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Correlation between Optical Absorption and Emission Bands of Cr^{3+} in MgO

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Abstract: The aim of this study is to show the correlation between optical absorption and emission energies bands of chromium ions in magnesium oxide. The luminescence and absorption of Cr^{3+} in MgO and MgO:Cr are studied in the present work. The main results of the paper include determination of optical absorption and emission energies bands of Cr^{3+} ions in MgO lattice, evaluation of the Huang-Rhys factor and the effective phonon energy. The increases of absorption and the decreases of emission bands are also discussed.

Key words: MgO, Cr, electron-phonon coupling, thermoluminescence, huang rhys factor

INTRODUCTION

Metal oxides have a wide-ranging importance in many areas of physics, geophysics, chemistry and technology. They are important as catalysts, as ceramics and high-Tc superconductors; they are potential fusion reactor materials and have relevance to micro-electronics (Kotomin and Popov, 1998).

The optical properties of the Cr^{3+} ion in bulk MgO have been thoroughly studied both experimentally and theoretically by Henderson and Imbush (1989), Dolgov *et al.* (2002) Kadri *et al.* (2007), Skvortsova and Trinkler (2009), Maghrabi *et al.* (2002), O'Neill and Henderson (1988), Karner *et al.* (2001), Groh *et al.* (1995) and Kantorovich *et al.* (2001). A great deal is known about its structure and the nature of its absorption and luminescence spectra.

The Cr^{3+} ion occupies a Mg site in the [Ar] d^3electronic configuration. Its three d electrons are well localized by a strong crystal field, so that the ion in the crystal strongly resembles the free ion (Bersuker, 1986; Stoneham, 1975). This is often exploited in the theory of transition ions (Bersuker, 1986). Since the defect is charged, cation Mg^{2+} vacancies are formed in the crystal to compensate (one vacancy for every two Cr^{3+} ions) these studies was confirmed in several works by Henderson and Imbush (1989), Dolgov *et al.* (2002), Henry *et al.* (1976) and O'Neill and Henderson (1988). This compensation leads to some of the chromium ions having different local environments of tetragonal and orthorhombic symmetries. At small Cr concentrations, most chromium ions are in octahedral (cubic) symmetry sites this results was confirmed by Skvortsova and Trinkler (2009).

The absorption spectrum was studied by several authors. Skvortsova and Trinkler (2009) and Imbusch *et al.* (1965) noted that this spectrum in the visible consists of two strong broad

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bands peaking at 620 nm (2.0 eV) and 445 nm (2.78 eV). Henderson and Imbush (1989), Larkin *et al.* (1973), Henry *et al.* (1976) and O'Neill and Henderson (1988) showed that the luminescence spectrum of cubic symmetry MgO:Cr^{3+} consists of a sharp R line at 1.77 eV (700 nm).

In the present study, the optical absorption and emission bands of Cr^{3+} have been identified; the Huang-Rhys factor and the effective phonon energy $\hbar\omega$ have been calculated. The correlation between absorption band probably responsible to the emission of Cr^{3+} has been discussed.

MATERIALS AND METHODS

Thermoluminescence and absorption measurements were carried out at the University of Science and Technology, Electronic Microscopy and Material Science Laboratory (2010). The samples used for the spectroscopic studies were 10×10×1 mm single-crystal plates of high optical quality. The first consist of the (001)-oriented MgO sample undoped but produced initially with 0.0011% of chromium, was polished by a chemo-mechanical treatment from Soekawa Chemicals Japan, a micro-probe analysis of this sample was previously discussed by Kadri *et al.* (2005, 2007). The second is MgO doped chromium (MgO:Cr); this last is obtained by thermal diffusion of small quantity of chromium (powders) at about 0.0031% of Cr in MgO; this operation needed 12 h at 1373K. The optical absorption measurements were performed at Room Temperature (RT). Concerning the luminescence characterization, the samples were irradiated by UV light (4.8 eV) for 10 min in air at 295 K. The emission spectrum is detected through a Spectrograph CP 200 (provided by JOBIN YVON company) connected to a CCD 3000 (Charge Coupled Device) and analyzed by SPECTRAMAX software by means of the Fourier self-deconvolution method.

RESULTS AND DISCUSSION

Optical Absorption Spectra of MgO and MgO:Cr

Figure 1 shows the optical absorption spectra of MgO and MgO:Cr samples in the visible region, this last contains the two bands of chromium ions which is our objective in

