

Microstructures and Dielectric Properties of SrTiO₃-Based BL Capacitor with Content of Ca

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Abstract

Microstructures and dielectric properties of (Sr_{1-x}Ca_x)TiO₃-0.006Nb₂O₅ (0.05 ≤ x ≤ 0.2) boundary layer ceramics were investigated. The samples fired in a reducing atmosphere(N₂) were painted on the surface with CuO paste for the subsequent grain boundary diffusion, and then annealed at 1100°C for 2 hrs. The metal oxide of CuO infiltrated by thermal diffusion from surface of sample presents continuously in not grain but only grain boundary, and makes up thin boundary phase.

The SEM photo. and EDAX revealed that CuO was penetrated rapidly into the bulk along the grain boundaries during the annealing. The average grain sizes is continuously increased as the content of substitutional Ca is increased from 5[mol%] to 15[mol%], but the average grain size of the sample with content of 20[mol%] Ca is slightly decreased.

In the samples with content of 10 ~ 15[mol%] Ca, excellent dielectric properties were obtained as follows; dielectric constant <25000, dielectric loss <0.3[%], and capacitance change rate as a function of temperature < ± 10[%], respectively. All samples in this study exhibited dielectric relaxation with frequency as a function of the temperature.

Key Words(중요용어) : A reducing atmosphere(환원분위기), Grain boundary diffusion(입계확산), Annealing(열처리), Dielectric relaxation(유전완화)

1. Introduction

A Boundary Layer(BL) capacitor material has been developed¹⁾, prepared by diffusion of mixtures of Bi₂O₃, PbO, B₂O₃ and so on into prefired semiconductive matrix material. When a semiconductive SrTiO₃ ceramic with metal oxide powders printed on it is heat-treated at a high temperature in air, the printed metal oxide diffuses into the grain boundaries of the semiconductive ceramics and changes the grain

boundaries to insulating layers.

Noticing this occurrence, Waku²⁾ invented the boundary layer dielectrics having a high apparent permittivity of 2×10^4 . The resulting material is very useful for capacitor application because the dielectric constant is large and has a small temperature dependence over a wide temperature range.

To explain these properties, a boundary layer model has been proposed^{2),3)}. In this model semiconductive SrTiO₃ materials are separated by an insulating layer. This layer consists of a second phase formed by reaction of the diffused mixture of oxides with the matrix material and two layers of oxidized SrTiO₃ matrix material on either side of the second phase formed by the

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firing treatment in air for the oxide diffusion. The thicknesses of the oxidized layers and the second phase layer depend on the preparation conditions.

At the present time, SrTiO₃ compositions with various dopants have been examined as the basic semiconductive ceramics of BL capacitors⁴⁾. The detailed microstructures and analysis of the grain boundaries of SrTiO₃-based BL capacitors have been reported in several papers.^{5,6,7)}

This paper deals with the microstructures and dielectric properties of (SrCa)TiO₃-Nb₂O₅ BL capacitor, which was prepared by diffusion of CuO, having an high apparent permittivity, low dissipation factor and the stable temperature coefficient of capacitance.

The pressed materials were fired to produce a coarse grained semiconductive ceramic, and a diffusion treatment was made to get a boundary layer structure. After being fired in a reducing atmosphere, metal oxides were painted on the surface and the samples were annealed at 1100°C for 2hrs and cooled. This treatment led to a very high apparent dielectric constant, high resistivity, and low loss factor at moderate frequencies.¹⁾

Measurement of the microstructures and dielectric properties as a function of temperature, frequency and contents of Ca have been carried out.

2. Experimental

2-1. Preparation of Samples

The starting chemical reagents used in this study were high purity materials of SrCO₃, CaCO₃, TiO₂, and Nb₂O₅, and CuO of small amounts were added. Here, Nb₂O₅ was added to form semiconducting grains. The basic formulation of compositions is (Sr_{1-x}Ca_x)TiO₃-0.006Nb₂O₅ (x=0.05, 0.1, 0.15, 0.2, respectively). The basic components were weighed respectively and the powder mixtures were milled for above 20 hrs in a alumina mortar using ethyl alcohol. After drying, the mixture was calcined at 1100°C for 2 hrs.

