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High pressure photoluminescence study of cerium-doped Lu_2SiO_5

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Abstract

We present the high pressure photoluminescence study of Lu_2SiO_5:Ce^{3+} in the pressure range up to 32 kbar, with pressure applied in sapphire anvil cell supplied. We have observed the red pressure shift of the Ce^{3+} emission equal to $-11.3\ cm^{-1}$/kbar for the $5d^1 \rightarrow F_{5/2}$ transition and $-7.7\ cm^{-1}$/kbar for $5d^1 \rightarrow F_{7/2}$ transition related to increase of the crystal field splitting of the $5d^1$ electronic configuration. We have found that local compressibility of Ce^{3+}–ligands system of Lu_2SiO_5 is more than two times smaller than the bulk material compressibility.

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1. Introduction

Materials doped with Ce^{3+} are characterized by the broad band emission related to the transition from the lowest state of the excited electronic configuration $5d^1$ to two states of the ground electronic configuration $4f^1$, the $^2F_{5/2}$ and $^2F_{7/2}$ splitted by the spin–orbit interaction. The energy of the emitting state is determined by the interaction of the d electron with the host lattice so the emission spectral range is strongly dependent upon the crystal field; it goes from the red in sulfide to the UV in fluorides [1]. The high hydrostatic pressure compresses the lattice and causes the increase of the interaction of localized electrons with ligands. This is a reason why high hydrostatic pressure is considered to be an effective tool for investigation of the $5d^1$ electron in the Ce^{3+} system and optical properties of Ce-doped materials.

Ce-doped Lu_2SiO_5 (LSO) is a well known scintillator utilizing $5d^1 \rightarrow 4f^1$ transitions of Ce^{3+} ions which has a quite high light yield considered to be about 25,000 photons/MeV, [2]. In LSO, cerium may occupy the two crystallographically distinct cation sites with oxygen coordination numbers equal to 6 and 7, both of C_1 symmetry, [3].

At ambient conditions the absorption spectrum of LSO:Ce^{3+} consists of at least three broad bands peaked at 360 nm, 300 nm and 260 nm related to radiative transitions from the ground state $^2F_{5/2}$ to the states of the excited electronic configuration $5d^1$ splitted by crystal field, [4,5]. The emission consists of two broad bands peaked at about 440 nm related to the transitions from the lowest $5d^1$ state to the $^2F_{5/2}$ and $^2F_{7/2}$ states belonging to the ground electronic configuration $4f^1$.

In this contribution high pressure ambient temperature photoluminescence spectra of LSO doped with Ce^{3+} are presented. Since Ce^{3+} in LSO needs the excitation in the UV range, we have used the pressure cell supplied with sapphire anvils. That determined the relatively low pressure limit.

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2. Experimental

The LSO:Ce^{3+} used in this work has been bought from CTI Molecular Imaging, Inc. (USA). Cerium concentration, measured by chemical analysis, is 0.11 mol%.

High pressure has been applied in the sapphire anvil cell. A silicone dimethylosiloxane oil has been used as a pressure transmitting medium. The emission of the R_1 and R_2 lines of ruby crystal has been used for pressure determination. The emission of Ce^{3+} has been excited using pulse excimer laser with wavelength 308 nm. The ruby R_1 and R_2 emissions have been excited by CW He–Ne laser.

The emission spectra of Ce^{3+} obtained at different pressures are collected in Fig. 1a. For each pressure the spectrum consists of two broad bands related to vibronicaly broadened transitions from the lowest state of the excited electronic configuration $5d^1$ to the $^2F_{5/2}$ and $^2F_{7/2}$ states belonging to ground electronic configuration $4f^1$. One observe the spin–orbit splitting of the ground electronic configuration which is approximately equal to $\Delta E = 2180 \pm 100\ \mathrm{cm}^{-1}$. One consider that the spin–orbit splitting ΔE in the Ce^{3+} ion is related to the spin–orbit coupling parameter ζ by following relation [6]

$$\Delta E = \frac{2l+1}{2}\zeta = 3.5\zeta \tag{1}$$

One observes the pressure induced red shifts of both bands. Energies of the respective peaks for different pressures are presented in Fig. 1b. One can see that the pressure shifts are not the same and are equal to $-11.3\ \mathrm{cm}^{-1}$/kbar and $-7.7\ \mathrm{cm}^{-1}$/kbar for the $5d^1 \rightarrow {}^2F_{5/2}$ and $5d^1 \rightarrow {}^2F_{7/2}$ transition, respectively. The difference equal to $-3.6\ \mathrm{cm}^{-1}$/kbar is related to the diminishing of the spin–orbit coupling with pressure. The average pressure shift of the emission is equal to $-\frac{6}{14}11.6 - \frac{8}{14}7.7 = -9.4\ \mathrm{cm}^{-1}/\mathrm{kbar}$.

