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Investigation of Mn^{2+} Diffusion in Lime (CaO) Using Electron Magnetic Resonance

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The electron magnetic resonance (EMR) technique was used to investigate the diffusion of Mn^{2+} in lime (CaO). The EMR absorption intensity was measured for several annealing times and three different temperatures of isothermal annealing: 1273, 1323 and 1373 K. The activation energy for diffusion, calculated from the experimental data using a theoretical model based on the Fick equation, was found to be $E_A = 266 \pm 27$ kJ·Mol^{-1}, about 30% larger than the activation energy for diffusion of Mn^{2+} in magnesia (MgO), a compound with the same crystal structure. The difference is attributed to the fact that the Ca^{2+} has a larger ionic radius than Mg^{2+}.

Keywords: *ceramics, electron magnetic resonance, calcium oxide, manganese, diffusion*

1. Introduction

Lime (CaO) is a ceramic material with many industrial applications, especially as a flux in steel manufacturing and in road construction, whose properties can be changed significantly by the presence of transition elements such as iron, chromium and manganese. Electron magnetic resonance (EMR) spectroscopy is a convenient method for studying these impurities within the CaO structure. In the present work, we investigate the diffusion of Mn^{2+} in CaO.

Analysis of the EMR spectrum of single-crystal manganese-doped calcium oxide[1] shows that divalent manganese ions substitutionally replace calcium ions in the lattice. The spectrum can be fitted to the Hamiltonian

$$\mathbf{H} = g\beta(H_xS_x + H_yS_y + H_zS_z) + A(S_xI_x + S_yI_y + S_zI_z) + (a/6)(S_x^4 + S_y^4 + S_z^4 - 707/16) \qquad (1)$$

with $g = 2.0009$, $A = -0.00808$ cm^{-1} and $a = 0.00059$ cm^{-1}.

The EMR spectrum of Mn-doped CaO powder[2] shows only the hyperfine sextet associated with the (–1/2, +1/2) transition, which is similar to the same sextet in single crystals, since a cubic crystal field will not split the ±1/2 Kramer doublet, except for a very small S^3 term[3].

The theory of ionic diffusion as applied to EMR measurements was developed by Davidson and Che[4]. Using the Fick equation, they showed that the intensity of the EMR spectrum may be expressed as

$$I = I_s - kt^{-1/2} \qquad (2)$$

where I_s is the saturation intensity and $k = cD^{-1/2}$, where c is a constant and D is the diffusion constant. The thermal behavior of the D factor can be described by an Arrhenius law: for each annealing temperature T, the value of k is obtained by fitting Equation 2 to the data points. A plot of ln k versus $1/T$ leads to the activation energy E_A.

2. Experimental Procedure

The manganese-doped samples used in this study were prepared from reagent grade $CaCO_3$ (Vetec, 99%) and MnO_2 (Carlo Erba, 92%) powders by grinding them together and then annealing the mixture in air. The starting composition corresponded to a 0.2% Mn/Ca atomic ratio. Magnetic resonance measurements were performed at room temperature and 9.50 GHz using a Varian E-12 spectrometer with 100 kHz field modulation.

3. Experimental Results and Discussion

A typical spectrum of Mn-doped CaO is shown in Figure 1. In principle, intensity data could be extracted from any of the lines in the powder spectrum; we chose the line indicated by an arrow in Figure 1. For the chosen line, the linewidth and the lineshape were the same, within experimental error, in all samples investigated, and thus the line amplitude was used as an accurate indicator of line intensity. The dependence of the line intensity on annealing time is shown in Figure 2 for three annealing temperatures; the best fits to Equation 2 are also shown. In the case of samples annealed at 1273 K, the data point for 0.25 h was excluded from the fitting because the annealing time was too short[4] for Equation 2 to be valid. Assuming that the activation energy is constant in the 1273 K-1373 K temperature range, a plot of ln k versus $1/T$ (Figure 3) yields an activation energy $E_A = 266 \pm 27$ kJ·Mol^{-1}. The fact that this value is about 30% larger than the activation energy $E_A = 203 \pm 24$ kJ·Mol^{-1} for diffusion

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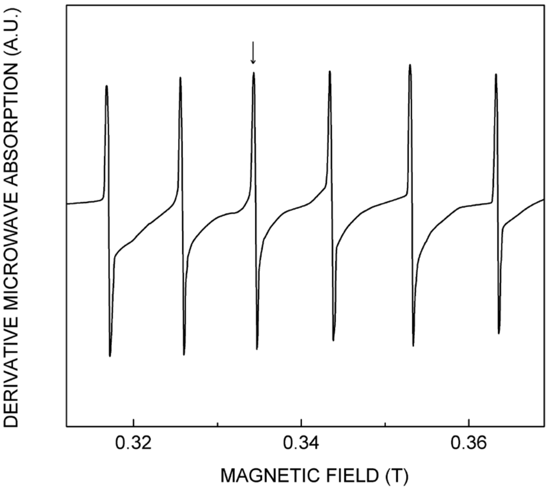

Figure 1. EMR spectrum of a Mn-doped CaO sample annealed for 2 h at 1273 K. The arrow shows the line used to measure the spectrum intensity.

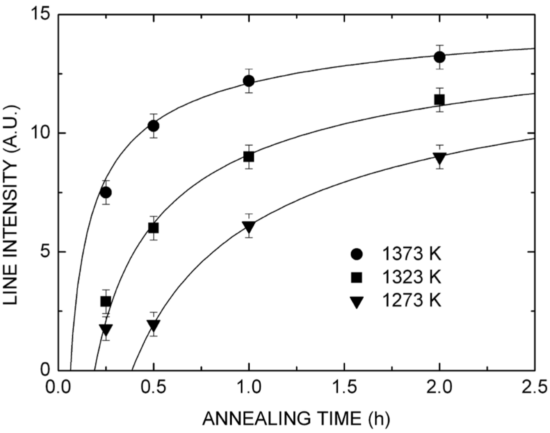

Figure 2. Intensity of the EMR spectrum of Mn^{2+} in CaO as a function of annealing time, for three annealing temperatures. The solid lines are fits to Equation 2.

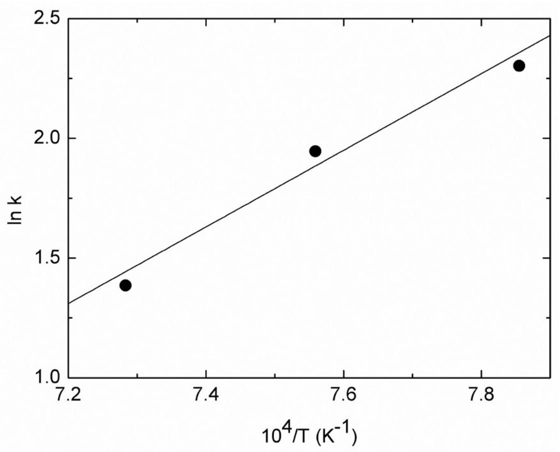

Figure 3. Arrhenius plot for the diffusion of Mn^{2+} in CaO. The solid line is a least squares fit to the data points.

of Mn^{2+} in magnesia (MgO)[5], a compound with the same crystal structure, is attributed to the fact the ionic radius of Ca^{2+}, 114 pm[6] is about 30% larger than the ionic radius of Mg^{2+}, 86 pm[6].

4. Conclusions

A fast, non-destructive method, based on EMR line intensity, has been used to determine the activation energy for diffusion of Mn^{2+} in CaO. This result should be useful in studies of the influence of manganese doping on the properties of lime.

Acknowledgments

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