A broken Born-Haber cycle in Ce^{3+} doped $MgAl_2O_4$*

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Magnesium mono-aluminate has been intensively studied due to its interesting spinel structure. It has a large number of unoccupied cation sites. There are totally 96 interstices with only 24 of them occupied by Mg^{2+} and Al^{3+}. $MgAl_2O_4$ spinel also has a high degree, up to 30%, of cation disorder and many oxygen vacancies. These defects can potentially form hole and electron traps in $MgAl_2O_4$ making it a suitable for photon energy storage applications.

V^{3+} centers, formed by three holes trapped at Mg^{2+} vacancies, have been shown to give afterglow emission at 520nm in $MgAl_2O_4$ spinel.[1] (Fig. 1a) The V^{3+} center emission is due to the recombination of electrons from conduction band and holes at the V^{3+} center, thus, the hole energy level is 2.4eV below the conduction band. The afterglow decay of the V^{3+} center in undoped $MgAl_2O_4$ can persist for 1 hour (Fig. 2a), and is due to hole traps at 238°C (1.5eV) and F-center-like electron traps at 41°C (0.95eV) (Fig. 3a) as identified by Lorincz et al.[1] in the thermoluminescence spectra.

Doping Ce^{3+} into magnesium mono-aluminate greatly enhances the V^{3+} center afterglow. The persistence time of the V^{3+} center afterglow at 520nm becomes longer than 10 hours in Ce^{3+} doped $MgAl_2O_4$ (Fig. 2b). Thermoluminescence spectra of undoped and Ce^{3+} doped samples have been studied. The samples are cooled down to –100°C and irradiated by UV mercury lamp for 30min in 10^{-3} torr vacuum. Two new thermal peaks are found at 14°C and 131°C which should correspond to two electron traps with 0.6eV and 1.1eV depths respectively. (Fig. 3b) These two electron traps are created by Ce^{3+} doping.

The integrated afterglow intensity of the V^{3+} centers increases by two to three orders of magnitude by doping with Ce^{3+}, which implies that the number of trapped electrons and holes in the Ce^{3+} doped sample are more than hundreds times larger than that of the undoped sample. The reason for the much higher population of the trapped charges in Ce^{3+} doped $MgAl_2O_4$ is that the Born-Haber cycle of the Ce^{3+}/Ce^{4+} in the $MgAl_2O_4$ is broken by the electron and hole traps. Therefore the electrons and holes aggregate at traps instead of completing the Born-Haber loop. The population of trapped electrons and holes are increased and the afterglow is enhanced.

1. A. Lorincz, M. Puma, F. J. James and J. H. Crawford, Jr. J. Appl. Phys., **53(2)**, 927 (1982)

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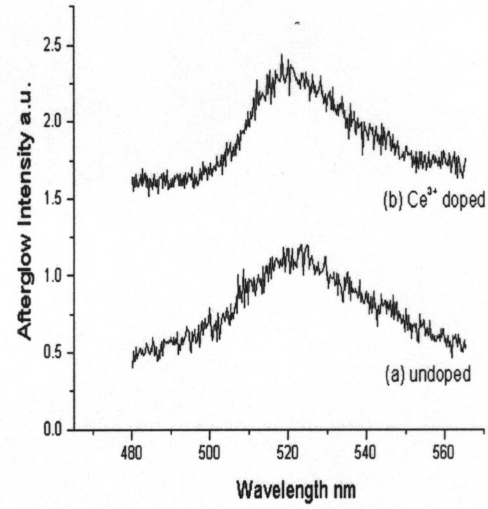

Fig. 1 Afterglow spectra (a) undoped sample, (b) Ce^{3+} doped sample of $MgAl_2O_4$.

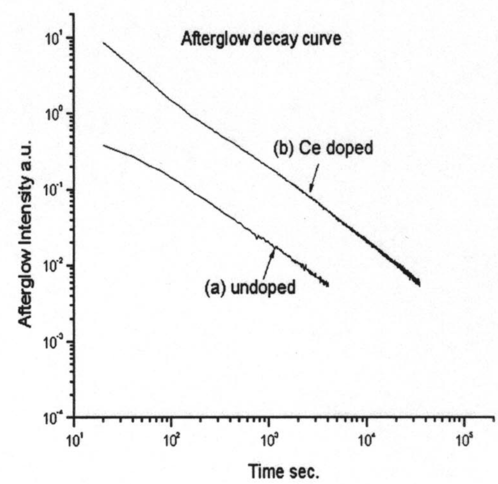

Fig. 2, Afterglow decay curve at 520nm of (a) undoped, (b) Ce^{3+} doped sample of $MgAl_2O_4$

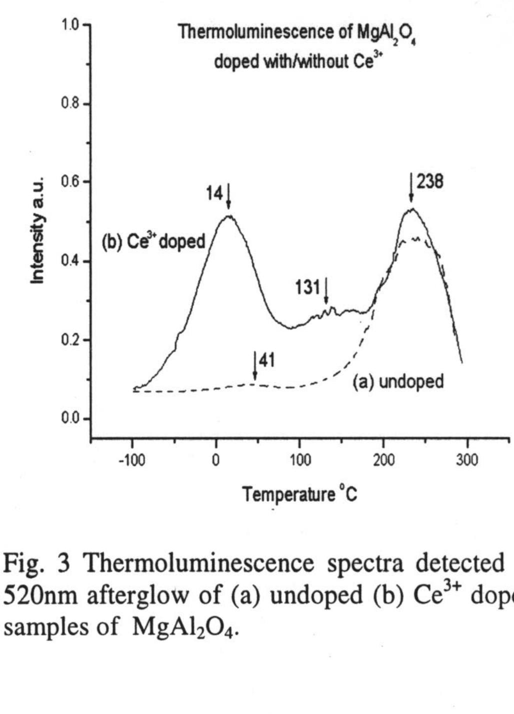

Fig. 3 Thermoluminescence spectra detected at 520nm afterglow of (a) undoped (b) Ce^{3+} doped samples of $MgAl_2O_4$.