The calcined powders were mixed with an

appropriate organic binder(an aqueous solution of 1.5[wt%] PVA), and pressed into 20[mm] diameter by 3[mm] thickness disks under pressure of 1500[kg/cm²]. The pressed disks were fired at 1350°C for 3 hrs in a reducing atmosphere (N₂ cylinder gas with a flow rate of 10[cm³/min]) and furnace cooled at about 100[°C/h] to room temperature.

After the firing, the samples were polished to 1[mm]-thickness and metal oxide of CuO was painted on the surface of the fired samples, then the samples were annealed again at 1100°C for 2 hrs to get the grain boundary diffusion and furnace cooled to room temperature. Diffused metal oxide was rapidly penetrated as a liquid phase along boundaries in post-sintering heat treatment.

After the secondary firing, samples for dielectric measurements were prepared by applying a silver electrodes pastes on both surface of tablets which were fired on for 20[min] at 800°C.

2-2. Measurements

The crystallographic structure of our sample was determined by X-Ray Diffraction(XRD) analysis using a Ni-filter and CuK α radiation. Grain growth behaviors of our samples were observed from one face of the sintered disks by using Scanning Electron Microscopy (SEM) after a specific heat treatment. The resistivity was measured by using High Resistance Meter(HP 4329A). Grain size was determined by Jeffrie's square measure method.

The dielectric constants and the dissipation factor were measured on the sintered disks by using a LCR Meter (YHP 4274A) in the temperature region -150°C to 200°C. The frequency dependence of the dissipation factor was measured by using an LF impedance analyzer(HP 4194A) in the frequency region 100[Hz] to 10[MHz].

3. Results and Discussion

3-1. Microstructures

Fig.1 shows the microstructures of a primary and secondary fired samples which have substitutional contents of Ca. The photo. of surface of our samples clearly reveal the grain boundaries

An interesting feature in this Fig.1 is the presence of a grain boundary phase in multiple grain junction. We can confirm by means of EDAX analysis that this phase is Ti-rich second phase which is not similar to composition in grain bodies. The apparent thickness of a second phase layer observed with SEM was found to be about 0.2 to $2\mu\text{m}$.

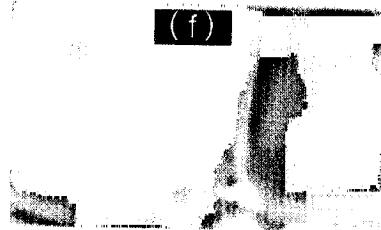
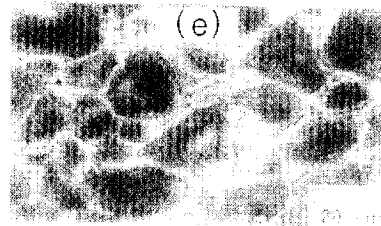
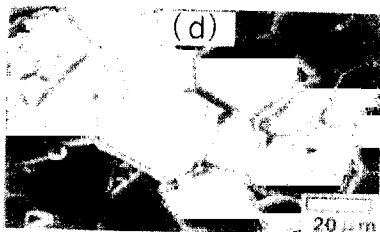
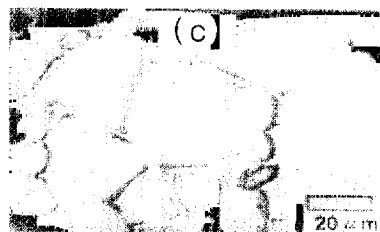
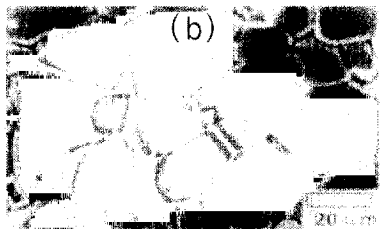
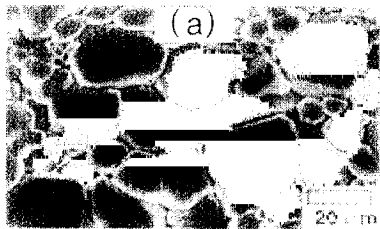


