

## ac conductivity analysis for a metal core-silver orthosilicate shell nanostructure

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Nanocomposites containing silver particles of diameter of 20 nm with silver orthosilicate crystals forming the shell with thickness around 21 nm closely packed in a silicate glass were prepared. The ac conductivity of samples subjected to different heat treatments were measured over the frequency range of 100 Hz to 6 MHz in the temperature range of 500–570 K. The data were analyzed by the Macdonald model based on Kohlrausch-related frequency response formalism designated as CK0. The reference system was taken as the glass-crystal composite containing a lithium orthosilicate crystalline phase. The shape parameter  $\beta_o$  for the reference system was found to be 0.33, whereas that for the nanocomposites was extracted to be 0.46. The former implied a one-dimensional lithium ion motion along the grain boundaries of the orthosilicate crystals, whereas the latter indicated that there was a one-dimensional silver ion motion in an effective two-dimensional structure in the shell surface because of a high stress condition along the radial direction of the core-shell composite.

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### I. INTRODUCTION

Nanostructured materials have occupied the center stage of research in recent times because of exotic properties exhibited by them which could be exploited to make useful devices.<sup>1–3</sup> Core-shell structured systems form a particular class and quite a few groups have investigated their properties. Most of these studies are related to magnetic interaction between the two phases present in the core and the shell, respectively.<sup>4–7</sup> We have recently synthesized nanocomposites comprising copper core-copper oxide shell structures.<sup>8</sup> The properties were ascribed to the creation of an interfacial amorphous phase. Our recent work involved the formation of a nanosized silver core with a silver orthosilicate shell both having dimensions of the order of 20 nm.<sup>9</sup> The latter system exhibited excitation of quantized acoustic modes as the temperature was raised. This was concluded from the analysis of the dc resistivity as a function of temperature. Generation of stresses on the orthosilicate shell due to thermal mismatch of the two phases was shown to be responsible for the above behavior.

In recent years a powerful data analysis method has been developed by Macdonald and applied to a large number of ionically conducting materials.<sup>10–14</sup> We have now applied this method to investigate the conduction mechanism in our system comprising silver core-silver orthosilicate nanostruc-

ture within a glass. Our interest has been to understand the effect of stress on the ionic transport in the orthosilicate shell. The details are described in this paper.

### II. EXPERIMENT

The specimen used was a melt-quenched glass of composition 15 Na<sub>2</sub>O, 15 Li<sub>2</sub>O, 12 CaO, 3 Al<sub>2</sub>O<sub>3</sub>, and 55 SiO<sub>2</sub> (in mol %). The glass was subjected to a Na<sup>+</sup>–Ag<sup>+</sup> ion exchange reaction by immersing the sample in a molten bath of AgNO<sub>3</sub> at 583 K for 6 h. Silver nanoparticles were grown within the glass by subjecting the latter to a reduction treatment in hydrogen at 673 K for 1/2 h. The glass powder was heat treated at 833 and 993 K, respectively, to grow the phase silver orthosilicate 2Ag<sub>2</sub>O·SiO<sub>2</sub>. Pellets of 1 cm diameter were prepared by cold pressing the nanocomposite powder at a pressure of 5 ton/cm<sup>2</sup>. The details of the sample preparation have been given earlier.<sup>9</sup> Silver paint (supplied by Acheson Colloiden B. V. Holland) was applied on both faces of the specimens. These formed the electrodes. The impedance was measured over the frequency range of 100 Hz–6 MHz using a Hewlett Packard HP 4192A impedance analyzer. Measurements were carried out over the temperature range of 500–570 K. This was necessitated by the level of sample resistance, which could be measured accurately by the impedance analyzer.

