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Luminescence of X-ray induced radiation defects in modified lithium orthosilicate pebbles with additions of titanium dioxide

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Modified lithium orthosilicate (Li_4SiO_4) pebbles with additions of titanium dioxide (TiO_2) are designed as a possible tritium breeder ceramic for the helium cooled pebble bed (HCPB) test blanket module. Additions of TiO_2 were chosen to enhance mechanical properties of the tritium breeder pebbles. The formation of radiation defects (RD) in the modified Li_4SiO_4 pebbles with a different content of TiO_2 was studied by X-ray induced luminescence (XRL) technique. After XRL measurements the accumulated RD were also analyzed by thermally stimulated luminescence (TSL) and electron spin resonance (ESR) spectrometry. XRL spectra consist of several bands with maxima at around 430, 490, 690, 700 and 800 nm. The XRL band with a peak at 490 nm could be associated with intrinsic defects in Li_4SiO_4 matrix whereas all the other maxima at lower photon energies are the result of the addition of TiO_2.

Keywords: lithium orthosilicate, titanium dioxide, X-ray induced luminescence, XRL, thermally stimulated luminescence, TSL, electron spin resonance, ESR

INTRODUCTION

Lithium-based ceramics are suggested as a possible tritium breeder material for the helium cooled pebble bed (HCPB) test blanket module of the International Thermonuclear Experimental Reactor (ITER) [1]. ITER is a large-scale scientific experiment intended to prove the viability of fusion as energy source. The easiest way to accomplish fusion reaction is the reaction between two hydrogen isotopes – deuterium (^2_1D) and tritium (^3_1T) (Eq. 1). The T-D fusion reaction

has a higher efficenty and probability in comparison to other reactions, such as D-D or T-T [2]:

$$({}^{2}_{1}D)+({}^{3}_{1}T)\rightarrow({}^{4}_{2}\mathrm{He}+3.57\ \mathrm{MeV})+({}^{1}_{0}n+14.1\ \mathrm{MeV}). \quad (1)$$

Deuterium can be extracted from sea water, while tritium resources on Earth are very limited and thus tritium breeding is an important issue for future nuclear fusion reactors [3]. The most promising way to produce tritium is by nuclear reactions (Eqs. (2) and (3)) [4, 5]:

$${}^{6}_{3}\mathrm{Li}+{}^{1}_{0}\mathrm{n}\rightarrow{}^{3}_{2}\mathrm{He}+2.1\ \mathrm{MeV})+({}^{3}_{1}T+2.7\ \mathrm{MeV}), \quad (2)$$

$${}^{7}_{3}\mathrm{Li}+{}^{1}_{0}\mathrm{n}\rightarrow{}^{3}_{2}\mathrm{He}+{}^{1}_{0}\mathrm{n}-2.4\ \mathrm{MeV}. \quad (3)$$

Modified lithium orthosilicate (Li_4SiO_4) pebbles with additions of titanium dioxide (TiO_2) are developed as a possible tritium breeder [6]. Due to addition of TiO_2, lithium metatitanate (Li_2TiO_3) was obtainted as a secondary phase [7]. Primarily researches show that mechancial properties of the modified Li_4SiO_4 pebbles with additions of TiO_2 were significantly improved compared to the reference samples – Li_4SiO_4 pebbles with 10 mol% lithium metasilicate (Li_2SiO_3) [7].

The tritium breeding ceramic during exploitation in the HCPB Test Blanket Module (TBM) will be under harsh operation conditions – neutron radiation (up to 2.4 MW m^{-2} or 10^{18}n $m^{-2}s^{-1}$), high temperature (up to 1193 K), and magnetic field (up to 7–10 T) [8, 9]. Under such conditions radiation defects (RD) and radiolysis products (RP) are induced in the tritium breeder by energetic neutrons, tritium ions, and helium ions as well as other processes. The accumulated RD and RP in the modified Li_4SiO_4 pebbles could play a crucial role in the behaviour of tritium release [10]. There is evidence that RD, such as E' centres, F^+ and F^0 centres (oxygen vacancy trapping one or two electrons), which may form during irradiation of lithium oxide (Li_2O), Li_4SiO_4 and Li_2TiO_3, may act as effective tritium scavengers [11].

In order to evaluate the formation of RD, the modified Li_4SiO_4 pebbles with a different content of TiO_2 were analysed by X-ray induced luminescence (XRL) technique. After XRL measurements the samples were also analyzed by electron spin resonance (ESR) and thermally stimulated luminescence (TSL) technique.

