Review of Rare Earth Doped BaTio3 in Multi-layer Ceramic Capacitor Current Development and Its Future Prospective

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Abstract

BaTiO3 works as an widely used dielectric material for multi-layer ceramic capacitor, the electric properties of it can be improved by doping rare earth elements. Different rare earth element atomic radius has different effect on both permeability and curie temperature. The intermediate atomic radius rare earth atoms have their unique dielectric properties but still unperfect as different rare earth elements have distinct characteristics. Based on these unperfects, polymer- ceramic hybrid ceramic can be a attainable way of achieving optimised dielectric properties.

Keywords

Rare earth, Multi-layer Ceramic Capacitor, permeability, curie temperature, polymer-ceramic hybrid.

1. INTRODUCTION

In recent years, the global electrical market is facing shortage of high performance of multilayer ceramic capacitors (MLCCs). [1] For dielectric material of MLCC, Barium titanate (BaTiO3) is one of the most used. These are benefited by its ferroelectric perovskite crystal structure. In this structure, Ti has relatively small atomic radius in the BaTiO3 lattice, so it can going off the centre of the site, the system ends up with more positive charge in one half of the cell and more negative charge in the other half, thus a dipole formed. It has high dielectric constant, low dielectric dissipation factor (DF) and excellent performance at high frequency. As the increasing demand of high-performance capacitor in consumer electronics, motor vehicles, aerospace, telecommunication industry. [2] This requires MLCCs which can stand various working environment and different properties may needs.

In this work, the effect of doping different RE onto BaTiO3 ceramics regarding the atomic radius of rare earths. Both advantages and disadvantages of intermediate radius of RE dopant are discussed and one of the possible solutions for both reducing the usage of rare earth and improving the electric properties of material is proposed.

2. EFFECT OF RE IN ABO3 CRYSTAL STRUCTURE

There have been many studies on doping rare earth (RE) ions and their compounds onto the ABO3 structure. RE atoms have subtle atomic radius in ABO3 crystal structure. Atsushi Honda et al.(2011) [3]point out this structure pulls RE at Ba site(RE_{Ba}) and RE at Ti site(RE_{Ti}) closer to the O site in BaTiO3, decreases the bond length thus decreases the binding energy of the whole system. This would significantly improve the insulating reliability of the ceramic dielectric material. The rare earth elements have variety of atomic sizes The larger ionic scale RE3+ (La, Sm) are likely to occupy the A site and smaller ionic scale RE3+ (Yb) are tend to occupy the B site.[4] And the ions have intermediate radius (Eu, Gd, Dy, Ho, Er) in between A site and B site can be the dopant of either or both Ba and Ti sites. This would greatly reduce the accumulation of oxygen vacancy (Vo) to improve the stability of MLCC. Also, research shows the stability of Vo is inversely proportional to solubility of RE in BaTiO3. This leads to higher solution energy.

The curie temperature is strongly depending on the volume of crystal unit cell that related to the size of doped ions. [5] Smaller ionic radius REs increases the curie temperature of capacitor, which narrow down the working temperature range of the capacitor. On the other hand, as stated by Shigeki SATO et al. (2004) [6], larger ionic radius RE (Tb, Gd) doped capacitors, the capacitance is more contingent on temperature variation and the ceramic will show less insulation to electrons thus the permeability decreases. So intermediate radius RE doped with BaTiO3 ceramic is a considerable choice for high performance MLCC.

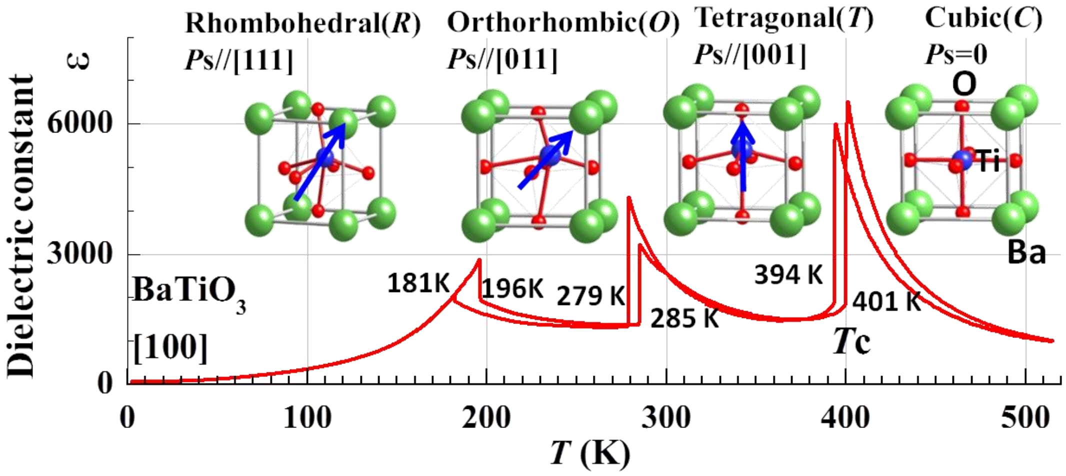

Figure 1. The schematic diagram of BaTiO3 crystal structure and dielectric constant shift with temperature as the Ti atom goes off centre. [27]

3. STUDY ON INTERMEDIATE RADIUS OF RE PARTICLE DOPED BATIO3

Base on a series of research done by Hiroshi KISHI et al.(2002) [7], Dysprosium(Dy) and Holmium(Ho) oxide ions have exhibit intermediate ionic radius and they perform dielectric properties in line with expectations of researchers and they exhibit different properties as Dy ions enhance the rate of ceramic condensation and boost the formation of shell structure. Using first-principles theoretical calculations and relative metadynamics methodology has been done by Robyn E. Ward (2019) [8], shows that the Dy is able to achieve better insulating reliability than Gd3+ does. This is contributed by the free movement of Dy3+ in between A site and B site. This quick diffusion makes better homogenized defects in the ceramic. So, less Dy is needed to trap the same quantity of Vo compering to other RE ions. The processing technics are also optimized.

