line at 567 nm which dominate the spectrum after a long delay time are a result of long-lived transitions in Sm^{3+} (Fig. 1).

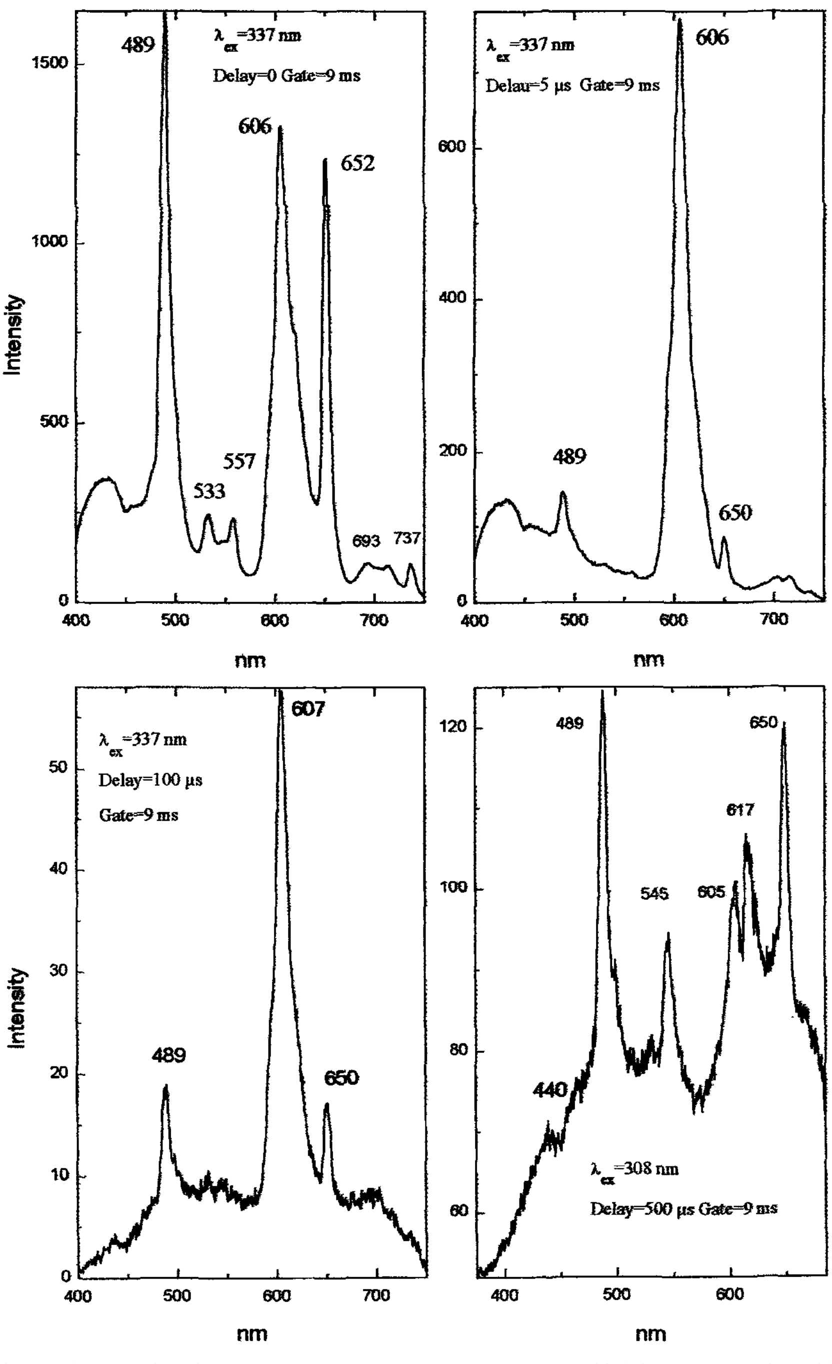

FIG. 2. Laser-induced time-resolved luminescence spectra of artificial scheelite activated by Pr.