Fig.1. The SEM photo. of samples sintered at reducing atmosphere(N_2)(a)x=0.05,(b)x=0.1,(c)x=0.15,(d)x=0.2) 2nd fired samples ((e)x=0.1,(f)x=0.05) with content of Ca

Fig.1 (e),(f) are the microstructures of secondary firing sample diffused by CuO. The metal oxide of CuO infiltrated by thermal diffusion from surface of sample presents continuously in not grain but only grain boundary, and makes up thin boundary phase as shown in SEM photo. After 2 hrs infiltration by a metal oxide of CuO at 1100°C , the boundary layer structure consists of an amorphous phase being similar to liquid phase. This reaction product of the metal oxide with the predominantly TiO_2 phases at the grain boundaries explains the very rapid penetration of the heavy metal between grain boundaries, giving a uniform distribution of material. An amorphous phase was presented at grain boundary, had completely retracted from the grain boundaries during furnace cooling.

During the second firing stage, high titania boundaries react rapidly during infiltration by the metal oxide forming amorphous phase having a thickness of about 0.1 to $2\mu\text{m}$ between grains. The nature of these boundary phases and their thickness account for the rapid penetration of the insulating phase between the boundaries.

This structure is quite similar to the model proposed by R. Wernicke³⁾, which has a 0.1 to 2 μm wide continuous insulating boundary phase. The structure of the diffused sample slowly furnace cooled from the metal infiltration temperature was found to be quite different from the first sintered samples.

Fujimoto and Kingery⁷⁾ had studied more precisely the microstructures and the diffused layer profile in such capacitor, materials at various stages in processing, using high resolution transmission electron microscopy and scanning transmission electron microscopy (STEM). Continuous liquid phases at the grain boundaries during the sintering and subsequent heat treatment stages were observed.

The average grain sizes of our samples with contents of Ca were shown in Fig.2. The average grain sizes are continuously increased as the content of substitutional Ca is increased from 5[mol%] to 15[mol%]. However, the average grain sizes of the sample containing a larger amount of substitutional Ca is slightly decreased. From these facts, we can suppose that substitutional Ca having atomic radius less than in contrast with Sr is displaced until 15[mol%], is saturated in further addition.

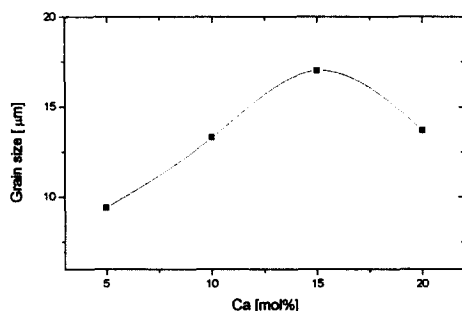


Fig.2. Grain sizes with contents of Ca

To investigate compositions in grain boundary, the EDAX analysis on the Fig.1(f) were illustrated in Fig.3.

The EDAX analysis indicates that Cu metal oxide infiltrated into the sample not present in grains but only grain boundary, form second phase in the grain boundary. After the second

firing process oxygen and metal oxide have been diffused to compensate the electric charge balance in a thin region adjacent to the boundaries.

Also, the barrier layer between the semiconducting grains, or between the grains and

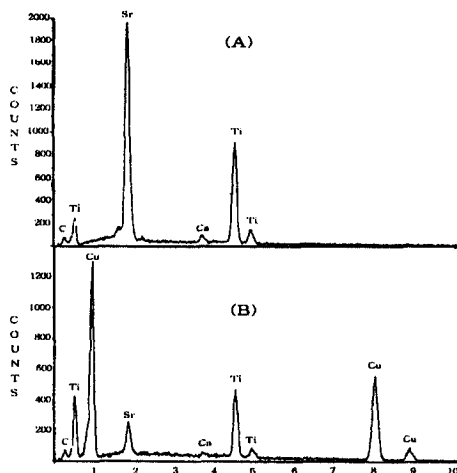


Fig.3. EDAX of 2nd fired sample($x=0.05$)

the intergranular layer, is due to a p-type surface layer overlying an n-type substrate. The conductivity of the n-type interiors of the grains is caused by the presence of donors formed by higher valency impurity ions or by the introduction of oxygen vacancies and Ti^{3+} ions through firing in a reducing atmosphere. The p-type outer layer is formed by acceptor ions, such as Mn^{3+} and Cu^{2+} , and by vacant A-sites created by the partial compensation for oxygen loss by the loss of A-site ions.

