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New High Dielectric Strength Materials: Micro/Nanocomposites of Suspended Au Clusters in SiO_2/SiO_2–Al_2O_3–Li_2O Gels

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Abstract: We have materials-designed, synthesized, processed and characterized micro-nanocomposite materials consisting of a suspension of Au clusters in insulating matrices of SiO_2 and of $SiO_2/Al_2O_3/Li_2O$, and we have tested this composite for high dielectric strength properties. The material was synthesized by the sol–gel method. The scientific approach to this research employs the percolation-theory expectation that at a critical topology of small metal elongated clusters amidst a ceramic or other insulating matrix, the dielectric constant will reach a peak as a function of some topological-geometric loci. Physical characterization of the material showed that the Au clusters were ellipsoid-like with average major axis of about 800 Å (200 Å minor axis). Chemical characterization suggests strongly that at least some of the Au clusters (particularly the very smallest ones) are positively charged. Dielectric constant measurements up to 10 kHz (over the temperature range of −100 to +100°C) have shown an average dielectric constant of 364–986 in the Au–$SiO_2/Al_2O_3/Li_2O$ (produced from eucryptite) and 5000 in the Au–SiO_2. The high dielectric constant results from the summation of the dipole moments of the clusters which appear ideally to be truncated octahedrals. Published by Elsevier Science Limited and Techna S.r.l.

1 INTRODUCTION

Materials which can serve to store charge in a high energy density fashion have emerged as important subjects for recent and innovative research. Conventional capacitors cannot at present satisfy the requirements for dielectric constant ($K_e > 200$), low dielectric loss (loss $\tan\Theta < 0.001$), and high stand-off potential ($V > 105$ V/cm) that are demanded for next-generation applications such as space-borne compact pulsers and directed-energy weapons discharge circuitry for electromagnetic propulsion.

A number of new-forum materials are being investigated for high-capacitance applications. These include Langmuir–Blodgett thin films (in ABABA super lattice configuration), block copolymers, thin film artificial (methane-grown) diamonds, polymer and polymer composites, as well as specially substituted perovskites, vycor glasses, and biological analogues having appropriate backbone structure to bond polar pendant groups. We have opted to select still another innovative (high-risk high-gain) approach to enhanced capacitance materials. We have shown through percolation and Dissado and Hill theory that a high-dielectric-constant low-dielectric-loss material is feasible by employing a micro-nanocomposite approach that entails small elongated metallic clusters of short inter-cluster distance within an insulating matrix.[1] A peak in the dielectric constant caused by equivalent summation of individual dipole moments is theorized to then occur at some topological condition of cluster–matrix geometry.

Current work in the Au-cluster area has indicated that the Au cluster itself assumes a truncated-octahedral or cubo-octahedral geometry (established from atomic force microscopy indentor techniques),[2] and that very small clusters such as Au_2 and Au_4 may indeed exist in a charged state[3–5] (perhaps because of the $6S^1$ electron being

