

Nearly constant loss in crystalline oxide-ion conductor $\text{Gd}_2\text{Zr}_2\text{O}_7$

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Abstract We present a study of the nearly constant loss regime in the oxide-ion conductor $\text{Gd}_2\text{Zr}_2\text{O}_7$ by using Impedance Spectroscopy measurements. At enough low temperature, between 173 and 253 K, the dielectric loss is found to be almost temperature and frequency independent within the whole experimental frequency range (10 Hz – 1 MHz). However, a symmetric and very broad relaxation peak is clearly resolved in the loss spectra. This peak shows a thermally activated peak frequency with activation energy $E_r=0.29\pm 0.02$ eV, and its origin is discussed in terms of previously proposed models for the nearly constant loss.

Keywords Ionic conductivity · Dielectric loss · Dielectric relaxation

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1 Introduction

In 1991, Nowick and coworkers reported the existence of a universal behavior in the low temperature conductivity of ionically conducting materials [1]. They found that an almost linear frequency dependence of the ac conductivity at the highest frequencies is ubiquitous in these materials, and that the frequency range where this linear relationship approximately holds extends towards lower frequencies when temperature is decreased. They also showed that this regime eventually covers the whole experimental frequency range at enough low temperatures, typically within 1 Hz and 1 MHz, though it has been observed in an even broader frequency range [2, 3]. An approximately linear frequency dependence of the ac conductivity at enough high frequencies had been reported earlier by Angell [4]. Even earlier, Macedo and Moynihan had approached the problem with the electric modulus representation and already showed the deviation from the Kohlrausch-Williams-Watts fits at enough high frequencies and/or low temperatures as the frequency dependence of the conductivity approaches a linear behavior [5, 6]. However, Nowick et al. were the first to recognize this linear frequency dependence as a universality in ionic conductors. Since then, this behavior is usually referred to as “second universality”, because the presence of a universal power-law frequency dependence (the so called Jonscher’s law) of the ac conductivity at higher temperatures / lower frequencies, was already well established at that moment [1, 7]. The imaginary part of the dielectric permittivity, or dielectric loss, $\varepsilon''(\omega)$, is related to the real part of the conductivity, $\sigma'(\omega)$, by

$$\varepsilon''(\omega) = \sigma'(\omega)/\varepsilon_0\omega \quad (1)$$

with ω the angular frequency and ε_0 the permittivity of vacuum. Thus a linear frequency dependence of $\varepsilon''(\omega)$ means a constant $\varepsilon''(\omega)$ value, and consequently the “second universality” is also known as “nearly constant loss” (NCL) regime [8].

For the last 20 years much work has been devoted to understand the origin and properties of the “second universality” in ionic conductors [9–15]. In 1999, Ngai pointed out [16] the correlation existing between the value of the NCL magnitude at low temperatures and the value of the dc conductivity σ_{dc} at room temperature. In particular, superionic conductors with technological interest for their application as electrolytes in solid state batteries and fuel cells usually show very high values of the NCL magnitude [14, 16–18]. Based on the different properties observed from experiment for the NCL in ionic conductors, Ngai proposed its physical origin might be due to the local displacements of the mobile ions at low temperature and/or high frequency before they are able to hop to available neighboring sites. Later on, León et al. found experimental evidence, in two different lithium ionic conductors, consistent with such an origin for the NCL contribution to the ac conductivity [13, 19, 20]. Ngai’s Coupling Model was shown to explain this finding, with the NCL behavior arising from caged ion dynamics, which result in a logarithmic time dependence of the mean square displacement and thus in a linear frequency dependence of the ac conductivity [21, 22]. Other different scenarios have been also proposed to explain the NCL properties [2, 23–25].

A key issue in order to definitely understand the nature and origin of the NCL might be the presence of additional, usually very weak, relaxations in the dielectric loss spectra at low temperature, that have been reported to occur in some “simple” ionic conductors [26]. Nowick et al. showed that in the case of “simple” systems, i.e. ionic crystals doped with dilute concentrations of aliovalent impurities, a conventional NCL behavior is not observed at low temperature since at least one relaxation peak appears in the dielectric loss. They also showed that this peak seems to smear out giving rise to a conventional NCL behavior in “complex” ionic conductors characterized by a high degree of disorder, i.e. when the concentration of impurities is largely increased, or in the case of ionic glasses [8, 26]. However, whether the relaxation peak in the dielectric loss evolves to a conventional NCL behavior, or both contributions may be always present and the NCL dominates the electrical response for “complex” systems, is not clearly established yet.

