Electrical properties of opal

M. Y. Xu, H. Jain, M. R. Notis

Department of Materials Science and Engineering, Lehigh University, Bethlehem, Pennsylvania 18015, U.S.A.

Abstract

The electrical conductivity (σ) of one natural and two synthetic opals has been determined from ac complex impedance analysis. The value of σ is lower and its activation enthalpy higher for the synthetic opals presumably because of a lower concentration of the Na^+ charge carriers. In contrast to σ, the dielectric constant (ϵ') of the synthetic opal is anisotropic and is dominated by the presence of water. Its value is higher perpendicular to the columns than parallel to the columns. With increasing temperature, ϵ' decreases for the latter case but increases for the former configuration because of the extra interfacial polarization when the charge carriers must cross the boundary between the columns.

Introduction

It is known that the physical properties of natural and synthetic materials can be significantly different. In the case of quartz, for example, the activation energy for electrical conductivity of the natural material, irrespective of its origin, is always found to be substantially lower than that of a synthetic quartz crystal, although structural techniques do not indicate any difference (Jain and Nowick, 1982a). The different electrical behavior of natural and synthetic quartz has been explained by the manner in which alkali ions associate with other defects in the respective crystals (Jain and Nowick, 1982a, 1982b); yet another possibility exists for structural differences arising from different growth conditions but being too small to be detected by available techniques. In view of this dilemma between structural and compositional factors, it is interesting to investigate a closely related but amorphous mineral, namely opal.

A typical natural opal is made of regularly packed monosize silica glass spheres (approximately 0.25 μm in diameter) with the space between the spheres also filled with silica but of much higher water content (Nassau, 1980). Synthetic opal, which was first prepared by Gilson (Nassau, 1980, chapter 22) and sometimes known as gilsonite, also consists of a similar packing of silica spheres, but the interstitial space in this case is uniformly filled with additional smaller-size zirconia spheres (Gauthier, 1986; Simonton et al., 1986). The commonly observed colors (or fire) in both kinds of opals are due to the diffraction-grating effect from regularly packed silica spheres (Nassau, 1980). Because of the special structure of synthetic opal, it is a good model system to study the overall dielectric behavior of a composite ceramic consisting of two components, one with a low dielectric constant and the other with a high one (silica and zirconia, respectively).

Experimental details

Samples

One natural white opal from South Australia and two synthetic platelike opals (manufactured by Nakazumi Crystal Laboratory, Japan) were used in this study. The chemical analysis of these samples as determined by plasma-emission spectroscopy is given in Table 1. A visual examination showed that each opal had the usual "fire" and was not isotropic but consisted of a columnar structure. In synthetic opals the columns were parallel to the sample thickness and could be distinguished by the diffracted color. An electron-microscope examination had shown earlier that the direction of packing of silica spheres is uniform within one column but is different between columns (Cowen et al., 1989). Simonton et al. (1986) have reported that the silica spheres are arranged on a hexagonal lattice when viewed along a column but on a square lattice when viewed in a perpendicular direction.

Electrical measurements

For both synthetic opals (S1 and S2), electrical properties were first measured with the electric field being perpendicular to the columns (which were parallel to the electrode plane). Because of the columnar structure of our opals, it was considered important to determine the relationship between the electrical properties and the macroscopic structural anisotropy shown by the colors. Accordingly, the same sample S2 was also studied with the electric field in the direction of the columns. The columns in the natural sample (N) were not as well aligned as in synthetic samples; nevertheless, on the average they were normal to the electric field.

All opal samples were polished on a 600-grit SiC paper to obtain uniform thickness. Next, Au electrodes were deposited on the top and bottom faces by vacuum evap-

TABLE 1. Chemical analyses (wt%) of opal samples

Element	Synthetic opal 1	Synthetic opal 2	Natural opal
Zr	2.4 ± 0.12	1.6 ± 0.2	—
Na	0.086 ± 0.004	0.079 ± 0.008	0.28 ± 0.01
Mg	0.068 ± 0.003	0.009 ± 0.001	0.028 ± 0.001
Al	—	—	0.32 ± 0.02
K	—	—	0.049 ± 0.002

oration. Pt wires were used to connect the Au electrodes to the ac bridge leads using flexible Ag paint. The ac conductance (G) and capacitance (C) were measured in the frequency range of 20 Hz to 100 kHz with a General Radio 1621 bridge assembly. At each temperature of measurement (±0.25 °C), the sample was equilibrated for at least 1.5 h in flowing, dried, high-purity He.