The lines of Er^{3+}, Tm^{3+} and Ho^{3+} are difficult to point out under 337 nm excitation because they have short decay times which are comparable with the decay of broad-band luminescence at the same spectral region. This problem was solved by using a dye-laser with 357 nm

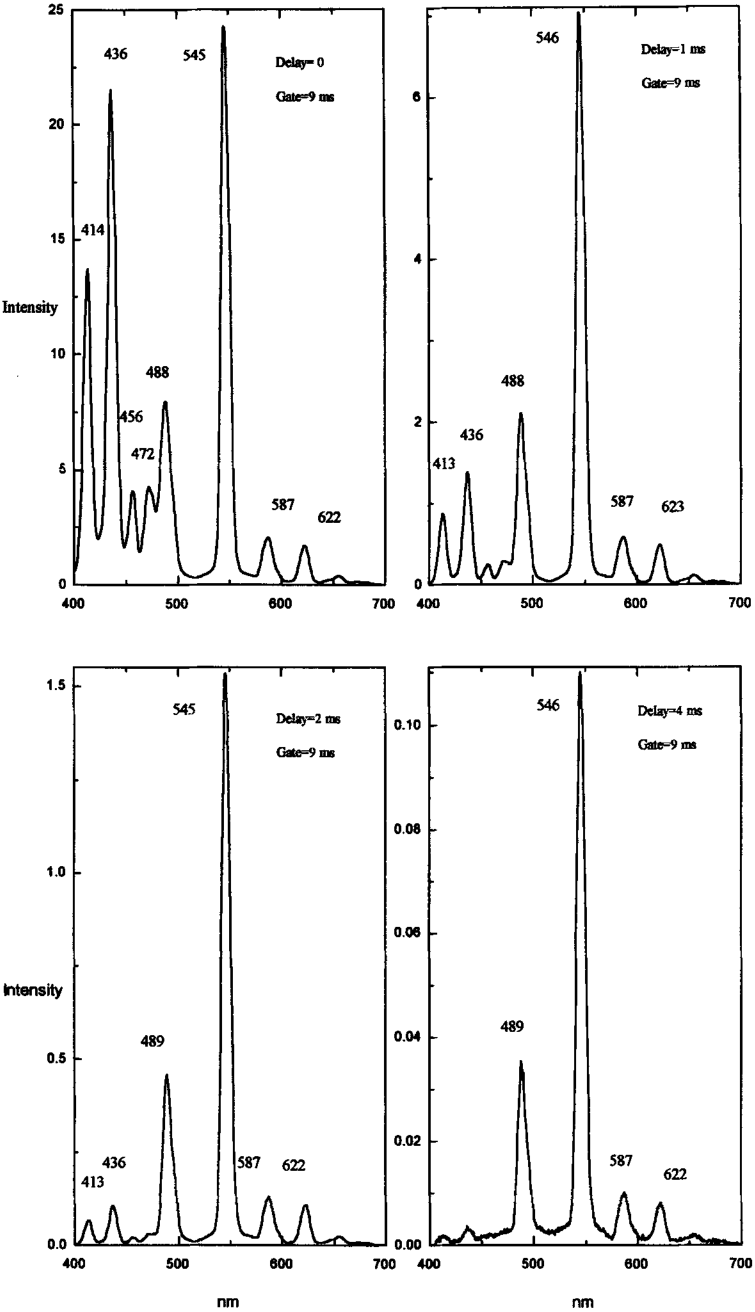

FIG. 3. Laser-induced time-resolved luminescence spectra of artificial scheelite activated by Tb (λ_{ex} = 337 nm).

excitation which is effective for *REE* but is not suitable for the excitation of the WO_4-centre (Fig. 6). These lines of *REE* are most clearly seen with a narrower gate-width when the luminescence of short-lived centres dominates. The characteristic lines of Er^{3+} at 527 and