EXPERIMENTAL

The modified Li_4SiO_4 pebbles with different contents of TiO_2 were fabricated by an enhanced melt-based process at the Karlsruhe Institute of Technology (Karlsruhe, Germany) [12]. The Li_4SiO_4 pebbles with 10 mol% Li_2SiO_3 were selected as reference material and fabricated by a melt spraying process at SCHOTT AG (Mainz, Germany) [13]. The specifications of the investigated pebbles are shown in Table 1. The pebbles were pre-annealed in previously studied condition [7]: at 1223 K for 3 weeks in air to reduce cracks and structural defects which may form during the fabrication process.

Table 1. **Specifications of the investigated Li_4SiO_4 pebbles**

Parameter	Sample #1	Sample #2	Sample #3	Sample #4
Phase composition	90 mol% Li_4SiO_4 10 mol% Li_2TiO_3	80 mol% Li_4SiO_4 20 mol% Li_2TiO_3	70 mol% Li_4SiO_4 30 mol% Li_2TiO_3	90 mol% Li_4SiO_4 10 mol% Li_2SiO_3
Primary component				
Li, wt%	22.3 ± 0.2	21.9 ± 0.2	20.5 ± 0.1	22.50 ± 0.05
Si, wt%	21.4 ± 0.05	18.3 ± 0.04	18.5 ± 0.1	24.4 ± 0.3
Ti, wt%	3.99 ± 0.02	8.03 ± 0.05	9.55 ± 0.01	–
Metallic impurities				
Pt, wt%	0.0059 ± 0.0002	0.0289 ± 0.0002	0.004 ± 0.0001	0.0052 ± 0.0003
Au, wt%	<0.0004	0.0156 ± 0.0001	<0.0004	<0.0004
Rh, wt%	0.0015 ± 0.0001	<0.0005	0.0017 ± 0.0002	<0.0005
Pebble diameter, μm	560–900	560–900	560–900	560–900

The micro-impurities of the noble metals – platinum (Pt), gold (Au), and rhodium (Rh) in the analysed samples can be explained with the corrosion of Pt alloy components, which are used both in the fabrication process [12].

For XRL measurements, the Li_4SiO_4 pebbles were crushed to fine powder and pressed in d = 10 mm pellets (pressure: up to 100 MPa, room temperature, air atmosphere). The optical image of the pebbles (Sample #1) and pellet is shown in Fig. 1. XRL spectra were recorded in high vacuum (lower than 10^{-5} Torr) at room temperature under X-ray tube irradiation (irradiation time: 15 min, W anode, anode voltage: 40 kV, anode current: 10 mA) and recorded with the Andor Shamrock B-303i spectrograph equipped with a CCD camera (Andor Du-401A-BV) for which the XRL spectra were not corrected to compensate for the sensitivity difference of the equipment.

For ESR spectrometry, the pellets after XRL measurement were crushed into fine powder. The ESR spectra were recorded by the Bruker Biospin X-band ESR spectrometer (microwave frequency: 9.8 GHz, microwave power: 0.2 mW, modulation amplitude: 5G, field sweep: 200 and 1000 G) operating at room temperature.

The TSL glow curves of the pellets after XRL analysis were measured from 293 to 773 K (heating rate: 2 K/s, high vacuum). The TSL intensity was detected with a photomultiplier tube (HAMAMATSU H8259) with a 300–550 nm bandpass filter. To acquire informxation about spectral distribution of TSL, the Andor Shamrock B-303i spectrograph with a CCD camera Andor DU-401A-BV was used simultaneously with a photomultiplier tube.x

RESULTS AND DISCUSSION

XRL spectra of the modified Li_4SiO_4 pebbles with additions of TiO_2

The XRL spectra of the modified Li_4SiO_4 pebbles with different contents of TiO_2 are shown in Fig. 2. In order to understand the influence of TiO_2 additions, the XRL spectrum of the reference pebbles with 10 mol% Li_2SiO_3 was also included.

The formation of XRL can be divided into three main stages – the formation (i.e. ionization), thermalization, and recombination of electron–hole pairs [14]. As X-ray photons hit the sample, the electrons are removed from the valance band and excited to the conduction band, thus holes form in the valence band. The process continues as electrons either recombine emitting photons with energy close to the band gap or become trapped in defects or impurities that are already present in the sample. In the last step, trapped electrons and holes recombine and emit photons of light.

