



Electron paramagnetic resonance study of exchange coupled Ce^{3+} ions in Lu_2SiO_5 single crystal scintillator



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HIGHLIGHTS

- $\text{Lu}_2\text{SiO}_5:\text{Ce}$ scintillator was studied by EPR.
- The work is focused on the incorporation and exchange coupling of Ce^{3+} ions.
- Three types of the $\text{Ce}^{3+}-\text{Ce}^{3+}$ exchange coupling were revealed.
- Corresponding spin-Hamiltonian parameters were estimated.

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ABSTRACT

The Ce^{3+} ions incorporation inside lutetium oxyorthosilicate (Lu_2SiO_5) single crystals was studied by electron paramagnetic resonance. Already known Ce1 and Ce2 centers originating from the lattice peculiarity allowing two lutetium sites coordinated by different number of the oxygen ions were detected. Remarkably, for the Ce2 center, the determined g^2 tensor is asymmetric and could not be diagonalized as compared to the Ce1 center, for which the three principal values and corresponding axes orientation have been determined and reported previously. Besides, the much weaker resonance lines found in spectra close to those coming from the Ce1 and Ce2, and following them under crystal rotation with respect to the direction of an external magnetic field, have been revealed as well. They were classified as doublets produced by the exchange coupled Ce^{3+} ions, creating the Ce1–Ce1, Ce2–Ce2 and Ce1–Ce2-like dimers. The corresponding spin–spin coupling constants were estimated. They are in the range 0.04 – 0.4 cm^{-1} . The Ce1, Ce2 and total dimer centers populations were calculated as 89%, 4.5% and 6.5%, comparing integral intensities of corresponding resonance lines.

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1. Introduction

The cerium-doped oxyorthosilicates (Lu_2SiO_5) attracted attention for years due to their unique physical properties advantageous for application in the scintillating detectors (Melcher et al., 2003). Their high light yield is worth noting as it is 3.5–4 times higher than that in bismuth germanate (Melcher and Schweitzer, 1992). Along with high density and short decay time, this scintillator is suitable for the fast detection of high-energy gamma rays (Melcher et al., 2003) and its optimization has been further pursued by divalent ion codoping (Blahuta et al., 2013; Yang et al., 2009). Therefore the knowledge of the Ce^{3+} ions distribution and incorporation inside the Lu_2SiO_5 (LSO) host is of great importance.

Up to now only few works reported electron paramagnetic resonance (EPR) results for the LSO:Ce (see for example (Blair et al., 2008; Buryi et al., 2013; Pidol et al., 2006)). In Pidol et al. (2006) and Buryi et al. (2013) the Ce1 and Ce2 centers embedded at Lu1 and Lu2 regular lattice sites were studied but no trustworthy information about the Ce2 center have been obtained yet. To the best of our knowledge no work was dedicated to the Ce^{3+} ions coupling investigation at all.

High concentration (ca. 0.04–0.5 mol.%) of the paramagnetic activation dopants in a material can lead to the exchange interactions between two (or more) neighboring spins as it is shown, for example, for the coupled $\text{Ce}^{3+}-\text{Ce}^{3+}$ ions in YAlO_3 and $\text{Y}_{0.7}\text{Lu}_{0.3}\text{AlO}_3$ (Buryi et al., 2015a, 2015b), LaCl_3 (Birgeneau et al., 1968), and $\text{Nd}^{3+}-\text{Nd}^{3+}$ ions in yttrium aluminum garnet (Lupei et al., 1995). Such an interaction causes the appearance of additional satellite lines in both EPR spectra (Birgeneau et al., 1968;

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Buryi et al., 2015a, 2015b) and transmission and emission optical spectra (Lupei et al., 1995) beside the central one.

The present work therefore focuses on classification and characterization of the observed Ce^{3+} centers in LSO single crystal host, including single ions and pairs (dimers).

2. Samples and experimental

Single crystals of LSO:Ce (0.04 mol.% of the cerium content) for the EPR measurements were grown by the Czochralski method in the iridium crucible in argon atmosphere. Since the lutetium oxyorthosilicate belongs to the monoclinic $C2/c$ space group (Gustafsson et al., 2001), the samples have been intently prepared in the shape of parallelepipeds with the faces parallel to the (a^*b) , (bc) and (a^*c) orthogonal planes. The a^* axis is not a crystallographic one and makes approximately 32° with the crystallographic a axis in the (ab) plane. The LSO crystal structure offers two regular cation sites, Lu1 and Lu2.

The continuous wave (CW) EPR measurements were performed on a Bruker X-/Q-band E580 FT/CW ELEXSYS spectrometer at X, Q-bands with the microwave frequencies 9.3–9.5 and 33–35 GHz, respectively, at temperatures of 10–30 K.

3. Results and discussion

EPR spectrum measured in LSO:Ce is shown in Fig. 1. In order to achieve better resolution, the spectrum was recorded at the orientation of an external magnetic field when $\angle(\mathbf{B}, \mathbf{c}) = -55^\circ$ in the (a^*c) plane (see also Fig. 1 in Supplementary Materials). The resonance lines corresponding to the Ce1 and Ce2 centers found at Lu1, and Lu2 regular lattice sites (Buryi et al., 2013; Pícol et al., 2006) (Fig. 1, insets B and C) are marked in the same way. Both Lu sites offer two magnetically non-equivalent positions for impurity ion. Therefore, the two groups of lines can be observed during sample rotation with respect to the external magnetic field direction (Figs. 1 and 2 in Supplementary Materials). Besides, the Ce1 and Ce2 resonance lines are accompanied by the number of weak satellites (Fig. 1, insets A and C). They will be discussed shortly.