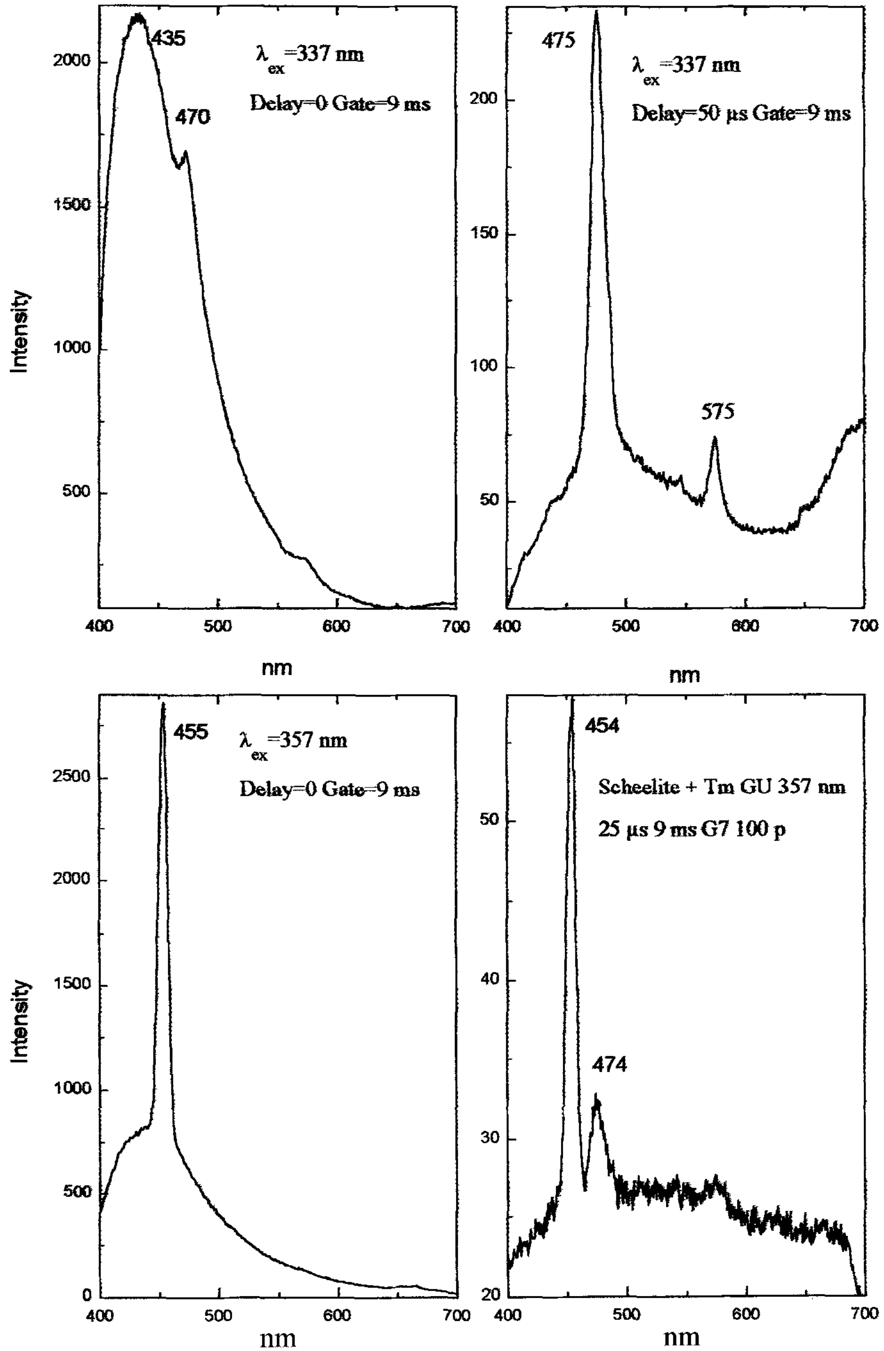

FIG. 4. Laser-induced time-resolved luminescence spectra of artificial scheelite activated by Tm.

551 nm, Tm^{3+} at 453 nm and Ho^{3+} at 542 nm are clearly seen.

