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Influence of addition of copper cadmium ferrite on the dielectric and electrical behavior of $BaSrTiO_3$ ceramics

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Abstract

Polycrystalline composites of (1 − x) ($Ba_{0.7}Sr_{0.3}TiO_3$)–x($Cu_{0.5}Cd_{0.5}Fe_2O_4$) (x = 0.15, 0.30, 0.45) were prepared by a modified wet chemical method. X-ray diffraction studies at room temperature confirmed the formation of polycrystalline composite with perovskite–spinel structure. Scanning electron micrographs also suggest polycrystalline microstructure with the grains of unequal size distributed throughout the pellet samples. Dielectric studies of the composites reveal that the effect of ferrite in the composites is to shift the ferroelectric–non-ferroelectric phase transition to higher temperature side. Complex impedance spectroscopy analysis indicated negative temperature coefficient of resistance behavior identical to semiconductors. The activation energy calculated from the temperature dependence of conductivity pattern shows that the conduction process can occur due to the hopping of electrons between Fe^{3+} and Fe^{2+}, leading to the contribution of both single and doubly-ionized oxygen vacancies.

Keywords: D. Perovskites; X-ray diffraction; Complex impedance spectroscopy; Negative temperature coefficient of resistance

1. Introduction

With the rapid development of portable electronic products and wireless technology, many electronic devices have evolved into collections of highly integrated systems for multiple functionality, faster operating speed, higher reliability, and reduced sizes. This demands the multifunctional integrated components, serving as both inductor and capacitor. As a result, low temperature co-fired ceramics (LTCC) with integrated capacitive ferroelectrics and inductive ferrites has been regarded as a feasible solution through complex circuit designs. However, in the multilayer LTCC structure consisting of ferroelectrics and ferrites layers, there are always many undesirable defects, such as cracks, pores and cambers, owing to the co-firing mismatch between different material layers, which will damage the property and reliability of end products [1]. A single material with both inductance and capacitance is desired for true integration in one element. For example, if the materials with both high permeability and permittivity are used in the anti electromagnetic interference filters, the size of components can be dramatically minimized compared to that of conventional filters composed of discrete inductors and capacitors. Because few phase material in nature can meet such needs [2], the development of ferroelectric–ferromagnetic composite ceramics is greatly motivated.

Recently, electronic composite materials have attracted many researchers and led to an improvement in the piezoelectric, piezomagnetic and mechanical properties, which are applicable for a particular application [3]. The electroceramic composite materials synthesized from two different phases account for the sum, combination and product properties [4]. In such composite materials, electromagnetic coupling occurs and accounts for an excellent magnetoelectric effect [5–7]. They are also significant for the fundamental research on novel coupling properties such as electro-optic, electro-magnetic and other couplings [8] and have potential applications in electromagnetic interference filters, capacitors, transducers and integral chip inductors. Ferrites and ferroelectric materials are used in a large family of microwave and millimeter wave devices. Many material systems, such as $BaTiO_3$/NiCuZn ferrite, $BaTiO_3$/MgCuZn

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ferrite, $Pb(Mg_{1/3}Nb_{2/3})O_3$–$Pb(Zn_{1/3}Nb_{2/3})O_3$–$PbTiO_3$/NiCuZn ferrite and $Bi_2(Zn_{1/3}Nb_{2/3})_2O_7$/NiCuZn ferrite, were investigated and found to exhibit fine dielectric and magnetic properties.

Ferrite devices typically have high figures of merit, large bandwidths, low insertion loss, and frequency agility [9]. Current ferrite components, however, present two critical problems for advanced system applications: large size and high cost. Ferroelectric components, on the other hand, provide solutions both in size and cost [10,11]. Size reduction arises from the large relative dielectric constants. These components are also tunable with the application of a modest voltage. Since the tunability is not as good as for ferrites, the voltage tenability and the low cost are advantageous for many applications. It is likely that ferrite–ferroelectric composites could be used to produce small, low cost, and highly tunable elements for microwave applications. Previous works on multifunctional ferrite–ferroelectric composite materials have emphasized static magnetization properties and complex permeability and permittivity [12–15]. $Cu_{0.5}Cd_{0.5}Fe_2O_4$ (CCF) has been in this was selected as magnetic material because it has high resistance, high magnetostriction coefficient, high Curie temperature and low dielectric permittivity and $Ba_{0.7}Sr_{0.3}TiO_3$ (BST) as a ferroelectric because it has high dielectric constant, high piezoelectric coefficient, high tunability and low dielectric loss. The objective of this work is to prepare a series of ferrite–ferroelectric composite materials with a systematic variation in the ferrite loading and to examine the temperature dependence of dielectric constant (ε') and dielectric loss, ac conductivity; and impedance spectroscopic studies.