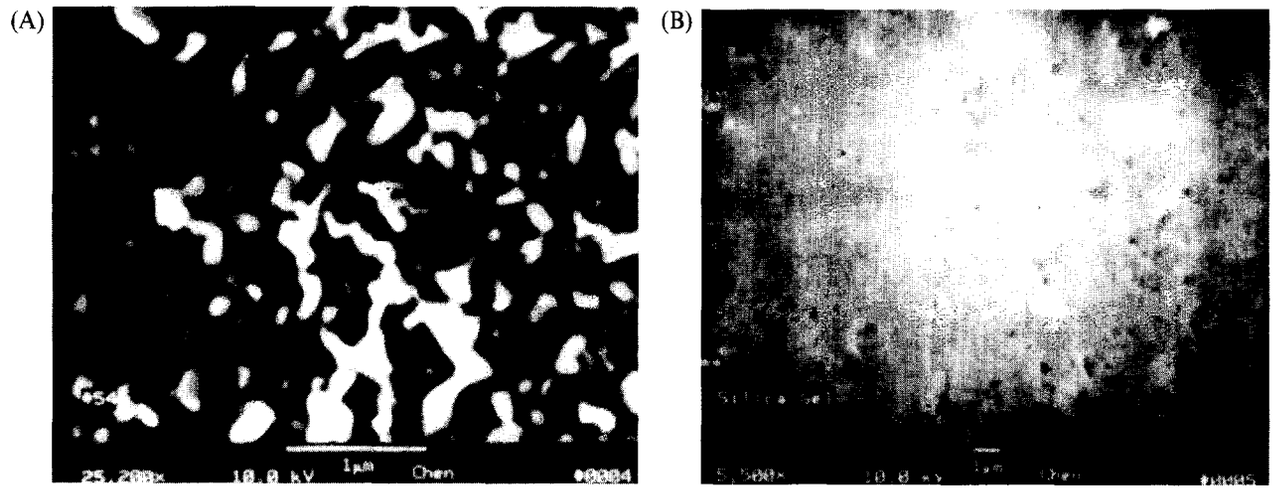

Fig. 1. (A) Scanning electron micrograph (SEM) of Au–SiO_2 micro-nanocomposite: 25000×. (B) SEM of silica gel without Au.

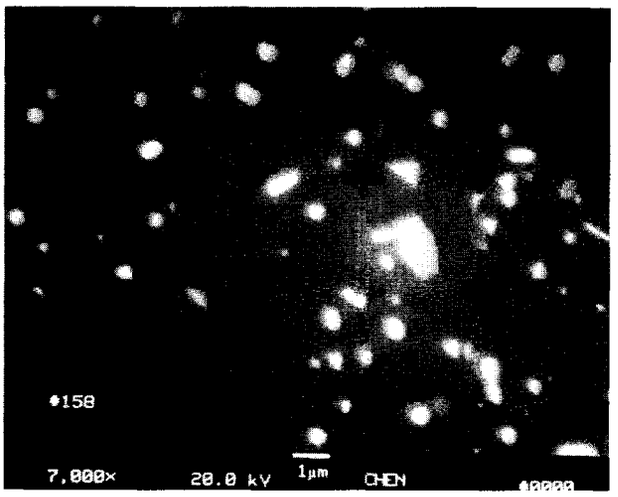

Fig. 2. Scanning electron micrograph of different Au–SiO_2 sample: 7000×.

ionized and the $5d^{10}$ electron being promoted to a 6S state, and a d–d dimeric bond being established.

2 EXPERIMENTAL PROCEDURES

Au was selected as the metallic constituent for the polyatomic cluster because of its very high electrical conductivity (resistivity $= 2.46\ \mu\Omega$ cm at 20°C) and its high polarizability and exceedingly high electronegativity (2.45 on the Pauling scale). The anharmonicity ($2b/a^2$) of Au is 4, and the elastic modulus for a 31 Å Au cluster is about 56 GPa; these additional criteria are also conducive toward Au being employed for the metallic cluster in a regime requiring an elongated or irregular

Table 1. Au–SiO_2/Al_2O_3/Li_2O micro/nanocomposite

Trial 1				
Silicate	Wt% Au	Anneal temperature(°C)	*K* (Measured)	*K* (Corrected)*
Spodumene	5.0	850	33.4	56.0
Eucryptite	2.5	1230	43.5	75.0
Eucryptite	5.0	1230	60.2	103.0
Spodumene	2.5	1230	16.5	26.7
Trial 2				
Eucryptite/slow	5.0	900	364.5	519.9
Eucryptite/fast+	2.5	900	969.0	1671.0
Eucryptite/fast+	2.5	900	12.6	20.3
Eucryptite/fast	5.0	900	9.8	13.5

Spodumene = $LiAl(SiO_3)_2$.
Eucryptite = $LiAlSiO_4$.
Slow and fast refers to the introduction of Au into gel.
*Refers to correction for porosity.
+The difference between these two samples was the vendor of origin, hence presumebly the two samples underwent different materials processing and thermal history.
Frequency of measurement = 1–10 kHz.
The major difference between Trial 1 and Trial 2 is the different annealing temperature which in three of the samples shown in Table 1 exceeded the melting point of Au and led to small grain size Au (which seems to enter into the grain bounderies). In both trials the matrix material is multiphase crystalline rather than a glass, as in the Au–SiO_2 micro/nanocomposite.

