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X-ray irradiated thermo- and radioluminescence, structural and thermal characterization of septarian (powder&bulk) from Madagascar

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ABSTRACT

The luminescence properties of septarian have been investigated for the first time in this study, which has been the subject of many studies in both geological and geophysical fields. This sediment with a calcium carbonate structure exhibited high luminescence properties with X-ray excitation. The radioluminescence (RL) and thermoluminescence (TL) properties were investigated as well as their structural (FT-IR, XRD), morphological (SEM), thermal (TG-DTA) and absorption (UV-Vis-NIR) properties of this sediment. The broad RL peak of septarian was observed at 640 nm. There was a significant increase in the RL intensities of the sifted samples compared with the bulk sample. The TL glow curves of septarian irradiated with X-rays exhibited intense main TL glow peak having the maximum temperatures at 116 °C and about 390 °C with a heating rate of 2 °C/s. Also; the TL kinetic parameters were reported; activation energy (E), frequency factor (s) and the order of kinetics (b) of the first peak have been determined in detail by using peak shape (PS) and Computerized Glow Curve Deconvolution (CGCD) methods. SEM and EDS analysis were performed for the two different layers of septarian. The light colored side with the amorphous structure of the sample has more impurities (such as Fe, Al, Zr, K) than the crystallized and darker side.

1. Introduction

Septarian nodules were formed in the Cretaceous Period millions of years ago. At this time of high sea level, volcanic eruptions in Madagascar destroyed the marine life sinking into the seawater and began to disintegrate. The minerals in the crusts and carcasses, the marine sediments that accumulate around the carcasses and form nodules or mud pits, pulled deposited. Eventually, as the ocean retreated, the sludge dried up and the molds inside the septic nodules began to shrink and crack [1]. In terms of shape, volume, and degree of shrinkage cracks are indicated a variable. The formation process that characterizes the Septarian concretions remains a mystery. A number of changing mechanisms in the earth crust have been suggested for the formation of septaria which is rich in point of the dehydration of clay and organic cores [2]. Septaria include crystals precipitated from circulating solutions, which is mostly calcite [3,4]. The crystallized structure in bright red and gold colors on the wall of the cavities in the septarites is due to siderite or pyrite coatings. Some septars may contain small calcite stalagmites and well-formed millimetric pyrite single crystals [5,6].

Although there are numerous geological and gemological studies on Septerian, there is no any optical, luminescence and thermal analysis studies of the sediment have been found in the literature review. The aim of this study is to investigate the characteristics of the Septerian (Dragon Egg) sample from Madagascar. In accordance with this purpose, RL, TL behaviors were investigated as well as their structural (FT-IR, XRD), morphological (SEM), thermal (TG-DTA) and absorption (UV-Vis-NIR) properties.

The lattice defects, impurity defects, structural defects and their distribution in the structure are responsible for the luminescence emission that is commonly observed in insulator minerals during excitation with many ways such as X-ray, ions, electrons, temperature, or light. In this respect, the radioluminescence is quite a convenient system for material characterization [7,8]. Radioluminescence (RL) in another saying X-ray excited luminescence is useful for determining defects of minerals. X-ray radiation penetrates and induces the whole

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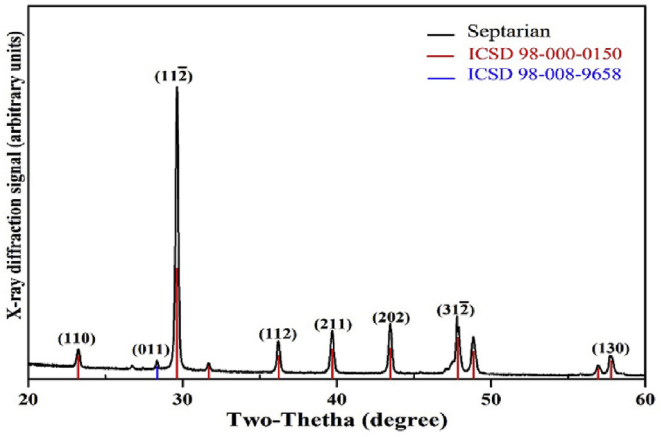

Fig. 1. X-ray diffraction (XRD) pattern of septarian.

sample, forming new luminescence defects.

The radioluminescence provides greatly enhanced spectral data by the volumetric excitation of the sample throughout, the setup of the system and data collection is relatively challenging. The luminescence emissions of minerals or phosphors were measured on a high-sensitivity wavelength multiplexed CCD (Charge Coupled Device) detector which is capable of detection between 200 and 1200 nm. Thus, in particular, the emission spectra of minerals with different impurity atoms can be determined in detail [9].

The TL kinetic parameters of septarian were determined through two methods used to analyze the thermoluminescence data. The main peak of the sample was observed at 116 °C. For the first time, the kinetic parameters of this peak were calculated by peak shape (PS) and computerized glow-curve deconvolution (CGCD) methods [10–12] in this study. Also, The RL spectrum was recorded for septarian. The peak maxima were observed at around 640 nm.