Fig.4 shows X-ray diffraction patterns of the mixed powder, calcined powder and first sintered sample with content of 15[mol%] Ca respectively. we could confirm that the perovskite phase was completely formed during the calcining.

3-2. Sintering Density and the Relative Resistivity

Fig.5 shows the relative density of the fired sample with content of Ca. The theoretical density was calculated from the lattice parameter obtained from X-ray diffraction analysis and basic formulation of compositions used in this

study.

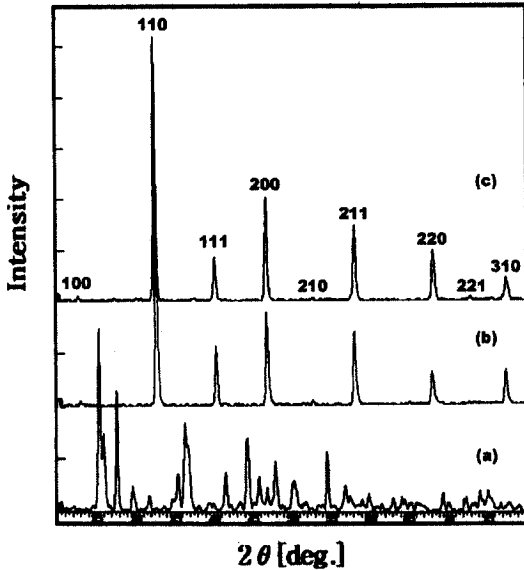


Fig.4. XRD pattern of sample(x=0.15)
(a)mixing powder, (b)calcining powder,
(c)1st firing powder

As shown in Fig.5, relative density is increased with substitutional content of Ca, but is slightly decreased in the samples with content of 20[mol%] Ca. It corresponds to results of crystallographic structure, that is to say, the relative density exhibits the most high value at substitutional content of 15[mol%] Ca having the most great average grain sizes, and is slightly decreased when Ca is displaced with content of 20[mol%] decreasing average grain size.

Fig.6 shows the resistivity of the reduced and second fired samples with content of Ca. Our semiconducting ceramics exhibit low relative resistance below $10^3[\Omega \cdot \text{cm}]$, and second fired samples exhibit relative resistance from 10^9 to $10^{11}[\Omega \cdot \text{cm}]$.

The resistivity of the main phase must be as small as possible in order to minimize the dissipation factor of the final body. The atmospheres used have varied from dry hydrogen, hydrogen-nitrogen mixtures, pure argon and nitrogen to air. Under suitable conditions donor

doped strontium titanate can form a distributed barrier structure after a single firing in air.

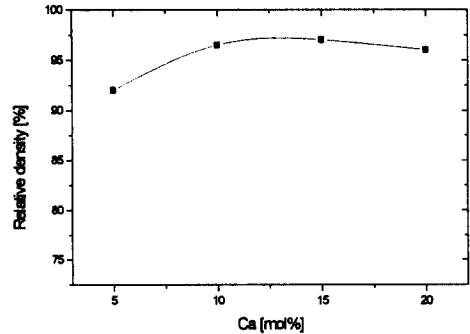


Fig.5. Relative Density of samples with content of Ca.

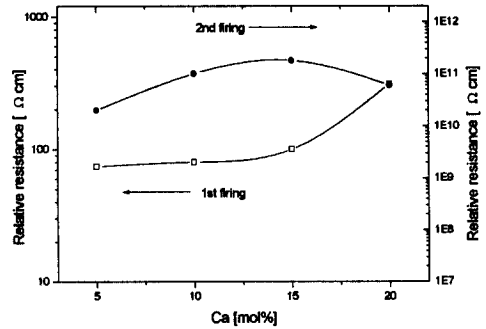


Fig.6. Relative Resistance of samples with content of Ca

It was reported that $(\text{Sr} \cdot \text{Ca})\text{TiO}_3$ ceramics which was sintered at atmosphere $\text{H}_2\text{-N}_2$ gases had the relative resistivity from 10^0 to $10^2[\Omega \cdot \text{cm}]$ being not similar to our samples which were sintered at atmosphere only N_2 gas⁸⁾. This indicates that the $\text{H}_2\text{-N}_2$ gases have reductive properties more than at atmosphere only N_2 gas.