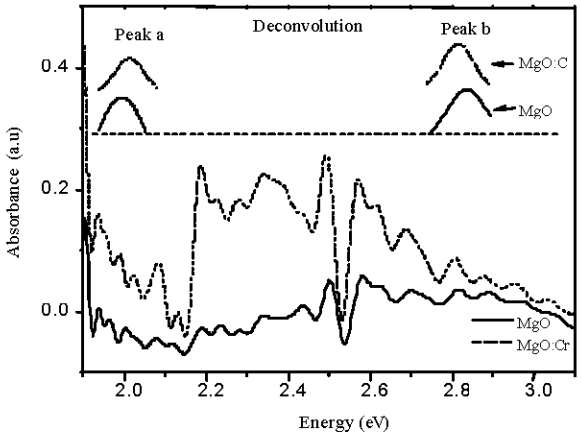

Fig. 1: Optical absorption spectra of MgO and MgO: Cr

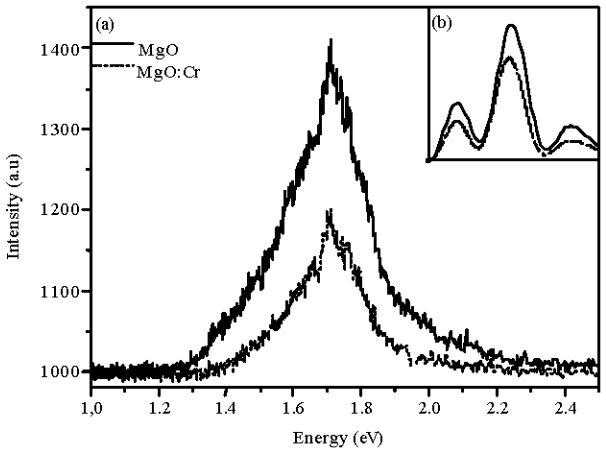

Fig. 2: Emission spectra of MgO and MgO:Cr measured at 295 K

this study. The spectra consist of two strong broads bands, the positions of absorption bands of chromium ions are indicated after deconvolution at approximately peak a at 620 nm (2.0 eV) and peak b at 440 nm (2.0 and 2.81eV), respectively.

The two broad bands peaking at 620 and 440 nm (2.0 and 2.81 eV) were attributed respectively to $^4A_2\ (t^3_2) \leftrightarrow {}^4T_2\ (t^3_2)$ and $^4A_2\ (t^3_2) \leftrightarrow {}^4T_1\ (t^3_2)$ transitions in the chromium ions in cubic sites, which agrees well with observations in $MgO:Cr^{3+}$ by several authors (Kadri *et al*., 2007; Kantorovich *et al*., 2001; De Castro, 1985). As the concentration of chromium ions increases, the optical absorption of bands at 620 nm (2.0 eV) and 440 nm (2.81eV) found to be increases.

Luminescence of Cr^{3+} Ions

The emission spectra of the MgO and MgO:Cr measured at room temperature (295K) reveals a broad band around 720 nm (1.72 eV) a full width at half-maximum (FWHM) of 0.238 and 0.208 eV for MgO and MgO:Cr respectively (Fig. 2a), after deconvolution in the sub region 1.6-1.85 eV of these spectra as shown in Fig. 2b; the emission bands of chromium at 720 nm (1.72 eV) was obtained. Chao, (1971) reported a red band which peaks at about 700 nm (1.77 eV) with vibrational sideband lines in the thermoluminescence spectrum of MgO and assigned the band to Cr^{3+} impurity, this result was already discussed by several authors (Kadri *et al*., 2005, 2007; Flecher and Leach, 1995; Kawaguchi, 2001). The spectra presented in Fig. 2 show that the intensities decreases with an increase of chromium concentration MgO lattice, this is a concentration quenching.

Electron-Phonon Coupling in MgO and MgO:Cr

In this section, the Huang-Rhys parameter S and effective phonon energy $\hbar\omega$ are estimated for MgO and MgO:Cr samples. These are the main two parameters ones describing the $\hbar\omega$ electron-phonon coupling. The parameter S is defined as the number of photons with energy excited in the absorption transition (Henderson and Imbush, 1989).

The quantities S and $\hbar\omega$ are related to the difference between the first absorption and corresponding emission bands peaks ΔE, i.e., the Stokes shift, as follows Henderson and Imbush (1989) and Torchia *et al*. (2004).

Table 1: Huang Rhys factor, E_{abs} and E_{em} for MgO and MgO:Cr

					E_{abs} (eV)Experimental			E_{abs}- E_{em} (eV)		
Samples	Cr (ppm)	T (K)	Γ (T)	S	Peak a	Peak b	E_{em} (eV)	Peak a	Peak b	2Sħω (eV)
MgO	11	295	0.238	7	2.00	2.81	1.72	0.28	1.09	0.35
MgO :Cr	42	295	0.208	6	1.99	2.80	1.72	0.27	1.08	0.30

$$\Delta E = (2S-1)\hbar\omega \tag{1}$$

The second equation required for extracting the values of S and ħω from the experimental spectral data is (Henderson and Imbush, 1989):

$$\Gamma(T) = 2.35\hbar\omega\sqrt{S\coth\left(\frac{\hbar\omega}{2kT}\right)} \tag{2}$$

where, Γ (T) is the full-width at half-maximum (FWHM) of the emission band at absolute temperature T. For the simplicity, we assume the same vibrational frequencies for all electronic states.

From the experimental absorption and emission spectra of MgO and Cr doped MgO single crystals, we estimate the Stokes shift ΔE and the FWHM of the $^2E \rightarrow {}^4A$ emission bands. The values of S and ħω can be readily obtained by solving Eq. 1 and 2. Table 1 collects the values of all parameters extracted from this study.

As seen from the Table 1, we estimated the experimental and calculated Stokes shiftΔE. If it is assumed that the excited state has the same effective frequency as the ground state, the energy for the luminescence peak E_{em} will be given by Henderson and Imbush (1989) and Kappers *et al.* (1970):

$$E_{em} = E_{abs} - 2S\hbar\omega \tag{3}$$

where E_{abs} is the energy of the absorption peak. From comparison between the experimental and calculated values presented in Table 1, we note that the absorption band around 620 nm (2.0 eV) (peak a) is responsible for the emission around 720 nm (1.72 eV) because the value of E_{abs}-E_{em} = 0.28 eV measured is comparable with 2Sħω eV calculated.

CONCLUSION

A complex study of Cr^{3+} in MgO and MgO:Cr was performed in the present paper. The absorption and emission bands of Cr^{3+} have been identified; the Huang Rhys factor S and effective phonon energy ħω were calculated (Table 1). The increases of absorption and the decreases of emission bands are due to the increased of chromium concentration. Using Equation (3), which correlated between absorption and emission energies bands of Cr^{3+}, we showed that the absorption around 2.0 eV (620 nm) is responsible to the emission around 1.72 eV (720 nm) peak a.

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