Journal of Alloys and Compounds 508 (2010) 453–456

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jallcom

Numerical study on dielectric permittivity for the ferroelectric ceramic with composition $KTa_{0.6}Nb_{0.4}O_3$

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ARTICLE INFO

Article history:
Received 22 January 2010
Received in revised form 21 August 2010
Accepted 24 August 2010

Keywords:
Ceramics
Perovskite
Dielectric
Debye theory
Ferroelectric

ABSTRACT

Based on the Debye theory, we have determined the evolution of the dielectric permittivity of the ceramic with composition $KTa_{0.6}Nb_{0.4}O_3$ as a function of temperature and frequency. This evolution shows that this composition exhibits a ferroelectric–paraelectric phase transition at 360 K with dispersion at high frequencies (10^6–6×10^8 Hz). A comparison between experimental and numeric calculation of dielectric permittivity for this solid solution has been suggested using a Gaussian distribution of the relaxation times, which was introduced in Debye relations. The numerical results were in agreement with experimental data.

1. Introduction

Perovskite ceramics of a general formula ABO_3 are widely used in various electronics and microelectronic devices. Among these electroceramics, complex perovskites, $A(B'B'')O_3$, are particularly attractive for various applications, such as microwave frequency resonators, multilayer capacitors, piezo-electric sensors, detectors, actuators and ferroelectric random access memories (FRAM) and electro-optic devices [1–5].

The ferroelectric materials are divided into two different classes: classical or relaxor ferroelectrics [6–8]. In particular, relaxor ferroelectrics have been widely investigated. Thanks to their interesting electrical properties, which can be employed in different technological applications [9–11]. The ferroelectric classic ceramics are much less complicated than relaxors so, several models have been developed describing their dielectric properties [12–15]. The solid solution $KTa_{1-x}Nb_xO_3$ that is one of the classical ferroelectric ceramic can be obtained from the oxides: $KTaO_3$ and $KNbO_3$, transparent ferroelectric material, by solid-state reaction. Its ferroelectric properties and variation with Ta/Nb ratios have been widely studied such as for $x = 0.4$ [16–18]. $KTa_{0.6}Nb_{0.4}O_3$ compound is denser than other compositions and presents ferroelectric and piezo-electric characters at room temperature. In addition, the $KTa_{0.6}Nb_{0.4}O_3$ can be used in the fabrication of agile circuits [19].

The aim of this work is to present a numerical model calculating the complex dielectric constant of the classical ferroelectric $KTa_{0.6}Nb_{0.4}O_3$ ceramic.

2. Experimental study

$KTa_{0.6}Nb_{0.4}O_3$ ceramic was prepared by solid-state reaction using the LiF additive. This method has been chosen because of the relative low sintering temperature and thus to decrease K_2O evaporation. The temperature sintered and the percent of LiF addition were optimised as the densification was optimal, at 1105 °C for 2.5 h and 1% of mass respectively.

The pellets have the shape of discs with dimensions 7 mm diameter and about 1 mm thickness. The compactness of the ceramic is close to 0.96 [17]. The dielectric measurements were performed on ceramic discs after deposition of gold electrodes on the circular faces by cathodic sputtering.

The permittivity ε'_r, shown in Fig. 1, was measured from 10^6 to 10^9 Hz using a HP8753A experimental setup [18].

This ceramic material presents a ferroelectric-paraelectric phase transition from tetragonal to cubic at $T_C = 360$ K.

3. The estimation method of the Gaussian–logarithmic distribution width of relaxation times

The Classic Debye theory of dispersion is valid for materials with single relaxation time (τ). In real materials such supposition is in general not true. In such cases, we must take into consideration the continuous distribution of relaxation times [20]. This distribution can be due to chemical inhomogeneity of ceramics which can cause an inhomogeneity in the distribution of ferroelectric microregion.

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doi:10.1016/j.jallcom.2010.08.092

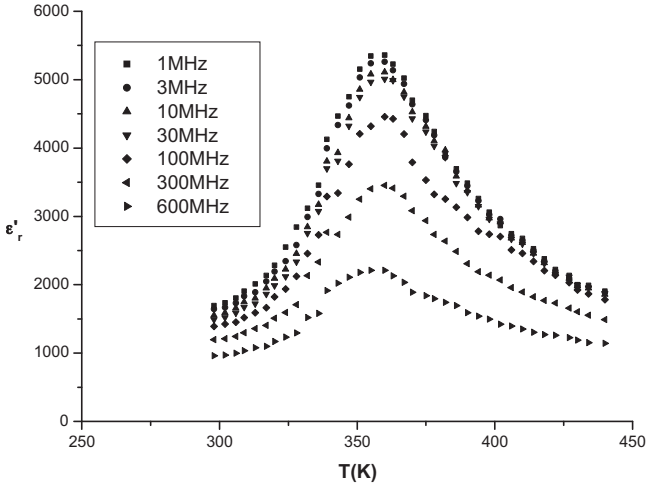

Fig. 1. Experimental obtained dependencies $\varepsilon'(T)$ for $KTa_{0.6}Nb_{0.4}O_3$, for various frequencies.