Luminescence spectra of scheelites enriched by Eu are represented in Fig. 7. The well-known

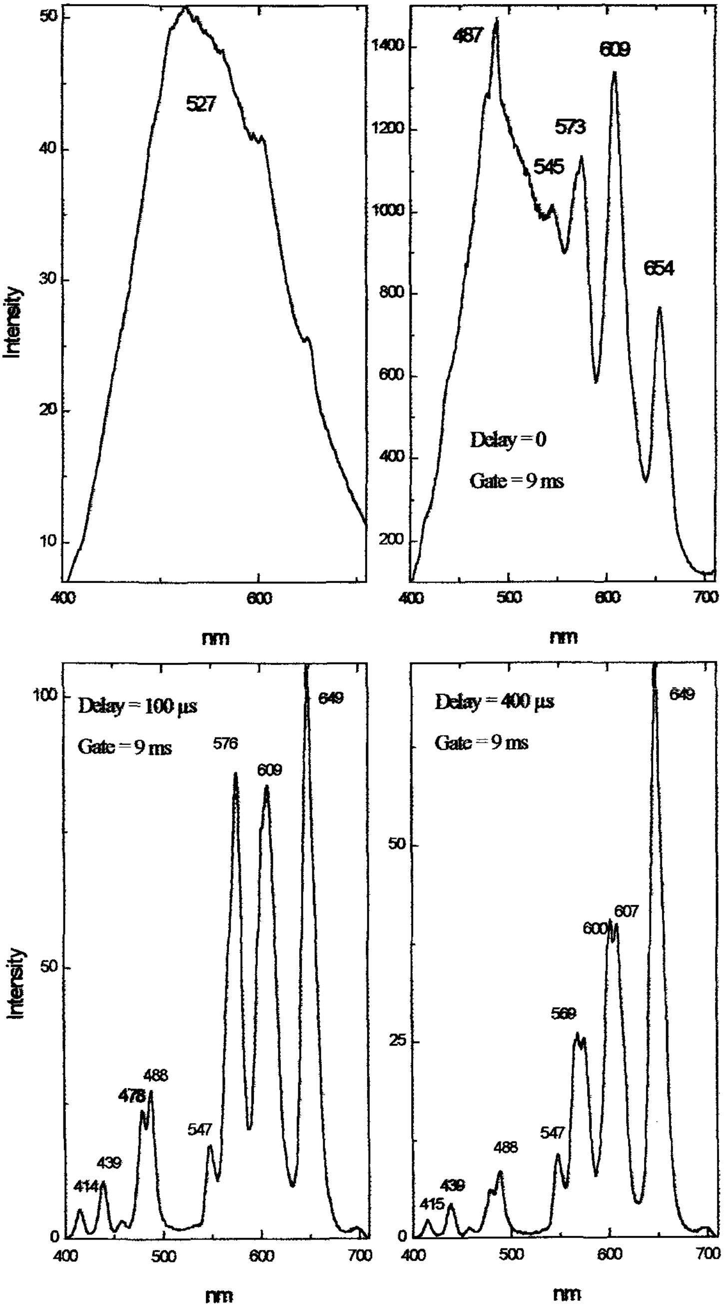

FIG. 5. Cathodoluminescence (*a*) and laser-induced (λex = 337 nm) luminescence spectra (*b*–*d*) of natural scheelite with different delays and gate widths (sample ZRK1).

characteristic line of Eu^{3+} is seen at 616 nm (Fig. 7*a*). Its relative intensity is stronger after a long delay time which is explained by longest decay time of Eu^{3+} in scheelite of 600 μs compared to other *REE*. Besides that, violet-blue band with λ_{max} = 430 nm is detected under

