A Novel Low-Temperature-Fired Multifunctional Varistor-Magnetic Material

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Outline

- Research Background
- Experimental Procedures
- Result and Discussion
- Summary
Research Background
Electronic devices are toward light and slim.

Example of typical metric sizes
Integrated passive device (ESD/EMI filter)

Multilayer capacitor/varistor-based integrated passive devices

T. M. Feichtinger, M. Rath, T. Pürstinger, G. F. Engel, “Highly integrated multilayer varistors for ESD/EMI filtering applications,” CARTS USA, 113-125, April 3~6, Orlando, FL (2006)

Mismatched densification kinetics, chemical reaction and thermal expansion mismatch between the layers could generate undesirable defects in cofiring process.

→ A multifunction material can avoid these problems.
→ Make ferrite exhibit varistor property.
Varistor property originated from Schottky barrier

N-type grains and p-type grain-boundaries would form Schottky barriers.

The microstructure of ZnO varistor

In ZnO varistors, two kinds of additive oxides are used to improve varistor property. One kind of cation dissolves in ZnO grains to increase the conductance of grains. The other one would segregate at the grain-boundaries, so-called varistor former.

Mayer reported that ferrites may exhibit varistor properties while Schottky barriers exist, which can be used to fabricate multifunctional varistor-magnetic devices.

CuCr$_{0.2}$Fe$_{1.8}$O$_4$ is an n-type semi-conductor, CuCr$_2$O$_4$ can store or release oxygen at different temperature or atmosphere. $V_2O_5$ can act as a varistor former and sintering aid in ZnO varistor. In this study, a low temperature-fired multifunctional varistor-magnetic ferrite material was prepared by adding $V_2O_5$ into CuCr$_{0.2}$Fe$_{1.8}$O$_4$ ferrites.

Experimental Procedures
CuCr_{0.2}Fe_{1.8}O_4 specimens were prepared using a conventional solid-state reaction and sintering process. V_2O_5 powders were added into the calcined powders with a composition expression, such as (100-x) mol% CuCr_{0.2}Fe_{1.8}O_4 + x mol% V_2O_5 (x = 0.5, 1, 2), abbreviate as CCFO05, CCFO1, CCFO2.
Result and Discussion
After calcination and sintering the specimen exhibit single spinel phase in X-ray diffraction patterns.
Density of the specimens

The theoretical density for the CCFO specimens are 5.37 g/cm³ ~ 5.42 g/cm³, CCFO05 cannot sinter at 900°C.
Average grain size increased with increasing sintering temperature and $V_2O_5$ addition.
Copper segregated at grain-boundaries

<table>
<thead>
<tr>
<th>Position</th>
<th>Cu</th>
<th>Fe</th>
<th>Cr</th>
<th>V</th>
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<tr>
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<td>2.03</td>
<td>90.00</td>
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<td>0.09</td>
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Energy dispersive spectroscopy (EDS) analyses results.

High-angle annular dark field (HAADF) image for CCFO1 sintered at 900°C.
The fracture specimen grain boundaries remained on the surface because of the relatively weak linkage between grains. XPS results show that grain-boundaries contain more Cu\(^{2+}\) than grain. Copper oxide with vacancies (Cu\(_{2-x}\)O, Cu\(_{1-x}\)O) are p-type semiconductor. The oxidization for copper oxide located at grain-boundaries can increase the acceptor concentration and the Schottky barrier height.
 Activation energy for the specimens

The activation energy for the grain was obtained through the impedance spectrum and Arrhenius equation.

$V^{5+}$ would solute into spinel structure and increase the donor concentration, which resulted in the semi-conductive grain.
Non-linear coefficients for the specimens

\[ \alpha = \frac{\log J_2 - \log J_1}{\log E_2 - \log E_1} \]

\( J_1 = 1 \text{mA/cm}^2, J_2 = 10^{1.5} \text{mA/cm}^2, E_1 \) and \( E_2 \) are the electric fields corresponding to \( J_1 \) and \( J_2 \), respectively.

Non-linear coefficient decreased with increasing grain size.
CuCr\textsubscript{0.2}Fe\textsubscript{1.8}O\textsubscript{4} ferrites were soft magnetic materials.

M-H curve for CCFO1 specimen sintered at 900°C. The coercive force and remanent flux density are 200Oe and 9.848emu/g, respectively.
Summer summery

- The addition of $V_2O_5$ can effectively reduce the sintering temperature of CuCr$_{0.2}$Fe$_{1.8}$O$_4$ ferrites to temperatures of lower than 950°C.
- $V^{5+}$ ions would dissolve into the grains and acted as donor dopant, which resulted in the semiconductive grain.
- The segregation of copper rich phase(s) at the grain-boundary may increase the acceptor concentration.