whether it is an "island" formation or a continuous film. In the first case practically strain-free support and coating could be expected; in the second case the coating and the support will also be strain-affected.

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Effect of voids on the electrical resistivity in lead zirconate–titanate ceramics

Lead zirconate–titanate (PZT) is an important ceramic material widely used for piezoelectric devices [1, 2]. Electrical conductivity which relates to the power loss of the devices is an important physical property. Previous investigators have only considered the resistivity problem from the standpoint of defect structure in PZT [3–5]. Because of differing fabrication techniques, complete densification is usually not achieved in ceramic materials. An understanding of the effects of voids or porosity on the electrical resistivity of PZT is necessary for a complete characterization of this property. Some work has been conducted to try to relate the ceramic microstructure of PZT to the other ferroelectric and piezoelectric properties [6–9].

The major problem encountered when studying the electrical properties of PZT is PbO loss during sintering. It has been reported that even a small amount of PbO loss from the system can cause appreciable differences in the electrical and physical properties [10]. Previous investigators attempted to control the grain size and porosity by varying the processing parameters, mainly the pressure, temperature, and time for hot-pressing and sintering. The PbO loss from the system is also affected by the process parameters. Therefore, the previous studies, while obtaining data on the effect of grain size and porosity, have not clearly demonstrated that the defect structure has remained constant. Holman and Fulrath [11] established the PbO activity for the $PbZrO_3$–$PbTiO_3$ system and determined the single-phase solid-solution width of the compounds in the system with temperature. Thus, a multi-phase packing powder technique was established that allowed reproducible processing of PZT compositions to a controlled and con-

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stant stoichiometry. In the present study, this fabrication procedure was employed to control the PbO loss from PZT during sintering.

The PZT samples were fine-grained ceramics is which the grain size (2 to 5 μm) was controlled by doping with 1 mol% Nb_2O_5. The composition was found to be $Pb_{0.99}\square_{0.01}(Zr_{0.52}Ti_{0.46}Nb_{0.02})O_3$, where □ is a lead vacancy. It was found that the addition of 5.5 wt% excess PbO enhances the sintering process and densities greater than the 99% theoretical value could be easily obtained. However, most polycrystalline ceramic materials are porous to some extent and this porosity greatly effects the mechanical, electrical, dielectric, piezoelectric and magnetic properties. In the present study, a model system containing a controlled amount of spherical voids (up to 15 vol%) in a highly-dense polycrystalline PZT matrix was used. Spherical voids of 110 to 150 μm diameter were introduced [8] by mixing with organic materials, cold-pressing and then decomposing the organics at 250° C for 12 h prior to sintering. The pellets were sintered at 1200° C for 8 h in a $PbZrO_3$ + 5 wt% ZrO_2 packing powder in an oxygen atmosphere at a pressure of 1 atm. The density of the sintered specimens was measured by both water displacement and geometric measurements.

Direct current (d.c.) bulk resistivity was measured by using a guard-ring method. Evaporated silver electrodes were used to provde ohmic contacts. The surfaces of all the specimens were ground to a depth sufficient to eliminate inhomogeneities due to any surface effects before electrodes were applied. A d.c. voltage provided by a dry cell was used for all measurements. The temperature range was 25 to 500° C. Bi-directional measurements were made and the results from each polarity were averaged to eliminate the thermoelectric contribution to the measured signal.

The influence of temperature on the resistivity of porous PZT is shown in Fig. 1, which shows a linear relationship between log resistivity and inverse absolute temperature. This behaviour is typical for a semiconductor, The resistivity (ρ)–temperature (T) relation,

$$\rho = \rho_0 \exp \frac{Q}{kT} , \qquad (1)$$

where ρ_0 is a constant, Q is the activation energy and k is the Boltzmann constant, was used to calculate the activation energy for conduction. The Q-value calculated from the slope of the straight line in Fig. 1 was found to be 1.4 eV. The values for the other specimens with different void contents lie on the same straight line indicating that voids have no measurable effect on electrical conduction. In a previous report [5], it was shown that the electrical conduction in PZT is due to the migration of holes contributed by the lead vacancies; however, for samples containing controlled amounts of artificially-introduced voids, the measured activation energies for conduction remain the same, as calculated from Fig. 1, indicating that the lead vacancies are still probably the major charge carriers for electrical conduction. Therefore, commercial PZT polycrystalline ceramics with void contents between 10 and 15 vol% are acceptable from the electrical resistivity point of view but are not from the point of view of the other electrical properties [8] such as dielectric constant and piezoelectric coupling factor.

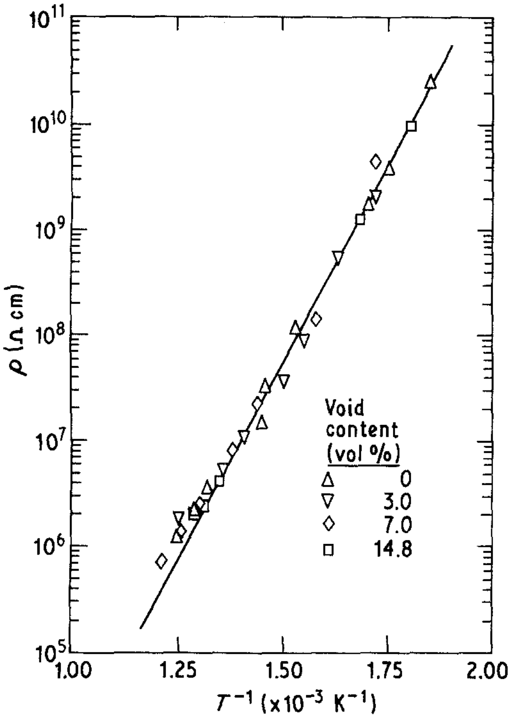

Figure 1 The temperature dependence of electrical resistivity of Nb-doped PZT ceramics with varying void contents.

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An EXAFS study of amorphous selenium

As part of our programme of study of amorphous chalcogenides we have investigated the extended X-ray absorption fine structure (EXAFS) of glassy selenium. X-ray diffraction studies of amorphous Se have already indicated peaks in the radial distribution function (RDF) at 2.34, 3.78 and 4.97 Å [1]. Structural models suggested for glassy Se indicate that it contains both chains and rings of varying lengths [2]. EXAFS is known to be particularly effective in the study of local structure in glasses [3]. Considering the diverse opinions on the structure of amorphous Se, we felt that an EXAFS study would be instructive.

Se glass was prepared from the 5N purity element (Koch-Light, UK). The K-edge absorption spectrum was recorded on a bent-crystal spectrograph using Mo radiation [4]. A Carl-Zeiss microdensitometer was used to record the trace with a linear reverse dispersion of 0.7 eV mm^{-1}.

Data up to 350 eV beyond the edge were amenable to analysis. Computation of the radial structure function was carried out using a Hanning window function and Eccles' procedure [5]. After background subtraction, the following steps were carried out:

(a) Data between 30 and 350 eV from the edge were Fourier transformed.
(b) The first few components were set equal to zero and data were back-transformed to k-space.
(c) Finally a transform to R-space was carried out to yield the radial structure function shown in Fig. 1.

Changes in the integration limits did not shift the positions of the peaks shown in Fig. 1, so that we feel sure that these do represent physical distances and are not computational artefacts. Uncertainties (± 0.02 Å) in the peak positions make estimation of phase-shifts difficult. Nevertheless, the fact that our values for various distances agree quite well with reported values indicates that these shifts are quite small.

In Fig. 1, the peak at 2.34 Å represents the usual Se–Se distance [1]. Apart from the peaks at

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