### III. RESULTS AND DISCUSSION

Figure 1 is a transmission electron micrograph for the specimen having a core-shell structure. In Fig. 2 we show the

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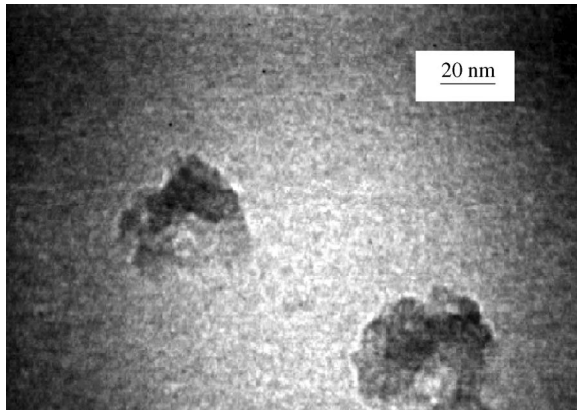


FIG. 1. Transmission electron micrograph for a silicate glass having a silver core-silver orthosilicate nanostructure.

variation of conductivity as a function of frequency for the specimen in which the orthosilicate shell was formed by giving heat treatment at 833 K for 1 h followed by 993 K for 3 h. As the temperature is raised the level of conductivity is found to increase. This is to be expected because the electrical transport arises due to an activated process involving silver ions. The data shown in Fig. 2 are typical for specimens in which the shell was grown by giving different heat treatments. Figure 3 shows the conductivity variation as a function of frequency for samples with shells grown by giving heat treatments for different durations. The conductivity is seen to decrease as the heating schedule is increased. This is consistent with the data reported earlier for dc resistivity.<sup>9</sup> In Fig. 4 is shown the conductivity variation as a function of frequency for a glass-ceramic specimen containing only the lithium orthosilicate phase.

The ac conductivity data for both the glass-ceramic sample (containing lithium orthosilicate phase) and the nanocomposites comprised of silver nanoparticles with silver orthosilicate shells were analyzed using the CK0 Kohlrausch frequency response model developed by Macdonald.<sup>10-14</sup> This model is based on a direct Fourier transformation of time-domain stretched-exponential response given by

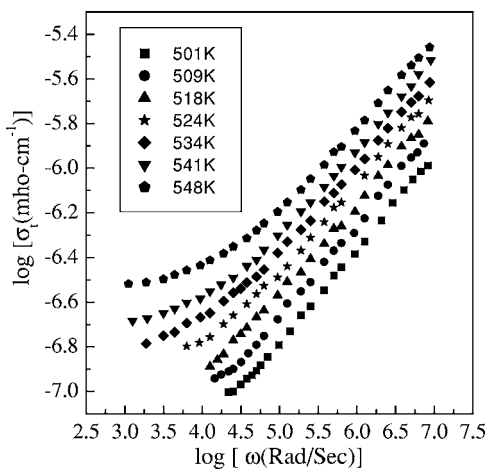


FIG. 2. Variation of electrical conductivity as a function of frequency for the specimen heat treated at 833 K/1 h followed by 993 K/3 h.

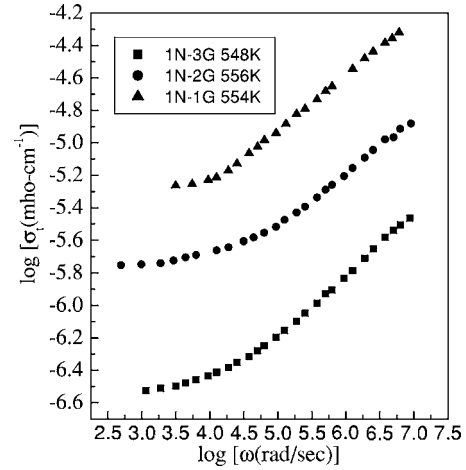


FIG. 3. Variation of electrical conductivity as a function of frequency for specimens with different heat treatments: 833 K/1 h+993 K/1 h, 833 K/1 h+993 K/2 h, 833 K/1 h+993 K/3 h.

$$F(t) = \exp \left[ - \left( \frac{t}{\tau_R} \right)^{\beta_o} \right], \tag{1}$$

where  $\beta_o$  ( $0 < \beta_o \leq 1$ ) is the stretching parameter and  $\tau_R$  is the characteristic conductivity relaxation time. For conductive systems, as in the present case,  $F(t)$  signifies the correlation function of the mobile charge carriers. The CK0 response at the complex modulus level may be written as

$$M_{CK0}(\omega) = M'_{CK0}(\omega) + iM''_{CK0}(\omega) \equiv i\omega \epsilon_V I_o(\omega), \tag{2}$$

where

$$M \equiv \frac{1}{\epsilon^*}, \tag{3}$$

$\epsilon^*$  is the complex dielectric permittivity,  $\epsilon_V$  is the permittivity of vacuum, and  $I_o(\omega)$  is the CK0 complex resistivity normalized response function satisfying the conditions  $I_o(0) = 1$  and  $I_o(\infty) = 0$ .