RESULTS

Both conductance and capacitance of the opal samples are strongly frequency dependent, typically as shown in Figures 1A and 1B for the natural opal at various temperatures. To separate electrode effects, $G(\omega)$ and $C(\omega)$ were analyzed in terms of complex impedance $Z^* = Z' - iZ''$ where

$$Z' = G/(G^2 + \omega^2 C^2)$$

and

$$Z'' = \omega C/(G^2 + \omega^2 C^2)$$

with ω (= $2\pi f$) as the angular ac frequency. To obtain the value of bulk conductivity free from any electrode polarization, Z'' was plotted against Z' as shown in Figure 2. The intersection of the high-frequency arc with the real axis gives the bulk conductance, which on multiplying with the geometrical factor (d/A', where d is sample thickness and A' is the electrode area) gives the bulk conductivity, σ (Jain et al., 1984). This value of σ was nearly the same as obtained from the plateau in Figure 1A. At the high-frequency end of the measurements where the electrode effects are negligible, capacitance is independent of frequency. This frequency-independent value of C, when divided by vacuum-equivalent capacitance, gives the relative bulk dielectric constant (ϵ') of the specific sample.

A convenient method of confirming that the values of σ and ϵ' are not affected by area-dependent electrode effects is to repeat the experiment on a given sample with the same fixed electrode area but with a different volume (thickness) (Jain and Nowick, 1982a). This experiment was carried out on synthetic opal S1. The results showed that upon reducing the thickness of this sample by a factor of 1.50, G and C at 284.5 °C increased by a factor of 1.53 and 1.48, respectively. This proved that our σ and ϵ' values represented the properties of the bulk of the specimen and that the capacitance from leads and stray sources was negligible. It also indicates that our results are reproducible within 2%.

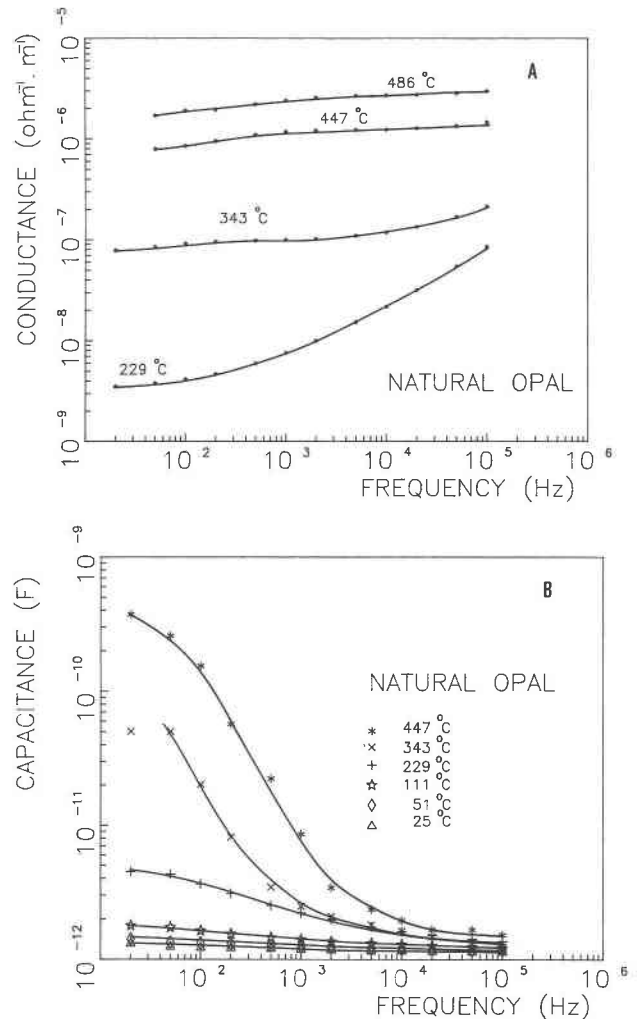The temperature dependence of bulk conductivity can

Fig. 1. Frequency dependence of (**A**) electrical conductance and (**B**) capacitance of a natural opal at the temperatures indicated.

