Optical and magnetic properties of defective MgO microcrystals

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Magnesium oxide is one of the most thoroughly studied metal-oxide materials in terms not only of a simple oxide system with rock-salt structure but also of structural defects. Recently, structure and properties of defects in MgO have attracted renewed interest in view of their intriguing electronic states, giving rise to a variety of optical, magnetic, and electron-emission properties. These new findings have revealed that our knowledge about defects in MgO is still incomplete, hence requiring further investigations on their structural and electronic properties.

It has been well recognized that MgO has several types of intrinsic defects or color centers, including oxygen and magnesium vacancies. Among other color centers, neutral oxygen vacancies (*F* centers) and positively charged oxygen vacancies (F^+ centers) have been extensively investigated during the past decades [1]. The *F* and F^+ centers exhibit broad photoluminescence (PL) bands peaking at ~2.3 eV (~500 nm) and ~3.2 eV (~400 nm), respectively, whereas the optical absorption of both types of centers is peaked essentially at the same energy of ~5 eV (~250 nm). In general, these *F*-type centers have been incorporated into MgO by the following two methods. One is by irradiation with energetic particles, such as neutron, electron and ions. The other method is by thermochemical reduction performed under highly reducing conditions at temperatures $T \geq$ ~2000 K, leading to stoichiometric deficiency in the oxygen sublattice.

Recently, we have proposed a simple but effective method to introduce *F*-type centers into MgO as an alternative to the conventional irradiation and thermochemical reduction methods [2]. The proposed method utilizes the solid phase reaction between simple oxides, such as SiO and B_2O_3, and Mg. When the Mg/Oxide mixture with a stoichiometric excess of Mg is heated under Ar atmosphere at 450–800 °C, substoichiometric MgO molecules are preferentially sublimated, forming colored micrometer-sized MgO crystals. The resulting MgO microcrystals show efficient PL emissions attributed to the *F* and F^+ centers. It should be worth mentioning that these colored MgO microcrystals exhibit a so-called random lasing effect (see Fig. 1), which is induced by multiple scattering in an amplifying disordered medium, even at room temperature.

We have found that thermally-induced ionization and carrier trapping play a vital role in the entire emission processes of the *F*-type centers especially at time scales longer than microseconds. In these time scales the PL decay profiles tend to exhibit a power-law behavior over more than 3–4 decades of time, implying thermally activated hopping and tunneling of the trapped electrons. Such delayed PL signals show two maxima in intensity at temperatures of ~130 K and ~300 K. This apparently anomalous temperature dependence is also indicative of the thermally stimulated emission processes of the originally photoexcited *F* and F^+ centers. The PL spectra above lasing threshold exhibit temperature-dependent broadening, demonstrating that the thermal vibrations of the crystal lattice affect the stimulated emission scheme as well. On the basis of these experimental results, a model of the photoexcitation, trapping and recombination processes of the F-type centers is presented.

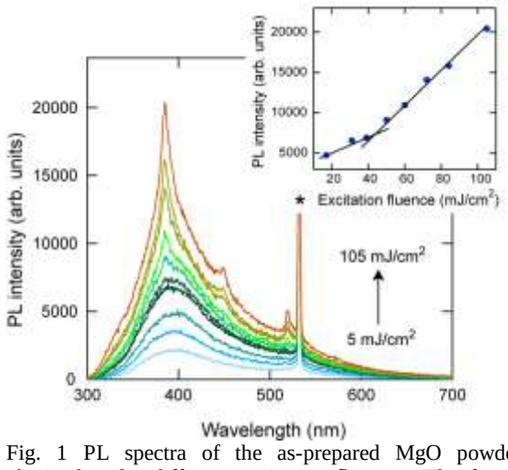

Fig. 1 PL spectra of the as-prepared MgO powder obtained under different excitation fluences. The fourth harmonic of a pulsed Nd:YAG laser (λex=266 nm) was used as an excitation source. The asterisk indicates the second harmonic (532 nm) of the Nd:YAG laser contaminated in the incident beam. The inset shows the excitation fluence dependence of the PL intensity at 384 nm.

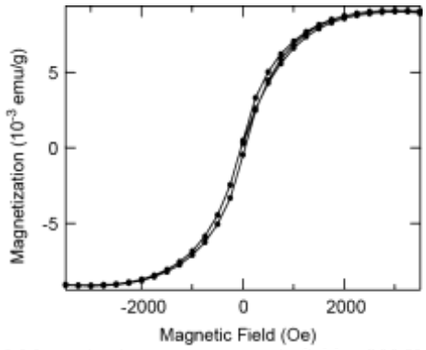

Fig. 2 Magnetization versus magnetic field at 300 K for the as-prepared MgO powder.

We have also found that room temperature ferromagnetism is observed in the lasing MgO microcrystals (see Fig. 2). Since the present MgO microcrystals do not explicitly contain magnetic metals such as Fe and Co, the present ferromagnetism most likely results from structural defects inside and/or at the surface of the oxide grains. The defect-related ferromagnetism has often been observed from other nanoscale closed-shell oxides such as ZnO and TiO_2 [3], which is referred to as d^0 ferromagnetism [4]. A possible origin of the observed ferromagnetism is also presented [5].

References

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