Study on Electric Properties of Gadolinium Nitrate Crystals

著者	ISODA Hiroshi, KAWASHIMA Riki
journal or publication title	Memoirs of the Muroran Institute of Technology
volume	58
page range	61-64
year	2009-02-20
URL	http://hdl.handle.net/10258/431

Mem. Muroran Inst. Tech., 58 (2008) 61～64

学 術 論 文

Study on Electric Properties of Gadolinium Nitrate Crystals

Hiroshi ISODA* and Riki KAWASHIMA*

(Received 20 June 2008, Accepted 7 November 2008)

Abstract

Frequency dependence of ac conductivity from 20Hz to 10MHz and time series of the conductivity at 2kHz along *c*-axis of gadolinium nitrate crystal $Gd(NO_3)_3 6H_2O$ were measured in the temperature range from 210K to 290K. Meta-stable phenomena were observed. Dynamical property given by the frequency dependence of the conductivity is compared to those in disorder system. Non-periodic instability (burst) was found in the time series data of the conductivity. The frequency dependence of the power spectrum densities is well represented by the power law $1/f^{\alpha}$. The exponent α is discussed with the nonlinear dynamical property.

Keywords : Gadolinium nitrate, Ac conductivity, Meta-stable phenomena, Nonlinear property

1. INTRODUCTION

Nonlinear and non-equilibrium phenomena were observed in many systems such as disordered ferromagnets[1], superconducting vortices[2], martensitic shape memory alloys[3], glass[4] and earthquakes[5]. The physical quantities in equilibrium state always show time variation in the vicinity of the average values, and the physical properties are characterized by the fluctuation[6]. The fluctuation could be closely related to inevitable thermodynamic instability[7]. Therefore the investigation of the thermodynamical instability could give a new information for unknown properties of the material. The behavior of the fluctuation was given by measuring the time variation of the physical quantities.

The rare earth nitrate crystals $R(NO_3)_3 6H_2O$ where R is rare earth element, form the triclinic symmetry with the space group $P\bar{1}$ above 193K[8]. Authors have studied the characteristic property of the rare earth nitrate crystals by electric measurement in the time successive procedures and the time series data between 210K and room temperature. In the successive measurements for the time variation of the electric properties in rare earth nitrate crystals, meta-stable and non-ergodic nonlinear properties were found[9]. By the measurements of time series for the ac conductivity at 2kHz, nonlinear dynamical property having deterministic chaotic one were also found in the rare earth nitrate[10]. In addition, the crystals show the distinct intermittent non-periodic oscillations (bursts) and the dependence of the rare earth element on the time series of the ac conductivity[11] [12]. However the instability in the rare earth nitrate crystal was not known sufficiently. In order to clarify the characteristic phenomena, we have measured frequency spectra of the ac conductivity in the frequency region from 20Hz to 1MHz and the time series of the conductivity at 2kHz at temperatures $210K \le T \le 290K$ along *c*-axis of $Gd(NO_3)_3 6H_2O$ crystal.

*Department of Materials Science and Engineering, Muroran Institute of Technology

2. EXPERIMENTAL

The crystal used for the present measurements was grown in a gadolinium nitrate aqueous solution by decreasing temperature. The size of sample A used for the measurements of the frequency spectra for the ac conductivity was 0.061±0.005cm in thickness and 0.591±0.005 cm^2 in area, and that of the sample B used for measuring the time series of the conductivity, 0.228±0.005cm in thickness and 0.228±0.005 cm^2 in area. The silver paste (Tokuriki Chem.Inst.P255) was used as a contact electrode. The good qualities of the electrodes and the specimens have been kept at the final stage of the experiment.

The ac conductivity in the frequency region from 20Hz to 1MHz was measured by using a computer controlled LCR meter (HP4284A) with a general purpose interface bus (GPIB). Time series data on the ac conductivity at 2 kHz were measured by using the digital lock-in amplifier (EG&G Princeton Applied Research, Model 5210) and an analog memory recorder (YOKOGAWA, AR1100).

The conductivity was measured at the sensitivity within $\pm 10^{-11}$ Ω^{-1} cm^{-1}. All the measurements were carried out under the isothermal condition and controlled by the computer within ±0.1K. For the time series data, 5000 data points were collected with a sampling time of 50 ms.