As a rule, the temperature dependency of relaxation time is of the Arrhenius type [21–22]

$$\frac{1}{\tau} = \frac{1}{\tau_0}\exp\left(\frac{-E_0}{kT}\right) \quad (1)$$

The other possible relation is the Vogel Fulcher relation [23–24].

$$\frac{1}{\tau} = \frac{1}{\tau_0}\exp\left(\frac{-E_0}{k(T-T_f)}\right) \quad (2)$$

where τ_0, E_0, and T_f are constants.

Assuming that distribution (in logarithm scale) of relaxation times takes place, we must calculate the integral:

$$\varepsilon^*(T) = \int_{-\infty}^{\infty} \varepsilon^*(T,\tau)y(\tau(T))d\tau \quad (3)$$

where $\varepsilon^*(T,\tau)$ is complex dielectric permittivity dependent on the temperature and the relaxation time τ; $y(\tau(T))$ is the temperature dependent distribution function of relaxation times.

$\varepsilon^*(T,\tau)$ is given by Debye relation with a single relaxation time depending on temperature.

$$\varepsilon^*(T,\tau) = \frac{\varepsilon_s(T) + \varepsilon_\infty(T) i\omega\tau_0(T)}{1 + i\omega\tau_0(T)} \quad (4)$$

where ε_s is the static permittivity, ε_∞ is the permittivity at very high frequencies, ω is the angular frequency and τ_0 is the means relaxation time.

We suggested that the distribution of relaxation times is a Gaussian distribution (in logarithmic scale). Below, it will be shown how it is possible to estimate the width of Gaussian–logarithmic distribution [25].

The Gaussian distribution of relaxation times can be described by the function:

$$y(\tau(T)) = \frac{1}{\sqrt{2\pi}\sigma(T)}\exp\left(\frac{-[\ln(\tau) - \ln(\tau_0)]^2}{[2\sigma(T)]^2}\right) \quad (5)$$

where τ_0 is the value around which the distribution takes place, $\sigma(T)$ is the temperature dependent half-width of the Gauss distribution. So, it is necessary to estimate this half-width from the experimental data. The method of estimating the width of Gaussian–logarithmic distribution of relaxation times was based on the diagrams $(\varepsilon' - \varepsilon_\infty)/(\varepsilon_s - \varepsilon_\infty)$ *vs* $\log(\omega\tau_0)$ (Fig. 2). The τ_0 value has been taken from the frequency at which the expression $(\varepsilon' - \varepsilon_\infty)/(\varepsilon_s - \varepsilon_\infty)$ is equal to 0.5.

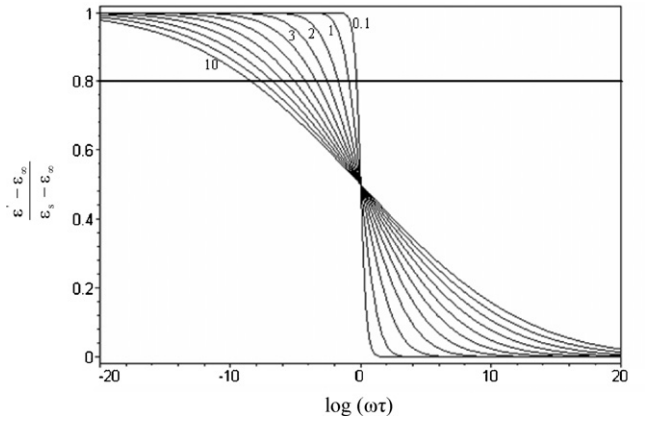

Fig. 2. Normalized plots of $(\varepsilon' - \varepsilon_\infty)/(\varepsilon_s - \varepsilon_\infty)$ *vs* $\log(\omega\tau_0)$ for various widths of Gaussian distribution $\sigma = 0.1, 1, 2, 3, \ldots, 10$.