Here we report on the dielectric loss data of an oxide-ion conductor, $\text{Gd}_2\text{Zr}_2\text{O}_7$, which has a large concentration of mobile oxygen vacancies and thus can be considered as a “complex” ionic conductor according to Nowick’s classification [26]. $\text{Gd}_2\text{Zr}_2\text{O}_7$ presents a highly disordered pyrochlore structure [27, 28] with oxygen vacancies at $48f$ sites which are known to be responsible for oxygen hopping and diffusion,

and shows a high ionic conductivity at high temperature ($\sigma_{dc} \sim 10^{-3}$ S/cm at 600 °C). In fact it has been proposed as a possible electrolyte material in solid oxide fuel cells to substitute currently used fluorites like yttria stabilized zirconia [29, 30]. We find that, as expected from its “complex” character, a broad relaxation peak dominates the loss spectra at enough low temperature. While the shape of the peak hardly changes with temperature, its maximum is thermally activated. The value obtained for the activation energy seems too low to be related to ion hopping processes, and is discussed in terms of previously reported models for the NCL.

2 Experimental

Samples were prepared by mechanically milling stoichiometric mixtures of high purity elemental oxides, as described in previous works [31]. Phase composition of milled samples was analyzed by X-ray power diffraction (XRD) in a Philips X’Pert diffractometer using Ni-filtered CuK_α radiation ($\lambda = 1.5418$ Å), and chemical reactions were considered completed when no traces of the starting reagents were observed by this technique. Impedance spectroscopy measurements were carried out on pellets (7 mm diameter and ~ 0.7 mm thickness) prepared by uniaxial pressing of the fine powders obtained by milling (sintering temperature = 1500 °C). Colloidal Pt-paint was coated on both faces to serve as electrodes, and measurements were made under N_2 gas flow to ensure an inert atmosphere. Impedance data were recorded over the 10 Hz–1 MHz frequency range, at selected temperatures between 173 and 500 K, by using a Novocontrol high resolution alpha analyzer.

3 Results and discussion

Figure 1(a) shows the frequency dependence of the real part of the ac conductivity in a log-log scale, at several fixed temperatures between 173 and 403 K. It can be observed that, below room temperature, the conductivity is almost linearly frequency dependent in the whole experimental frequency range, which is the NCL regime reported by Nowick et al. as a universal regime in ionic conducting materials [1, 26]. As a guide to the eye, the dashed line in the figure represents the linear frequency dependence for the conductivity. At the highest temperatures, although a NCL still dominates the electrical conductivity at 403 K in the highest frequency decade, the ac conductivity departs from a linear dependence at low frequencies, crossing over to sublinear (power-law) frequency dependence, with the power exponent changing from approximately 1 to 0.6 with increasing temperature or decreasing frequency. This is due to the increasing probability of ion hopping and the onset of long range ion diffusion [13, 19, 32–34]. The presence of an activated hopping diffusion

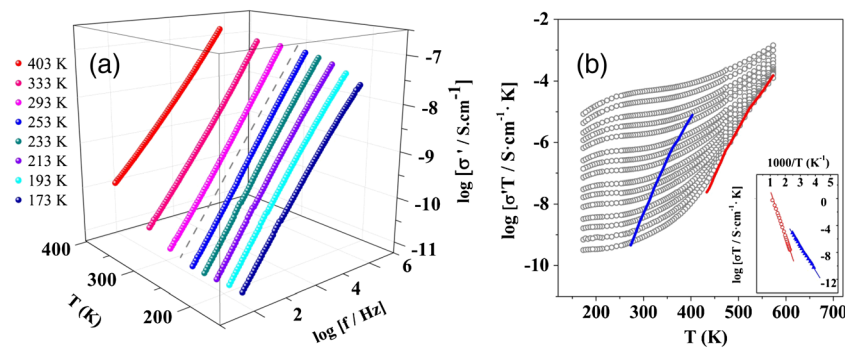


Fig. 1 (a) Frequency dependence of the real part of the conductivity, $\sigma'(\omega)$, in a log-log scale, for several temperatures between 173 K and 403 K. *Dashed line* in the figure represents a linear frequency dependence, $\sigma'(\omega) \sim \omega$. (b) Temperature dependence of the real part of the conductivity at several fixed frequencies (22 Hz, 48 Hz, 107 Hz, 210 Hz, 522 Hz, 1 kHz, 2 kHz, 5 kHz, 10 kHz, 20 kHz, 55 kHz, 110 kHz, 210 kHz, 525 kHz, and 1 MHz, increasing frequency from bottom to