be described well in terms of an Arrhenius equation:

$$\sigma = (A/T)\exp(-H/kT),$$

where A, the pre-exponential factor, and H, the activation enthalpy, are experimentally determined quantities and kT has the usual meaning. The values of H and A, obtained from the slope and intercept of ln σT vs. $1/T$ plots shown in Figure 3, are given in Table 2 for the three opals. The error bars for A and H have been determined from the uncertainties in actual measurements. In our early experiments, σ was found to decrease with time, particularly at high temperatures, and the results during cooling did not reproduce those obtained during heating. Capacitance also decreased but by a very small amount. The activation enthalpy of σ during heating was approximately 0.2 eV; exact values could not be ascertained as σ was changing with time. This irreversible behavior was not too surprising considering that opals contain signifi-
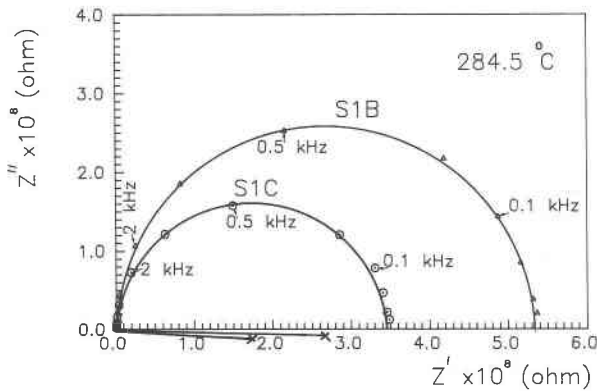
Fig. 2. Complex impedance plot for synthetic opal sample S1 at 284.5 °C. S1B sample is 1.50 times thicker than the S1C sample.
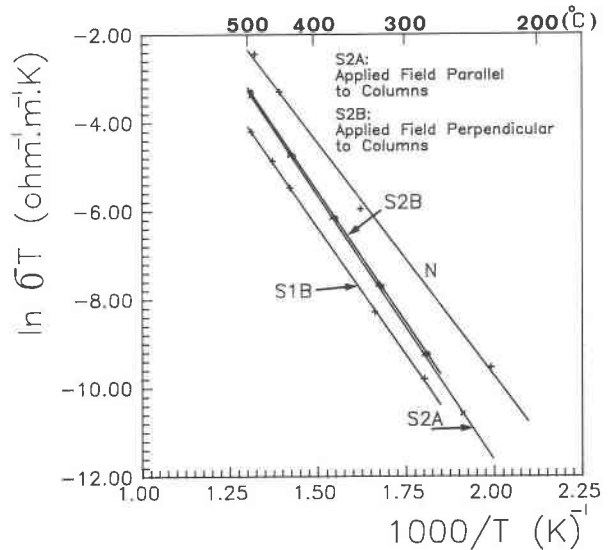

Fig. 3. Arrhenius plot of electrical conductivity of two synthetic (S1 and S2) and one natural (N) opal. The electric field was perpendicular to the columns for S1B, S2B, and N samples, but parallel for the S2A sample.

cant amounts of water that evaporates upon heating (Segnit et al., 1965). Upon heating, an opal would lose water, but the rate and temperature of loss vary from sample to sample. It is possible that the low value of H during heating represents ionic motion in physically absorbed water. In order to obtain consistent values of σ and ϵ', in our subsequent experiments we first heated the specimen to 500 °C (typically for ∼15 h) and maintained the temperature until σ reached a stable value. After this treatment, the value of σ was reproducible during heating and cooling and thus could be considered as a property of opal itself and, therefore, could be included in the results given in Table 2.

As expected, ϵ' shows much weaker temperature dependence. However, it is interesting that whereas ϵ' increases with increasing temperature for all the samples for which electric field was perpendicular to the axis of columns, the opposite was true when the field was parallel to the columns (see Fig. 4).

DISCUSSION

Electrical conductivity

It is clear from Figure 1 that both G and C are strongly frequency dependent and that the results would be inaccurate if the bulk conductivity or dielectric constant were obtained from fixed frequency measurements. The present frequency-dependent measurements have allowed us to obtain σ and ϵ' values that represent the properties of the opal structure rather than the interface between the opal and the Au. From these data, one would like to determine the mechanisms and characteristics of the electrical phenomena. Since opal is primarily a silica-based material, it is natural to first compare the present data with those of silica glass (Bansal and Doremus, 1986) or crystalline quartz (Jain and Nowick, 1982a). The electrical conductivity in crystalline or amorphous silica is primarily due to the migration of alkali impurities and perhaps H^+ or OH^- in some cases. Furthermore, the activation enthalpy for conductivity is sensitive to the

method of preparation and the presence of other impurities (Owen and Douglas, 1959; Doremus, 1969). This sensitivity makes the interpretation of conduction in silica a complex problem. For all the present opal specimens, we find that H is approximately 1.00 eV, suggesting that very likely the same ionic species are responsible for ionic conduction in all the three kinds of specimens. The magnitude of conductivity is 2 to 3 orders of magnitude higher than that found in fused silica, which can be understood from the much higher impurity content in our opals. The chemical analysis (Table 1) shows Na as the dominant monovalent cation in all the three opals, and its concentration is more than two orders of magnitude higher than in commercially pure silica glass (Doremus, 1969; Rothman et al., 1982). Since the mobility of Na is the highest among commonly found impurities in silica (Doremus, 1969), we may conclude that electrical conduction in our samples is most likely due to the migration of Na ions.

