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Vacancy relaxation in cuprous oxide ($Cu_{2-x}O_{1-y}$)

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ABSTRACT

Phonons are produced when an excited vacancy in cuprous oxide (Cu_2O) relaxes. Time resolved luminescence was used to find the excited copper vacancy (acceptor) and oxygen vacancy (donor) trap levels and lifetimes. It was also used to determine the typical energy and number of phonons in the phonon pulses emitted by vacancies. The vacancy properties of cuprous oxide are controlled by several synthesis parameters and by the temperature. We directly demonstrate the absorption of light by oxygen vacancies with transient absorption. Copper and oxygen vacancies behave differently, in part because the two kinds of traps capture carriers from different states. For example, the copper vacancy luminescence lifetime is around 25 times greater at low temperature. However, both kinds of vacancy luminescence are consistent with a Poissonian multiple phonon emission model.

1. Introduction

1.1. Applications of cuprous oxide and importance of its stoichiometry

Cuprous oxide (Cu_2O) is composed of highly abundant elements [1,2] and presents a 2.17 eV direct bandgap at room temperature [3]. Such characteristics make the material a candidate for scalable application in solar energy conversion technologies that range from photovoltaics to photocatalytic water splitting [4–6]. Recent reports also suggest that point defects may aid such technologies by acting as donors or acceptors [4,7–9].

Frequently, electronic devices are based on the junction of *p*-type and *n*-type materials. In cuprous oxide, the type is determined by the nonstoichiometry of the structure and by doping. The known nonstoichiometries are copper vacancy sites and oxygen vacancy sites. Cuprous oxide is typically *p*-type because copper vacancies are electron acceptors. Oygen vacancies, however, are electron donors. Oxygen vacancies are typically a minority defect.

In response to experimental reports, Scanlon and Watson have asked, "Is undoped n-type cuprous oxide fact or fiction?" [10] On a theoretical basis, they conclude that it is fiction. However, annealing experiments suggest the removal of oxygen vacancies (as opposed to dopants) converts *n*-type samples to *p*-type [7,4]. There have been several literature reports of geological samples of cuprous oxide which have luminescence from oxygen vacancies, but not from copper vacancies [11–13].

Cuprous oxide and Ag_2O are the only materials with achiral octahedral (O_h) symmetry. As a result of the *d* structure of the valence band and the *s* structure of the conduction band in these two materials [14], exciton radiative decay is suppressed. Cuprous oxide has a more convenient phase diagram than Ag_2O [15,16]. Therefore, cuprous oxide is a favored material for the investigation of the fundamentals of Wannier-Mott excitons, including the scattering of excitons with other excitons [17,18], phonons [19], and photons [20], or the formation of Bose-Einstein condensates [21,19]. Using samples the same or similar to those reported here, we previously investigated exciton photoionization [20] and multiphoton excitation of excitons [22]. Since excitons can decay at vacancies, low vacancy concentration cuprous oxide can be desirable for exciton research.

Here, we use a geological sample and reproducible synthetic samples to investigate whether the exclusive presence of oxygen

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Table 1
Cuprous oxide synthesis parameters. Purity: refers to copper precursor purity. AD: anneal duration. CR: cooling rate; ramp rate of the furnace during annealing. Power: floating zone furnace lamp power. GR: growth rate.

Symbol	Thickness (mm)	Purity	AD (days)	CR (C/min)	Power (%)	GR (mm/h)	Diameter (mm)
A	2.0	Geological					
B	0.61	0.999	4	Quench	55.4	7	5
C	2.3	0.999			55.4	7	5
D	1.8	0.999	4	5	55.4	7	5
E	0.74	0.9999	7	5	56.5	3.5	6.35
F	0.24	0.99999	3	5	55.8	3.5	5

vacancy luminescence might indicate the sample is *n*-type. We conclude that the mechanism of relaxation at the two vacancy types is different, so the absence of copper vacancy luminescence does not indicate an absence of copper vacancies.

Trapping and recombination of carriers at defects, which leads to luminescence, reduces the photocurrent in cuprous oxide solar energy devices [1]. Therefore the elimination of vacancy luminescence is desirable. On the other hand, sub-bandgap absorption may be used to capture sunlight which would otherwise be lost in traditional solar energy devices. The presence of vacancies induces absorption below the bandgap, as we demonstrate below.