2. Impedance formalism

The electrical properties of the materials are investigated by a complex impedance spectroscopy (CIS) technique. This technique has a special significance in the analysis of electrical properties of a material because it enables us to examine the correlation of properties (viz. conductivity, dielectric behavior, relaxation characteristics, etc.) with microstructures (i.e. bulk material and grain boundary contributions, etc.) [16]. Further, it is an elegant non-destructive technique that separates the barrier properties attributing to grains (bulk) from grain boundaries, where each of them has different relaxation time. As a result, a separate semicircle in the complex impedance spectrum is formed.

As it is well established that impedance spectroscopy is an effective method to study (a) properties of the intragranular and interfacial regions and their interrelations, (b) their temperature and frequency dependent phenomena in order to separate the individual contributions from the total impedance and (c) their interfaces with electronically conducting electrodes [17–19,16,20], each impedance parameter can be used to highlight a particular aspect of the response of a sample. More interestingly, the impedance measurements enable us to eliminate the error, if any, due to stray frequency effects. The frequency dependence of various impedance parameters of a material can be described via the complex permittivity (ε^*), complex impedance (Z^*), complex admittance (Y^*), complex electric modulus (M^*) and dielectric loss or dissipation factor ($\tan\delta$) [18]. They are in turn related to each other as follows:

$\varepsilon^* = \varepsilon' - \varepsilon''$, where $\varepsilon' = (-Z'')/\omega C_0(Z'^2 + Z''^2)$ and $\varepsilon'' = Z'/\omega C_0(Z'^2 + Z''^2)$

$M^* = M' + jM'' = (1/\varepsilon^*) = j\omega\varepsilon_0 Z^*$; $Z^* = Z' - jZ'' = (1/jC_0\varepsilon^*\omega)$; $Y^* = Y' + jY'' = j\omega C_0$ and $\tan\delta = (\varepsilon''/\varepsilon') = (M''/M') = (Z''/Z') = (Y'/Y'')$ ($\omega = 2\pi f$ is the angular frequency, $'$ and $''$ mark the real and imaginary part of complex parameters (ε^*, Z^*, M^* and Y^*), C_0 is the geometrical capacitance, $j = \sqrt{-1}$. These relations offer a wide scope for a graphical representation of various impedance parameters under different experimental conditions (i.e. temperature, frequency, etc.). The use of function Z^* and Y^* is particularly appropriate for the resistive and/or conductive analysis where the long-range conduction dominates, where as the ε^* and M^* functions are suitable when localized relaxation dominates. So the plotting of a.c. data in terms of impedance, electric modulus and dielectric permittivity simultaneously gives a complete assignment of all the physical processes taking place in the material [21].

3. Experimental procedures

3.1. Preparation of the composites

Piezoelectric phase, BST powder as reported by us [22] was synthesized by sol gel method using barium acetate, strontium acetate, and titanium (IV) isopropoxide as precursors. The magnetic phase, CCF was prepared by citrate precursor method as reported by us [23]. Then, both the calcined powders $(1 - x)$ BST–x CCF with $x = 0$, 0.15, 0.30, 0.45 and 1.00 were mixed together and ball milled for 48 h in acetone medium. The powder composites were uniaxially pressed into cylindrical pellets of diameter ~10 mm and thickness ~1 mm using a hydraulic press at a pressure of 8 MPa and sintered at 850°C for 2 h.

3.2. Structural characterization

The crystal structures were examined by an X-ray diffraction (XRD) technique using a Philips Analytical, X'pert-MPD, employing CuKa radiation under the conditions 50 kV and 40 mA. The samples were scanned at an interval of 0.038°/min for 2θ in the range 10°–70°. The identification of the peaks was carried out using the Topas23 refinement program. Microstructural examination of the fractured surface of the ceramics was carried out by scanning electron microscopy (SEM) using a JEOL 6300 scanning electron microscope.

3.3. Electrical characterization

For dielectric measurements, the disk-shaped samples were ground on SiC paper to reduce the thickness to less than 1 mm and coated with silver paste. Dielectric constant, loss tangent and impedance were determined by PSM1735 Impedance Analyzer at frequencies of 1 kHz–10 MHz; samples were