The XRL spectra of the Li_4SiO_4 pebbles with 10 mol% Li_2SiO_3 consist of one band with maxima at 490 nm (2.5 eV). Previously, K. Moritane et al. [15] published similar results for Li_2SiO_3, Li_4SiO_4 and SiO_2 under He^+ ion beam irradiation and attributed these bands to E' centers and some variants of oxygen deficiency centers (ODCs). The paramagnetic E' centre (≡Si·) is an unpaired electron localized in a single silicon sp^3 orbital, where the "·" represents an unpaired electron and symbol "≡" bands with three oxygen atoms [16]. The XRL spectra of the modified Li_4SiO_4 pebbles with additions of TiO_2 are

Fig. 1. The modified Li_4SiO_4 pebbles with additions of TiO_2 (Sample #1) – left, and pressed pellet – right

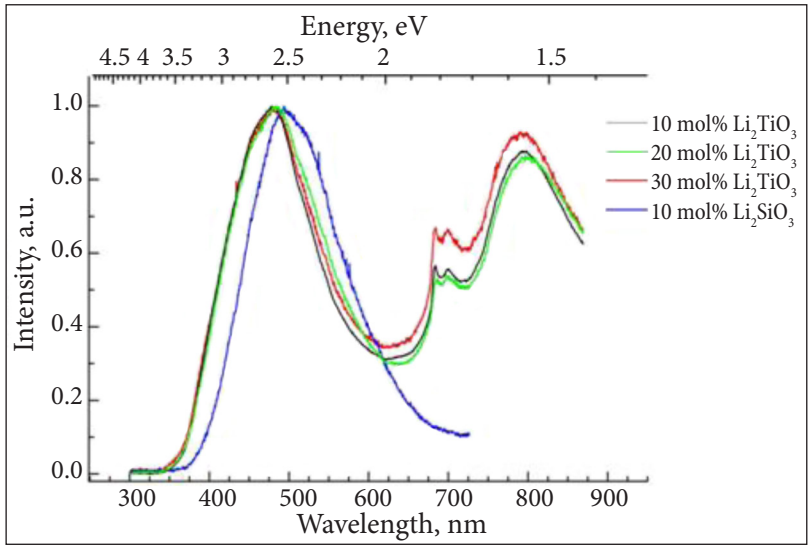

Fig. 2. Normalized XRL spectra of the Li_4SiO_4 pebbles with different chemical composition

more complicated and contain at least five bands (Fig. 3). In order to separate these bands, the energy-based Gaussian functions were used and deconvoluted spectrum contains four main bands with wavelenght 430 nm (2.9 eV), 490 nm (2.5 eV), 690 nm (1.8 eV), and 800 nm (1.55 eV). The band around 690–700 nm seems to contain two overlapped narrow peaks – 690 (1.8 eV) and 700 nm (1.77 eV). Some addition of the second order of 490 nm band is present in the red emission bands, as a diffraction grating spectrometer was used to acquire spectra. The band with wavelength 490 nm (2.5 eV) could be attributed to the primary phase – Li_4SiO_4, while other bands might be associated with additions of TiO_2. The cathodoluminescence (CL) spectra of Li_2TiO_3 were measured by V. Correcher and M. Gonzalez [17] and broad emission bands around 430, 470, and 700 nm were detected. While R. Plugaru et al. [18] detected a sharp and intense emission around 800 nm for TiO_2 (at 800 nm for rutile and 820 nm for anatase).

The XRL spectra of the modified Li_4SiO_4 pebbles with additions of TiO_2 depending on the measurement time are shown in Fig. 4A. The obtained results show the XRL intensity decreases as irradiation time increases. As an