3-3. Dielectric Properties

3-3-1. Temperature Dependence of Dielectric Constants

Temperature dependence of dielectric constants and $\tan \delta$ of our $(\text{Sr} \cdot \text{Ca})\text{TiO}_3$ systems with content of Ca were shown in Fig.7. Dielectric constants are not obviously varied until substitutional content of 15[mol%] Ca, but our

sample with content of 20[mol%] Ca reveals distinct decrease.

This suggest that an appropriate amount of Ca in order to get high dielectric constants is less than 20[mol%]. This is due to the fact that in which accord with the results of structural study which the resistivity and relative density in our samples reveal the most high values at content of 15[mol%] Ca.

This phenomenon indicates that thermally diffused Cu glass phase from surface of samples and TiO_2 phase in boundary layer react actively in the second firing process, dielectric constant increase in accordance with the increment of capacitance caused by the second phase which consist of continuous liquid phase, but when displace contents of Ca is more than 15[mol%], dielectric constants decrease as thickness of dielectric layer due to the rapid penetration of metal oxide increase.

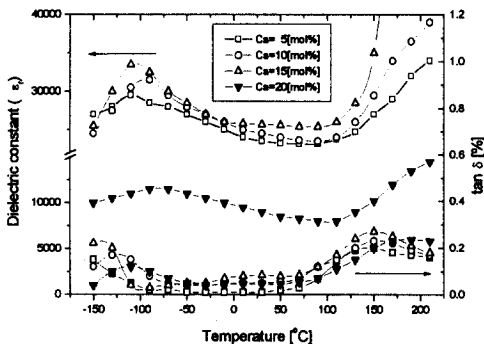


Fig.7. Dielectric constant and dielectric loss with content of Ca as a function of temperature

We can see an rapid increase of dielectric constant in the region of high temperature($>100^\circ\text{C}$). It is considered that the resistance of $(\text{Sr} \cdot \text{Ca})\text{TiO}_3$ diffusion layer is decreased with increasing temperature, and the thickness of boundary layer affecting to dielectric constant is thinned, resultantly the dielectric constants of our samples are rapidly increased.

Dielectric loss as a function of temperature is rapidly increased in the range of temperature

both below -50°C and above 80°C . Dielectric loss is due to the conversion of the movement of charges into vibrations of the lattice. This can occur from a multiplicity of causes, particularly, as with ceramics, when the microscopic structure is complex. In general, the dissipation factor in the ceramic dielectrics is affected by crystallinity of grain, impurities, lattice defects, and porosity of bulk, etc. Both ionic and electronic polarizability involve simultaneous changes in charge distribution round every ion in the lattice. Although, in the case of hopping processes dependent on the presence of defects, the situation is more and less different. Each defect causes an adjustment in the surrounding ions relative to their states when the defect is absent.

Also, porosity results in internal surfaces that are an important source of loss because the surfaces of ceramics contain a high concentration of defects due to the transition from a solid crystal structure to a gas phase. A dense pore free structure is therefore a prerequisite for a low loss dielectric.

It seems likely that the relatively large $\tan \delta$ in the range of low temperature is attributed to imperfection of crystals caused by phase transition, in the range of temperature above 80°C , is attributed to decrease of resistance in diffusion layer, oxidation layer, which is conformed during second fired stage as temperature increase.

Although the $\tan \delta$ of our samples are not widely different with contents of Ca, are slightly increased by increasing the ratio of Ca/Sr. This could be explained by the following facts that re-oxidation of grain boundary is easily carried out because of addition of Ca during the second firing, the resistance of newly formed boundary layer affects to $\tan \delta$.

It can be also observed in Fig.7 that the dielectric losses of our all samples is below 0.05 in the region of room temperature. The dissipation factor is generally taken as an indication of the quality of a particular type of capacitor. These dissipation factors of our samples are acceptable values for high

permittivity (high-K) ceramic capacitor.

