Impedance Spectroscopy Models for X5R Multilayer Ceramic Capacitors


School of Materials Science and Engineering, Chonnam National University, Gwangju 500-757, Korea
*LCR Material Development Group, Samsung Electro-Mechanics, Suwon 443-743, Korea

(Received August 24, 2012; Accepted September 27, 2012)

ABSTRACT

High capacitance X5R MLCCs based on BaTiO$_3$ ceramic dielectric layers exhibit a single broad, asymmetric arc shape impedance and modulus response over the wide frequency range between 1 MHz to 0.01 Hz. Analysis according to the conventional brick-layer model for polycrystalline conductors employing a series connection of multiple $RC$ parallel circuits leads to parameters associated with large errors and of little physical significance. A new parametric impedance model is shown to satisfactorily describe the experimental spectra, which is a parallel network of one resistor $R$ representing the DC conductivity thermally activated by 1.32 eV, one ideal capacitor $C$ exactly representing bulk capacitance, and a constant phase element (CPE) $Q$ with complex capacitance $A(i\omega)^\alpha$ with $\alpha$ close to 2/3 and $A$ thermally activated by 0.45 eV or ca. 1/3 of activation energy of DC conductivity. The feature strongly indicate the CK1 model by J. R. Macdonald, where the CPE with 2/3 power-law exponent represents the polarization effects originating from mobile charge carriers. The CPE term is suggested to be directly related to the trapping of the electronic charge carriers and indirectly related to the ionic defects responsible for the insulation resistance degradation.

Key words: MLCC, X5R/X7R, impedance spectroscopy, dispersed conduct, CK1 model

1. Introduction

MLCC (Multi-layer Ceramic Capacitor) is the most important passive component in electronic devices such as cellular phones, personal computers and digital displays. The development trend of MLCC is miniaturization with increasing capacitance.¹ Fig. 1, top right, illustrates how the interdigitated electrode configuration of MLCCs results in high overall capacitance. The multi-layer structure of $n$ electrode layers is electrically a parallel network of $(n-1)$ thin layer capacitors $C_{\text{layer}} = \varepsilon_r\varepsilon_0 A/t$, where $\varepsilon_r$, $\varepsilon_0$, $A$, and $t$ are the permittivity, relative dielectric constant, electrode area, and dielectric layer thickness. MLCCs in the electronic circuits are represented by the equivalent circuit indicated in Fig. 1: in addition to the capacitor ($C_{\text{dielectric}}$), ESR (equivalent series resistance) and ESL (equivalent series inductance) originating from the inner and outer electrodes are connected in series, which addresses the high-frequency non-ideal performance.

The real dielectric material does not behave as an ideal capacitor but exhibits a complex permittivity, $\varepsilon' = \varepsilon' - i\varepsilon''$. The non-zero imaginary capacitance component ($\varepsilon''$) is responsible for the power dissipation. In addition to the dielectric dissipation represented by $\varepsilon''$ or $\tan \delta = \varepsilon''/\varepsilon'$, the oxide dielectric material is usually of a finite non-zero DC conductivity ($\sigma_{dc}$) or not infinite DC resistivity ($\rho_{dc}$), which may also represent the insulation resistance (IR) ($R_{\text{insulation}}$) of the capacitors. In the first place, the parallel electrical network of thin multi-layer structure of MLCCs to obtain high capacitance as $(n-1)\varepsilon_r\varepsilon_0 A/t$ as shown in Fig. 1, consequently reduces the overall resistance by the same geometrical factor, i.e. $\rho_{dc} \pi A(n-1)$. The grain boundaries of the polycrystalline ceramic dielectric layer and the dielectric/metal interfaces are often supposed beneficial for IR characteristics due to the formation of highly resistive depletion layers of Schottky barriers as in ZnO varistors or BaTiO$_3$ PTCR components. Similar explanation has been given for the grain boundary impedance of polycrystalline solid electrolytes.² The equivalent circuit with three $RC$ parallel circuits as shown in Fig. 1, bottom, is thus widely applied to polycrystalline electroceramics. The measurements of AC response or equivalent time-dependent electric response of MLCCs according to the equivalent circuit with one or multi-relaxation responses are not experimentally viable due to the high resistance and the long relaxation time ($\tau = RC$). Therefore, IR tests are usually performed by monitoring resistance after applying the specific voltage, e.g. 6.3 V for the specified time e.g. 60 sec. Similarly, the characterization of the dielectric properties of MLCCs is limited to the comparison of the measurement values at one fixed fre-
quency, e.g. 1 kHz. A parametric characterization of the frequency-dependent dielectric behavior of MLCCs in connection with the processing variables is highly desirable but a technique yet to be developed. Moreover, conventional linear impedance spectroscopy should be applied as a diagnostic tool to the degradation phenomena and nonlinear electrical response of MLCCs with micrometer-thick dielectric layers for testing and operating AC and DC conditions of MLCCs, e.g. AC 0.5 V and DC 10 V. In the meantime, one may exploit the experimentally viable high-temperature measurements in order to characterize the MLCCs in relation with the processing conditions. Since the basic transport properties are generally strongly thermally activated with well-defined activation energies, the extrapolation to lower temperature can provide the fundamental information regarding the IR and its degradation at operation conditions.