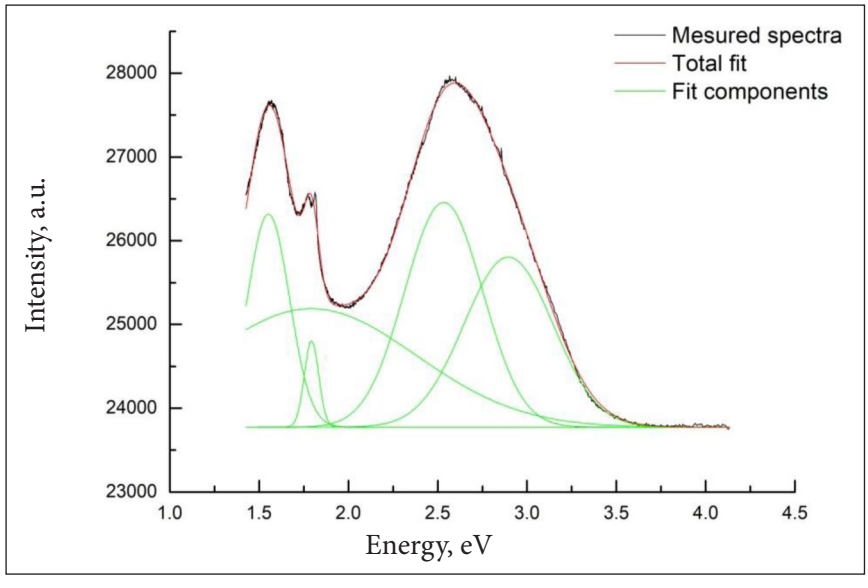

Fig. 3. Deconvoluted XRL spectrum of the modified Li_4SiO_4 pebbles with additions of TiO_2 (Sample #2)

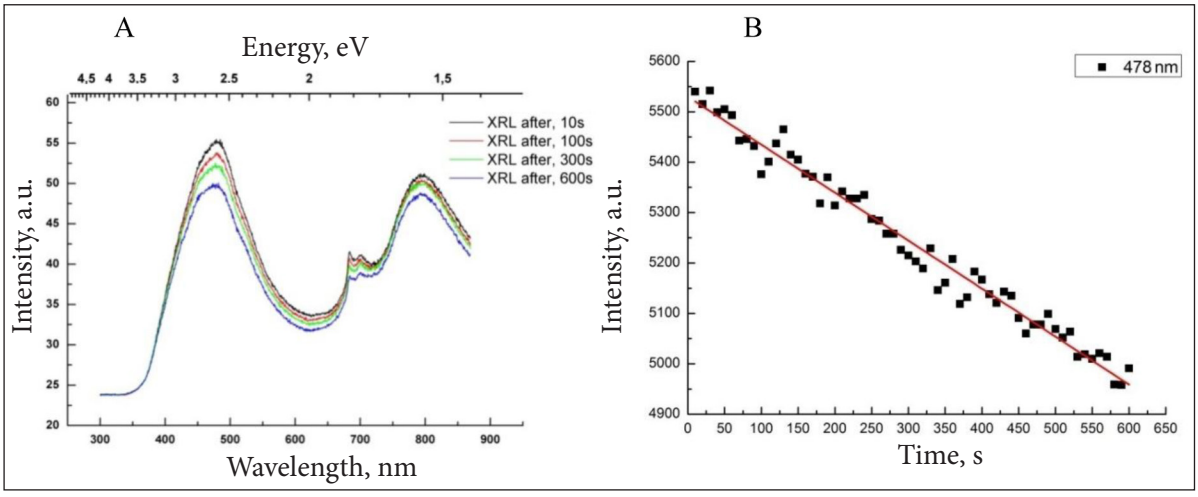

Fig. 4. XRL spectra of the modified Li_4SiO_4 pebbles with additions of TiO_2 (Sample #1) (A) and intensity of maximum with wavelength 478 nm (B) depending on irradiation

example, the intensity of the maximum with wavelength 478 nm (2.59 eV) depending on irradiation time is shown in Fig. 4B. Such decrease in intensity could be associated with the formation and recombination processes of defects present in the samples. V. Grismanovs et al. [19] reported similar effect in Li_2O and related it to oxygen vacancies introduced by annealing.

To supplement the obtained results of XRL technique and to analyse the formed electron and hole centres, the modified Li_4SiO_4 pebbles with additions of TiO_2 after XRL measurements were also investigated with ESR spectrometry and TSL technique.