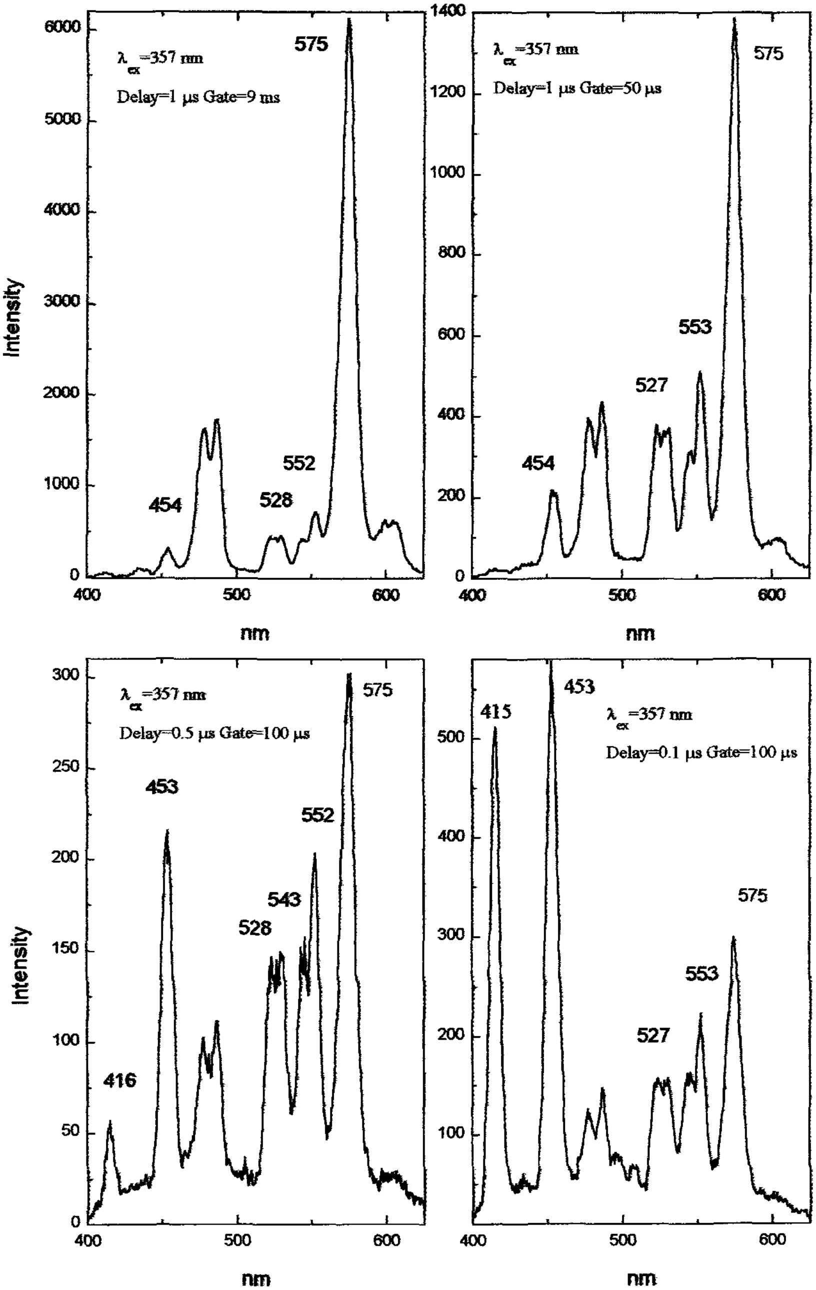

Fig. 6. Laser-induced luminescence spectra of the same natural scheelite as in Fig. 5 with different λ_{ex} = 357 nm.

337 nm excitation which is dominant at a narrow-gate width of several μs (Fig. 7*b*). This blue emission may not be ascribed to intrinsic luminescence because the latter has a short-wavelength charge transfer excitation band peaking at 240 nm with an excitation edge starting from 300 nm. Consequently, it may not be excited by 337 nm. Apart from this, the band is