From Debye theory, it is well known that the plot $(\varepsilon' - \varepsilon_\infty)/(\varepsilon_s - \varepsilon_\infty)$ *vs* $\log(\omega\tau_0)$ for all materials should be the same if we assume the single relaxation time. The distribution of relaxation times leads to deviation from such model plot. So, it is possible to estimate the width of Gaussian distribution (σ) using such normalized plots; the procedure based on comparing the experimental of $(\varepsilon' - \varepsilon_\infty)/(\varepsilon_s - \varepsilon_\infty)$ *vs* $\log(\omega\tau_0)$ with the theoretical ones can be used.

Then it is possible to find the relation between the value of σ and the shape of normalized plot. For this purpose in the last figure (Fig. 2) the horizontal line has been plotted. The value 0.8 has been chosen arbitrarily, intersection of this line with plots gives us the relation between σ and the value of $\log(\omega\tau)$ for which $(\varepsilon' - \varepsilon_\infty)/(\varepsilon_s - \varepsilon_\infty) = 0.8$. We can obtain in such way the relation as:

$$\log(\omega\tau) = a + b\sigma \quad (6)$$

with: $a = -0.27069$ and $b = -0.74139$.

The obtained dependency between $\log(\omega\tau)$ and σ is linear which permits us to determine the dependency $\sigma(T)$ for real materials as well.

4. Results for KTN-($KTa_{0.6}Nb_{0.4}O_3$)

The experimental data for $KTa_{0.6}Nb_{0.4}O_3$ at various temperatures have been taken from ref [18] and the diagram in Fig. 1 has been constructed using this data. We have assumed that $\varepsilon_\infty = 608$,

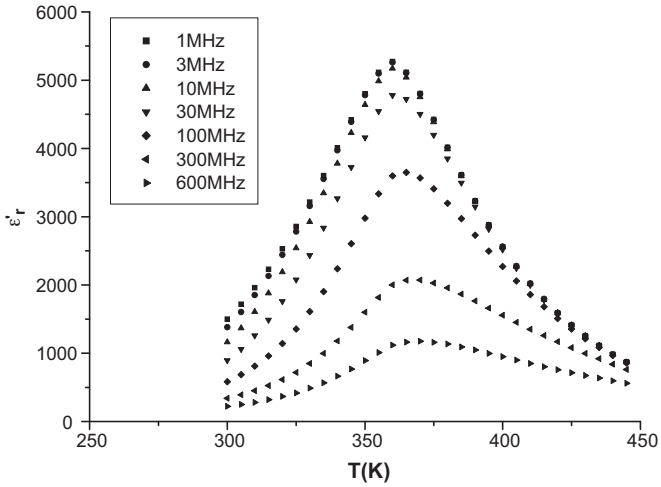

Fig. 3. Numerical obtained dependencies $\acute{\varepsilon}$ (T) for $KTa_{0.6}Nb_{0.4}O_3$, in the frequency range 10^6–6×10^8 Hz.