ESR spectra of the modified Li_4SiO_4 pebbles after XRL measurements

The ESR spectra of the modified Li_4SiO_4 pebbles with 10 mol% Li_2TiO_3 before and after XRL measurements are shown in Fig. 5. After XRL measurements, in the ESR spectra at least three first derivative signals with g-factors 2.019 ± 0.001, 2.003 ± 0.001, and 1.93 ± 0.01 were detected. ESR technique uses quantum effects in order to detect electron spin switches as the changing magnetic field increases the energy gap for electrons under constant radiation of microwaves. There is a resonance event with a specific energy gap when

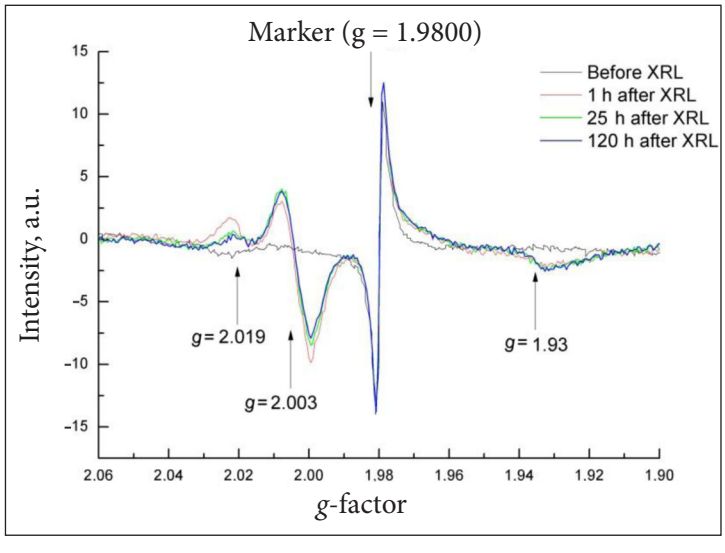

Fig. 5. ESR spectra of the modified Li_4SiO_4 pebbles with additions of TiO_2 (Sample #1) before and after XRL measurements

electrons switch the spin; thus these spectra can be observed. Dependence of resonance events on interactions inside measured material described with Zeeman and Starks effects can be used for the identification of paramagnetic RD and for better understanding of their structure.

Previously, similar ESR signals were detected and described for pure Li_4SiO_4 [10], Li_2TiO_3 [20], and TiO_2 [21]. Therefore, the ESR signal with g-factor 2.003 most likely could be associated with E' centres (SiO_3^{3-} or TiO_3^{3-}), and relatively small signals around 1.93 might be related to Ti^{3+} centres [22], while the unstable ESR signal at 2.019 could be associated with oxygen related defects.

TSL glow curves of the modified Li_4SiO_4 pebbles after XRL measurements

The TSL glow curve (measured with a photomultiplier tube) of the modified Li_4SiO_4 pebbles with 10 mol% Li_2TiO_3 after XRL measurement is shown in Fig. 6. Two major peaks at 365 and 650 K were detected. TSL measurements involve the heating of the sample and detection of emitted light from electrons and hole recombination processes. Two Gaussian peaks suggest at least two energy depth "traps" in the pebbles with addition of TiO_2.

To acquire information about recombination centres responsible for TSL emission, the TSL spectra were measured. However, no signal was detected while measuring luminescence with a CCD camera and spectrometer. Most likely, luminiscence intensity was below the detection limit of the system.

Previously, the correlation between tritium release processes and thermally annealing RD were detected [10] and thus it can be suggested that these defects could play a significant role in tritium diffusion and release behaviour. On the basis of obtained results of XRL technique, it was shown that the formation processes of RD in the modified Li_4SiO_4 pebbles with additions of TiO_2 slightly differ from the reference pebbles with 10 mol% Li_2SiO_3. Due to the additions of TiO_2, additional XRL bands were detected, which can be associated with TiO_2 or Li_2TiO_3. To identify the formed electron and hole centres, ESR and TSL technique were used, however for precise identification of RD additional measurements need to be done. Therefore, all results also clearly confirm the necessity of further study of the radiation effects in the modified pebbles.