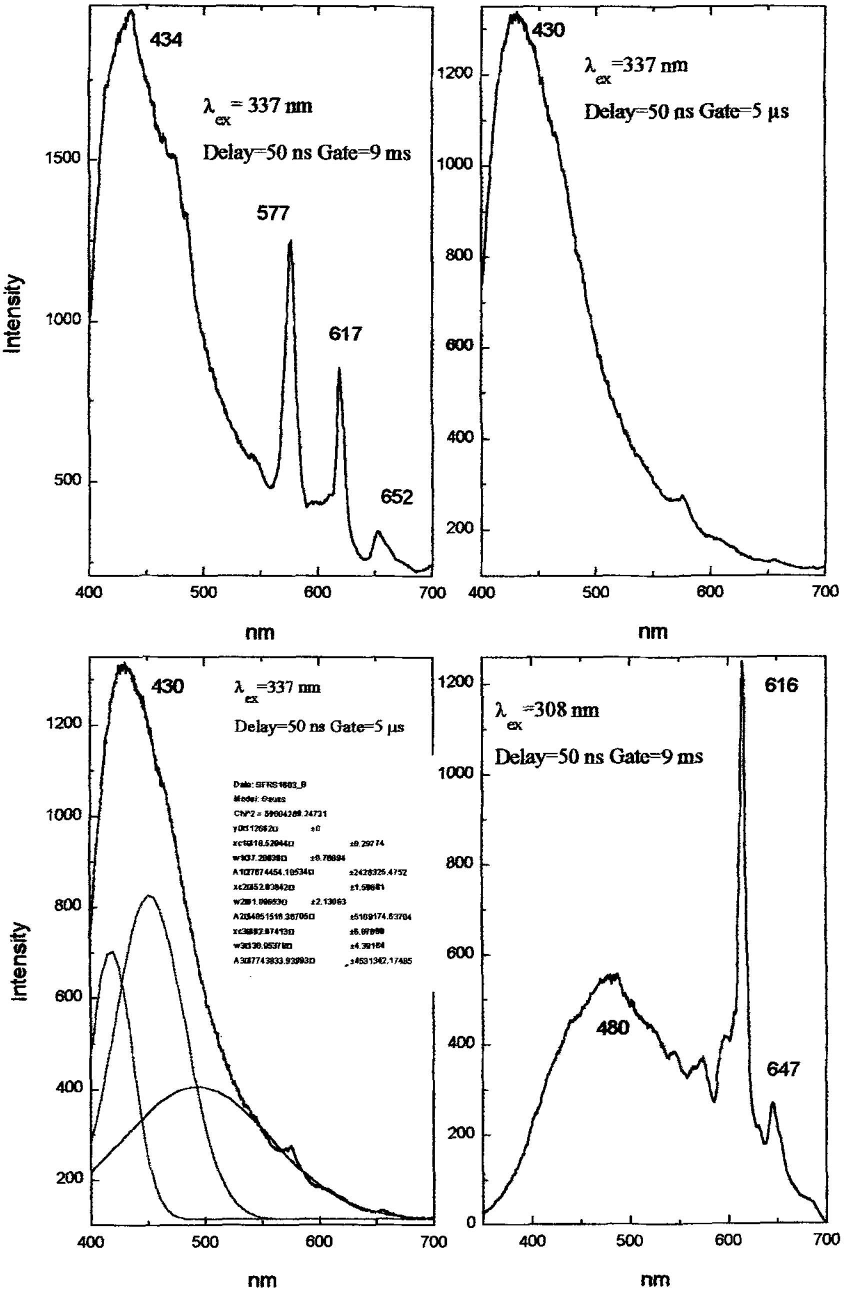

FIG. 7. Laser-induced time-resolved luminescence spectra of natural scheelite enriched by Eu. Spectral fitting of the narrow blue band is presented (c) (sample FRS16).

not excited by excimer laser (308 nm) (Fig. 7*d*) which is suitable for excitation of intrinsic WO_4^{2-} and defect WO_3 complexes (Koepke *et al.*, 1993)

This violet-blue emission spectrum was fitted to a sum of Gaussian functions using a curve-fitting method (Fig. 7*c*). A best result was