3. RESULTS AND DISCUSSION

3.1. Frequency dependence of ac conductivity

The Frequency dependence of ac conductivity along *c*-axis was measured from 20 Hz to 1MHz at temperatures between 290K and 210K in both cooling and heating cycles of four measuring runs (1)〜(4) using the sample A. Figure 1 shows the real component σ'(*T*) of the complex conductivity σ* (σ* = σ' + *i*σ'') derived from the experimental data at 1 kHz.

As seen from Fig.1, σ'(*T*) in cooling and heating cycles of run (1) shows appreciable temperature variation with thermal hysteresis in the region between 280K and 230K. The temperature variation of σ'(*T*) as observed in the following runs (2) and (3) suggests an existence of meta-stable phase in the crystal. The phase seems to disappear asymptotically. At the run (4), the meta-stability behavior appeared in the first time. The temperature dependence of σ'(*T*) shoes the same behavior observed in the first runs.

The behavior of meta-stable phase in other rare earth nitrate crystals was dependent on the rare earth ion R^{3+} in $R(NO_3)_36H_2O$; non-periodic oscillation of appearance for meta-stable phase in $Sm(NO_3)_36H_2O$[9]; rapid disappearance of the phase in $La(NO_3)_36H_2O$[13], $Nd(NO_3)_36H_2O$[14], $Tb(NO_3)_36H_2O$[15] and $Er(NO_3)_36H_2O$[16]; complex behavior appearance of the phase in $Eu(NO_3)_36H_2O$[17] and $Yb(NO_3)_36H_2O$ [18].

Figure 2 shows the frequency dependence of σ'(ν) in the logarithmic scale within the range 20Hz≤ ν ≤ 1MHz at several temperatures 288K, 273K, 253K, 233K and 214K in cooling(1) of the first measuring run. The σ'(ν) increases with increasing frequency ν at 253K and 233K in cooling(1). The frequency dependence of σ'(ν) was analyzed by power law, $\sigma' \propto \nu^{s}$, where *s* is frequency exponent. The value of the exponent *s* was estimated from the local slope $-\partial \ln \sigma'(\nu)/\partial \ln \nu$ in Fig.2.

The temperature variation of the frequency exponent *s*(*T*) was given in Fig. 3 in the frequency region 10kHz ≤ ν ≤ 100kHz. As the temperature increases, the value of *s* decreases and is nearly equal

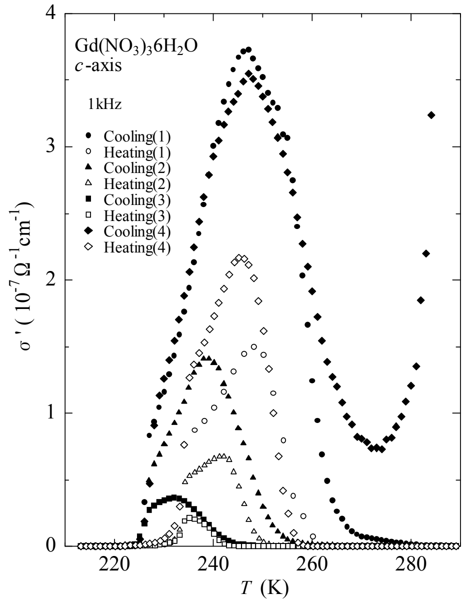

Figure 1 The real part σ' of the complex conductivity σ* at 1 kHz along *c*-axis of $Gd(NO_3)_36H_2O$ crystal at temperatures between 290K and 210K in both cooling and heating cycles of four measuring runs.

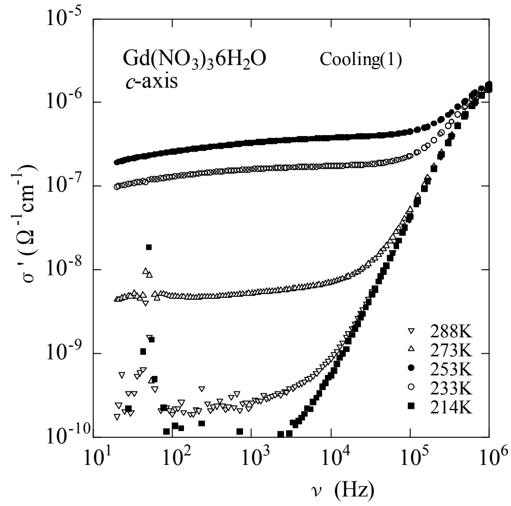

Figure 2 Frequency dependence of the conductivity σ' along *c*-axis of $Gd(NO_3)_36H_2O$ crystal at several temperatures in the cooling(1) of the measuring runs.

to 0 for meta-stable phase. The value $s \le 1$ has been obtained in a frequency dependent conductivity in disordered materials, such as an amorphous semiconductor and glass material[19]. The σ'(ν) in the meta-stable phase shows similar behavior as that of the nearly constant loss in ionic conducting glass[20]. The value $s \approx 2$ of the frequency exponent *s* corresponds to the frequency response of Debye relaxation process [21].