MLCCs with X7R/X5R specifications are suited for bypass and coupling purposes, filtering, frequency discrimination, DC blockage, and as voltage transient suppression elements. The temperature range for the 15% capacitance is for X7R between −55°C and +125°C and for X5R between −55°C and +85°C, respectively, which is controlled by dopant concentrations or compositions. There have been several reports of impedance spectroscopy using the multiple RC models for X7R/X5R MLCCs do not indicate the clearly distinguished multiple responses. In this work, a reassessment of the multi-RC brick-layer-model analysis applied for the X7R/X5R type MLCCs is made based on the measurements on 10 µF 1608 size X5R MLCC chips produced by Samsung Electromechanics. The problems associated with the previously reported model analysis are illustrated. A new impedance model for X5R MLCCs is suggested which describes the spectral feature successfully with all the parameters representing well-defined physical quantities.

2. Experimental Procedure

Ni-electrode MLCC chips with 1608 size (1.6 mm × 0.8 mm × 0.8 mm) of 10 µF provided by Samsung Electromechanics were used. The dielectrics based on BaTiO3 powders was formulated to meet the X5R specifications which results in the characteristic core-shell structure. The chips were prepared by the standard nickel electrode MLCC fabrication procedures: Machined green chips underwent binder burnout and were fired at various peak temperatures, followed by a reoxidation process. The MLCC chips were mounted on a closed cycle refrigerator (CCS-400/202, Janis, USA) and the impedance response was measured using a frequency response analyzer combined with a high impedance interface (Solartron 1260/1296, UK) over the frequency range of 10 MHz to 10 mHz using AC 0.5 V in the

![Fig. 1. Schematic illustration for the principle of high capacitance of MLCCs (top right) and the MLCC equivalent circuit in electronic circuits with ESR and ESL. The ceramic dielectric layer of polycrystalline microstructure (top left) is also represented by the brick-layer-model with three Rs and Cs representing bulk (B), grain boundary (GB), and electrode (EL) associated impedance.](image-url)
temperature range of $-70^\circ$C to $221^\circ$C. The impedance spectra were analyzed using a commercial fitting program, Zview (Scribner Ass. Inc., USA).

3. Results and Discussion

Fig. 2 represents the capacitance of an X5R chip as a function of temperature at different frequencies. The broad temperature dependence is shown to satisfy the X5R specification ($\pm 15\%, -55 < T/\circ\text{C} < +85$). The capacitance values at high frequencies above $10^3$ Hz are affected by the large extra inductance ($\sim 5\ \mu\text{H}$) (ESL+) as well as resistance (ESR+) due to the extended lead wire of the measurement setup in addition to those intrinsic in MLCCs as shown in Fig. 1.

Fig. 3(a) shows the complex plane representation of the impedance measured at temperatures higher than the Curie temperature of BaTiO$_3$, $120^\circ$C. The spectra above $200^\circ$C represent an almost complete, slightly deformed semicircular shape over the frequency range down to $10^2$ Hz. The modulus representation of the spectra is shown in Fig. 3(b), where $M^* = 1/C^* = i\omega Z^*$. The intercepts of the arcs thus represent the capacitance variation with temperature, which is also indicated in the Bode plots of real capacitances, $C^*$ in Fig. 3(c). It should be noted that high frequency impedance data become vanishingly small due to the short-circuiting via parallel capacitors but magnified by the frequency factor in the modulus presentation. Responses associated with much smaller resistance and relaxation times can be visually distinguished better in the modulus representation. The ‘tucked-in’ high frequency arcs in the modulus spectra are the response of the series resistance (ESR+) and inductance (ESL+). The high frequency data around 1 MHz was further afflicted by the instrumental artefact and not shown. The smooth arc shape spectra both in impedance and modulus representations of X5R MLCC chips thus indicate the absence of multi-processes with distinguished relaxation times.

