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Ceramics International 39 (2013) 2171–2173

CERAMICS INTERNATIONAL

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Short communication

Measurement of small concentrations of manganese in cadmium oxide (CdO) using electron magnetic resonance

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Received 21 June 2012; accepted 8 July 2012
Available online 7 August 2012

Abstract

Electron magnetic resonance (EMR) line widths of Mn^{2+} in CdO were measured in samples doped with small concentrations (up to 1.0 mol%) of Mn. The line width of one of the lines, which corresponds to the $|1/2\ 1/2> \leftrightarrow |-1/2\ 1/2>$ transition, was found to change in a predictable way with Mn concentration, according to the theoretical equation $\Delta H_{pp}=2.05+370f(1-f)^{42}$, where ΔH_{pp} is the line width in mT and f is the Mn concentration in mol%. The experimental results show that the technique can be used to measure, rapidly and nondestructively, small concentrations of Mn in commercial CdO.

Keywords: B. Impurities; C. Magnetic properties; D. Batteries; Electron magnetic resonance

1. Introduction

Cadmium oxide (CdO) is a compound with many industrial applications, among them in electrodes, semiconductor devices and phosphors, whose electrical and mechanical properties can be changed significantly by the presence of additives such as manganese, copper, antimony, lithium, nickel, aluminum, titanium and tin [1–7]. In many applications, therefore, it is important to know the concentration of Mn impurities in CdO. This contaminant may be present in the raw material or may be introduced in the manufacturing process.

The usual methods of determining Mn concentration in CdO samples are chemical analysis and atomic absorption spectroscopy. Although they are accurate, both methods are destructive and relatively slow. The present work proposes the use of electron magnetic resonance (EMR), an essentially nondestructive method, to measure small concentrations of Mn in CdO.

The intensity of the absorption spectrum is the EMR parameter most closely related to the impurity concentration. It depends, however, on several instrumental parameters that are often difficult to determine accurately, e.g., the applied microwave power and the cavity-filling factor. The line width of the absorption spectrum is another parameter that is related to the impurity concentration and that, within certain limits, is independent of instrumental parameters. The present study, therefore, proposes the use of the EMR line width as a reliable parameter for measuring absolute concentrations. All Mn ions are assumed to be present as Mn^{2+}, which is the most stable valence state [8] in CdO.

2. Background

Analysis of the EMR spectrum of manganese-doped cadmium oxide [8] shows that divalent manganese ions substitutionally replace cadmium ions in the lattice. For manganese concentrations larger than about 0.08 mol%, the spectrum can be fitted to the Hamiltonian

$$\mathbf{H} = g\beta\vec{H}.\vec{S} + A\vec{S}.\vec{I} \quad (1)$$

with $g=1.999$, $A=7.8$ mT.

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http://dx.doi.org/10.1016/j.ceramint.2012.07.102

The theory of dipolar broadening in diluted solid solutions was developed by Kittel and Abraham [9] and extended by de Biasi and Fernandes [10] to take exchange interactions into account. Its main results can be summarized as follows:

(i) the line shape is a truncated Lorentzian;
(ii) the peak-to-peak first derivative line width may be expressed as

$$\Delta H_{pp} = \Delta H_0 + \Delta H_d = \Delta H_0 + c_1 f_e \quad (2)$$

where ΔH_0 is the intrinsic line width, ΔH_d is the dipolar broadening, c_1 is a constant and f_e is the concentration of substitutional ions of the paramagnetic impurity not coupled by the exchange interaction, which can be expressed as

$$f_e = f(1-f)^{z(r_c)} \quad (3)$$

where f is the impurity concentration, $z(r_c)$ the number of cation sites included in a sphere of radius r_c and r_c is the effective range of the exchange interaction.

The fact that ΔH_{pp} is a function of concentration means that EMR line width data may be used to measure small concentrations of paramagnetic impurities in nonmagnetic hosts in a fast, nondestructive manner. In fact, the method has already been used to measure small concentrations of Mn in lime [11]. In the present work, the same method is applied to the Mn^{2+}:CdO system.

3. Experimental procedure

The manganese-doped samples used in this study were prepared from reagent grade CdO (Carlo Erba, 99%) and MnO_2 (Carlo Erba, 92%) powders by grinding them together and then firing the mixture for 24 h at 1100 °C in air. Room-temperature X-ray diffraction patterns matched the spectrum of cadmium oxide within experimental error. No other phases were detected.

All magnetic resonance measurements were performed at room temperature and 9.50 GHz using a Varian E-12 spectrometer with 100 kHz field modulation. The microwave power was 5 mW and the modulation amplitude was 0.1 mT. The magnetic field was calibrated with an NMR gaussmeter. The error in the measurement of the magnetic field attributable to finite line width of the NMR sample was of the order of 0.003 mT; the difference between the field at the NMR sample and at the EMR sample, as verified by removing the microwave cavity and moving the NMR probe across the air gap, was less than 0.001 mT.

4. Experimental results and discussion

The spectra of typical samples are shown in Figs. 1 and 2. All the lines are easily identified as corresponding to specific spin transitions predicted from the spin Hamiltonian given by Eq. (1). In principle, concentration data can be extracted from any of the lines in the powder spectra.

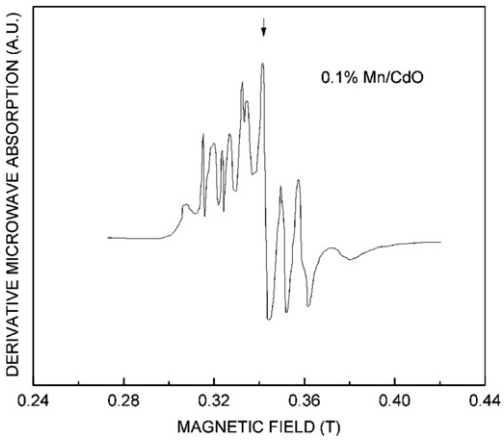

Fig. 1. EMR spectrum of a CdO sample doped with 0.1 mol% Mn. The arrow shows the line used to measure the line width of the spectrum.

