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# Evaluation of defects in cuprous oxide through exciton luminescence imaging

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ABSTRACT

The various decay mechanisms of excitons in cuprous oxide ($Cu_2O$) are highly sensitive to defects which can relax selection rules. Here we report cryogenic hyperspectral imaging of exciton luminescence from cuprous oxide crystals grown via the floating zone method showing that the samples have few defects. Some locations, however, show strain splitting of the *1s* orthoexciton triplet polariton luminescence. Strain is reduced by annealing. In addition, annealing causes annihilation of oxygen and copper vacancies, which leads to a negative correlation between luminescence of unlike vacancies.



## 1. Introduction

Owing to the positive parity of the valence and conduction bands, the primary luminescence mechanism in cuprous oxide is emission of two negative parity particles. The strongest process is the decay of an orthoexciton into a 0.014 eV ${}^2\Gamma_{12}^-$ phonon and a photon [1]. In addition, there is polariton luminescence from the quadrupole quantum mixing of the orthoexciton with a photon [2]. Under mechanical stress, the orthoexciton triplet state is split, and so is its luminescence [3]. The paraexciton can also begin to produce direct luminescence under stress owing to breaking of the positive parity of the band structure [3,4]. These properties are unique to $Cu_2O$ and $Ag_2O$, the two cuprite structure materials.

On one hand, deliberate application of strain to cuprous oxide can be useful for increasing luminescence [5], trapping excitons in a potential [6,5], initiating transverse (negative parity) phonon emission [7], or distinguishing otherwise degenerate states [8]. On the other hand, unwanted strain increases Auger recombination [9–11] and breaks the unique symmetry of cuprite structured crystals. Under practical experimental conditions, cuprous oxide is metastable. The thermodynamic phase is cupric oxide [12] which appears in inclusions when cuprous oxide crystals are cooled too quickly [13–16]. In this report, interfacial stress between the cuprous oxide and the cupric oxide inclusions is a source of strain [17].

Luminescence at 1.9477 eV has previously been described as "very weak" and resolvable only at temperatures below 4.2 K [1]. Very little is known about this luminescence, except that it is thought to be extrinsic. This is not discussed in most luminescence studies, probably because most CCD spectrometers have narrow spectral ranges that cannot cover this line and the better known luminescence lines simultaneously.

Cuprous oxide is nonstoichiometric [18–20]. Excitons bind to vacancies in the crystal and then undergo radiative decay [21]. The dominant luminescence is from copper vacancies $V_{Cu}^-$. There are also two types of oxygen vacancy luminescence, from $V_O^{1+}$ and $V_O^{2+}$. Vacancies are useful for increasing the conductivity of cuprous oxide [22–25]. However, the luminescence produced by vacancies indicates that vacancies reduce the lifetime of excitons [21,26]. The simultaneous existence of both copper and oxygen vacancies occurs because real samples are not perfectly equilibriated. Ultimately, low temperature equilibration conditions should lead to elimination of the minority defect.

In this paper, we investigate the spatial distribution of defects in large cuprous oxide crystals developed for optical applications

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[27] to demonstrate the high quality of floating zone synthesis methods. We also describe the underlying defect/exciton and defect/defect interactions.

## 2. Materials and methods

### 2.1. Samples

A crystal of cuprous oxide was grown using the floating zone method as previously described [13]. The starting material was 99.9% Cu rods with a 5 mm diameter. The crystal was grown in air at 7 mm/h using two oxidized rods rotating at 7 rpm in opposite directions. In this study, an as-grown sample and a sample annealed at 1045 °C for 5 days with a 5 °C/min ramp rate are compared. The samples were polished. In Ref. [13], these samples are shown as Fig. 8 (a, d) and contribute to Fig. 7.

### 2.2. Luminescence measurements

The samples were placed in an optical microscopy cryostat (Montana Instruments Cryostation). Thermal contact was established with VGE-7031 varnish. The stage temperature was about 5.7 K, with a stability of about 5 mK. The temperature dependence of cuprous oxide luminescence has been well characterized [28]. The samples were in vacuum. A scanning microscope with a 50X, 13 mm working distance objective was used to image the samples through a single window. The samples were illuminated through the objective using a reflection from a beamsplitter with 4.3 mW (measured between the objective and the beamsplitter) of 532 nm light from a Coherent Verdi G18 laser. Luminescence from the sample passed back through the objective, was partially transmitted through the beamsplitter, passed through a 532 nm long-wavelength-passing dielectric filter, and was collected in a fiber. The spectrum was recorded with an Andor 303 mm focal length Czerny-Turner spectrograph and DU420A-BEX2-DD CCD camera.

