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Electron Spin Resonance Study of Chicken Eggshell Transformation

[1]Piyapong Pankaew, [2]Weeranut Kaewwiset, [3]Ekachai Hoonnivathana, [4]Pichet Limsuwan and [4]Kittisakchai Naemchanthara

[1]*Division of Science, Faculty of Science and Technology, Rajamangala University of Technology Phra Nakhon, Bangkok, 10800, Thailand*
[2]*Department of Physics, Faculty of Liberal Arts and Science, Kasetsart University, Kamphaeng Saen Campus, Nakhon Pathom 73140, Thailand*
[3]*Department of Physics, Faculty of Science, Kasetsart University, Bangkok 10900, Thailand*
[4]*Department of Physics, Faculty of Science, King Mongkut's University of Technology Thonburi, Bangkok 10140, Thailand*

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ABSTRACT

The chicken eggshell was firstly prepared by crushing and then calcining in air at different temperatures from 200 to 1300 °C for 4 hours at an interval of 100°C. The ESR spectrum of the eggshells revealed an additional sextet signal, that corresponding of the Mn^{2+}. Each Mn^{2+} peak splits into doublet, which results from the calcite structure of chicken eggshell. At temperature increased up to 700°C, the intensity of sextet signals increased. The six doublet peaks of Mn^{2+} ions became the six singlet peaks after heating at 900°C. This result is due to chicken eggshells are no longer calcite at 900°C, but become cubic structure of CaO. The ESR spectra of chicken eggshells relating to different g-values for organic carbon was found to be in the range of 2.0068 to 2.0023 $\pm$ 0.0004. The ESR study can indicate the phase transformation of chicken eggshell ($CaCO_3$) to CaO for heating temperatures from 200-1300°C.

Key words: Calcium Carbonate, Phase Transformation, Eggshells, Electron spin resonance.

INTRODUCTION

Electron spin resonance (ESR) is a method of microwave absorption spectroscopy used in physics and chemistry and is being used in earth sciences [5]. It is a very sensitive method for detection of free radicals. On the other hand ESR is one of the most advanced accurate and precise techniques. It is characterized by non-destructive study of structure and behavior of materials. The chicken eggshell consists of calcium carbonate (94%), calcium phosphate (1%) and organic matter (4%). Thus, the objective of in this work is to investigate the phase transformation of chicken eggshell using ESR spectroscopy. Its temperature effect was also investigated.

Materials and Methods

Sample Preparation:

The eggs were obtained from Charoen Pokphand Foods, (CPF) public company limited, Bangkok, Thailand. The eggs were removed their membranes and washed with distilled water to remove impurities. The shells were dry in air for a few days and then were ground into fine powder. To investigate temperature effect, these powdered eggshells were calcined at the range from 200 to 1300 °C for 4 h with a rate of 5 °C/min.

Sample Characterization:

Eggshell was required to measure the ESR spectra in the X-band with the Bruker spectrometer, Model E500 at 0.5 mT field (100 kHz) modulation amplitude and time constant 0.035 s TE_{011} mode cavity. About 50 mg of before and after heated in quartz probe tube with stopcocks was placed in the instruments. The experimental setting were used: central magnetic field 350 mT; sweep width 12 mT; microwave power 1 mW; modulation frequency 100 kHz; modulation amplitude 0.10 mT; receiver gain $1x10^5$; sweep time 84; time constant 0.3 s; number of scans 30.

In this study, the oxidation state of Mn^{2+} was determined using an electron spin resonance technique. The Mn^{2+} ions have to 5 unpaired electrons in d-orbital and thus can be detected. Two standard samples, DPPH and MgO: Mn^{2+} was used to calibrate applied magnetic filed positions. The evaluation of spin Hamiltonian parameters of ESR

Corresponding Author: Piyapong Pankaew, Division of Science, Faculty of Science and Technology, Rajamangala University of Technology Phra Nakhon, Bangkok, 10800, Thailand.
E-mail: piyapong.p@rmutp.ac.th

spectra can be accomplished by fitting of theoretically line positions to the measured spectrum. The ESR spectra of powder samples before and after heated were studied. The measurements were performed in X-band frequency (~9.04 GHz).

Results and Discussions

Chicken eggshells were accurately weighed before keeping it in the ESR sample tube so that the intensity of signals could be compared before and after heating temperature. The ESR spectrum of chicken eggshells before heating temperature was recorded and shown in Fig. 1. The ESR spectrum of the eggshells consists an additional sextet signal, that corresponding of the Mn^{2+} spectrum are very good agreement with the manganese-doped CaO [2]. The weaker pair of peaks occurred between the main peaks are so-called the forbidden transitions in which both electron and nuclear spin state change, i.e. $\Delta m_s = 1$, $\Delta m_I = 1$. Each Mn^{2+} peak splits into doublet, which results from the calcite. There are two magnetically inequivalent Mn^{2+} paramagnetic centers due to two different Ca^{2+} sites occupied by Mn^{2+} ions in trigonal symmetry, arising from the distortion of oxygen octahedrons of nearest neighbors [4]. Between spectra 3 and 4 of Mn^{2+} were paramagnetic center which have on the chicken eggshells but not appear on the other calcium carbonate. The peak of paramagnetic center chicken eggshells was identified as an organic carbon.