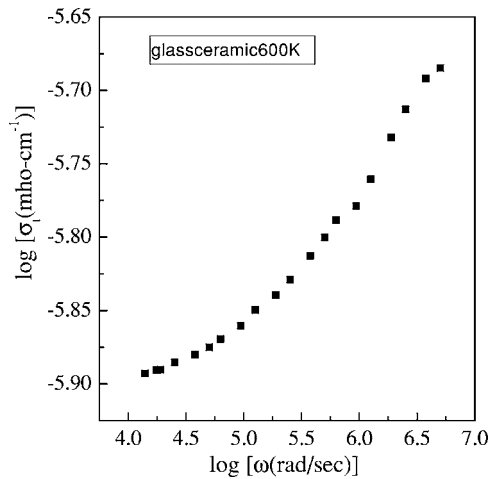


FIG. 4. Variation of electrical conductivity as a function of frequency for a glass-ceramic specimen containing only the lithium orthosilicate phase.

TABLE I. Parameters extracted by fitting experimental data to CK0 model.

Specimen	Temperature (K)	$\rho_{dc}$ ( $\Omega$ cm)	$\tau_o$ (s)	$\epsilon_\alpha$	$\beta_o$
Core-shell structure					
Heat treatment 833 K/1 h+ 993 K/1 h	509	$1.6 \times 10^8$	$2.8 \times 10^{-3}$	25.1	0.526
	518	$2.8 \times 10^7$	$4.1 \times 10^{-4}$	25.2	0.464
	529	$1.9 \times 10^7$	$8.9 \times 10^{-5}$	25.0	0.481
	538	$1.1 \times 10^7$	$4.2 \times 10^{-5}$	25.3	.585
	546	$1.0 \times 10^7$	$5.8 \times 10^{-5}$	25.0	0.509
	554	$8.8 \times 10^6$	$6.9 \times 10^{-5}$	25.3	0.436
	570	$3.9 \times 10^6$	$2.4 \times 10^{-5}$	25.2	0.455
Heat treatment 833 K/1 h+ 993 K/2 h	521	$1.4 \times 10^7$	$5.0 \times 10^{-5}$	23.9	0.431
	533	$9.6 \times 10^6$	$4.5 \times 10^{-5}$	24.0	0.419
	543	$6.4 \times 10^6$	$2.7 \times 10^{-5}$	24.1	0.428
	550	$4.6 \times 10^6$	$2.0 \times 10^{-5}$	24.1	0.424
	556	$3.4 \times 10^6$	$1.8 \times 10^{-5}$	24.4	0.399
Heat treatment 833 K/1 h+ 993 K/3 h	501	$5.1 \times 10^7$	$2.7 \times 10^{-4}$	23.3	0.458
	509	$4.4 \times 10^7$	$3.8 \times 10^{-4}$	23.4	0.444
	518	$2.7 \times 10^7$	$1.9 \times 10^{-4}$	23.4	0.449
	524	$1.6 \times 10^7$	$9.3 \times 10^{-5}$	23.8	0.456
	534	$1.2 \times 10^7$	$6.5 \times 10^{-5}$	23.8	0.460
	541	$9.5 \times 10^6$	$5.7 \times 10^{-5}$	23.8	0.451
	548	$6.3 \times 10^6$	$3.5 \times 10^{-5}$	24.0	0.459
Glass-ceramic sample containing lithium orthosilicate	535	$1.2 \times 10^7$	$5.2 \times 10^{-6}$	2.8	0.33
	551	$6.2 \times 10^6$	$2.6 \times 10^{-6}$	2.7	0.33
	566	$3.4 \times 10^6$	$1.4 \times 10^{-6}$	2.9	0.33

In the above  $I_o(\omega)$  is related to the parameters  $\rho_0$  [the dc value of the complex resistivity  $\rho(\omega)$ ],  $\tau_0$  (the characteristic relaxation time), and  $\beta_o$  [the stretching parameter as given in Eq. (1)].