Nevertheless, the impedance spectra of X5R or X7R MLCCs with similarly broad single relaxations have been analyzed using multiple RC parallel circuit models. The approach was not limited to the conventional three RC models for bulk, grain boundary, and electrode responses. Additional RC elements were employed to address the effects from the core-shell structure into a total of four RCs. Additional holmium doping was supposed to cause
another RC making five RC elements in total. The broad overlapped spectral feature can be represented by the multiple RCs with small difference in relaxation times. The more elements employed, the better the apparent fit or the smaller $\chi^2$ goodness-of-fit values would result. Note that this is also the principle of the numerical Kramers-Kronig fitting which can be performed without physical significance in the elements.

The analysis using three ideal RC elements of the data in the present work provided the results shown in Fig. 4. Note that the resistance data below 180°C or larger than ca. 2.2 of $1000/T$ are associated with large errors due to the obviously limited spectral range for the modeled three RC responses (See Fig. 3). The results, however, are presented to illustrate that a proper modeling could extend such analysis limits considerably, as will be shown below in Fig. 5. When the results above 180°C are considered, the three $R$ elements exhibit Arrhenius behavior with activation energies of 0.53 eV for $R_1$, 0.68 eV for $R_2$ and 1.5 eV for $R_3$, respectively. The magnitudes of $R_2$ and $R_3$ are comparable and they are higher than $R_1$ by almost two orders of magnitude. The parameter $C_1$ is shown to be higher than $C_2$ by almost one order of magnitude, and both exhibit the negative temperature dependence expected for the bulk dielectric constant of BaTiO$_3$ according to Curie-Weiss law. However, $C_3$, which is associated with larger errors, exhibits the opposite temperature dependence, crossing with $C_2$. The behavior is in contrast with the generally observed three-RC cases where the relation $C_1 = C_2 = C_3$ is mainly responsible for the behavior $r_1 < r_2 < r_3$ as shown in Fig. 4(c). Due to the temperature dependent capacitance contribution, the relaxation times exhibit significantly different thermally activated behavior from those of $R$: 0.94 eV for $r_1$, 1.17 eV for $r_2$, and 1.20 eV for $r_3$. The activation energy values of $r$'s become similar. Note that the $R_3$ element contributes as a major impedance element and is associated with $C_3$ with the opposite temperature dependence to $C_1$ and $C_2$. According to the Mott-Schottky space charge theory for the resistive grain boundary and electrode impedance, the activation energy difference between $R_2$ and $R_1$ or $R_3$ and $R_1$ parameters represents the Schottky barrier potentials at grain boundaries and electrodes. However, with the capacitance behaviors completely out of the scheme, such an attribution is hardly justifiable. Fig. 4(d) indicates that the errors associated with these parameters are as large as 10% to 30% even for the high temperature spectra covering sufficiently the model response. The $\chi^2$ values, representing the goodness-of-fit, is shown to be less than 0.004, indicating that the fit parameters can describe the overall spectral feature rather well. The fit residuals $(Z_{exp} - Z_{fit})/Z_{fit}$ for both real and imaginary impedance $Z$ were very small for the spectra limited below 1 MHz with the high frequency instrumental artefact being cut-off. The more RC elements are used, the better the apparent fit of the spectra becomes. This is also the principle of numerical Kronig-Kramers test algorithm. However, the parameters with a small difference in the time constants are of little physical significance and thus subject to large statistical errors.

In this work a new impedance model for the behavior of X5R MLCCs is suggested, as shown in Fig. 5(a). In the first
place, no separation of responses connected in series is attempted. For such overlapped broad spectra, so-called ‘distributed elements,’ such as Cole-Cole or more general Havriliak-Negami impedance model as Eq. (1) may be phenomenologically employed:

\[
Z_{HN} = \frac{R_{HN}}{1 + (i\omega \tau_{HN})^{\gamma}}
\]

where \( \gamma = 1 \) for the Cole-Cole model which can be also represented by the parallel circuit of resistor \( R \) and \( Q \), a constant phase element (CPE) with complex capacitance \( A(i\omega)^{\alpha-1} \). In such phenomenological approaches, the power-law frequency exponents are arbitrarily adjustable parameters and do not have a clear physical meaning.