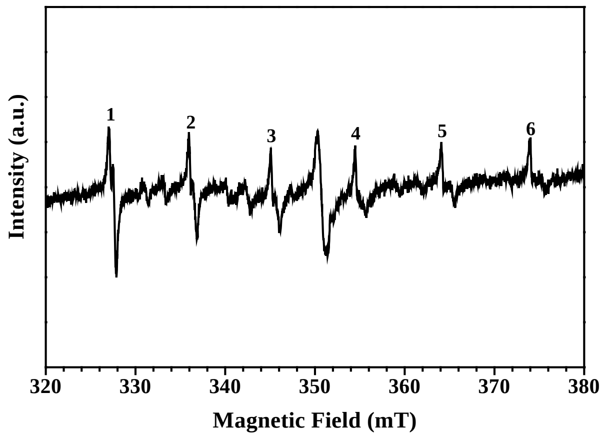

Fig. 1: ESR spectra of chicken eggshells before heating temperature.

The ESR spectrum of chicken eggshells before and after heating at temperature ranges of 200-1300 °C was recorded and shown in Fig. 2 and 3. The chicken eggshell was assigned as K. The intensity of the sextet signals are strongly enhanced when chicken eggshells were heated at different temperatures. The intensity of sextet signals increased as the temperature increased up to 700°C and decreased after chicken eggshells were heated higher than 700 °C. However, it was found that after heating at 900 °C, the six doublet peaks of Mn^{2+} ions became the six singlet peaks as shown in Fig. 3. This result is due to chicken eggshells are no longer calcite at 900°C, but become cubic structure of CaO [4]. On the other hand, the intensity of organic carbon of chicken eggshells was strongly enhanced after heating temperatures were increased up to 700 °C. At 800 °C, the intensity of organic carbon rapidly decreased. It is still present in a very small amount in the chicken eggshells annealed at 900 °C and it was disappeared at 1000 °C as shown in Figs. 3 and 4.

The ESR spectra of chicken eggshells correspond to different g-values for organic carbon can be calculated and it was found to be in the range of 2.0068 to 2.0023 ± 0.0004. Fig. 5 shows the g-values as a function of heating temperatures for organic carbon in chicken egg shells. It is seen that the g-value of the organic carbon rapidly decreased from 2.0068 to 2.0023 corresponded to the heating temperature range from 200-600°C. The g-value gradually decreased with increasing heating temperatures from 600-900 °C. The decreased of the g-value with heating temperature approximately follows a 1/T (heating temperature) relationship. The variation of g-value with heating temperature was similar to those found by Hillman *et al*. [1] for other organic carbon radical signals on cereal grains. In the case of the higher heating temperatures, the g-values (2.0068–2.0023) are typical of those found for π-type aromatic hydrocarbon radicals.

Fig. 6 shows the variation of peak-to-peak line width (ΔHpp) with heating temperature range of 200-1300°C of organic carbon in chicken egg shells. The results show that ΔHpp decreased from 1.123 to 0.269 mT for heating temperatures range of 200-600°C. At higher annealing temperatures ΔHpp line width is constant. This result is due to the phase transformation from $CaCO_3$ to CaO for heating temperatures from 200-1300°C as previously discussed in Fig. 2 and 3.

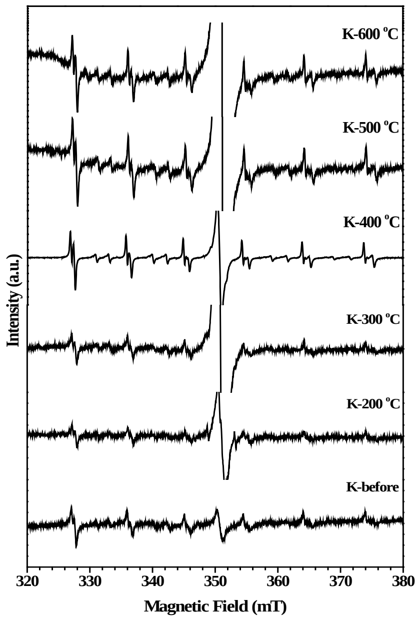

Fig. 2: ESR spectra of chicken eggshells before and after heating at temperatures of 200-600 ^{o}C.

