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Thermal dependence of luminescence lifetimes and radioluminescence in quartz

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ABSTRACT

During time-resolved optical stimulation experiments (TR-OSL), one uses short light pulses to separate the stimulation and emission of luminescence in time. Experimental TR-OSL results show that the luminescence lifetime in quartz of sedimentary origin is independent of annealing temperature below 500 °C, but decreases monotonically thereafter. These results have been interpreted previously empirically on the basis of the existence of two separate luminescence centers L_H and L_L in quartz, each with its own distinct luminescence lifetime. Additional experimental evidence also supports the presence of a non-luminescent hole reservoir *R*, which plays a critical role in the predose effect in this material. This paper extends a recently published analytical model for thermal quenching in quartz, to include the two luminescence centers L_H and L_L, as well as the hole reservoir *R*. The new extended model involves localized electronic transitions between energy states *within* the two luminescence centers, and is described by a system of differential equations based on the Mott–Seitz mechanism of thermal quenching. It is shown that by using simplifying physical assumptions, one can obtain analytical solutions for the intensity of the light during a TR-OSL experiment carried out with previously annealed samples. These analytical expressions are found to be in good agreement with the numerical solutions of the equations. The results from the model are shown to be in quantitative agreement with published experimental data for commercially available quartz samples. Specifically the model describes the variation of the luminescence lifetimes with (a) annealing temperatures between room temperature and 900 °C, and (b) with stimulation temperatures between 20 and 200 °C. This paper also reports new radioluminescence (RL) measurements carried out using the same commercially available quartz samples. Gaussian deconvolution of the RL emission spectra was carried out using a total of seven emission bands between 1.5 and 4.5 eV, and the behavior of these bands was examined as a function of the annealing temperature. An emission band at ~3.44 eV (360 nm) was found to be strongly enhanced when the annealing temperature was increased to 500 °C, and this band underwent a significant reduction in intensity with further increase in temperature. Furthermore, a new emission band at ~3.73 eV (330 nm) became apparent for annealing temperatures in the range 600–700 °C. These new experimental results are discussed within the context of the model presented in this paper.

1. Introduction

The experimental technique of time-resolved optically stimulated luminescence (TR-OSL) is an important tool for studying luminescence mechanisms in a variety of materials, and finds extensive applications in the field of luminescence dosimetry and luminescence dating [1–8]. While continuous-wave optically stimulated luminescence (CW-OSL) measurements are more common in quartz applications, TR-OSL is a valuable probe in the study of recombination and/or relaxation pathways in the material.

During TR-OSL measurements the stimulation is carried out with a brief light pulse, and the signals from several pulses are summed to obtain a typical TR-OSL curve consisting of a buildup of

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the signal during the pulse, followed by the subsequent decrease when the optical stimulation is turned off. The decaying part of the luminescence signal is usually analyzed with a linear sum of exponential decays, and is characterized by the corresponding luminescence lifetimes. Several researchers have studied the temperature dependence of luminescence lifetimes and luminescence intensity from time-resolved luminescence experiments in quartz (see for example, [9–13] and references therein). Luminescence lifetimes for unannealed quartz of sedimentary origin (for convenience hereafter referred to as sedimentary quartz) are typically found to remain constant at ~42 μs for stimulation temperatures between 20 °C and 100 °C, and then to decrease continuously to ~8 μs at a stimulation temperature of 200 °C. This decrease of the luminescence lifetime with stimulation temperature is usually described within the framework of the well-known phenomenon of thermal quenching of luminescence in quartz. Thermal quenching has also been observed in both thermoluminescence (TL) and CW-OSL experiments on quartz [14,15], and is commonly described using the Mott–Seitz mechanism (see for example [16–18] and references therein).

Several experimental studies have shown that time resolved luminescence from sedimentary quartz annealed below 500 °C is dominated by a single exponential component, with a luminescence lifetime τ_H~42 μs, which is independent of irradiation dose [10–13,19]. However, when sedimentary quartz samples are annealed at temperatures above 500 °C, one observes that the effective luminescence lifetime decreases continuously thereafter to a characteristic value of τ_L~32–35 μs [9,11,20–22]. These results have been interpreted previously empirically by proposing the existence of two separate luminescence centers L_H and L_L in quartz, each with its own distinct luminescence lifetime τ_H and τ_L correspondingly. In addition, the existence of a non-luminescent hole reservoir R has been proposed, on the basis of the predose effect exhibited by this material. The predose effect is usually interpreted empirically on the basis of thermal transfer of holes taking place between the distinct luminescence centers in quartz.