Fig.8 shows variation of capacitance as a function of temperature. As shown in Fig.8, the temperature coefficients of capacitance exhibit very stable values with $< \pm 10\%$ in the temperature range from -30°C to 90°C . This indicates that dielectric constants of pure SrTiO_3 presenting paraelectric phase in the temperature region of above -160°C reveals negative temperature coefficients that the relative permittivity decrease with increasing temperature due to Curie-Weiss law⁹⁾⁽¹⁰⁾. The liquid phase forming secondary phase in the grain boundary reveals positive temperature coefficients that the relative permittivity increase with increasing temperature.

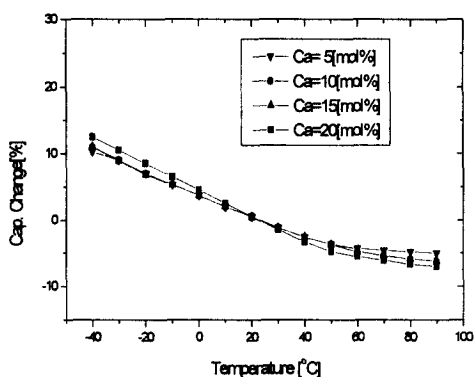


Fig. 8. Capacitance Change as a function of temperature

These facts suggest that the complementary effects of both liquid phase with Cu and paraelectric phase of $(\text{Sr} \cdot \text{Ca})\text{TiO}_3$ grains make our samples to exhibit stable temperature characteristics. Also, temperature coefficients are not nearly affected with the content of Ca. It is clear that in our system with ABO_3 , when an appropriate value for B is used, the obtained dielectrics exhibit not only high permittivity but stable temperature coefficients.

3-3-2. Frequency Dependence of Dielectric Constants

Fig.9 shows capacitances as a function of

frequency, which reveals very stable frequency characteristics until 10^6 [Hz].

It is generally reported that useful frequency for evaluation of the ceramic dielectrics is the frequency of range from 10[Hz] to 10[MHz]⁷⁾.

In our samples, the frequency characteristics of capacitance may be relatively stable because all samples have not ferroelectric but paraelectric properties in around room temperature. The types of polarization in ceramic dielectrics may be interface, space charge, and orientation polarization. Even if our samples may be affected to space charge polarization by drift of impurities, ions, and lattice vacancies, it's influence may be very small.

The measured frequency dependence of the capacitance indicates that these samples have dielectric properties that depend on frequency in accordance with Maxwell-Wagner theory¹¹⁾, in which important parameters include the conductivity and grain size of the $(\text{Sr} \cdot \text{Ca})\text{TiO}_3$ ceramics.

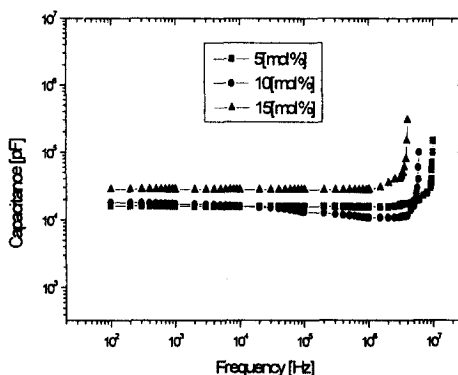


Fig.9. Capacitance of samples as a function of frequency

Also, it can be described that frequency dependence in the boundary layer (BL) structure is affected by dielectric relaxation in each other dielectric layer, relaxation frequency (f_m :Hz) in the boundary layer ceramics consisting of both n-type semiconductor and p-type insulation layer can be described by the relative resistivity (ρ) in the semiconductor region and the permittivity (ϵ)

in low frequency like following equation.

$$f_m = 1.8 \times \frac{10^{12}}{\epsilon\rho} \text{ [Hz]}$$

This equation explains that relaxation frequency decrease with increasing the resistivity in the semiconductor region, accords with the resistivity properties as illustrated in Fig.6.