A columnar structure on a macroscopic scale and the consequent visual anisotropy were present in all the opals, but Figure 3 shows that the electrical conductivity of synthetic specimen S2 is identical for the directions parallel

TABLE 2. Pre-exponential factor and activation enthalpy for electrical conductivity

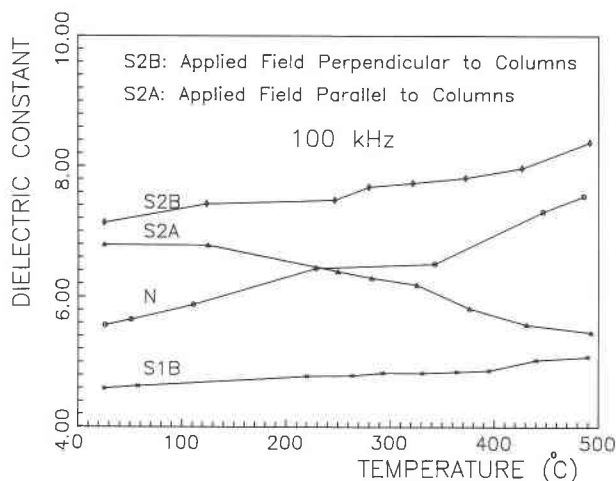| Sample	Field relative to columns	A (ohm^{-1}·m^{-1}·K)	H (kJ/mol)
Synthetic, S2A	Parallel	2.1 ($\pm$ 0.1) × 10^5	99.4 $\pm$ 0.2
Synthetic, S2B	Perpendicular	2.0 ($\pm$ 0.1) × 10^5	98.7 $\pm$ 0.2
Synthetic, S1B	Perpendicular	5.3 ($\pm$ 1.1) × 10^4	95.7 $\pm$ 0.2
Natural, N	Perpendicular	8.7 ($\pm$ 2.6) × 10^4	87.8 $\pm$ 0.3

Fig. 4. Temperature dependence of dielectric constant of two synthetic (S1 and S2) and one natural (N) opal. The electric field was perpendicular to the columns of S1B, S2B, and N samples, but parallel for the S2A sample.

and perpendicular to the columns. That is, in spite of the columnar structure, σ is isotropic as expected for the migration of Na$^+$ in amorphous silica. The columnar structure results from the difference in stacking of silica spheres. However, the stacking is of cubic-close-packed type and, hence, σ is isotropic. On the other hand, each column shows a different diffraction color depending on its relative orientation with respect to the incident light and can be distinguished from the neighboring column.

The activation enthalpy for electrical conductivity is the same for the two synthetic opals, but the level of conductivity and hence the pre-exponential factor are different by a factor of ~4. This latter observation would appear inconsistent with the same concentration of Na given by the average chemical analysis listed in Table 1. However, we must recognize that an opal is not a homogeneous material but consists of silica spheres embedded in another glassy matrix. Considering that during the growth of opal, relatively pure silica spheres precipitate out, leaving behind an impurer matrix, we believe that the current-carrying Na ions are primarily present in the matrix phase. Then the Na ions migrate in the interconnected matrix, and the conductivity of the sample is determined by the volume fraction of the matrix and the Na$^+$ concentration partitioned (not averaged over the whole sample) into the matrix. The level of conductivity in S2 samples is higher than in S1 because the former has a greater volume fraction of the matrix and/or its matrix retains a greater fraction of Na$^+$. The ac conductivity value used in determining H does not appear to contain any significant effects of interfacial polarization (such as a strong frequency dispersion), which is consistent with the idea that Na$^+$ migrates in the matrix and not from one silica sphere to the next.

The higher value of σ and lower value of H for the natural sample compared to the two synthetic samples

are analogous to the behavior of quartz crystals studied by Jain and Nowick (1982a, 1982b). Their explanation for the difference between the natural and synthetic quartz was based on the ratio of the mobile Na$^+$ concentration to the concentration of charge-compensating unassociated Al (which substitutes on a Si site). This ratio is nearly one for natural quartz but much smaller than one for synthetic quartz. A similar explanation may be given for the present results. However, unlike quartz crystals, the structure of silica glass is not well defined. Addition of Na to silica glass is accommodated by the production of nonbridging oxygen, which continually modifies the structure making it more open (Hakim and Uhlmann, 1971). Therefore, it is tempting to believe that the lower activation enthalpy for natural opal is due to the higher concentration of Na$^+$ and consequently to a more open structure, rather than due to the difference in relative concentrations of Na$^+$ and nonbridging oxygen.

