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Observation of color center peaks in calcium fluoride

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ABSTRACT

Alkali halides such as calcium fluoride all have color center defects that absorb light in the visible region. Using a moncochromator equipped, aberration corrected, scanning transmission electron microscope (STEM) we recorded spectra showing the time evolution of the generation of F and H centers in calcium fluoride. The final stage of electron beam irradiation is the formation of metallic calcium nanoparticles. High resolution low loss spectra for the Vacuum Ultraviolet region were also recorded.

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1. Introduction

The development of the new generation of monochromators has made it possible to record energy loss spectra with an energy resolution of 10 meV from regions less than 1 nm across [1]. This is almost an order of magnitude improvement over what was possible with monochromators in the electron gun [2]. It is unlikely that this spectacular change will result in the observation of new features on inner shell edges, or even in the low loss region dominated by collective excitations. The width of any feature in the energy loss spectrum is ultimately governed by the lifetime of the excitation that generally decreases for higher excitation energies. In practice even for inner shells with binding energies as low as 100 eV the lifetime broadening is approximately 100 meV, as shown by Krause and Oliver [3]. This does not mean that improved energy resolution has no value. Narrower peaks mean higher signal/noise or signal/background so making it possible to observe small peaks, such as pre-edge features that are signs of charge transfer.

The main benefit of improved energy resolution is a narrower zero loss peak, making it possible to detect excitations in the band gap of insulators and semiconductors and to define the conduction band offset more precisely. The reduction in the tails of the zero loss peak is more significant than the improvement in full width half maximum though in practice the two are connected, a narrower zero loss as defined by the FWHM will mean less intense tails. When trying to detect a feature in the band gap that might be 10^{-4} or 10^{-5} the intensity of the zero peak, it is important that the tails be at that level or lower. A clear band gap region obviates the need for elaborate (and controversial) modeling of the tails of the zero loss peak.

Electron and X-ray irradiation can produce a variety of defects in alkali halides that all show optical luminescence [4]. These defects have been characterized by both absorption and emission spectroscopy. More precise identification of the nature of the defect has been made possible by optically detected Electron Paramagnetic Resonance (EPR) [5] and polarization measurements as a magnetic field was varied [6].

Calcium Fluoride or fluorite can either appear as a colorless crystal or can have a natural purple color. This color has been attributed to calcium trapped at defects on {111} cleavage planes [7]. Optical emission and characterization of radiation-induced defects in fluorite has been extensively studied. The stable defects are not necessarily the same as in the alkali halides. In addition to the F center, where an electron is trapped at the site of a missing fluorine ion, defects such as V_k centers and H centers where an electron is trapped at an F_2 fluorine molecule are also possibilities [5,8]. The difference between these defects is that an H center is at an existing fluorine ion lattice site, whereas a V_k center is at a

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vacant position between two sites. Patterson [9] concluded that the probability of production of F centers was low. Williams et al. [5] studied both time resolved optical emission and absorption following electron bombardment. On the basis of optically detected Electron Paramagnetic Resonance (EPR) they concluded that the lowest energy state was a F–H center pair. Using polarization measurements in a magnetic field Call et al. were able to show that the fluorescence could be attributed to an H center [6]. More recently Lindner et al. [10] used femtosecond laser absorption to probe the dynamics of the self-trapped excitons.

The first measurements of the Vacuum Ultraviolet reflection that can be directly compared to energy loss spectra up to 40 eV were performed by Stephan [11]. Other spectra were published shortly there after [12,13], the measurements of Rubloff [12] having slightly better energy resolution. The most recent VUV reflection results and dielectric function results are those of Barth [14]. They are not that different from the results reported by Rubloff [12], though there are some differences in the heights of the various peaks. There have been many calculations of the energy bands in CaF_2, some of which in addition calculated the real and imaginary parts of the dielectric function, or a joint density of states that can be directly compared with experimental measurement. [15–21]. Given the strong exciton at the band onset, many body techniques should be used to calculate the dielectric response, though the agreement with experiment does not extend over a wide range. [22,23].

Given the large band gap there has recently been renewed interest in CaF_2 for vacuum ultraviolet components. However both electron beam and excimer laser exposure [24] were shown to generate calcium nanoparticles that severely degraded optical performance.

Using the Nion UltraSTEM with a monochromator we were able to record spectra with much improved energy resolution compared with the VUV reflection measurements. In particular the sharp excitonic peak at the onset of the conduction band threshold was readily observable. Radiation induced defects that would emit in the optical region were observed to increase with prolonged exposure to the electron beam. We observed a peak in the band gap at 2.5 eV corresponding to the F center and a peak at 4.6 eV that could be attributed to the H center. Even higher levels of electron irradiation led to expulsion of the fluorine, leaving behind Ca metal as identified by the metallic density of states and the volume plasmon.