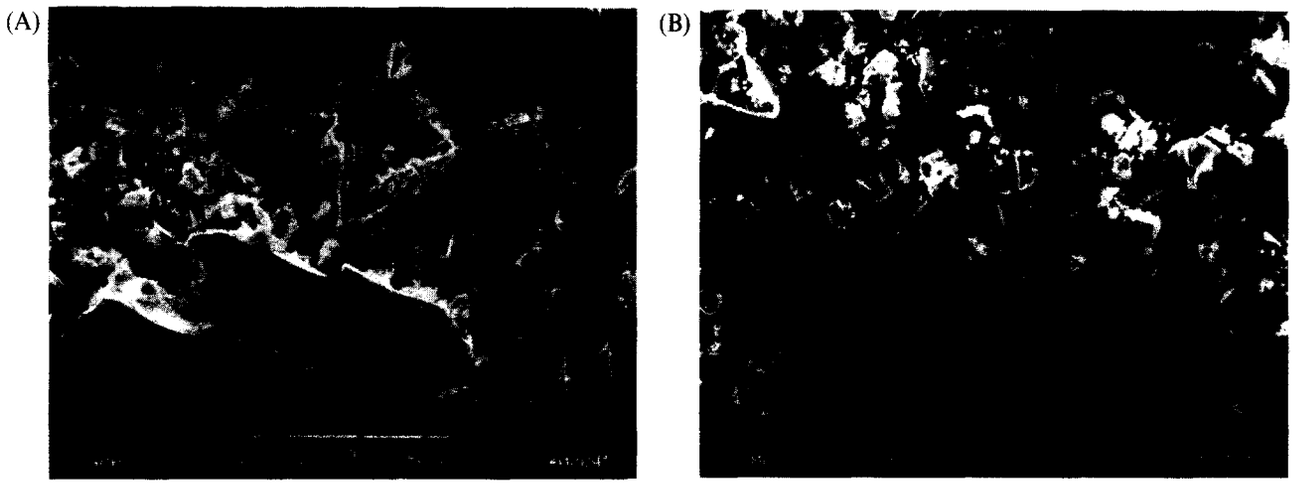

Fig. 3. (A) Scanning electron micrograph of Au–$SiO_2/Al_2O_3/Li_2O$ sample: 400×. (B) SEM of same sample at 500×.

flocculate for high dipole-moment effects. (Even if the Au $5d^{10}6S^1$ electron configuration becomes ionized to Au^+ (a closed shell configuration) it should still be at least marginally polarizable.)

The sol–gel method[1,6] (employing tetramethyloxysilane) was selected as the preparation and processing technique of choice. Citric acid was employed to reduce $AuCl_3$ to Au. Special emphasis was devoted to: dehydration drying; speed of introducing Au; acidity or basicity of catalyst; gelling time; and molar ratio of alkoxide to water. Silica gel (SiO_2) was employed as the matrix material initially for simplicity of its network-type structure and to be able to dwell on the abundant silica gel technical literature. A composite gel of $SiO_2/Al_2O_3/Li_2O$ was also employed for the purpose of ensuring charge compensation (Li_2O) and fostering dangling bond homogeneity.

Figure 1(a) gives a scanning electron microscope (SEM) photograph of the Au particles in the SiO_2 gel matrix, shown at 25,200×. The average dimensions of ellipsoidal-like particles are 800 Å for the major axis and 300 Å for the minor axis. The minimum cluster dimension for the major axis was approximately 100 Å. The inter-cluster distance varied from 300 to 2000 Å.

Figure 1(b) gives an SEM photo of the SiO_2 glass *without* Au. Figure 2 shows the Au flocculates at 7000× and supports the interpretation that the Au clusters take on a truncated octahedral geometry.[2] Independent studies[3–5] employing ESCA indicated micrograph of the Au–$SiO_2/Al_2O_3/Li_2O$ composite (Fig. 3).