top). Inset: Arrhenius plot of the conductivity values at the crossover point between hopping conductivity and nearly constant loss behavior (*blue solid triangles*) and dc conductivity values (*red open circles*). *Solid lines* in inset and main panel are fits to an Arrhenius law for dc conductivity values (*red*), and crossover points between hopping conductivity and nearly constant loss behavior (*blue*)

process is more evident in Fig. 1(b), which shows isochronal ac conductivity data as a function of temperature in an Arrhenius plot. At high temperatures, in the dc conductivity regime, conductivity is found to be frequency independent and shows a thermally activated behavior with activation energy $E_{dc} = 1.32 \pm 0.04$ eV (see red line in Fig. 1(b) and red open circles in its inset). When decreasing the temperature, and first for the highest frequencies, the ac conductivity enters into the power law frequency dependent regime and it departs from the dc conductivity value. Finally, at enough low temperature, the ac conductivity is dominated by the NCL contribution and shows very weak temperature dependence, which has been often reported in the past as a feature of the NCL regime [2, 16, 17, 23, 35]. The NCL regime has been previously proposed to arise from caged ion dynamics, when ions do not have enough thermal energy or time to overcome the potential barrier and hop to neighboring vacant sites [21, 22]. A thermally activated crossover from the NCL to the ac conductivity due to ion hopping (see blue line in Fig. 1(b) and blue solid triangles in its inset) was already reported for this material [34], similar to that found in other ionic conductors [13], and its activation energy of about 0.71 ± 0.04 eV has been proposed to be the

potential barrier needed for independent ion hopping [21, 36]. The much larger value observed for the dc conductivity activation energy is interpreted in terms of the additional energy needed for dc or long range ion transport to take place due to the existence of ion-ion interactions during the hopping dynamics [14, 37].

The NCL behavior is better observed in Fig. 2(a), showing the dielectric loss ϵ'' as a function of frequency. Note that, below room temperature, the dielectric loss varies as much as a factor of 2 while the frequency changes over five orders of magnitude. The NCL behavior can be also observed from the plot of the real part of the dielectric permittivity ϵ' as a function of frequency (see Fig. 2(b)). According to the Kramers-Kronig relations, the dielectric loss in the NCL regime is given by [38]:

$$\epsilon''(\omega) = -\frac{\pi}{2} \frac{d\epsilon'(\omega)}{d \ln(\omega)}, \tag{2}$$

what results in an almost logarithmic dependence of ϵ' on frequency if the dielectric loss is nearly constant. In fact we

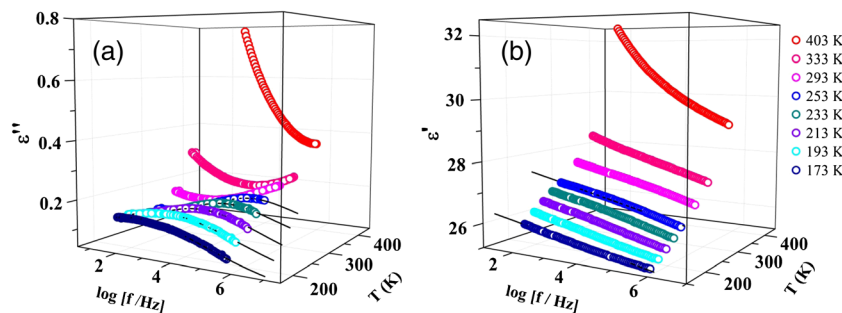


Fig. 2 (a) Dielectric loss spectra at several fixed temperatures between 173 K and 403 K. *Solid lines* are best fits according to Eq. (3) (see text) with fit parameters shown in Table 1. (b) Frequency dependence of the