2. Materials and methods

Purple flourite was obtained from Minas Gerais, Brazil and prepared by gently disaggregating a fragment under methanol. 1 μL of the suspension was then added to a lacey carbon grid. The spectrometer was calibrated by recording zero loss peaks with a 20 V offset between them. Areas 8 nm across were imaged at 100 kV using a 5th order aberration corrected probe with a convergence of 30 mrad. The probe size on the specimen was about 0.1 nm with a current of 5–6 pA. An image from a typical region showing a thin flake from which EELS spectra were recorded is shown as Fig. 1.

Spectra were recorded at a dispersion of 20 meV/channel over a range of 30 eV using a 5 mm spectrometer entrance aperture. The full width half maximum for the zero loss peak was measured as 20 meV for a 0.5 s exposure with the beam going through vacuum, for the spectra from the specimen with longer acquisition times this was degraded to about 40 meV due to shifts in the position of the zero loss. To minimize radiation damage some spectra were taken with a 2 s acquisition time while the beam was scanned across a square 8 nm wide. Other spectra were taken by summing the results from 20 0.5 s acquisitions for a total acquisition time of 10 s.

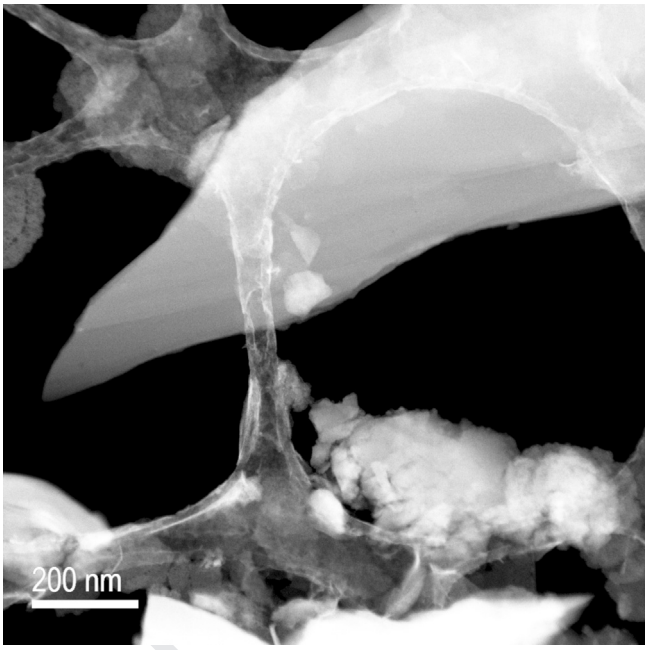

Fig. 1. Image showing a typical fluorite flake from which spectra were recorded.

3. Results and discussion

The production of defects by the electron beam happens rapidly. Fig. 2a shows the first spectrum recorded when the electron fluence was less than 300 electron/Å^2. The band onset marked by an excitonic peak at 11.83 eV is clearly visible. There is also a double peak due to defects at 2.55 eV and 2.72 eV. Comparing with Fig. 2b, the spectrum taken at the end of the damage series, the peaks at energies above the band gap are unchanged apart from relative intensities. The positions of these peaks are listed in Table 1. In the band gap region the peak at just under 3 eV is very apparent. There are also new peaks at 1.7 eV and 4.6 eV, as well as a very large peak at 9.5 eV, which has a low energy shoulder at 8.12 eV. This peak shifts to 8.5 eV after prolonged exposure and the band gap region is entirely filled (Fig. 4). Fig. 3a and 3b show two series of spectra with time showing how the peaks in the band gap increase with radiation exposure. In Fig. 3b the growth of the peak at 4.6 eV is more apparent.

The peak at 11.83 eV agrees with VUV measurements and can be attributed to an exciton at the onset of the conduction band. DFT calculations considerably underestimate the band gap, and only Bethe Salpeter [22] or GW [23] calculations put the onset at the correct energy and show the excitonic peak.

Peaks at the positions shown in Table 1 have been reported by Rubloff [12], but many are missing in Barth's measurements [14]. Only the major peaks are apparent in Stephan's results [11]. Both Barth [14] and Rubloff [12]relate the peaks they observe to results from band structure calculations [15–17]. The valence band mainly comes from F p states, and the lower parts of the conduction band have a d like character from empty Ca d states. The triplet between of peaks at 13.75 eV, 14.88 eV and 17.65 eV can be attributed to transitions from p-like valence band states to conduction band d states. Their energy separation is close to the energy separation of flat parts of the conduction bands at the Γ point, as shown by the VASP calculations of Cadalano [21]. The weak peak at 15.19 eV might be due to an indirect transition, allowed in electron

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