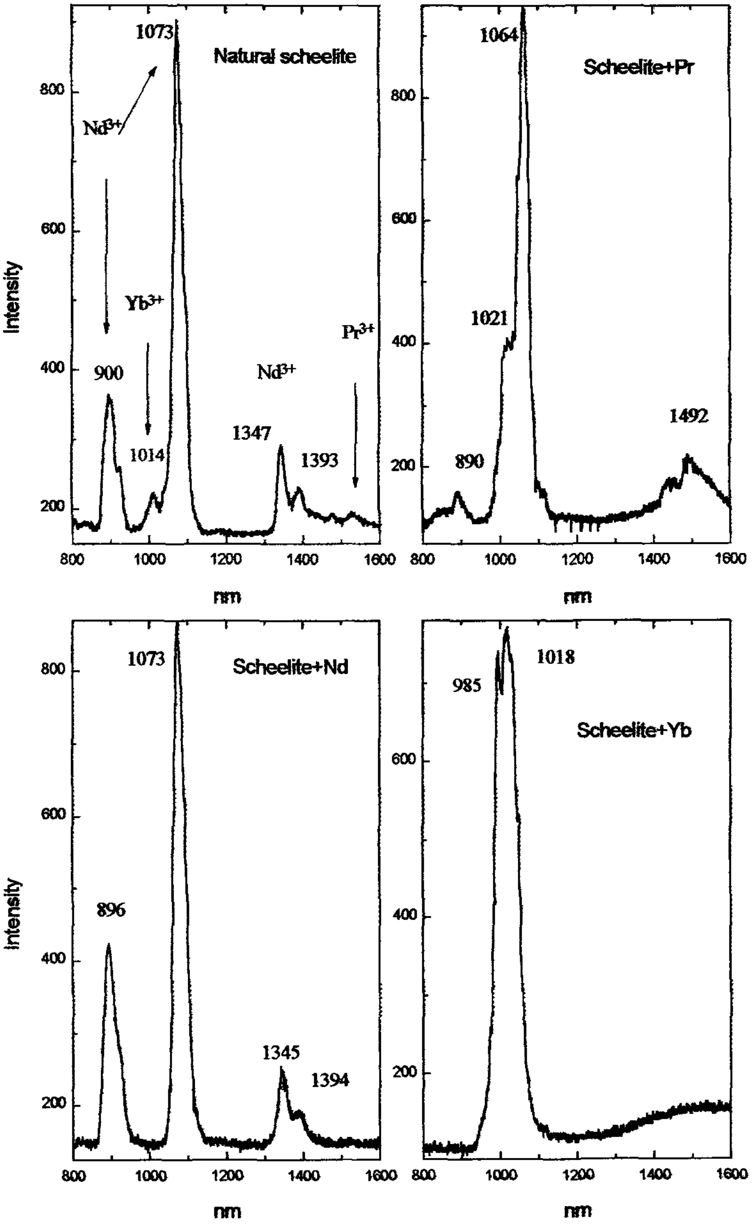

FIG. 8. Laser-induced luminescence spectra of natural and artificially activated scheelites in the near IR region.

achieved when it is assumed that the emission band is a superposition of three Gaussian bands and the fit is satisfactory. A band with $\lambda_{max} \approx$ 500 nm and half-width of $\approx$ 130 nm in natural scheelites is most probably connected with MoO_4 luminescence. The narrow bands with $\lambda_{max} \approx$ 418 nm and $\lambda_{max} \approx$ 452 nm have spectral-kinetic parameters suitable for Ce^{3+} and Eu^{2+}, respectively, which have not been determined previously in scheelite because they are hidden by intrinsic luminescence. The fact that in time-resolved spectra they are mostly prominent with a narrow gate-width, is supported by evidence from the shorter decay time of Eu^{2+} and Ce^{3+} compared with other *REE* and intrinsic scheelite luminescence.

Figure 8 represents scheelite luminescence in the near IR range of the spectrum. Luminescence of Nd^{3+}, Yb^{3+} and Pr^{3+} are detected in the spectral range up to 1.6 µm.

Conclusion

By using laser-induced time-resolved spectroscopy of natural and synthetic scheelite we were able to detect and ascribe various luminescence lines to a variety of *REE*. The selectivity of detection is possible by using different time delays after excitation, different gate-widths and different excitation wave-numbers. The technique described here allowed detection of *REE* in samples where they are hidden by intrinsic luminescence and are therefore not visible in the steady-state spectra. Luminescence of Pr^{3+}, Er^{3+} and Tm^{3+} are confidently detected in natural scheelite, even in low concentrations and in the presence of Tb^{3+}, Dy^{3+} and Sm^{3+} which conceal them in steady-state spectra. Luminescence of Ho^{3+} and Yb^{3+} is detected in natural scheelites for the first time.

From these preliminary studies, luminescence of Eu^{2+} and Ce^{3+} is identified, but a more detailed investigation is in progress to further investigate this process.

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