But Dy doped sample features less stable comparing to Ho doped sample while temperature is above 1280 °C. The Ho doped sample, on the other hand, shows less effected by the temperature coefficient of capacitance. The atomic radius of rare earth element has a critical effect on the dielectric constant and (TCC) of the material which allows rare earth doped capacitors work in diverse thermal environment.

Table 1. The ionic radius of rare earth ions [26]

rare earth ions radius	ionic radius (pm$\times 10^{-2}$)
La3+	1.032-1.36
Ce3+	1.01-1.34
Nd3+	0.983-1.27
Sm3+	0.958-1.24
Eu3+	0.947-1.12
Gd3+	0.938-1.107
Dy3+	0.912-1.083
Ho3+	0.901-1.12
Er3+	0.89-1.062
Yb3+	0.868-1.042
Lu3+	0.861-1.042

Table 2. The ionic radius of A/B site ions [25,26]

A/B site ion radius	ionic radius (pm$\times 10^{-2}$)
Ba2+	1.35-1.61
Ti4+	0.61

4. CURRENT ISSUES OF RE DOPED BATIO3

A large part of the rare earth element relatively expensive and the prices are higher (few are much higher) than none-ferrous metals and metals widely used in modern industry. [9] Besides, they have high extraction and processing cost, limited proven resource inventory and uneven geographical distribution, affected by regional political economy. [10] These all give more uncertainty the development of RE doped BaTiO3. Also, the mining and processing of rare earth have negative effects on the local environment. So, reduce the usage amount of RE is a problem that must be faced in RE doped BaTiO3 future development. Moreover, the doping also can affect the curie temperature of the material. The curie temperature is strongly depending on the volume of crystal unit cell that related to the size of doped ions. [11] Because of the intermediate ionic radius rare earth oxide (for example: Holmium, Dysprosium oxide) doped BaTiO3 has higher meticulous grain densities, which enhance the dielectric constant of ceramic. [12] So, in order to get high dielectric constant, the species of rare earth ions are limited, and the curie temperature of the ceramics are in limited range. Under this condition, the application temperature and the function of ceramics sometimes can be conflict. This issue needs to be balance cost of solving these problems, at the same time, regarding the price of rare earth material. In addition, the lifespan between different intermediate size rare earth ions doped MLCC is likely to be attributed to the unbalanced electron charges and feature of grain boundary [13]

5. FUTURE PROSPECTIVE OF DIELECTRIC BATIO3

So as before all these drawbacks have not been overcame yet, one of the feasible solutions which is the simplest way is to reduce the concentration of rare earth raw material. Hybrid materials (polymer- ceramic hybrid in this case) are composite materials consist two types of different materials integrate in molecular scale and nano parameter. Usually one material is organic, and the other is inorganic. [14] In this case, the BaTiO3 as a filler diffuse into the polymer matrix. This forms a core-shell structure which the centre core is original ceramic, the shell around it is alternatively doped with polymer. [15] This provides better affinity between two materials and makes ceramic filler in molecule scale more evenly distributed into the polymer matrix structure.[16] The polymer cross-linked structure offers higher elevated mechanical strength of the hybrid material plate in MLCC. Polymers are easy to process, with low cost and high capability, despite having relatively low dielectric constant comparing to the inorganic materials such as BaTiO3. Additionally, polymers have lower breakdown strength (E_b) from 100 to 300 kV/cm [17] inter doped BaTiO3 with meticulous grains result in higher breakdown strength and relative permittivity.[18] Therefore the hybrid of polymer and BsTiO3 ceramic is a favourable way to improve to breakdown electric field strength of MLCC. The ideal polymer with good dielectric properties are non-polar plastics with a symmetrical structure and truly covalent bonds.[19] So, it is critical to select the potential species of polymer that satisfy the application requirements. Though current research study, Polyvinylidene Fluoride (PVDF) is an outstanding semi-crystalline polymer that have great dielectric constant and energy density (U_e) (min:6, max:9)value among variety of common polymer and plastic material [20] that are by the greatly polarized carbon–fluorine bond. The bonding energy of it is 485KJ/mol [19] with the bond length of 135 pm [21]. Besides, it has good thermal resistance that can perform at 150 though it is thermoplastic. It also has strong mechanical strength which against the fatigue and cripes and easy to be processed. [20]

In order to combine the beneficial dielectric properties of two material together as much as possible, several instruments have been attempted.

The conventional way of composting BaTiO3 and polymer in nano or micro by solid dissolving and surface coating is unideal. The loss of energy capacitance and increasing attrition rate caused by unhomogenised and defect interface of two phases lead to finite improvement of dielectric properties. However, applying PVDF as the polymer. Polymer grafting [22] [23] [24] is a new way of solving this issue, it has a relative accuracy control of the thickness of shell costing. [33] All of these technics shown above are expected to optimise the genal dielectric properties of the sample.

6. CONCLUSION

This review discussed the how rare earth work as dopants improve the dielectric properties at of MLCC. The curie temperature and permeability vary with the atomic radius of the dopants thus effected by the rare earth element species. As the imperfections of pure RE doped BaTiO3, a feasible solution for future development of MLCC ceramic has been raised.

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