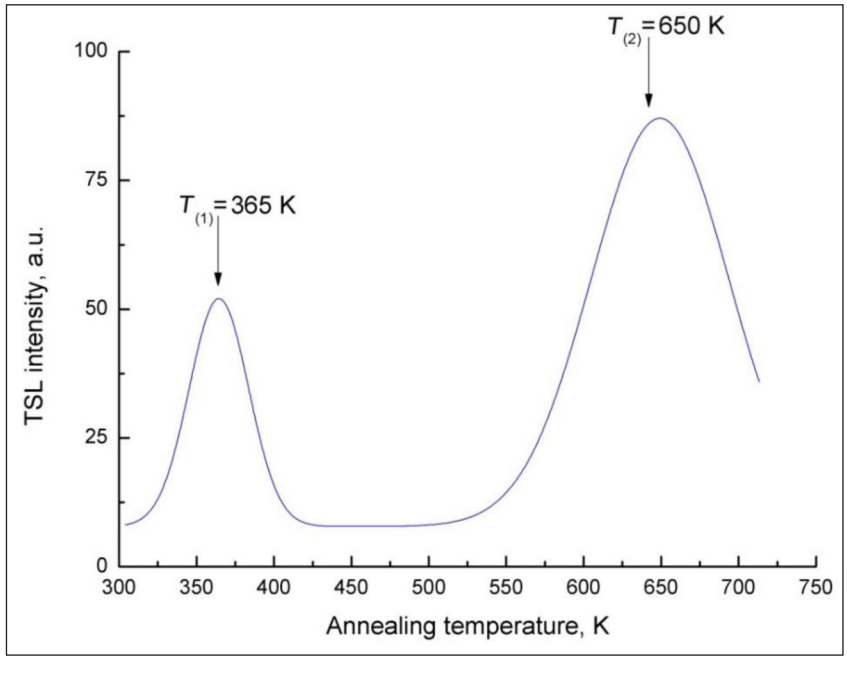

Fig. 6. TSL glow curve of the modified Li_4SiO_4 pebbles with addition of TiO_2 (Sample #1) after X-ray irradiation (15 min)

CONCLUSIONS

In this research, the formation of radiation defects in the modified Li_4SiO_4 pebbles with different contents of TiO_2 was studied by XRL, ESR and TSL techniques. The obtained results of XRL indicate that a similar process occurs in the modified pebbles as in the Li_4SiO_4 pebbles without addition of TiO_2. In the XRL spectra of the modified pebbles the maxima around 430 nm (2.9 eV), 490 nm (2.5 eV), 690 nm (1.8 eV), 700 nm (1.77 eV), and 800 nm (1.55 eV) were detected. Whereas in the spectra of the pebbles without addition of TiO_2, only one band with maxima at 490 nm (2.5 eV) was detected (which could be associated with intrinsic defects). Most likely, other bands are the result of the addition of TiO_2. However, additional analysis is required to identify the origins of these maxima.

In the ESR spectra of the modified pebbles, the formation of at least three first derivative ESR signals with g-factors around 1.93, 2.003, and 2.019 were detected and they were attributed to Ti^{3+} centres, E' centres, and oxygen related defects, respectively. From obtained results of TSL two peaks can be distinguished at 365 and 650 K, thus electrons are localised in traps with at least two energy levels. However, all above-mentioned results also clearly confirm the necessity in further study of the radiation induced effects in the modified mixed two-phase Li_4SiO_4–Li_2TiO_3 tritium breeder pebbles.

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RENTGENO SPINDULIŲ SUKELTŲ DEFEKTŲ LIUMINESCENCIJA MODIFIKUOTUOSE LIČIO ORTOSILIKATO RUTULIUKUOSE SU TITANO DIOKSIDO PRIEDAIS

Santrauka

Modifikuoti ličio ortosilikato (Li_4SiO_4) rutuliukai su titano dioksido (TiO_2) priedais yra suprojektuoti kaip galima tričio bryderio keramika, skirta heliu aušinamam rutuliniam įkrovos tęstiniam apvalkalo moduliui. TiO_2 priedai parinkti taip, kad būtų pagerintos tričio bryderio rutuliukų mechaninės savybės. Spinduliuotės defektų formavimasis modifikuotuose Li_4SiO_4 rutuliukuose su įvairiu TiO_2 priedų kiekiu buvo analizuotas rentgeno spindulių sukelta liuminescencijos (XRL) technika. Atlikus XRL matavimus sukaupti spinduliuotės defektai taip pat buvo analizuoti termiškai stimuliuojama liuminescencija (TSL) ir elektronų sukimosi rezonansu (ESR). XRL spektras susideda iš keleto juostų su 430, 490, 690, 700 ir 800 nm. XRL juosta su maksimumu prie 490 nm gali būti susieta su būdingais Li_4SiO_4 matricos defektais, kai visi kiti maksimumai su mažesne fotonų energija yra TiO_2 priedų įvedimo rezultatas.

Raktažodžiai: ličio ortosilikatas, titano dioksidas, rentgeno spindulių sukelta liuminescencija (XRL), termiškai stimuliuojama liuminescencija (TSL), elektronų sukimosi rezonansas (ESR)

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