3.2. Time series of ac conductivity

Figure 4 shows the time dependence of the fluctuation Δσ' of the real part σ' of the complex conductivity σ* at 2kHz along *c*-axis of the $Gd(NO_3)_36H_2O$ crystal at several temperatures in the

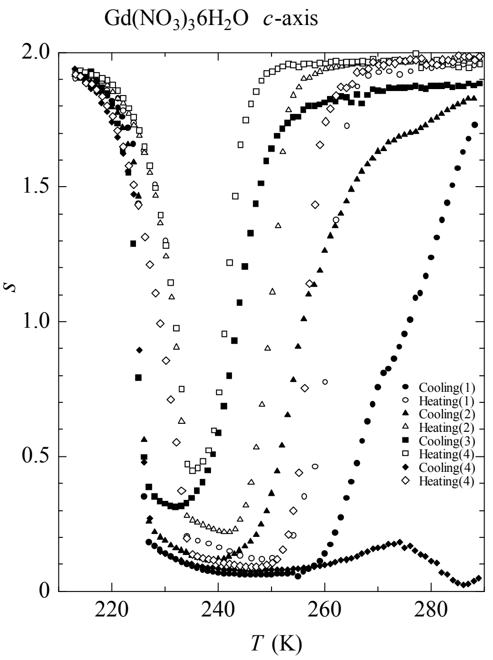

Figure 3 Frequency exponent $s(T)$ of the power law in the frequency spectra of the ac conductivity in the frequency region 10kHz～100kHz in both cooling and heating cycles of four measuring runs.

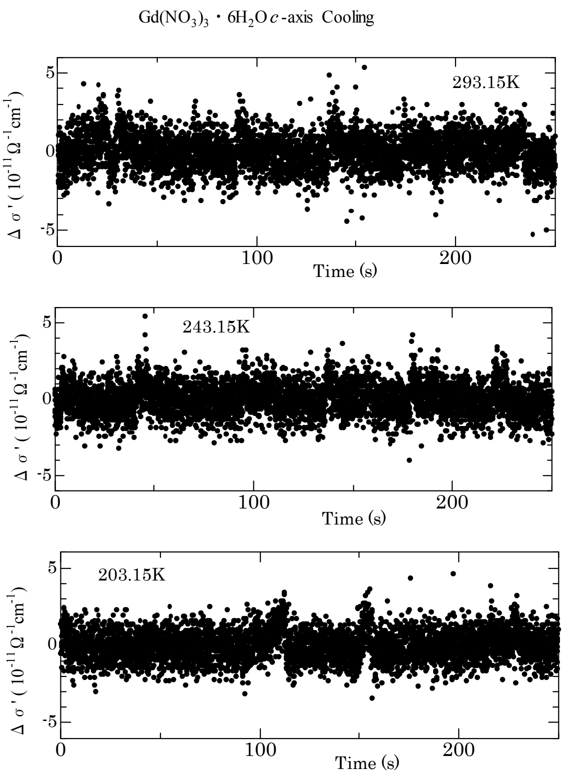

Figure 4 Time series of the fluctuation Δσ' for the real part σ' of the complex conductivity σ* at several temperatures in cooling cycle measured at 2 kHz with a sampling time 50 ms along c-axis of $Gd(NO_3)_3 6H_2O$ crystal.

cooling cycles, where Δσ' is given as Δσ' = σ' - <σ'>. The average value <σ'> was obtained from 5000 data points of σ' at the temperature. The set of the data Δσ' is represented by {Δσ'}. As shown in Fig.4, the non-periodic unstable oscillations (bursts) appear in the time series data {Δσ'} at several temperatures, 293.15K, 243.15K and 203.15K in cooling, respectively.