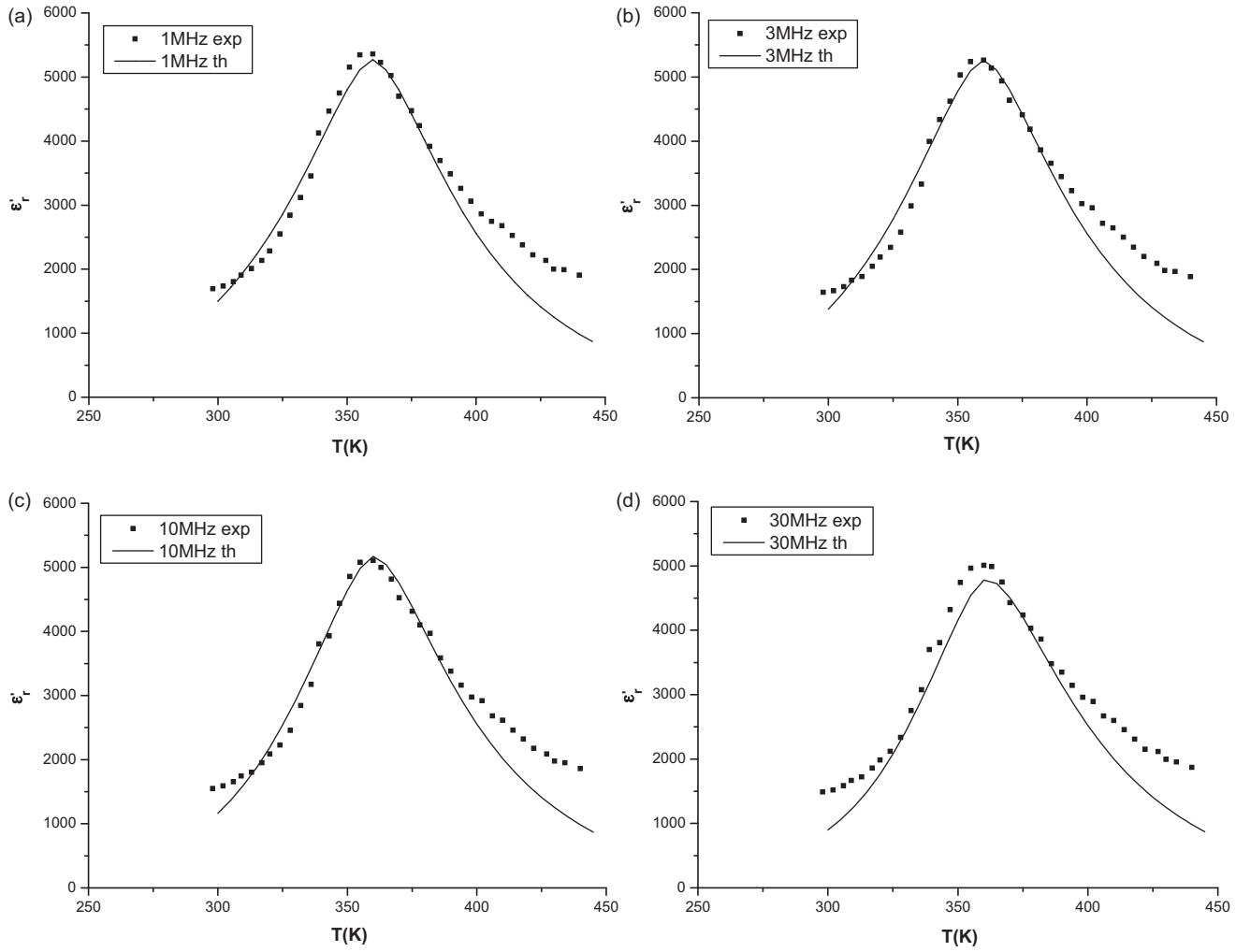

Fig. 4. Comparison between numerical and experimental obtained dependencies $\acute{\varepsilon}$ (T) for $KTa_{0.6}Nb_{0.4}O_3$, for various frequencies: (a) 10^6 Hz, (b) 3×10^6 Hz, (c) 10^7 Hz and (d) 3×10^7 Hz.

while ε_s fulfils the generalized Curie–Weiss law in the form:

$$\frac{1}{\varepsilon_s} = A + B|T - T_m|^{\gamma} \tag{7}$$

where: $A = 0.17 \times 10^{-3}$, $B = 3.2659 \times 10^{-7}\ K^{-1}$, $T_m = 360$ K, $\gamma = 1.65$.

At every temperature, the frequency has been found at which $(\varepsilon' - \varepsilon_\infty)/(\varepsilon_s - \varepsilon_\infty) = 0.8$. Next, we can obtain the dependency of the logarithm of the mean relaxation time at the temperature. The dependency obtained in such a way is well described by Eq. (1) with: $\tau_0 = 2{,}995 \times 10^{-12}$ s and $E_0 = 0.231$ eV (the dependency is Arrhenius type).

As a result, the construction of the diagram $(\varepsilon' - \varepsilon_\infty)/(\varepsilon_s - \varepsilon_\infty) = f(\log(\omega\tau_0))$ for $KTa_{0.6}Nb_{0.4}O_3$ becomes possible. Next, we can find the $\sigma(T)$ dependency using the procedure described above. The obtained relation can be expressed as:

$$\sigma(T) = a + bT + cT^2 + dT^3 \tag{8}$$

with $a = 30.580$, $b = -0.229\ K^{-1}$, $c = 5.889 \times 10^{-4}\ K^{-2}$ and $d = -5.116 \times 10^{-7}\ K^{-3}$.

Similar calculation for SBN and PMN compound was presented by Skulski [25]. It has been shown that $\sigma(T)$ dependency in PMN follows the equation:

$$\sigma(T) = \frac{\sigma_\infty}{(T - T_\sigma)^n} \quad (\sigma_\infty, T_\sigma, \text{and } n \text{ are constants}), \tag{9}$$

and for SBN, this variation is polynomial as:

$$\sigma(T) = a + bT + cT^2 (a, b \text{ and } c \text{ are constants}). \tag{10}$$

Compared to these studies, the $\sigma(T)$ variation in $KTa_{0.6}Nb_{0.4}O_3$ is like BSN with third degree polynomial (Eq. (8)).

