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Optical Materials

Laser cooling of solids containing local centers with electric dipole allowed transitions: a feasibility study

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ABSTRACT

Various insulating materials containing local centers with electric dipole allowed transitions were studied under excitation in the long-wavelength tail of the absorption spectrum ("laser cooling regime"). Though no actual cooling was detected, spectra with a strong anti-Stokes component were observed which demonstrate the possibility to employ electron–phonon bands of electric dipole allowed transitions for optical refrigeration. The mechanisms responsible for the absence of observable optical refrigeration are discussed.

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1. Introduction

The problem of finding new materials where the optical refrigeration or laser cooling of solids employing phonon-assisted anti-Stokes fluorescence may be achieved is of significant interest. Since the first successful experimental results were obtained with Yb^{3+}-doped glass [1], many exciting achievements were reported: laser cooling was observed in different materials including rare earth doped insulating glasses and crystals, organic dye solutions [2], and semiconductors [3,4]; see [5–8] for reviews. The most successful results were obtained with $^2F_{7/2}$–$^2F_{5/2}$ transitions of Yb^{3+} ions in insulating glasses and crystals.

All experimental observations of laser cooling in insulating solids containing local fluorescent centers employed 4f–4f transitions of triply-charged rare-earth impurity ions that are parity-forbidden as electric dipole and occur only due to admixture of opposite-parity states of the 4f5d configuration [9]. The low oscillator strength of 4f–4f transitions requires arranging a long optical path of the exciting light inside the laser-cooled samples and limits the possibility to obtain laser cooling of small samples.

The goal of our experiments was to find out whether it is possible to employ electric dipole allowed radiative transitions of local centers in insulating solids for optical refrigeration. We report the results of spectroscopic feasibility studies of laser cooling via the phonon-assisted anti-Stokes emission in various materials containing local centers of different nature whose electric dipole allowed transitions provide broad electron–phonon bands in the emission spectra. The concept proposed here is to cool via allowed electronic transitions with moderate vibronic coupling. Such a laser cooling mechanism is therefore similar to that studied in experiments with organic dye solutions [2], where the electron–phonon emission of dye molecules was responsible for cooling. On the other hand it differs from an earlier proposal to use an allowed electronic transition free of vibronic coupling in combination with a phonon-coupled step to effect Raman cooling [10]. Though no laser cooling was detected in all materials studied, the observations support the possibility of using broad electron–phonon emission bands of electric dipole allowed radiative transitions for optical refrigeration of solids.

2. Experiment

The experiments were performed with three kinds of samples: alkali halide crystals (NaF and LiF) containing different aggregate fluorescent centers, single crystals containing Eu^{2+} ions and with polyethylene terephthalate (PET) containing fluorescein dye molecules.

Aggregate color centers in NaF and LiF crystals were formed by ionizing irradiation. NaF crystals were irradiated with X-ray Cu Kα for 1–3 h. LiF crystals samples were prepared by γ-radiation and irradiation with electron beam from electron accelerator. The most

significant LiF samples #5 and #7 were prepared by electron irradiation. Formation process of various color centers depends on the temperature of irradiation and storage of the crystal, composition of the initial material, ionizing radiation quanta energy and irradiation dose. The γ-radiation source was radioactive isotope ^{60}Co. Linear accelerator with electron energy of 5–7 MeV was used to carry out the electron irradiation [11–13]. Different kinds of crystalline materials containing Eu^{2+} ions were also examined of which CaF_2:Eu and CaS:Eu are discussed here. As an example of an organic dye-doped fluorescent material, the commercial polyethylene terephthalate (PET) samples were studied.

Most of the optical measurements were performed at room temperature. For measurements with thermally-isolated crystals the samples were mounted in vacuum in the sample chamber evacuated with a turbo vacuum pump (cold finger liquid helium refrigerator chamber was used).

Fluorescence was excited with diode-pumped solid state (DPSS) lasers (λ = 457, 473, 532, 543 nm), semiconductor lasers (λ = 405, 746 nm), He–Ne laser (λ = 632.8 nm), or with a DPSS laser-pumped CW R6G/DCM dye laser (Coherent CR-599); typical power of all lasers was of about 40–80 mW. The fluorescence was detected with a double-grating monochromator and a photomultiplier operating in a photon-counting regime (corrected for the system spectral response) or with a grating spectrometer equipped with a CCD camera.