With \( \alpha \) and \( \gamma \) not equal to zero or one, the model can describe an arbitrarily asymmetric arc-type response as the impedance spectra with the low-frequency-limiting frequency power-law exponent \( \alpha \) and the high-frequency limiting slope \(-\alpha \gamma\). The model analysis provides one well-defined resistance \( R \) corresponding to the magnitude of arcs. The peak frequencies of Havriliak-Negami impedance can be estimated as follows

\[
\omega_{HN}\tau_{HN} = \left[ \tan\left( \frac{\pi}{2(\gamma+1)} \right) \right]^{1/\alpha}
\]

An ‘effective’ or ‘average’ capacitance may be estimated as \( \phi_{HN} = (RC)^{-1} \) with reference to the ideal \( RC \) parallel circuit. It may be surprising that even with such arbitrarily adjustable parameters the spectra shown in Fig. 3(a) could not be satisfactorily fitted. The origin of such failure is the nearly frequency-independent high frequency capacitance indicated in Fig. 3(c), which clearly deviates from the prescribed frequency dispersion as \( \omega^{-\alpha} \). Frequency-independent or negligibly dependent capacitance at high frequency range and the emerging frequency dispersion with lowering frequency was successfully described by the parallel connection of two constant phase elements \( Q \)'s with distinct power-law exponents. The new model shown in Fig. 5(a), thus consists of five fit parameters besides ESL+ and ESR+. The \( Q \) elements with \( A \) and \( \alpha \) parameters, respectively and \( R \) are all connected in parallel. Thus the \( R \) element clearly represents the DC resistance, named as insulation resistance, \( R_{\text{insulation}} \).

An example of the analysis is shown in Fig. 5(a) and the fit results are represented as a function of temperature in Figs. 5(b) and (c), in a similar fashion as for the brick-layer model analysis in Fig. 4. The comparison of the two analyses clearly shows that the new model results in the fit parameters with substantially small errors. At the high temperature range all the errors of the parameters are less than 2 % and increase only up to 10 % at lowest temperature for the analysis, where only very small part of arcs were measured. The goodness-of-fit, \( \chi^2 \), is in the order of \( 10^{-4} \), smaller by one order of magnitude than the three \( RC \) model case. Such excellence is partly due to the adjustable power-law exponents of two \( Q \) elements.

If the exponents do not exhibit any systematic tendency or specific values, they may be simply adjustable parameters,

Fig. 5. (a) Example of impedance analysis using the new parametric model for X5R MLCC. The circles are experimental data and guideline is the simulation using fit results indicated in the equivalent circuit. The response of the \( R_{\text{insulation}} Q_{\text{dielectric}} \) parallel circuit with peak frequency 0.341 Hz and \( R_{\text{dispersion}} Q_{\text{dispersion}} \) with 1.57 Hz are presented in comparison. (b) Parameters of \( \phi_{\text{dielectric}} \) and \( \phi_{\text{dispersion}} \). (c) Percentage errors of the parameters and \( \chi^2 \) goodness-of-fit.
possibly correlated, for a better apparent fit. The presence of such arbitrary, ill-defined parameters makes the principle of the analysis rather weak and definitely reduces the information content obtainable from the fitting analysis. In the present analysis, one CPE or Q element was fitted with $\alpha$ values very close to but slightly in excess of 1. Nearly ideal capacitor behavior of this element is responsible for the frequency-independent high frequency capacitance in the spectra and exhibit a well-defined Arrhenius behavior defined activation energy of 0.45 eV, which is close to 1/3 of the activation of the DC conductivity, Fig. 6(b). The behavior of $Q_{\text{dispersion}}$ with fixed $\alpha$ value of 2/3 in parallel to the ideal capacitor corresponds to the CK1 model by J. R. Macdonald, which suggests the specific shape parameter $\beta_{\text{KWW}} = 1/3$ in the Kohlrausch-Williams-Watts (KWW) stretched-exponential temporal response, 

\[
\phi(t) = \exp\left[-(t/\tau_{\text{KWW}})^{\beta_{\text{KWW}}}\right]
\]

on top of Jonscher’s universal dielectric response (UDR) power-law,\textsuperscript{14} original modulus formalism (OMF) by Mohri et al.,\textsuperscript{15} the coupling model by Ngai and Kannert,\textsuperscript{16} and ‘jump relaxation’ or ‘MIGRATION’ framework by Funke et al.\textsuperscript{17,18}