Recently Pagonis et al. [20] presented a new kinetic model for thermal quenching in quartz which is based on the Mott–Seitz mechanism. In this model all recombination transitions are localized within the recombination center (in contrast to delocalized models in which all charge transitions take place via the conduction and valence bands [18]). In later work Pagonis et al. [21] developed analytical expressions for the luminescence intensity observed during and after the short pulses used during a TR-OSL experiment. These analytical expressions were derived by assuming that the traps are well below saturation, and were compared with the numerical solutions of the system of differential equations.

The specific goals of the present paper are

(a) To expand the recently published quartz model of Pagonis et al. [20,21], in an effort to include the experimentally observed lifetimes τ_H and τ_L for sedimentary quartz samples.
(b) To describe mathematically the experimentally observed decrease of the luminescence lifetime from a value of τ_H~42 μs for unannealed sedimentary quartz samples, to a value of τ_L~32 μs for samples annealed above 500°C.
(c) To describe mathematically the experimentally observed decrease of the luminescence lifetime with the stimulation temperature used during a TR-OSL experiment.
(d) To carry out a quantitative comparison of the modeled results from parts (b) and (c) above, with published experimental data for a commercially available quartz sample.
(e) To supplement the published TR-OSL data with new radioluminescence (RL) data obtained using the *same* commercial quartz samples, after annealing at elevated temperatures.

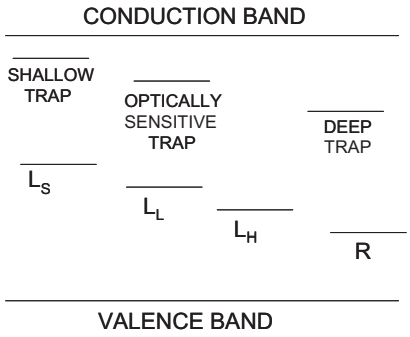

Fig. 1. A model for luminescence lifetimes in quartz from Ref. [9], showing the 3 radiative luminescence centers denoted by L_H, L_L and L_S and the non-radiative luminescence center R. Centers L_H, L_L and R are dominant in sedimentary quartz.

2. Luminescence lifetimes in quartz: the T_H, T_L and T_S components

This section presents an overview of experimentally observed luminescence lifetimes in quartz samples. Fig. 1 shows a simple energy scheme model which has been proposed based on extensive experimental studies of luminescence lifetimes in quartz (see for example Galloway [9]; Chithambo and Galloway [19]; Chithambo and Ogundare [22]). The energy scheme in Fig. 1 consists of three independent radiative luminescence centers denoted by L_H, L_L and L_S, and a non-radiative luminescence center denoted by R. These radiative centers are associated with distinct characteristic lifetimes denoted by τ_H, τ_L and τ_S correspondingly (Galloway [9]). It is also assumed that all three luminescence centers contribute to the experimentally observed optically stimulated luminescence and that the experimentally observed lifetime will depend on which of the three centers is dominant.

According to this energy scheme, time resolved luminescence from sedimentary quartz annealed below 500 °C is dominated by a single component with a luminescence lifetime τ_H ~42 μs [9–13]. It is believed that high temperature annealing of quartz samples above ~500°C causes the redistribution of holes between the non-radiative center R and the three radiative centers denoted by L_H, L_L and L_S. As a result of this redistribution of holes, luminescence from centers other than L_H becomes more important.

In the rest of this paper, the discussion and model will concern sedimentary quartz samples, and will therefore refer only to luminescence centers L_H, L_L and their distinct characteristic lifetimes τ_H, τ_L correspondingly. In addition, the non-radiative hole center R will also be discussed in the context of the model.

3. The new model

This section summarizes the main points of the recent model of Pagonis et al. [20,21], and the model is extended to the case of two luminescence centers. The physical basis of explaining thermal quenching within the model is based on the Mott–Seitz mechanism. The model involves electronic transitions between energy states *within* the recombination center. The original model of Pagonis et al. [21] is shown in Fig. 2. Fig. 2a shows the configurational diagram for thermal quenching processes based on the Mott–Seitz mechanism, while Fig. 2b shows the proposed electronic transitions taking place within the model.

In this paper we extend the model shown in Fig. 2a, to include the two independent luminescence centers L_H and L_L, as well as the non-radiative hole reservoir R. Fig. 3 shows the new extended model, which is also based on the Mott–Seitz mechanism. The arrows in Fig. 3 indicate the electronic transitions which are likely