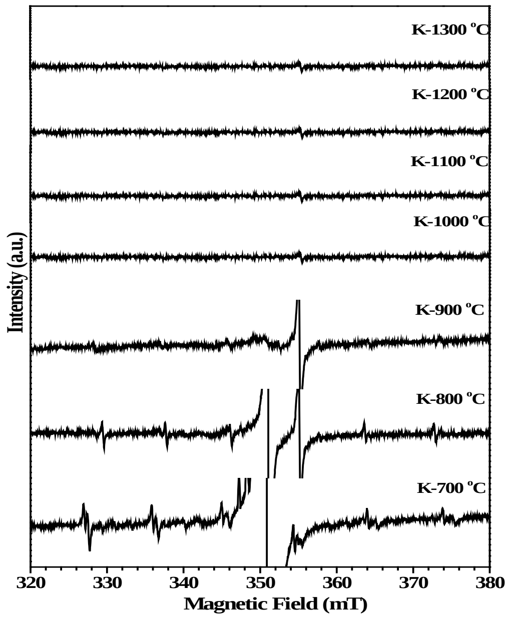

Fig. 3: ESR spectra of chicken eggshells after heating at temperatures of 700-1300 ^{o}C.

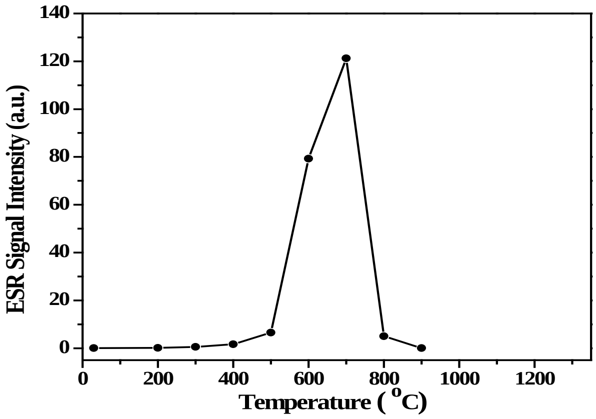

Fig. 4: Variation of the intensity of heat induced ESR signal with heating temperatures.

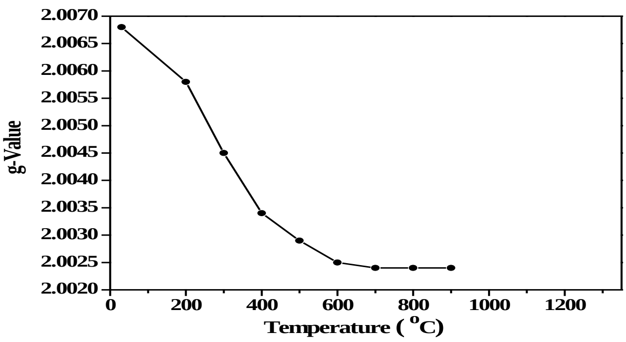

Fig. 5: Variation in g-Values of heat induced ESR signal with heating temperatures.

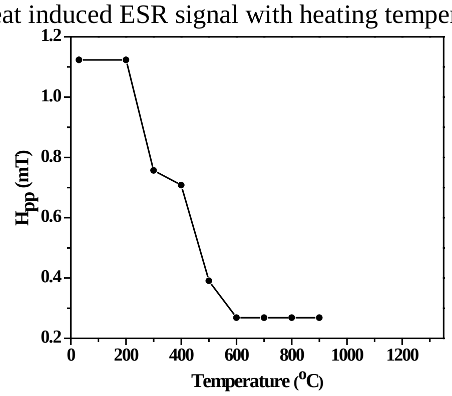

Fig. 6: Variation of the peak-to-peak line width (ΔHpp) values of heat induced ESR signal with heating temperatures.

Conclusion:

In the present investigation, the phase transformation of powdered eggshells calcined at temperatures ranges of 200-1300 °C was indicated by electron spin resonance (ESR) technique. The ESR spectrum of the eggshells revealed an additional sextet signal, that corresponding of the Mn^{2+}. Each Mn^{2+} peak splits into doublet, which results from the calcite structure of chicken eggshell. At temperature increased up to 700°C, the intensity of sextet signals increased. The six doublet peaks of Mn^{2+} ions became the six singlet peaks after heating at 900 °C. This result is due to chicken eggshells are no longer calcite at 900°C, but become cubic structure of CaO. The ESR spectra of chicken eggshells relating to different g-values for organic carbon was found to be in the range of 2.0068 to 2.0023 ± 0.0004. It is seen that the g-value of the organic carbon rapidly decreased from 2.0068 to 2.0023 corresponded to the heating temperature range from 200-600°C. The g-value gradually decreased with increasing heating temperatures of 600-900 °C. The variation of peak-to-peak line width (ΔHpp) with different temperatures of organic carbon in chicken egg shells revealed ΔHpp decreased from 1.123 to 0.269 mT for heating temperatures range of 200-600°C. At higher annealing temperatures ΔHpp line width is constant. This result is due to the phase transformation from $CaCO_3$ to CaO for heating temperatures from 200-1300°C.

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