The pre-factor $A_{\text{dispersion}}$ multiplied by the absolute temperature is shown to exhibit an Arrhenius behavior of the well-defined activation energy of 0.45 eV, which is close to 1/3 of the activation of the DC conductivity, Fig. 6(b). The behavior is a straightforward consequence of $\alpha=2/3$ in $Q_{\text{dispersion}}$. The pre-factor $A_{\text{dispersion}}$ corresponds to the AC conductivity, $\sigma_{ac}$ from the relation $\sigma = \sigma_{dc} + \sigma_{ac}$. The KWW function with the shape factor $R_{\text{KWW}}=1/3$ in Eq. (2) corresponds to the frequency power-law exponent $\alpha = 2/3$ for the limited frequency range. Experimental observation of $\alpha$ values close to 2/3 in ionic conducting glasses was also reported by Sidebottom et al.\textsuperscript{19} Macdonald suggests the universal nature of the shape parameter, which can be derived from constraint theory depending on the effective dimensionality of the space in which mobile charges move, i.e. 1/3 in three dimension, and applies to various types of the ionic conductors.\textsuperscript{20-22}

The essential aspect of the CK1 model is the separation of constant dielectric capacitance corresponding to the bulk dipolar components is simulated in Fig. 5(a) with the peak frequency indicated as 0.341 Hz. The deviation from the semi-circular response with peak frequency 1.57 Hz in Fig. 5(a). The temperature dependence of the spectra and exhibit a well-defined Arrhenius behavior 

Fig. 6. (a) Temperature dependence of relaxation times ($\tau$) of $R_{\text{dispersion}}Q_{\text{dielectric}}$ and $R_{\text{dispersion}}Q_{\text{dispersion}}$. (b) DC conductivity from $R_{\text{dispersion}}$ and AC conductivity from $A$ of $Q_{\text{dispersion}}$. 

An almost ideal RC semicircular response of $R_{\text{dispersion}}C_{\text{dielectric}}$ components is simulated in Fig. 5(a) with the peak frequency indicated as 0.341 Hz. The deviation from the semi-circular response in the experimental spectrum is successfully addressed by another CPE, indicated by $Q_{\text{dispersion}}$. The element substantially deviates from the ideal capacitor behavior indicated by $\alpha$ values ranging from 0.6 to 0.7. The relaxation times $\tau = \omega \phi_{\text{peak}}$ of RQ elements can be estimated as $(RA)^{1/\alpha}$. The simulated response of the $R_{\text{dispersion}}Q_{\text{dispersion}}$ parallel circuit is shown by the depressed arc of Cole-Cole type response with peak frequency 1.57 Hz in Fig. 5(a). The temperature dependence of $\tau$ of $R_{\text{dispersion}}Q_{\text{dielectric}}$ and $R_{\text{dispersion}}Q_{\text{dispersion}}$ is presented in Fig. 6(a) as 1.49 eV and 1.45 eV, respectively.

The activation energy mainly reflects that of $R_{\text{dispersion}}$ shown in Fig. 6(b) and includes the temperature dependence of $A$ and $\alpha$ shown in Fig. 5(b).

The narrow distribution of $\alpha$ parameter values between 0.6 to 0.7 is suggested to have a physical significance. The values can be considered to be close to 0.667 or 2/3. The behavior of $Q_{\text{dispersion}}$ with fixed $\alpha$ value of 2/3 in parallel to the ideal capacitor corresponds to the CK1 model by J. R. Macdonald, which suggests the specific shape parameter $\beta_{\text{KWW}} = 1/3$ in the Kohlrausch-Williams-Watts (KWW) stretched-exponential temporal response, 

\[
\phi(t) = \exp\left[-(t/\tau_{\text{KWW}})^{\beta_{\text{KWW}}}\right]
\]

on top of Jonscher’s universal dielectric response (UDR) power-law,\textsuperscript{14} original modulus formalism (OMF) by Mohri et al.,\textsuperscript{15} the coupling model by Ngai and Kannert,\textsuperscript{16} and ‘jump relaxation’ or ‘MIGRATION’ framework by Funke et al.\textsuperscript{17,18}