real part of the permittivity, $\epsilon'(\omega)$, for several temperatures between 173 K and 403 K. *Solid lines* are best fits to Eq. (2) in the text

can see in Fig. 2(b) that this logarithmic dependence approximately holds in the whole experimental frequency window below room temperature. Moreover, we can check the consistency of the experimental data by using Eq. (2) and estimate the value of the dielectric loss at a given temperature from the slope of ε'' vs $\ln(\omega)$. We did that for the data at 173 and 253 K, and obtain $\varepsilon''=0.16\pm 0.02$ within this temperature range, in good agreement with the experimental data for the dielectric loss in Fig. 2(a). It is however obvious in Fig. 2(a) the presence of a very broad and nearly symmetric relaxation peak in the dielectric loss at the lowest temperatures, whose characteristic frequency decreases when decreasing the temperature. Note that the presence of this dielectric relaxation process is obscured in the conductivity vs frequency plot (Fig. 1(a)) but becomes evident in the dielectric loss representation. In order to obtain the amplitude and characteristic relaxation time of this relaxation process we have fit the experimental dielectric loss data at the different temperatures to the following equation:

$$\varepsilon^*(\omega) = \varepsilon' - i\varepsilon'' = \varepsilon_\infty + \frac{C}{(1 + (i\omega\tau)^\alpha)^\beta} - iA, \quad (3)$$

where the dielectric permittivity is described as a superposition of a high frequency dielectric permittivity (ε_∞), a Havriliak-Negami type [39] relaxation process of amplitude C and characteristic relaxation time τ , and a possible additional contribution of a strictly constant loss of amplitude A . Solid lines in Fig. 2(a) are best fits to Eq. (3), and the parameters obtained from the fits for the different temperatures between 173 and 253 K are given in Table 1. We find from the fits that the value of A is negligible at all temperatures. In fact, the quality of the fits is improved if one considers $A=0$, even though the use of one parameter less. The values obtained for the fractional exponents α and β are consistent with the observation of a very broad and symmetric relaxation peak in the dielectric loss spectra. The value of the exponent β is found to be 1 at all temperatures (except for the highest one, where we have fixed the value in the fit since there are not enough experimental points at high frequencies to resolve the

Table 1 Results from the fits of the dielectric loss spectra at different temperatures to Eq. (3) in the text

T (K)	α	β	$\log [\tau$ (s)]	C
173	0.223 ± 0.003	1	-3.38 ± 0.03	1.84 ± 0.02
193	0.228 ± 0.002	1	-4.22 ± 0.02	1.97 ± 0.02
213	0.248 ± 0.002	1	-5.09 ± 0.01	1.95 ± 0.01
233	0.238 ± 0.002	1	-5.74 ± 0.01	2.19 ± 0.02
253	0.216 ± 0.003	1 ^(*)	-6.50 ± 0.03	2.60 ± 0.04

(*) The value $\beta=1$ was fixed in the fit at $T=253$ K (see text)

peak shape unambiguously). This indicates that the peak in the loss spectra is indeed symmetric and that the relaxation process could be described by using a Cole-Cole function for the relaxation process [40]. The value of the exponent α is also found to be almost temperature independent (see inset to Fig. 3) but much smaller ($\alpha=0.23\pm 0.02$), which indicates that the loss peak is actually very broad as experimentally observed. A value $C=2.2\pm 0.4$ is obtained for the amplitude of the relaxation process, much smaller than the value of the high frequency permittivity value in this temperature range ($\varepsilon_\infty=26\pm 2$), and seems to decrease slightly when decreasing temperature. Finally, the temperature dependence of the characteristic relaxation time τ is plotted in the main panel of Fig. 3 in an Arrhenius fashion. The solid line in this plot is a fit to a thermally activated behavior for the relaxation time, from which an activation energy $E_\tau=0.29\pm 0.02$ eV can be estimated. Therefore, the NCL behavior results in $\text{Gd}_2\text{Zr}_2\text{O}_7$ from a very broad relaxation peak in the loss spectra, that can be described by a Cole-Cole function, and whose relaxation time is thermally activated. The origin of this relaxation process is unclear. The activation energy E_τ seems to be too low to be related to oxygen hopping reorientation processes. Broad relaxation peaks in the loss spectra with similar values for the activation energy were obtained by Nowick et al. in other “complex” ionic conductors characterized by a high degree of disorder, like Gd- and Y-doped ceria, and it was proposed to be originated from coordinated ion motions by less than an atomic spacing, described as “rocking motions” [26]. Such a description is somehow similar to the concept of “jellyfish fluctuations” introduced by Jain et al. [2]. Other authors have also reported the presence of a broad relaxation process in the NCL regime of several borate glasses [41, 42]. These collective relaxation modes, such as rocking motions or jellyfish fluctuations, are possible in the realm of cage dynamics as the