The temperature changes of thermally-isolated samples were detected by monitoring the fluorescence intensity (usually in the anti-Stokes part) under the laser on/off switching conditions and comparing it with the calibration temperature dependences of corresponding fluorescence measured under the weak (few milliwatts) excitation with the samples placed in air inside a variable temperature optical chamber. The very existence of fluorescence under the excitation in the long-wavelength tail of the absorption spectrum is due to excitation of ground electronic state vibronic levels by phonons thus covering the energy deficit between the electronic excited state and the photon energy. Thus the calibration dependence may be approximated by an activation curve, $\exp(-\Delta E/kT)$, where ΔE is the energy difference between the exciting photons energy and the zero-phonon transition. Laser cooling would result in the fluorescence transients after switching the laser excitation on (decrease of intensity from its initial value). In case of optical heating the fluorescence transient would be the increase of intensity in the course of optical pumping. The accuracy of our experiments made it possible to detect the temperature changes of about 1 K.

3. Experimental results and discussion

3.1. Color centers in alkali halide crystals

Aggregate color centers in alkali halide crystals often exhibit efficient fluorescence due to dipole-allowed electronic transitions [9]. The strong electron–phonon interaction in these centers results in broad emission bands. Probably, the best studied are the aggregate luminescent centers in LiF (see [14] for review) and NaF [15] crystals. Color centers in LiF crystals were studied in detail because these crystals were used as a medium for tunable solid state lasers [11–13] and other applications. The existence of different kinds of luminescent centers and the possibility to vary their relative concentration by changing the irradiation, annealing and bleaching conditions make these crystals attractive from the point of view of finding a medium in which laser cooling may be observed.

The centers, whose excitation in the long-wavelength tail of the absorption spectrum results in anti-Stokes emission that is stronger than the Stokes one, are of interest here. This means that the excitation should occur lower in energy than the fluorescence band maximum. The anti-Stokes emission occurs due to the population of vibronic levels of the centers ground electronic state by room-temperature phonons followed by absorption of a photon with energy below that of the zero-phonon transition in the center. Obviously, the centers possessing the narrower emission band (about 1000 cm^{-1}) width are preferred because for very broad emission bands (more than 2000 cm^{-1}) excitation at energies below their maximum occurs too far below the location of zero-phonon transition and does not result in significant fluorescence at room temperature.

In Fig. 1 the fluorescence spectra of X-ray irradiated NaF crystals containing F_3^+ aggregate centers [15] under the excitation at different wavelengths are shown. The fluorescence spectra shape does not depend on excitation wavelength. It may be clearly seen that under longer wavelength (595–610 nm) excitation the integral of anti-Stokes emission intensity (classified here as emission at wavelengths shorter than that of the laser) is significantly stronger than that of the Stokes fluorescence. This in principle admits the possibility of laser cooling of NaF crystals containing F_3^+ centers since more photons are emitted with energies exceeding the energy of absorbed ones than with lower energies. Thus in the fluorescence process of F_3^+ centers more phonons are annihilated than created, provided non-radiative and energy transfer processes are absent. An obviously negative feature of the spectrum can be clearly seen however under excitation at 610 nm. Excitation at this wavelength produces fluorescence at longer wavelengths than that of F_3^+ centers. This fluorescence is due to a different type of aggregate centers, the variety of which exists in the irradiated samples. The Stokes emission in these centers is obviously accompanied by creation of phonons and heating of the sample. The relative contribution of different kinds of aggregate centers to the spectrum strongly depends on the sample growth conditions, X-ray irradiation conditions and on optical bleaching of the samples in the
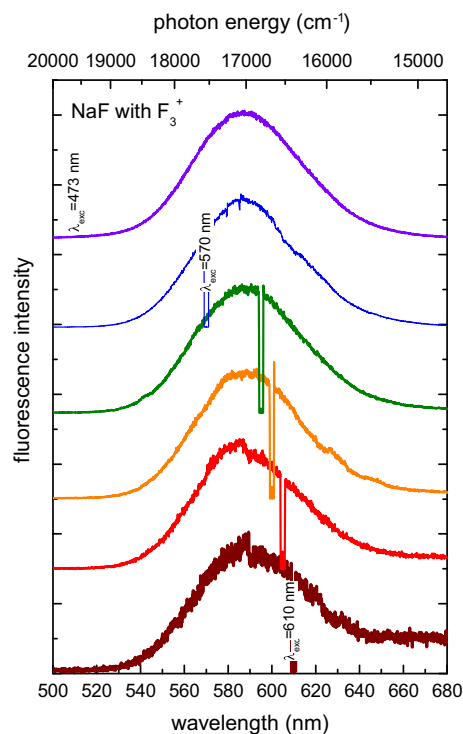

Fig. 1. Fluorescence spectra of F_3^+ centers in X-ray irradiated NaF sample excited at different wavelengths (473, 570, 595, 600 and 610 nm), including those in the long-wavelength tail of the absorption spectrum. Spectrometer blocked while scanning through the laser wavelength, T = 295 K.