The pre-factor $A_{\text{dispersion}}$ multiplied by the absolute temperature is shown to exhibit an Arrhenius behavior of the well-defined activation energy of 0.45 eV, which is close to 1/3 of the activation of the DC conductivity, Fig. 6(b). The behavior is a straightforward consequence of $\alpha=2/3$ in $Q_{\text{dispersion}}$. The pre-factor $A_{\text{dispersion}}$ corresponds to the AC conductivity, $\sigma_{ac}$ from the relation $\sigma = \sigma_{dc} + \sigma_{ac}$. The KWW function with the shape factor $R_{\text{KWW}}=1/3$ in Eq. (2) corresponds to the frequency power-law exponent $\alpha = 2/3$ for the limited frequency range. Experimental observation of $\alpha$ values close to 2/3 in ionic conducting glasses was also reported by Sidebottom et al.\textsuperscript{19} Macdonald suggests the universal nature of the shape parameter, which can be derived from constraint theory depending on the effective dimensionality of the space in which mobile charges move, i.e. 1/3 in three dimension, and applies to various types of the ionic conductors.\textsuperscript{20-22}

The essential aspect of the CK1 model is the separation of constant dielectric capacitance corresponding to the bulk dipolar
lar dielectric constant of the material, independent of the frequency in the usual experimental range, from the frequency-dispersion effect originating from the mobile charge carriers. Note that the model can describe the wide frequency range feature including the high frequency part which is not visible in the complex impedance representation as in Fig. 3(a). When the analysis is limited to the frequency range with the only appreciable impedance magnitude, the spectrum may be described by a Cole-Cole or Havriliak-Negami model only without parallel $Q_{\text{dielectr}}$. The peak frequency 0.263 Hz of the experimental spectrum is lower than that of $R_{\text{model}}Q_{\text{dielectr}}$ parallel circuit, 0.341 Hz. The lower peak frequency or higher effective capacitance can be attributed to the additional capacitance contribution by $Q_{\text{dispersion}}$. It should be noted that the often-practiced dielectric capacitance estimation from the peak frequency can lead to a significant overestimation, as in the example of Fig. 5(a), 30% by the factor 0.341/0.263=1.3.

The superiority of the CK1 model in fitting many experimental data sets for ionic glasses, polycrystalline materials, single crystals and supercooled liquids, has been recently emphasized in a short summary by J. R. Macdonald. The significance of the present work is more than providing another example of the successful application of the model. The previous work suggests the dispersion behavior should be ascribed to the ionic motion in ionically conducting materials. The conduction mechanism in the crystalline oxide dielectric materials as in MLCCs, however, could be ionic, electronic, or mixed-conducting. The DC conductivity of BaTiO$_3$-based dielectric material in X5R MLCC chips obtained from $R_{\text{model}}Q_{\text{dielectr}}$ in the present work is considered predominantly electronic. In the above analysis the activation energy of 1.32 eV of DC conductivity was attributed to the polaron hopping conduction via deep acceptors. Therefore, the element $Q_{\text{dispersion}}$ is likely to be related to the trap charge densities observed e.g. by thermally stimulated depolarization currents (TSDC). In the temperature range below 220°C, the electronic trap charges are associated with the oxygen vacancies in dipoles. The element $Q_{\text{dispersion}}$ can be thus further related with the ionic defects responsible for the IR degradation.

It should be mentioned that the CK1 model has been successfully applied in the authors' lab (Chonnam National University) to various ceramic systems in different types of solid state electrochemical cells, in conjunction with other polarization effects due to grain boundaries and electrodes. The present work and other results from mixed-conducting systems strongly suggest that the CK1 model can be applied to semiconducting materials with a hopping conduction mechanism as well as ionic conductors. The results may not be so surprising since the hopping conduction of electronic carriers and ionic conduction are phenomenologically very similar. In the present work, in essence, the CK1 model alone describes the entire experimental spectral range and all the parameters are relevant for the bulk crystalline properties. Several samples of the same lot exhibited quite similar characteristics. The electrical effects of the grain boundaries, core-shell structure or electrodes that multiple $RC$ models attempted to describe are not explicitly shown. The formation of Schottky barriers along the grain boundaries and at semiconductor/electrode contacts depends on the electronic structures of the material and of the interfaces, and thus may not be presumed in advance. Other MLCC specifications such as Y5V and C0G show another distinct low frequency response under the similar measurement condition and thus allows the construction of two $RC$ models in the first approximation. The generic difference in the impedance feature between different types of MLCCs will be reported elsewhere.