To determine if our samples are a relaxor, we measured the temperature variation of the relative permittivity at different frequencies for composition with content of 15[mol%] Ca as shown in Fig.10. The Curie point lies -100°C to -30°C range depending on the frequency. Our samples show a pronounced change in permittivity with frequency at temperatures near the Curie point.

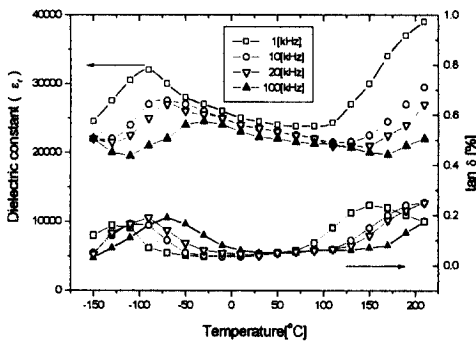


Fig.10. Dielectric constants and dielectric losses as a function of temperature and frequency.

High-k dielectrics generally show a gradual fall in permittivity with frequency over the range 10^2 to 10^8 [Hz]. Relaxors are a class of dielectric in which the temperature of the peak of the dielectric constant depends on frequency. They also show a broadening of the permittivity peak as a function of temperature, that is to say, diffuse phase transitions.

All relaxors contain two or more species of ion on the same site, as in our system $(Sr_{1-x}Ca_x)TiO_3$, and it appears likely that their behaviour arises from fluctuations in composition between microscopic regions. While there is general agreement that the diffuse transitions are

due to fluctuations in Curie point between different regions within the grains of the ceramic, there is still discussion as to whether the fluctuations are in chemical composition or in lattice behaviour. This results in range of Curie points and so accounts for the diffuse transitions.¹²⁾ The substituted titanates behave as relaxors with diffuse phase transitions, an effect which seems to be due to inhomogeneity on a microscopic scale within individual crystals.

It is clear that our samples with diffuse phase transition are relaxors as shown in Fig.10. These relaxation characteristics are due to the structural defects on the A-site vacancies such as Sr^{2+} , Ca^{2+} , etc by substitutional Nb^{5+} ions in which greatly reduces the oxygen vacancy concentration and increases the A-site vacancy concentration to the extent of one vacant site for every Nb^{5+} ions so as W. Johnson et al.¹³⁾ suggest. The other hand, A.N. Gubkin et al.¹⁴⁾ reported that broad curie region was caused by compositional fluctuation, random distribution of positive ions within sublattice, etc.

Therefore, it is suggested that broad curie region in our system is caused by compositional fluctuations and structural defects on the B-sites due to the vacancies of A-sites.

4. Conclusion

In our $(Sr_{1-x}Ca_x)TiO_3-0.006Nb_2O_5$ BL ceramic materials, the following facts were observed.

The metal oxide of CuO infiltrated by thermal diffusion from surface of sample presents continuously in not grain but only grain boundary, and made up thin boundary phase. The average grain sizes was continuously increased as the content of substitutional Ca is increased from 5[mol%] to 15[mol%], but the average grain size of the sample with content of 20[mol%] Ca was slightly decreased.

XRD analysis results showed that the samples used in this study have the cubic perovskite structure. The relative densities had a excellent value above 96% in most samples. Our semiconducting ceramics exhibited low resistivity

below $10^3[\Omega \cdot \text{cm}]$, and second fired samples exhibited resistivity from 10^9 to $10^{11}[\Omega \cdot \text{cm}]$.

Dielectric constants were not obviously varied until substitutional content of 15[mol%] Ca, but our sample with content of 20[mol%] Ca revealed distinct decrease as a function of temperature. Although the $\tan \delta$ of our samples were not widely different with contents of Ca, were slightly increased by increasing the ratio of Ca/Sr. The temperature coefficients of capacitance exhibited very stable values with $< \pm 10\%$ in the temperature range from -30°C to 90°C . The dielectric losses of our all samples were below 0.05 in the region of room temperature. Capacitances as a function of frequency revealed very stable characteristics until 10^6 [Hz]. We could confirm that our samples with diffuse phase transition were relaxors. From the results of these experiments, we could suggest that our BL ceramics were able to be used as high-k ceramic capacitors which exhibited high dielectric constants, low dielectric loss, and stable temperature coefficients and frequency characteristics.

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