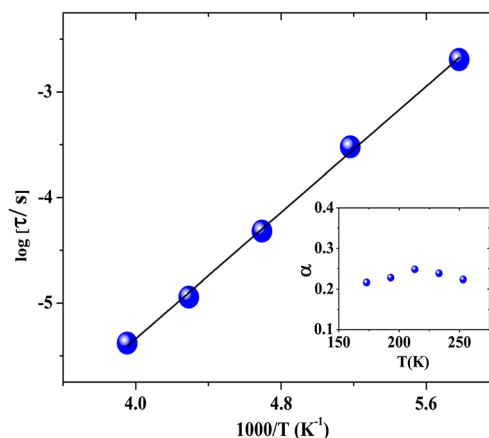


Fig. 3 Arrhenius plot of the relaxation time τ as obtained from fits of the dielectric loss to Eq. (3) in the text. Inset shows the temperature dependence of the Cole-Cole parameter α as obtained from the same fits. Solid line in the main panel is a fit to an Arrhenius law from which an activation energy $E_\tau=0.29\pm 0.02$ eV is obtained

origin of the NCL [21], but a clear explanation remains elusive for the observed thermally activated behavior of the broad dielectric loss peaks giving rise to the NCL behavior at low temperatures in “complex” ionic conductors.

4 Summary and conclusions

We have studied the nearly constant loss regime in the oxide-ion conductor $\text{Gd}_2\text{Zr}_2\text{O}_7$. Below room temperature the conductivity vs frequency plots show almost linear frequency dependence in a frequency range that extends towards low frequencies as the temperature decreases. We found that the dielectric loss is not completely frequency independent, but a well defined relaxation peak exists in the loss spectra. The observed peak is very broad, symmetric, and can be described by a Cole-Cole relaxation function for the dielectric permittivity. The attempts to separate two different contributions to the dielectric loss, namely a relaxation peak and a strictly constant loss term, from the fits to experimental data, show that only the relaxation peak exists. While the spectral shape of the dielectric loss peak is almost independent of temperature, the peak frequency is thermally activated. This behavior is similar to that reported in other “complex” ionic conductors with a large concentration of mobile ions. In fact, it has been previously proposed that the loss peak broadens and effectively become a NCL behavior as the concentration of mobile ions is increased [26]. The value obtained for the activation energy of the relaxation peak is too low to be related to ion hopping dynamics, and the NCL response is interpreted as due to collective motions of caged ions at low temperatures and short times, before hopping processes become statistically relevant.