Figs. 3 and 4 show the spectrum of the theoretical dielectric permittivity calculated with the relaxation times obtained from the Gaussian distribution function in the frequency range 10^6–6.10^8 Hz (Eq. (3)). These dielectric permittivity spectrums have approximately the same evolution that obtained experimentally [17]. In fact, like the experimental dielectric permittivity a dispersion behavior was observed at different frequency (Fig. 4).

Fig. 4 presents a comparison between numerical and experimental dielectric permittivity for some frequencies (1, 3, 10 and 30 MHz). In these spectrums, we notice that the difference between experimental and numerical result becomes more important with increasing frequency.

5. Conclusions

Ferroelectric $KTa_{0.6}Nb_{0.4}O_3$ ceramic, synthesized by a solid-state reaction technique was investigated. The frequency dependence of the dielectric loss peak was found to obey an Arrhenius law with activation energy of 0.231 eV. This result is in agreement with experimental data as the solid solution $KTa_{0.6}Nb_{0.4}O_3$ is a classical

ferroelectric. Analyses of the real part of the dielectric permittivity with frequency were performed, assuming a Gaussian distribution of relaxation times. The width of the Gaussian distribution of relaxation times fulfills a polynomial form. In the present work, we have presented a study of dielectric permittivity for a classical perovskite ferroelectric. We intend in the future to continue our study for other classical and relaxor ferroelectric and to find an explanation for relaxor phenomena.

References

[1] J. Toulouse, R.K. Pattnaik, Phys. Rev. B 65 (2001) 24107.
[2] Y.-C. Chen, S.-M. Tsao, C.-S. Lin, S.-C. Wang, Y.-H. Chien, J. Alloys Compd. 471 (2009) 347.
[3] P.-C. Juan, C.-H. Wang, Microelectron. Eng. 86 (2009) 1845.
[4] T.A. Jain, K.Z. Fung, J. Chan, J. Alloys Compd. 468 (2009) 370.
[5] U. Kushnir, O. Rabinovitch, Sens. Actuators A 150 (2009) 102.
[6] L.E. Cross, Ferroelectrics 76 (1987) 241.
[7] L. Khemakhem, A. Kabadou, A. Maalej, A. Ben Salah, A. Simon, M. Maglione, J. Alloys Compd. 452 (2008) 451.
[8] J. Hao, Z. Xu, R. Chu, W. Li, G. Li, Q. Yin, J. Alloys Compd. 484 (2009) 233.
[9] T. Tsurumi, K. Sejima, et al., Jpn. J. Appl. Phys. 33 (1994) 1959.
[10] A. Chen, Y. Zhi, J. Appl. Phys. 91 (2002) 1487.
[11] A.A. Bokov, Z.G. Ye, J. Mater. Sci. 41 (2006) 31.
[12] P.Q. Mantas, J. Eur. Ceram. Soc. 19 (1999) 2079.
[13] O.G. Zaldívar, A.P. Barranco, F.C. Piñar, R.L. Noda, L.V. Molina, Scripta Mater. 55 (2006) 927.
[14] A.S. Verma, R.K. Singh, S.K. Rathi, J. Alloys Compd. 486 (2009) 795.
[15] V. Ciancio, F. Farsaci, P. Rogolino, B. Physica, Condens. Matter 405 (2010) 175.
[16] H. Khemakhem, J. Ravez, A. Daoud, Ferroelectrics 188 (1996) 51.
[17] H. Khemakhem, J. Ravez, P. Dubernet, A. Daoud, Phase Transit. 54 (1996) 199.
[18] H. Khemakhem, J. Ravez, A. Daoud, Status Solidi Phys. (a) 161 (1997) 557.
[19] V. Laur, A. Rousseau, G. Tanné, P. Laurent, S. Députier, M. Guilloux-Viry, F. Huret, IEEE Trans. Ultrason. Ferroelectr. Freq. Control 53 (2006) 2280.
[20] A.E. Glazounov, A.K. Tagantsev, A.J. Bell, Phys. Rev. B 53 (1996) 11281.
[21] Z. Kutnjak, C. Filipic, et al., Phys. Rev. Lett. 70 (1993) 4015.
[22] A.K. Tagantsev, Phys. Rev. Lett. 72 (1994) 1100.
[23] D. Viehland, S.J. Jang, et al., Philos. Mag. B 64 (1991) 335.
[24] E. Courtens, Phys. Rev. B 33 (1986) 2975.
[25] R. Skulski, Physica A 274 (1999) 361.