The response at the complex dielectric constant level arising from mobile charges can be written as

$$\epsilon_{CK0}(\omega) = \epsilon'_{CK0}(\omega) - i\epsilon''_{CK0}(\omega) \equiv \frac{1}{M_{CK0}(\omega)}. \quad (4)$$

It is usually found that  $\epsilon'_{CK0}(\omega) = 0$ . Hence the data fitting in this model requires the addition of a parallel component representing the high frequency limiting dielectric constant,  $\epsilon_\alpha$ .

The parameters extracted by fitting the full complex experimental conductivity data to the CK0 model delineated as above are summarized in Table I. From this table we find the value of  $\beta_o = 1/3$  for the glass-ceramic sample. This implies that the silver ion motion occurs along one dimension.<sup>14</sup> In the present system this is realistic because the lithium ions will move along the grain boundaries of the lithium orthosilicate phase. The value of  $\epsilon_\alpha$  is found to be around 2.8, which is temperature independent. This being the high frequency limiting dielectric constant is also a reasonable value because it is known that this value for pure SiO<sub>2</sub> glass is  $\sim 3.8$ .<sup>15</sup>

For the core-shell structured system containing a metallic silver core with silver orthosilicate nanoshells, it is also found that the  $\epsilon_\alpha$  is temperature independent. The value of  $\epsilon_\alpha$  is, however, much larger than that in the glass-ceramic sample as discussed above. This arises due to the presence of metallic silver particles and the consequential space-charge polarization at the metal-silicate interface. The value of  $\beta_o$  is found to be around 0.5—in fact, the average taken over all the temperatures is 0.46. This suggests two possibilities viz. either (i) silver ion motion occurs in a two-dimensional structure with only one of these two dimensions being appropriate for motion or (ii) it is a case of field-free relaxation for which the predicted theoretical value is  $\beta_o = 3/7 = 0.43$ .<sup>14</sup> The second case has been investigated by stress relaxation experiments in which the probe field is a stress and the change of this as a function of time is recorded and analyzed. In the present case, however, a stressed condition in the sample system is maintained, while the effect of applied electric field is monitored as a function of frequency. The stress condition will affect the conducting response, but it is definitely not a case of stress relaxation. We therefore rule out the second of the two possibilities listed above. We elucidate the first possibility as follows.

TABLE II. Summary of activation energies for dc conduction as determined from ac conductivity data and comparison with earlier results (Ref. 9).

Specimen	Activation energy (eV)	
	From ac conductivity analysis	From dc measurements (Ref. 9)
Glass-ceramic sample with lithium orthosilicate	0.6	0.8
Nanocomposite	0.9	0.9
833 K/1 h+993 K/1 h	1.0	1.0
833 K/1 h+993 K/2 h	1.1	1.2

The externally applied electric field can be resolved into three components—one along the radial direction of a spherical core and two others along mutually perpendicular directions in a plane tangential to the radius. Because of a high stress condition along the radial direction in which different nanoparticles meet, the movement of silver ions will become difficult. This will effectively reduce the system to a two-dimensional structure and the motion executed only along one of them. This mechanism is consistent with the conclusion we had drawn earlier from the dc resistivity results over a wider temperature range.<sup>9</sup> The discontinuous changes of dc resistivity were ascribed to the excitation of quantized Lamb modes, which were effective along the circumference of the shells concerned. The movement of silver ions—the way it has been described on the basis of ac conductivity analysis—is therefore consistent with our earlier discussion. We have determined the activation energies for dc conduction from the dc resistivity results extracted by the present model from the ac conductivity data. These are summarized in Table II. We find that two sets of results are in satisfactory agreement with each other.

#### IV. CONCLUSIONS

ac conductivity of nanocomposites comprised of silver nanoparticles of diameter  $\sim 20$  nm with silver orthosilicate shells with a thickness  $\sim 21$  nm in a silicate glass matrix was

measured in the frequency range of 100 Hz–6 MHz at temperatures varying from 500 to 570 K. The data were analyzed on the basis of Kohlrausch related frequency response model designated as CK0. The glass-ceramic sample containing the lithium orthosilicate crystals was used as the reference. The shape parameters  $\beta_o$  for the reference system was found to be  $\sim 0.33$ , whereas it was  $\sim 0.46$  for the core-shell nanostructured system. The former is consistent with the one-dimensional motion of lithium ions along the crystal grain boundaries. The latter indicates that there is a one-dimensional silver ion motion in an effective two-dimensional structure in the shell surface because of the high stress condition along the radial direction of the core-shell composite.

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