The probability distributions of the fluctuation {Δσ'} show continuous line shapes. The power spectrum densities were calculated from the time series data {Δσ'}[10]. The power spectral densities of the fluctuation {Δσ'} at temperatures show the random broad peaks in the statistical frequency region from 1Hz to 10Hz and the continuous line shape below 1Hz. In the statistical frequency region 0.1～1Hz, the continuous part of the power spectra is proportional to $1/f^{\alpha}$, where f is the statistical frequency in the power spectra and α is the exponent of the power law. The values of α were estimated by calculating the local slopes of the power spectra in the temperature region 210K ≤ T ≤ 290K. The temperature dependence of the exponent α is given in Figure5 for cooling and heating cycles. In Fig.5, the value of α is nearly equal to 2 and the power spectra are assigned to the thermal noise [22]. The values of α in the light rare earth nitrates ^{57}La ～^{64}Gd are approximately equal to 2 with exception of ^{59}Pr [12]. In the case of the heavy rare earth nitrates, the values of α were nearly equal to 1, so that this is assigned to the f^{-1} noise [12] [23].

To study the non-periodic unstable oscillation (the burst), the data {Δσ'} were analyzed in detail by using the nonlinear dynamical method. The nonlinear dynamical property of the system was specified by a fractal dimension derived from N data point of the time series according to the simple procedure of Grassberger and Procaccia [24]. For an arbitrary embedding dimension n, the σ_i' and σ_j' are pseudo-vectors defined by

$$\sigma_i'=\{\sigma'(t+i\tau_N),\sigma'(t+(i+1)\tau_N),\cdots,\sigma'(t+(i+n-1)\tau_N)\}, \quad (1)$$

where the value of τ_N is a fixed time increment between successive measurements. In the present measurement, τ_N corresponds to the sampling time 50 ms. Spatial correlation of the attractor embedded in a phase space of n-dimensions is defined by

$$C(r)=\frac{1}{N^2}\sum_{i,j=1}^{N}\theta(r-|\sigma_i'-\sigma_j'|) \quad , \quad (2)$$

where $\theta(x)$=0 if x<0 and $\theta(x)$=1 if x>0. Thus the correlation integral $C(r)$ counts the number of pairs whose distance $|\sigma_i'-\sigma_j'|$ is smaller than a given r.

The correlation integral $C(r)$ were calculated for the time series data {Δσ'} at temperatures for the embedding dimension n = 1 ⋯ 20 by using the supercomputer (Hitachi SR8000) of Hokkaido University. The correlation integral $C(r)$ behaves as power of r for small r : $C(r) \propto r^d$, where d is a correlation exponent. The values of d at each embedding dimension n were obtained from the slope

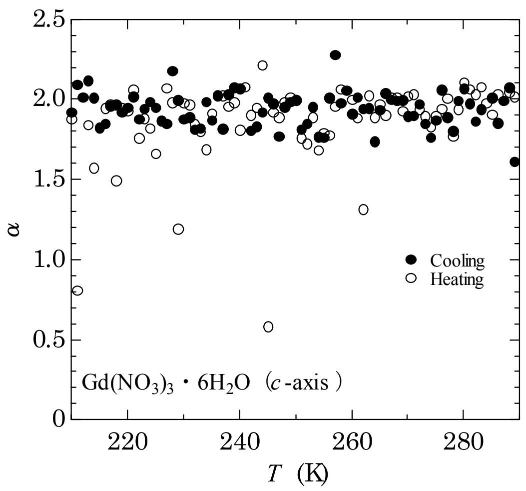

Figure 5 Temperature dependence of the exponent α in the power law $1/f^{\alpha}$ for the power spectral densities of the fluctuation {Δσ'} in the statistical frequency region 0.1Hz≤f≤0.5Hz for both cooling and heating cycles of four measuring runs, where f is the statistical frequency.

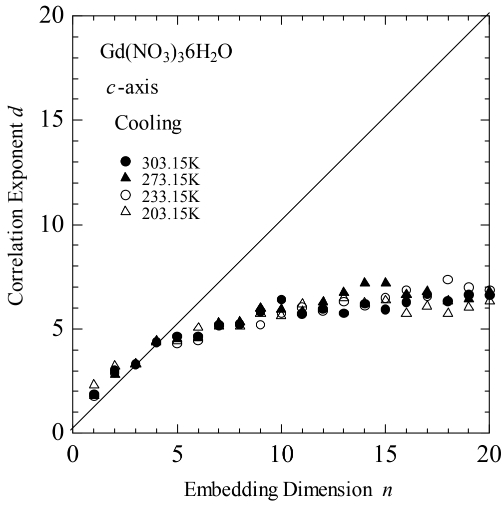

Figure 6 Correlation exponent d versus dimension n of the embedding space.

of $\ln C(r)$ versus $\ln r$. Figure 6 shows the dependence of the correlation exponent d on the embedding dimension n at the several temperatures in cooling cycle. In the case of the random noise, d is equal to n ($d = n$) so that the relation is shown as the straight line in Fig.6. As seen from Fig.6, d shifts to the asymptotic value as n increases.