3. Discussion

Energy of the lowest state of the $5d^1$ electronic configuration of the Ce^{3+} ion in solid is diminished by the quantity of depression energy, E_{depr} [1], which can be considered as the sum:

$$E_{\mathrm{depr}} = -C \cdot Dq + E_{\mathrm{cen}} \tag{2}$$

In this equation, coefficient C describes the crystal field d^1 splitting and depends on the symmetry of crystal field. E_{cen} is the centroid shift related to changes in the ligands polarization that accompanies the $4f^1$–$5d^1$ transition. In the standard crystal field model $Dq \propto \frac{1}{R^5}$, [7] whereas according to the ligand polarization model, [8], $E_{\mathrm{cen}} \propto \frac{1}{R^6}$. R is the average distance between the Ce^{3+} ion and ligands. Considering that the energy of $5d^1 \rightarrow 4f^1$ transition, $E_{\mathrm{d-f}}$ is a sum of the energy of the free ion and depression energy, and that pressure changes only depression energy one obtains [9]:

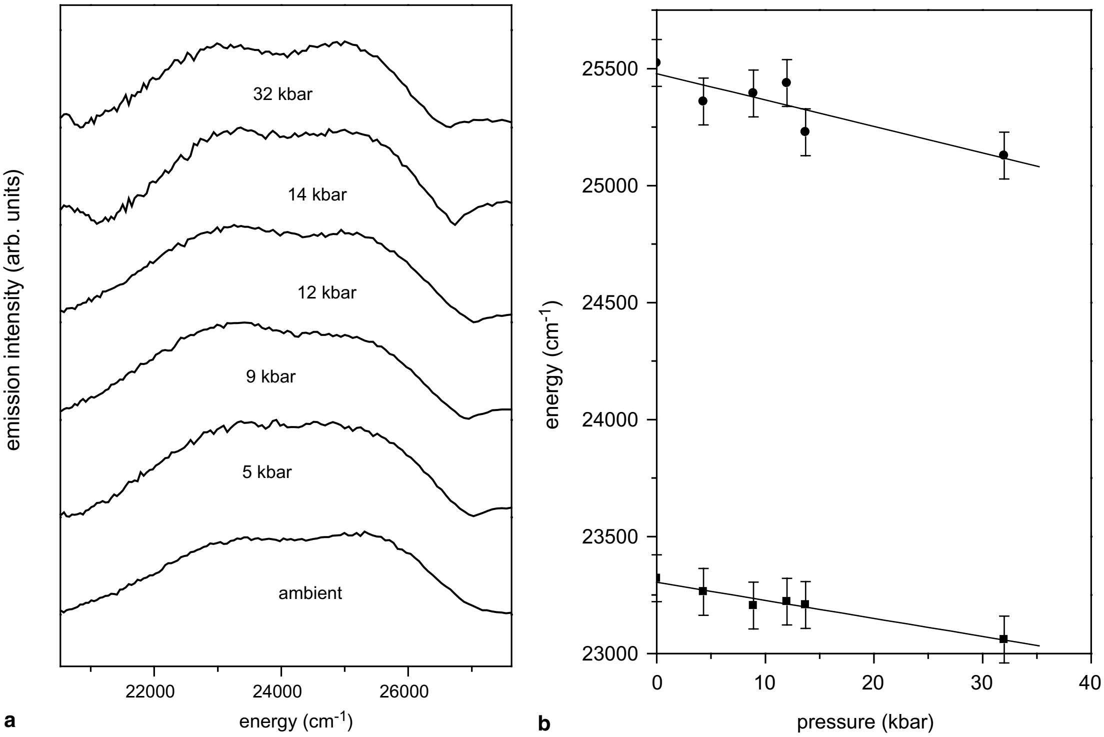

Fig. 1. (a) Room temperature emission spectra of LSO: Ce^{3+} obtained for different pressures and (b) energies of the emission peaks related to the $5d^1 \rightarrow {}^2F_{5/2}$ and $5d^1 \rightarrow {}^2F_{7/2}$ transitions versus pressure. Solid lines correspond to the linear least square fits.