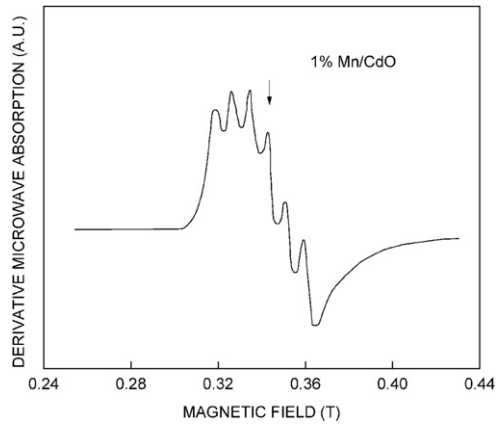

Fig. 2. EMR spectrum of a CdO sample doped with 1 mol% Mn. The arrow shows the line used to measure the line width of the spectrum.

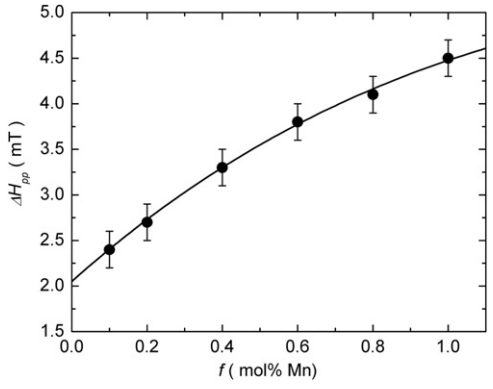

Fig. 3. Concentration dependence of the line width, ΔH_{pp}, in Mn-doped CdO. The curve is theoretical (see Eq. 3); the dots represent experimental data.

We chose the line indicated by an arrow in Figs. 1 and 2, which corresponds to the $|1/2\ \ 1/2> \leftrightarrow |-1/2\ \ 1/2>$ transition, because it is the most intense.

The line width of the $|1/2\ 1/2> \leftrightarrow |-1/2\ 1/2>$ transition is shown in Fig. 3 as a function of Mn concentration. The experimental data are fitted well by the theoretical

equation [12]

$$\Delta H_{pp} = 2.05 + 370 f (1-f)^{42} \quad (4)$$

where ΔH_{pp} is the line width in mT and f is the Mn concentration in mol%.

Using Eq. (4), it is possible to determine the Mn concentration in a given CdO sample from the experimental values of the manganese $|1/2\ 1/2> \leftrightarrow |-1/2\ 1/2>$ transition line width.

5. Conclusions

A fast, nondestructive method, based on the measurement of the EMR line width of Mn^{2+} is proposed to determine small concentrations of Mn in CdO. Its usefulness, compared to more traditional methods such as chemical analysis, appears to be limited only by the fact that it requires fairly sophisticated equipment.

References

[1] V. Bilgin, I. AkyuzI, S. Kose, F. Atay, Characterization of Mn-incorporated CdO films grown by ultrasonic spray pyrolysis, Semiconductor Science and Technology 21 (2006) 579–585.

[2] R.K. Gupta, F. Yakuphanoglu, F.M. Amanullah, Band gap engineering of nanostructure Cu doped CdO films, Physica E 43 (2011) 1666–1668.

[3] Z. Serbetçi, R.K. Gupta, F. Yakuphanoglu, Preparation and characterization of nanorods Sb doped CdO films by sol–gel technique, Journal of Sol–Gel Science and Technology 61 (2012) 477–483.

[4] R.K. Gupta, Z. Serbetçi, F. Yakuphanoglu, Bandgap variation in size controlled nanostructured Li–Ni co-doped CdO thin films, Journal of Alloys and Compound 515 (2012) 96–100.

[5] R.K. Gupta, K. Ghosh, R. Patel, S.R. Mishra, P.K. Kahol, Preparation and characterization of highly conducting and transparent Al doped CdO thin films by pulsed laser deposition, Current Applied Physics 9 (2009) 673–677.

[6] B. Saha, R. Thapa, K.K. Chattopadhyay, Bandgap widening in highly conducting CdO thin film by Ti incorporation through radio frequency magnetron sputtering technique, Solid State Communications 145 (2008) 33–37.

[7] Z.Y. Zhao, D.L. Morel, C.S. Ferekides, Electrical and optical properties of tin-doped CdO films deposited by atmospheric metalorganic chemical vapor deposition, Thin Solid Films 413 (2002) 203–211.

[8] R.F. Shinde, S.K. Date, X-Band EPR studies of hyperfine and superhyperfine structure of Mn^{2+} ions in polycrystalline CdO, Material Chemistry and Physics 24 (989) 71–81.

[9] C. Kittel, E. AbrahamsE, Dipolar broadening of magnetic resonance lines in magnetically diluted crystals, Physical Review 90 (1953) 238–239.

[10] R.S. de Biasi, A.A.R. Fernandes, The ESR line width of dilute solid solutions, Journal of Physics C 16 (1983) 5481–5489.

[11] R.S. de Biasi, M.L.N. Grillo, Measurement of small concentrations of manganese in lime (CaO) using electron spin resonance, Journal of the American Ceramic Society 86 (2003) 195–196.

[12] R.S. de Biasi, M.L.N. Grillo, Influence of manganese concentration on the electron magnetic resonance spectrum of Mn^{2+} in CdO, Journal of Alloys and Compounds 485 (2009) 26–28.