X7R and X5R type MLCCs belong to the same category and differ only in the temperature range for the maximum 15% capacitance variation. They exhibit similarly indistinguishable, broad single response as shown in Fig. 3, but X7R MLCCs present pronounced asymmetry in the impedance spectra with the peak clearly shifted on the low frequency side. The spectral feature and the extended temperature range from +85°C for X5R to +125°C can be ascribed to the formation of the core-shell structure more predominantly in X7R than in X5R. The feature has invoked the modeling with additional $RC$ for the core-shell structure. Skewed spectra can be described by the generalization $R_{\text{model}}Q_{\text{dispersion}}$ to Havriliak-Negami model, Eq. (1), with two power-law exponents. The symmetric Cole-Cole type response of the X5R MLCCs investigated in this work, Fig. 5(a), corresponds to $\alpha = 2/3$ and $\gamma = 1$. The asymmetric spectral feature of X7R MLCCs may be described in terms of Cole-Davidson function with $\alpha = 1$. Being modified mainly by dopant concentrations, the difference between X5R and X7R should be the matter of the degree in the skewness. It should be noted, however, that the KWW equation (Eq. (3)) with one shape parameter $\beta$ can be approximated as the HK model with multiple choice of the two power-law exponents, $\alpha$ and $\gamma$. There can be thus additional $\alpha$ and $\gamma$ values besides the approximate form exploited in this work, i.e. $\alpha = 2/3$ and $\gamma = 1$, for the shape parameter $\beta = 1/3$ in KWW form of the CK1 model. Relations between KWW function in the time domain with parameters $\tau_{\text{KWW}}$ and $\beta$, Eq. (3), and those of HK models in the frequency domain with parameters $\tau_{\text{HK}}, \alpha$ and $\gamma$, Eq. (1), have been sought after but those satisfying a wide parameter and frequency range are not generally known. Recently two HK models are shown to describe the Fourier transform of KWW function, that is, multiple set of 4 parameters, $\alpha_i$, $\gamma_i$, $\alpha_y$, $\gamma_y$ for one shape parameter $\beta$. X7R and X5R MLCCs can be represented by $\alpha$ and $\gamma$ values generally different from one. Further investigation on the impedance spectroscopy of X7R/X5R MLCCs is under progress using the HK model. The possibility of a more general application of the CK1 model should be examined although the inapplicability of the CK1 model to X7R/X5R type MLCCs with the pronounced microstructural inhomogeneity is also expected. In any case, power-law exponents and time constants as well
as well-defined dc resistance and the capacitance are expected to be the useful parameters interrelating the electrical properties, microstructure, and preparation variables such as compositions and heat-treatment schedules in X7R/X5R MLCCs.

4. Conclusion

Impedance spectroscopy can be an important tool to characterize both the dielectric and conductive behaviors of MLCCs. The application of multiple RC models to X7R/X5R type MLCCs is poorly supported in view of an apparently single distributed relaxation process. A new impedance model consisting of one R, almost ideal C, and a CPE Q in parallel has been successfully applied, where all the parameters represent well-defined physical quantities. The R element provides the DC conductivity with the activation energy of 1.32 eV which is ascribed to the small polaron conduction of deep acceptors. Nearly ideal C element is shown to be exactly consistent with high frequency capacitance values following Curie-Weiss law. The Q element is found with a power-law exponent close to 2/3, and the prefactor A representing high frequency AC conductivity thermally activated by the activation energy close to 1/3 of that of the DC conductivity. The model turns out to be the approximate parallel has been successfully applied, where all the parameters are also associated with oxygen vacancies in dipoles.

Acknowledgments

This work was supported by Samsung Electromechanics Co. Ltd., Korea and also by grant (KRF-2008-531-D00006) of National Research Foundation of Korea funded by the Korean government (MEST).

REFERENCES