4. SUMMARY

The time successive processes of the electric properties of the $Gd(NO_3)_36H_2O$ crystal were studied by two different experimental methods. The frequency dependence of the ac conductivity was analyzed by the power law ν^s. The value of the exponent s depends on the temperature and the measurement cycles. The meta-stable structure was discussed in terms of the exponent s.

The power spectrum densities were calculated form the time series of the ac conductivity. The frequency dependence of the power spectrum densities is well represented by the power law $1/f^{\alpha}$. The obtained value α≈2 corresponds to the thermal noise. The nonlinear dynamical analyses were carried out. The analyses indicate that the correlation exponent deviated from the value of the random noise as the embedding dimension n increases.

In the present study, it confirms that the electric property measured for $Gd(NO_3)_36H_2O$ shows the nonlinear non-equilibrium phenomena, and that the fluctuation, generated in the rare earth nitrate crystal, has both the chaotic feature and the effect of rare earth element.

REFERENCES

(1) D. Lorenzo, D. Gianfranco, M. Alessandro and Z. Stefano, Phys. Rev. B 65 (2002),144441.
(2) S. Field, J. Witt, F. Nori and X. Ling, Phys. Rev. Lett. 74(1995), p.1206-1209.
(3) E. Vives, J. Ortín, L. Mañosa, I. Ràfols, R. Pérez-Magrané, and A. Planes, Phys. Rev. Lett. 72(1994), p. 1694-1697.
(4) T. Komori, H. Yoshino and H. Takayama, J. Phys. Soc. Jpn. 68 (1999), p. 3387-3393.
(5) J. P. Sethna, K. A. Dahmen and C. R. Myers, Nature 410(2001), p. 242-250.
(6) L. D. Landau and E. M. Lifshitz, Statistical Physics (New York: Wesley, 1958).
(7) P. Glansdorff and I. Prigogine, Thermodynamic theory of structure, stability and fluctuations (New York:Wiley, 1971).
(8) R. Kawashima, M.Sasaki, S.Satoh, H.Isoda, Y.Kino and Y.Shiozaki, J.Phys.Soc.Jpn. 69(2000), p. 3297-3303.
(9) R. Kawashima and Y. Matsuda, J.Phys.Soc.Jpn.59 (1990), p.3727-3731.
(10) R. Kawashima, S. Nishimura and H. Isoda, Physica B183(1993), p.135-144.
(11) R. Kawashima, R. Hattada and H. Isoda, J.Phys.Soc.Jpn.68(1999), p. 1143-1147.
(12) R. Kawashima, J. Fukui, K. Haruki and H. Isoda, J.Phys.Soc.Jpn.72(2003), p.2477-2480.
(13) R. Kawashima, T. Saitoh and H. Isoda, J.Phys.Soc.Jpn.62(1993), p.4529-4530.
(14) R. Kawashima, M. Hattori and H. Isoda, J.Phys.Chem.Solids 55 (1994), p.1331-1335.
(15) R. Kawashima, S. Nasukawa and H. Isoda, J.Phys.Soc.Jpn.64(1995), p.1439-1440.
(16) R. Kawashima, J.Phys.Soc.Jpn.60(1991),p. 342-343.
(17) R. Kawashima, T. Sasaki and H. Isoda, J.Phys.Soc.Jpn. 63(1994), p. 2008-2009.
(18) R. Kawashima, R. Takahashi and H. Isoda, J.Solid State Chem.121(1996), p.74-78.
(19) A. K. Jonscher, Dielectric Relaxation in Solids (Chelsea Dielectric Press:London, 1983).
(20) K. L. Ngai and C. León, Phys. Rev. B 66(2002), 064308.
(21) V. V. Daniel, Dielectric Relaxation (Academic Press,London, 1967).
(22) P. Dutta and P. M. Horn, Rev.Mord.Phys. 53(1981),p. 497-516.
(23) R. Kawashima, T. Okubo and H. Isoda, J.Solid State Chem. 177(2004), p. 2223-2230.
(24) P. Grassberger and I. Procaccia, Physica 9D(1983),p. 189-208.