2. Experimental details

The X-ray diffraction (XRD) pattern and phase analysis of septarian were performed under the room temperature by a PANanalytical Empyrean X-ray diffraction equipment and X'Pert High Score Plus program, are demonstrated in Fig. 1 and Table 1. The PANanlytical Empyrean X-ray diffraction equipment is projected to plural purpose configurations. The X-ray tube which is part of this device set to work at 10–60 kV rated voltage, 8–60 mA rated current and 6 kW max rated output phase control. Established divergence slit size in X-ray generator is 0.4785(°). The voltage and current values of this device were set to 45 kV and 40 mA respectively. Cu-Kα (1.5405 Å) was used as the radiation source. For qualitative analysis, XRD patterns were recorded in the interval of 20°- 60° (2θ) at a speed of 0.0445°/s.

For the RL measurements of the bulk and powder septarian samples, excitation was made with a Machlett OEG-50A X-ray tube operated at a maximum experimental level of 30 kV and 15 mA. Luminescence detection system is conducted with a Yobin Yvon spectrometer, coupled to a liquid nitrogen cooled CCD detector. The irradiated samples for TL analysis were readout in the dark room with a RA94 Reader/Analyzer system at a linear heating rate of 2 °C/s from 50 °C up to 400 °C in a N_2 atmosphere. The nitrogen atmosphere during recording the data was employed to reduce spurious signals from the air and to improve thermal contact between the sample holder and heater planchet. Also, low heating rates were used to prevent any temperature lag. Optical absorption spectra of the sample were recorded at room temperature in the wavelength region of 200–2000 nm using Perkin-Elmer Lambda 950 spectrophotometer. The FTIR spectra were recorded for absorbance in the region 600–2500 cm^{-1} using an Agilent Technologies Cary 660 Spectrometer with room temperature. The thermal analysis (TG-DTA) of samples was performed Hitachi SII Exstar 7300 thermal analyzer. The thermal behavior of bulk septarian was studied in the temperature range of 25–1100 °C at a heating rate of 10 °C.min^{-1} in the air atmosphere. Scanning electron microscopy (SEM-EDS) images were used to examine the morphology of Septarian by using a Carl Zeiss 300 VP.

3. Results and discussion

3.1. Structural and morphological properties

3.1.1. XRD pattern of septarian

The X-ray diffraction (XRD) pattern and phase analysis of septarian were performed and demonstrated in Fig. 1 and Table 1. The result of phase analysis for sample X'Pert High Score Plus program was showed that planes of the *Calcium Carbonate* ($CaCO_3$) such as (110), (112), (211) and (202). The crystal structure was defined as the space group P1-21/c1, space group number: 14 and the lattice parameters were calculated from the XRD data on the basis of the septarian. The lattice parameters were calculated for monoclinic sample: a,b,c values 6.3340 Å, 4.9480 Å, 8.0330 Å respectively. Besides, there is a *Silicon Dioxide* (SiO_2) phase in the structure.

3.1.2. FT-IR spectrum of septarian

The FTIR-ATR investigation was mainly performed to collect qualitative information about the main components and unknown materials organic-inorganic materials present in the powdered septarian sample. Calcite, aragonite, and vaterite transmittance values of $CaCO_3$ group minerals are observed in the FTIR spectrum of septerian.

In the Fig. 2, the characteristic peaks of calcite were noticed at 711 and 1399 cm^{-1}. From this point to around 1475 cm^{-1}, vibrational bands were defined to the characteristic in-plane bending and

Table 1
The peak ID report of septarian (ICSD card no: 98-000-0150 and 98-008-9658).

2θ	Phase ID	Height (%)	d(Å)	h k l
23.240	$CaCO_3$	7.7	3.82441	1 1 0
28.286	SiO_2	100.0	3.15253	0 1 1
29.624	$CaCO_3$	100.0	3.01317	1 1 $\bar{2}$
31.632	$CaCO_3$	3.0	2.82627	2 0 $\bar{2}$
36.297	$CaCO_3$	12.9	2.47303	1 1 2
39.746	$CaCO_3$	6.4	2.26603	2 1 1
43.550	$CaCO_3$	6.6	2.07647	2 0 2
47.883	$CaCO_3$	22.6	1.90009	3 1 $\bar{2}$
48.887	$CaCO_3$	10.6	1.86155	2 2 $\bar{2}$
57.082	$CaCO_3$	0.8	1.61223	0 3 $\bar{1}$
57.921	$CaCO_3$	5.7	1.59085	1 3 0

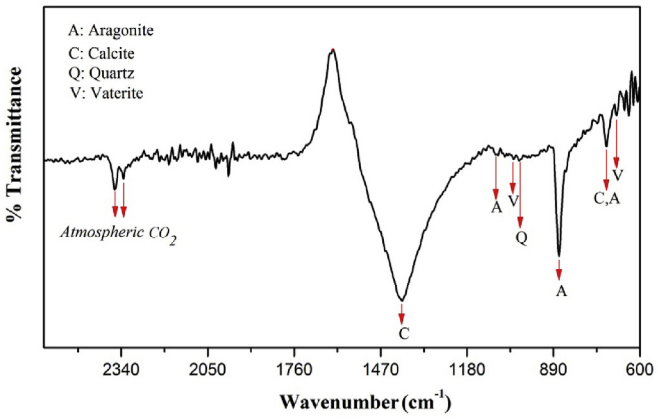

Fig. 2. FTIR spectrum of septarian.