Dielectric constant

Since the synthetic samples contain a couple of percent of zirconia (relative dielectric constant $\epsilon' \simeq 21$), we expected their ϵ' values to be significantly higher than for the natural sample. However, the results show (Fig. 4) that the room-temperature ϵ' value for the natural sample is intermediate between the two synthetic samples. This suggests that the contribution to total dielectric constant from ZrO$_2$ spheres is not significant. Assuming $\epsilon' = 3.9$ for pure silica and $\epsilon' = 21$ for ZrO$_2$, we used various mixing models to determine the net dielectric constant of opal (Cowen et al., 1989). The upper-limit approximation of the parallel model predicted $\epsilon' = 4.1–4.3$, which is much lower than the observed value. The dielectric constant for the natural sample is also significantly higher than the reported value of 3.9 for pure silica. Therefore, there should be an additional source of polarization in both the natural and the synthetic opals. In this regard we note from the work of Owen and Douglas (1959) that the dielectric constant of silica is dominated by the presence of water in a rather complex manner. Higher values of ϵ' in all of our samples are, as expected, a result of the presence of water. Andeen et al. (1974) have shown that for vitreous silica $\epsilon' = 3.8073 + (2.72 \times 10^{-22})N$, where N is the concentration of hydroxyl ions. Then, for example, if all the increase in ϵ' of the S1 sample from the ideal value of 3.8073 can be attributed to its water content, N should be (2.88×10^{21})/cm^3. However, for the reasons given below, an interfacial polarization also contributes to ϵ' of this sample, and the calculated value of N is an upper limit. Since our measurements were conducted after heating the samples at 500 °C for ~15 h, the water responsible for electrical polarization is likely to be chemically bonded in the structure.

Unlike silica glass, opal is a composite structure, and therefore, interfacial polarization is another likely reason for its higher ϵ'. Interfacial polarization develops when charge carriers cannot migrate freely across an interface and is expected to scale with the conductivity of the sam-

ple. We find this to be true for the two synthetic samples, but the natural opal, in spite of its highest conductivity, has lower ϵ' than the S2 sample. Furthermore, as discussed above, most of the electrical conduction occurs in the continuous matrix phase. Therefore, polarization at the interface between the silica spheres and the matrix does not appear to be a major factor in producing high ϵ' values for opals. There is, however, another interfacial polarization that becomes important when the electric field is applied perpendicular to macroscopic columns. Figure 4 shows that although σ was isotropic with respect to the columnar structure, ϵ' and its temperature dependence are not. ϵ' is greater when the field is perpendicular to columns than when it is parallel. Also, ϵ' in the former case increases with temperature but decreases for the latter case. This behavior can be explained as follows: There is a small but significant interfacial polarization that appears when a few charge carriers move across the boundary between columns. As the mobility of charge carriers increases with temperature, this polarization and, hence, ϵ' also increase. The effect of such a polarization, however, is minimal on σ. When the applied field is in the direction of columns, the charge carriers do not migrate across any boundary, and the interfacial polarization does not exist. In this case, the orientational polarization arising presumably from water in the sample decreases as the dipoles tend to become more random at higher temperature. The orientational polarization is present in all the samples, but when the field is perpendicular to the columns, interfacial polarization dominates, giving a net positive temperature coefficient.

CONCLUSIONS

A comparison of the electrical conductivity of two synthetic and one natural opal shows that in opal the most likely charge carriers are Na^+ ions that predominantly migrate in a vitreous matrix phase. The level of conductivity is higher and the activation enthalpy is lower for the natural sample than for the synthetic samples. This is attributed to the higher Na concentration and to consequently more nonbridging oxygens and more open structure in the natural opal.

The dielectric constant of all the opals is greater than that of pure silica, most likely because of the presence of water, which is also the reason for the variation of ϵ' from one sample to the other. The presence of ZrO_2 spheres in synthetic opal has insignificant effect on its dielectric con-

stant. Whereas electrical conductivity of opals is isotropic, the dielectric constant and its temperature dependence are not isotropic. When the electric field is perpendicular to the columns in opal, an interfacial polarization sets in which increases the dielectric constant. In this case, ϵ' increases with temperature. In contrast, ϵ' parallel to the columns is dominated by orientational polarization, presumably of water molecules, and, therefore, decreases with increasing temperature.

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