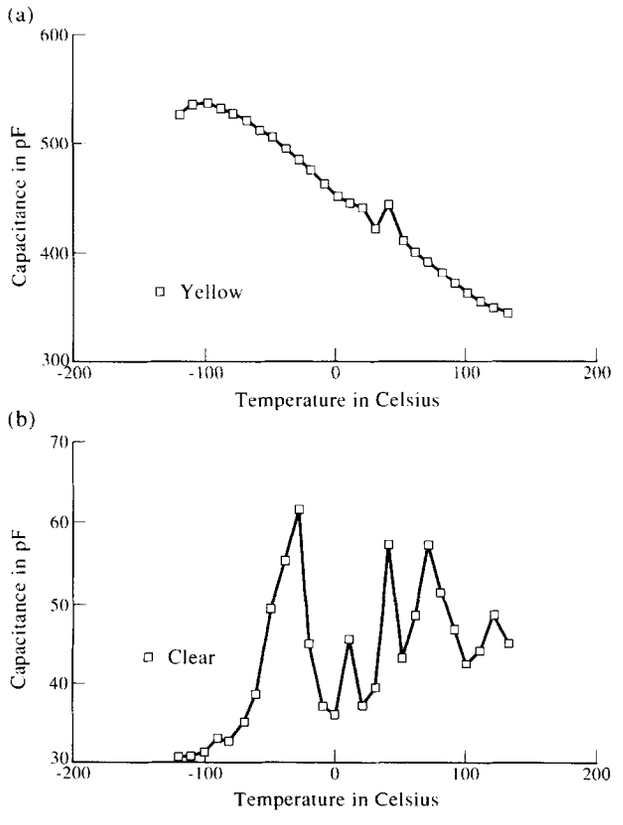

Fig. 4. Capacitance in pf vs temperature in °C for Au–SiO_2 gel sample.

3 EXPERIMENTAL RESULTS

3.1 Au–SiO_2 gel

Figure 4(a) gives the value of capacitance vs temperature for the Au–SiO_2 gel micro/nanocomposite, showing a broad maximum at −100°C; Fig. 4(b) gives the data of capacitance vs temperature for SiO_2 gel *without* the presence of Au showing an irregular pattern.

3.2 The Au–$SiO_2/Al_2O_3/Li_2O$

The Au–$SiO_2/Al_2O_3/Li_2O$ work employed both spodumene ($LiAl\,[SiO_3]_2$)[2] and eucryptite ($LiAlSiO_4$) as the source of the silicate, and varied the rate of introduction of Au into gel. The approach utilized Li_2O to foster charge compensation.

The pertinent data for the Au–SiO_2/Al_2O_3/Li_2O samples are presented in Table 1. In trial 1, the synthesized materials showed a smaller grain-size which was engineered for lower porosity. It is believed that at least a moderate proportion of the Au diffuses into grain boundaries during processing. The value of K_e is corrected for the measured porosity in the last column of Table 1.

The major difference between trial 1 and trial 2 is the different annealing temperature which in the three samples (identified by 1230°C in the third column) exceeded the melting temperature of Au and led to small grain size. In both trials the resulting yield is multiphase crystalline rather than a matrix glass as in the Au–SiO_2 nanocomposite.

4 CONCLUSIONS

We conclude that both the Au–SiO_2 gel techniques, and the Au–SiO_2/Al_2O_3/Li_2O render materials with high dielectric constant at frequencies of 1–10 kHz.

We have concluded that the mathematical treatment given in Refs 1, 7, 8 and 9 including the two-potential solution of Laplace's equation and the Claussius Mossoti relation for polarizability, $\alpha = [3E_o\ (K_e-1)/N(K_e+2)]$, validly describes our data. It appears that the Au-suspended system is a non-linear dielectric in which the polarization, P, is a function of the electric field, E, i.e. $P_x = P_x\ (E_x, E_y, E_z)$.

REFERENCES

1. VEZZOLI, G. C. & CHEN, M. F., Nanophase and nanocomposite materials (ed. S. Komarneni, J. C. Parker & G. J. Thomas). *Mat. Res. Soc. Symp. Proc.*, **286** (1993) 271–279.
2. MONTEJANO-CARRIZALES, J. M. & MORAN-LOPEZ, J. L., *Nanostruct. Mater.*, **1** (1992) 397–409.
3. KHANNA, S. N. & JENA, P., *Nanostruct. Mater.*, **1** (1992) 137.
4. SCHLZE, W., WINTER, B. & GOLDENFELD, T., *Phys. Rev.*, **B38** (1988) 12937.
5. CASLAVSKA & CASLAVSKA, Max Planck Institute, Stuttgart, Private communication, January 1994.
6. BRINKER, C. J. & SCHERER, G. W., *Sol Gel Science*. Academic Press, New York, 1990.
7. LIU, R., YAO, S. & CROSS, L., *J. Appl. Phys.*, **71** (1992) 1.
8. LIU, R., YAO, S. & CROSS, L., *J. Mater. Sci.*, **16** (1981) 2037.
9. LIU, R., YAO, S. & CROSS, L., *Proc. Roy. Soc. London*, **A380** (1983) 131.