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References

1. W. Lee, J. Liu, A. Nowick, Phys. Rev. Lett. **67**, 1559 (1991)
2. H. Jain, S. Krishnaswami, O. Kanert, J. Non. Cryst. Solids **307–310**, 1017 (2002)
3. P. Lunkenheimer, A. Loidl, Phys. Rev. Lett. **91**, 207601 (2003)
4. J. Wong, C. Angell, *Glass: structure by spectroscopy* (Dekker, New York, 1976), p. 750
5. F.S. Howell, R.A. Bose, P.B. Macedo, C.T. Moynihan, J. Phys. Chem. **78**, 639 (1974)
6. C.T. Moynihan, J. Non. Cryst. Solids **172–174**, 1395 (1994)
7. A.K. Jonscher, Nature **267**, 673 (1977)
8. A.S. Nowick, A.V. Vaysleyb, W. Liu, Solid State Ionics **105**, 121 (1998)
9. S. Estalji, O. Kanert, J. Steinert, H. Jain, K. Ngai, Phys. Rev. B **43**, 7481 (1991)
10. X. Lu, H. Jain, J. Phys. Chem. Solids **55**, 1433 (1994)
11. D.L. Sidebottom, P.F. Green, R.K. Brow, J. Non. Cryst. Solids **203**, 300 (1996)
12. J. Dyre, T. Schröder, Rev. Mod. Phys. **72**, 873 (2000)
13. C. León, A. Rivera, A. Várez, J. Sanz, J. Santamaria, K.L. Ngai, Phys. Rev. Lett. **86**, 1279 (2001)
14. C. León, K. Ngai, A. Rivera, Phys. Rev. B **69**, 134303 (2004)
15. W. Dieterich, P. Maass, Solid State Ionics **180**, 446 (2009)
16. K. Ngai, J. Chem. Phys. **110**, 10576 (1999)
17. A. Rivera, J. Santamaria, C. León, J. Sanz, C.P. Varsamis, G. Chryssikos, K. Ngai, J. Non. Cryst. Solids **1024**, 307–310 (2002)
18. C. León, M. Lucia, J. Santamaria, F. Sánchez-Quesada, Phys. Rev. B **57**, 3 (1998)
19. A. Rivera, C. León, J. Sanz, J. Santamaria, C. Moynihan, K. Ngai, Phys. Rev. B **65**, 224302 (2002)
20. A. Rivera, C. León, C. Varsamis, G. Chryssikos, K. Ngai, C. Roland, L. Buckley, Phys. Rev. Lett. **88**, 125902 (2002)
21. K. Ngai, C. León, Phys. Rev. B **66**, 064308 (2002)
22. C. León, J. Habasaki, K.L. Ngai, Z. Für Phys. Chemie **223**, 1311 (2009)
23. W. Dieterich, P. Maass, M. Schulz, Eur. Phys. J. Spec. Top. **161**, 79 (2008)
24. K. Funke, P. Singh, R.D. Banhatti, Phys. Chem. Chem. Phys. **9**, 5582 (2007)
25. J. Macdonald, Phys. Rev. B **66**, 064305 (2002)
26. A. Nowick, B. Lim, Phys. Rev. B **63**, 184115 (2001)
27. K.J. Moreno, A. Fuentes, M. Maczka, J. Hanuza, U. Amador, J. Santamaria, C. León, Phys. Rev. B **75**, 184303 (2007)
28. M.R. Díaz-Guillén, K.J. Moreno, J.A. Díaz-Guillén, A.F. Fuentes, K.L. Ngai, J. Garcia-Barriocanal, J. Santamaria, C. Leon, Phys. Rev. B **78**, 104304 (2008)
29. P.K. Moon, H.L. Tuller, Solid State Ionics **28–30**, 470 (1988)
30. J. Chen, J. Lian, L. Wang, R. Ewing, R. Wang, W. Pan, Phys. Rev. Lett. **88**, 105901 (2002)
31. K.J. Moreno, G. Mendoza-Suárez, A.F. Fuentes, J. Garcia-Barriocanal, C. León, J. Santamaria, Phys. Rev. B **71**, 132301 (2005)
32. K.L. Ngai, C. Leon, Solid State Ionics **125**, 81 (1999)
33. K.L. Ngai, J. Habasaki, Y. Hiwatari, C. Leon, J. Phys. Condens. Matter **15**, S1607 (2003)
34. M.R. Díaz-Guillén, J.A. Díaz-Guillén, A.F. Fuentes, J. Santamaria, C. León, Phys. Rev. B **82**, 174304 (2010)
35. J.R. Macdonald, J. Chem. Phys. **116**, 3401 (2002)
36. K. Tsang, K. Ngai, Phys. Rev. E. **56**, R17 (1997)
37. K. Ngai, G. Greaves, C. Moynihan, Phys. Rev. Lett. **80**, 1018 (1998)
38. C.J.F. Böttcher, P. Bordewijk, *Theory of Electric Polarization. Vol. 2, Dielectric Polarization* (Elsevier, Amsterdam, 1978)
39. S. Havriliak, S. Negami, J. Polym. Sci. Part C Polym. Symp. **14**, 99 (2007)
40. K.S. Cole, R.H. Cole, J. Chem. Phys. **9**, 341 (1941)
41. D.M. Laughman, R.D. Banhatti, K. Funke, Phys. Chem. Chem. Phys. **11**, 3158 (2009)
42. D.L. Sidebottom, M. Bassett, Z. Für Phys. Chemie **223**, 1161 (2009)