Since the electron spin of a single Ce^{3+} ion is $S = 1/2$, the Ce1 and

Ce2 EPR spectra could be described by the spin-Hamiltonian consisting of the Zeeman term only:

$$\hat{H} = \beta \mathbf{B} \mathbf{g} \mathbf{S}, \quad (1)$$

where β is the Bohr magneton, \mathbf{g} is the g tensor, \mathbf{S} is the spin operator and \mathbf{B} is the magnetic field.

Following the procedure described in Supplementary Materials, one obtains:

$$g_1^2 = \begin{pmatrix} 3.205 & -2.306 & 1.531 \\ -2.306 & 1.739 & -0.553 \\ -1.656 & -0.553 & 1.093 \end{pmatrix}, \quad (2)$$

$$g_2^2 = \begin{pmatrix} 3.592 & 2.306 & 2.154 \\ 2.306 & 1.840 & 0.553 \\ -1.968 & 0.553 & 1.330 \end{pmatrix}, \quad (3)$$

where $g_{1,2}^2$ are the g^2 tensors for each Ce2 magnetically non-equivalent position. As one can see, both tensors are asymmetric and thus they cannot be diagonalized (Meilman and Samoilovich, 1977). Subsequently, it is impossible to derive directly the principal values of the g tensor and principal axes orientations as well. The principal values will be rather roughly estimated further from the improved fit of the powder spectrum recorded in Buryi et al. (2013) (Fig. 2).

The spectra in Fig. 1, insets A and C, contain mentioned above unknown contributions (assigned as 1–8) of much lower intensity. They are almost symmetrically placed with respect to the Ce1 and Ce2 lines. Moreover, as one can see in Fig. 1 in Supplementary Materials, the lines 1–5 (Fig. 1, inset A) follow the Ce1 lines all over the angular variations without crossing them. Since Ce^{3+} belongs to the rare-earth elements and all its isotopes have zero nuclear spin, the mentioned satellite lines 1–5 cannot be referred to either hyperfine or superhyperfine structure. They cannot be related also to the single Ce^{3+} ions with somewhat perturbed local surroundings because, for instance, in Y_2SO_5 (Kurkin and Chernov, 1980), the Ce^{3+} g factors do not differ much from those obtained in Buryi et al. (2013) and Pícol et al. (2006) despite the different local crystal field strength. Most probably, few Ce^{3+} ions inside the

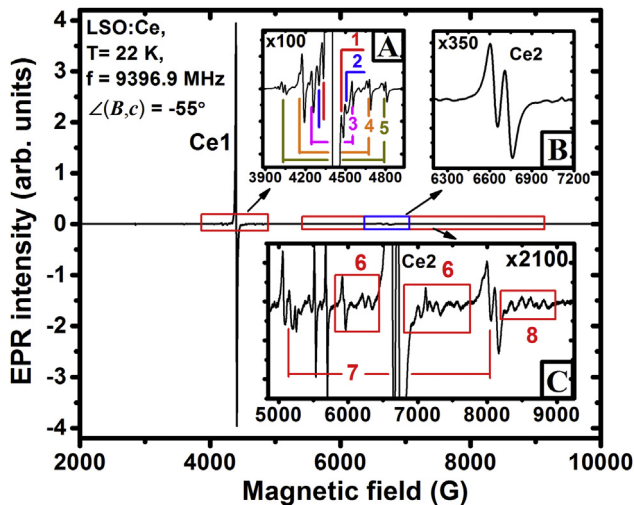


Fig. 1. EPR spectrum measured in $\text{Lu}_2\text{SiO}_5:\text{Ce}$ at X band. Inset A demonstrates doublets around the central line Ce1 (numbered from 1 to 5), originating from the coupled Ce1 ions. The inset B shows lines from the Ce2 center. In the inset C, the resonance lines produced by the two types of $\text{Ce}^{3+}-\text{Ce}^{3+}$ dimers are stressed: numbers 6,8 assign the doublets generated by the Ce2–Ce2 coupled ions and number 7 denotes the doublet of resonance lines originating from the Ce1–Ce2 coupled ions.

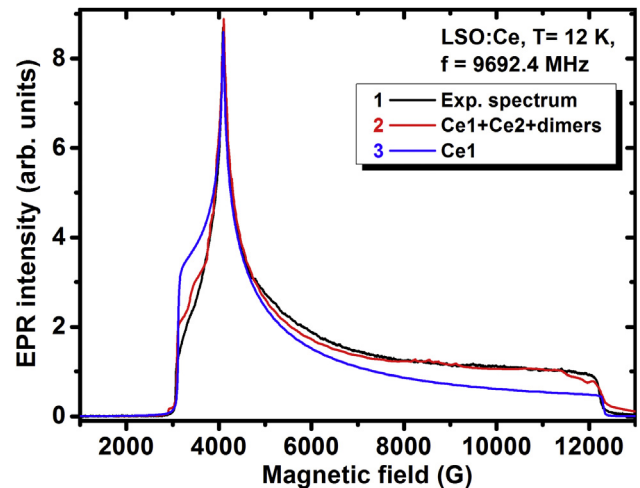


Fig. 2. X-band FS ESE spectrum (“1”) measured in LSO:Ce powder at $T = 12$ K (Buryi et al., 2013); “2” is the simulated spectrum (Stoll and Schweiger, 2006) with initial parameters for the single Ce1, Ce2, two Ce1–Ce1, one Ce2–Ce2 and one Ce1–Ce2 dimer centers whereas “3” is the simulation with the parameters for the Ce1 center only (Buryi et al., 2013).

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