1.2. Physics of relaxation in cuprous oxide

Excitation above the bandgap can lead to relaxation into a variety of states, which include (in order of decreasing energy): 1. electron-hole plasma; 2. the "yellow" exciton series; 3. excited oxygen vacancy states; 4. excited copper vacancy states; 5. excited vibrational states; 6. the ground state. This is not an exhaustive list. Owing to the high conduction and valence band symmetry, the electron-hole plasma cannot be investigated optically. Relaxation from the exciton states to vibrational states or the ground state has, however, been studied using luminescence [23].

As there are a large number of states in the system, the coupling between states can be quite complex. In this paper, we are measuring relaxation from excited vacancy states to vibrational states. Since vacancies are fixed at particular lattice site, they are less sensitive to the environment than Wannier-Mott excitons. We assume vacancies always relax the same way. Therefore, variations observed in vacancy relaxation are explained by changes in the behavior of the higher lying states which are causing the vacancy state to become occupied.

1.3. Structure of this article

Section 2 summarizes the preparation of the samples. Section 3 describes how the luminescence was recorded. Section 4 describes the luminescence spectrum. Section 5.1 gives the theory of the temporal evolution of the luminescence. Section 5.2 gives the theory of the luminescence spectrum. Section 5.3 describes control of the luminescence lifetime by different synthesis methods. Section 5.4 describes control of the excited energy level of vacancies by different synthesis processes. Section 5.5 explains the number and energy of the phonons emitted by vacancies. Section 5.6 describes the phonon pulses produced by vacancies. Section 6 shows the temperature dependence of the luminescence results. Section 7 demonstrates direct absorption by oxygen vacancies using a transient absorption technique.

2. Material: cuprous oxide synthesis (the optical floating zone method)

For this experiment, we selected six samples covering a wide range of synthesis conditions with the goal of demonstrating variability in the results. As a "guide to the eye" throughout this paper, the samples are labeled A to F in order of increasing expected quality. Expectations were based on our previous measurements of vacancies and inclusions [24,25].

Sample A is a natural sample selected for its suspected poor quality. Most exciton research in cuprous oxide uses naturally mined samples. A was mined at the Ray Mine, Arizona, USA [26] and purchased from Arkenstone, Richardson, Texas, USA.

Samples B–F were prepared by oxidation, floating zone crystallization, and (excepting C) annealing as previously described [24]. Polycrystalline feed and seed rods of cuprous oxide were obtained through thermal oxidation of copper metal rods. Oxidation occurred in a furnace at 1045 °C for 3 days. Crystal growth was conducted in an optical image furnace (CSI-FZ-T-10000-H-VI-VP) equipped with four 300 W tungsten halide lamps. All samples were grown in air. During growth, the feed and seed rods were counterrotating at 7 RPM. B, D, E, and F were annealed post growth at 1045 °C. The samples were polished on two parallel faces with a process discussed elsewhere [27]. The detailed synthesis parameters are listed in Table 1.

To summarize our previous results, we initially compared the intensity of copper vacancy luminescence across samples [24]. Images of B, C, and D are shown in Fig. 8 of [24]. We assumed that the luminescence intensity increases with the copper vacancy concentration. The vacancy luminescence is the most sensitive qualitative probe of stoichiometry available.

3. Experimental: luminescence methods

We used a 35 fs regeneratively amplified titanium doped sapphire laser. The laser output was converted to 500 nm using an optical parametric amplifier and a β-barium borate second harmonic generator. We selected 500 nm as the excitation wavelength because it is comparable with wavelengths widely used in the literature. Previous experiments have used continuous wave argon-ion and intracavity doubled neodymium-based excitation lasers. We used 0.4 to 1 mW of laser power to excite each sample. The laser pulsed at a repetition rate of 2 kHz. The beam diameter was about 1 mm. The peak irradiance was about 10^{13} W/m^2.

The samples were mounted with VGE-7031 varnish on a sapphire window. The sample assembly was placed in vacuum in a cryostat held at 3.2 K, except where other temperatures are specified below. The luminescence was collected in a transmission geometry. We used two detectors. The first was a fiber coupled, 300 mm focal length spectrograph. The spectrograph was equipped with 150 and 1800 groove/mm gratings. These were used for vacancy and exciton luminescence, respectively. The spectrograph data was recorded with a CCD. The second detection system was for time resolved luminescence. It included a 150 mm focal length spectrograph with a 50 groove/mm grating. The time resolved spectra were recorded using a Hamamatsu streak camera operating in single photon counting mode. Luminescence intensities were not intended to be comparable across samples. The efficiency