The background was subtracted from the spectrum. During background measurements, the laser beam was blocked. To obtain a consistent spectrum, it was necessary to wait approximately 15 min for the stage temperature to stabilize after the sample was illuminated.

Exciton luminescence for each sample was recorded over a $25 \times 25$ square grid of locations with a spacing of 20 μm for 30 s using a 1200 grooves/mm grating. This process took about 7 h per sample. For the exciton luminescence, the manufacturer specifies an instrument resolution of 372 μeV.

Vacancy luminescence, which has no spectrally narrow features, was recorded using a 150 grooves/mm grating over a square grid of locations with a spacing of 28 μm. Since a more efficient, coarser grating was used, only one second was required to collect a good vacancy luminescence spectrum and it was possible to easily sample a larger number of locations.

Our previous study [13] was designed to compare room temperature copper vacancy luminescence across samples. To achieve this, each sample was placed at the same distance along the optical axis from the objective. In this experiment, we investigate variations in luminescence within samples, including lines best observed at temperatures below 10 K [28]. The design of the cryostation does not permit each sample to be placed at precisely the same location along the optical axis, so direct comparisons of luminescence brightness between samples are not possible. When changing between samples, the microscope was refocused to optimize the efficiency with which the luminescence was collected. All measurements reflect conditions near the sample surface because the laser light has a short absorption length [29]. Since excitons and exciton polaritons propagate differently [2], the different types of luminescence come from slightly different volumes, with the highest density and greatest brightness occurring at the laser spot.

### 2.3. Analysis methods

In summary, the phonon-assisted luminescence is modeled. The residuals are used to determine the brightness, energy, and width of the orthoexciton polariton luminescence. Analysis is performed for each location in the hyperspectral image.

Excitons in these conditions are Maxwell–Boltzmann distributed [30–32]. They can decay into a phonon/photon pair if the phonon has negative parity. There are also three and four particle complications [1]. Phonon-assisted luminescence was modeled using the Maxwell–Boltzmann equation for the spectral irradiance $I$ as a function of energy $E$ [33]:

$$I(E) = A(|E - E_c|)^{1/2} e^{-(E-E_c)/k_B T}; \quad (1)$$

Here $A$ is the brightness, $E_c$ is the orthoexciton ground state energy minus the phonon energy, and $k_B$ is the Boltzmann constant. We only analyzed the most efficient luminescence, which is linked to emission of the ${}^2\Gamma_{12}^-$ phonon. The other phonon-assisted luminescence peaks do not significantly overlap with this peak at 5.7 K [28]. We also tried adding a constant background term to the model, but concluded that the background was adequately accounted for by the experimental background subtraction. The remaining error in the spectrum baseline after the background subtraction procedure contributes to error in the results. For each of 625 locations on each sample, the model was applied between 2.0180 and 2.0300 eV to avoid the region $E < E_c$, where the model is invalid, and to avoid the 2.0318 eV orthoexciton polariton luminescence which could skew the fit.

The orthoexciton polariton luminescence, which intrinsically has a very narrow spectral width [34,2], can typically be modeled by a Gaussian. The width of the Gaussian is determined by the spectrometer resolution. In this study, we are searching for deviations from the typical luminescence spectrum owing to sample defects. These deviations can cause a Gaussian model, or any other single peaked model, to fail, so for each location we computed the residual brightness after subtracting Eq. (1). Next we computed the sum over energies of the residual brightness, the residual brightness square weighted mean energy, and the likewise weighted standard deviation energy of the spectrum between 2.0300 and 2.0335 eV. These three statistics describe the brightness, energy, and width of the orthoexciton polariton luminescence respectively. No assumption is made about the structure of the polariton luminescence in the analysis.

For the defect linked luminescence near 1.95 eV we do not have a line shape model. To evaluate it, we summed brightness in the spectrum between 1.9443 and 1.9478 eV.

We modeled vacancy luminescence with a double Gaussian. The first Gaussian described the copper vacancy luminescence. The second Gaussian described the $V_O^{2+}$ luminescence. There are two limitations of the model: First, as in previous studies, silicon based detectors do not detect the low energy tail of the copper vacancy luminescence very efficiently. Second, the $V_O^{1+}$ luminescence appears indistinctly between the other two peaks. The oxygen vacancy luminescence line shape has been described in more detail using a multiple phonon emission model [35].

## 3. Results and discussion

### 3.1. Exciton luminescence

The cuprous oxide lattice has octahedral $O_h$ symmetry (not chiral $O$ symmetry). Crystals with this point group are not birefringent. Fig. 1 shows that the as-grown sample had birefringence near its