JOURNAL OF MATERIALS SCIENCE 27 (1992) 4219–4222

Spectroscopic cathodoluminescence studies of Mg–PSZ

C. LEACH, C. E. NORMAN*
Department of Materials, Imperial College of Science, Technology and Medicine, Prince Consort Road, London SW7 2BP, UK

Cathodoluminescence (CL) techniques have been used to examine the microstructure of a magnesia–partially stabilized zirconia. Spectroscopic analysis of the visible light emitted under electron bombardment, coupled with monochromatic imaging techniques have distinguished the luminescent monoclinic zirconia from the grain-boundary silicate phase, commonly believed to be forsterite. The CL spectrum of the grain-boundary silicate was found to differ from that of pure synthetic forsterite suggesting the presence of modifiers. Lowering the specimen temperature allows the grain-boundary silicate phase to be more easily distinguished.

1. Introduction

Magnesia–partially stabilized zirconia (Mg–PSZ) is a ceramic material commonly used for the fabrication of wear-resistant parts, particularly in the paper and oil industries [1, 2]. The microstructure of this ceramic is complex (see Fig. 1), comprising cubic zirconia grains containing tetragonal zirconia precipitates, with monoclinic zirconia grains heterogeneously precipitated at the cubic grain boundaries. Impurities, principally silica, retained either by design or cost-cutting exercises during powder preparation, react to form secondary phases, notably crystalline forsterite (Mg_2SiO_4), at the cubic zirconia grain boundaries. The development and characterization of the microstructure of Mg–PSZ have been well documented in the literature (e.g. [3, 4]) and will not be considered further here. The ceramic is particularly tough, with contributions coming from, *inter alia*, crack deflection, crack blunting and transformation toughening. This latter process is peculiar to zirconia-based ceramics and is due to the volume expansion of tetragonal zirconia as it tranforms to the monoclinic phase under some stress-relieving influence such as a propagating crack tip. Mg–PSZ shows R-curve behaviour [5] but is susceptible to relatively rapid failure during fatigue-type loading [6]. A knowledge of the relative amounts and the distribution of the various phases of zirconia within the ceramic's microstructure can, therefore, yield a great deal of information as to the state of that ceramic. This information can be obtained in part by several methods such as X-ray diffraction [7], transmission and scanning electron microscopy, Raman spectroscopy [8] and cathodoluminescence (CL). The latter technique is the subject of this paper.

CL uses a high-energy beam of electrons in, say, an SEM to excite electronic transitions across the forbidden energy gap, thereby creating electron–hole pairs. Subsequent recombination of these beam-induced carriers occurs by electronic transitions directly between the conduction and valence bands and via states introduced into the band gap by impurities and a variety of defects. If sufficient of these transitions is radiative then the photons which are emitted can be collected, detected and analysed using a monochromator to obtain a spectrum of the target material. By using a voltage analogue of the CL signal level to drive the grid of the SEM screen it is possible to form a CL image of the target material, either using all the emitted luminescence (panchromatic), or using only a narrow range of photon energies (monochromatic). In this way spatially inhomogeneous distributions of different phases, impurities or defects can be recorded.

Whilst the electron beam can excite all the available luminescence mechanisms, it will, however, tend to excite transitions in the outermost, least strongly bound electrons of the target atoms. These electrons are very sensitive to their surrounding electronic environment and so the energies of the transitions are not so well defined as, for instance, in the case of inner-shell transitions which give rise to characteristic X-ray emissions. This can present problems in identifying the exact origins of the transitions observed in the CL mode and is perhaps the biggest drawback in CL analysis. The technique does, however, possess the advantages of relatively high spatial resolution (of the order of 1 μm), the possibility of varying the depth of the excitation below the sample surface and, in the absence of competing non-radiative recombination centres and strong self-absorption, the ability to detect efficient recombination centres in concentrations as low as 10^{15} atoms cm^{-3} [9]. Cooling the target material is usually advantageous, tending to decrease the activity of non-radiative centres thereby increasing the luminescence efficiency.

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* *Present address*: C.N.R., Maspec Institute, Via Chiavari 18/A, 43100 Parma, Italy.

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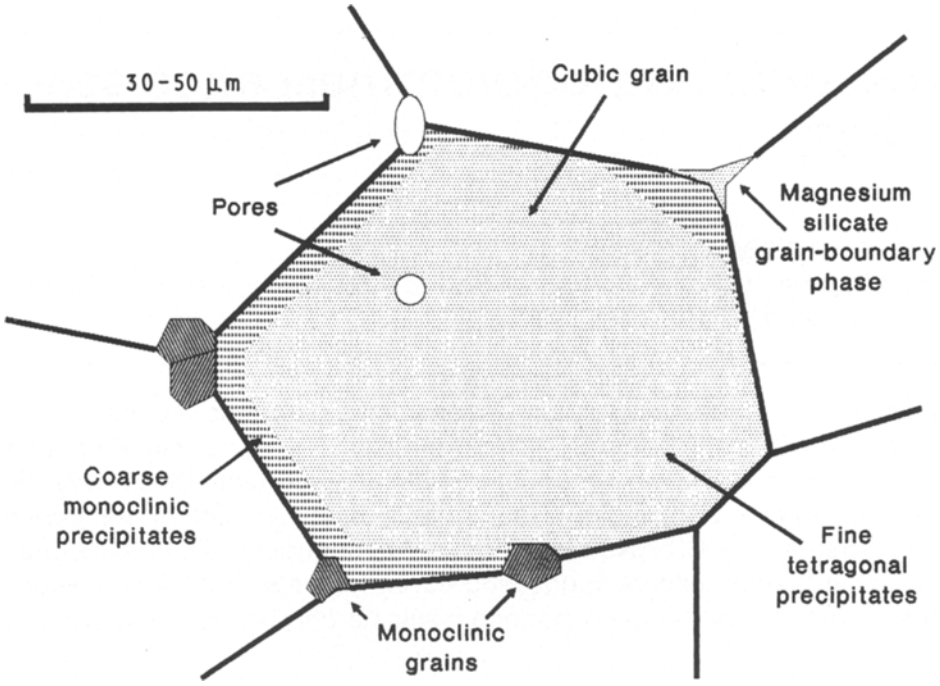


Figure 1 Microstructure of Mg–PSZ.

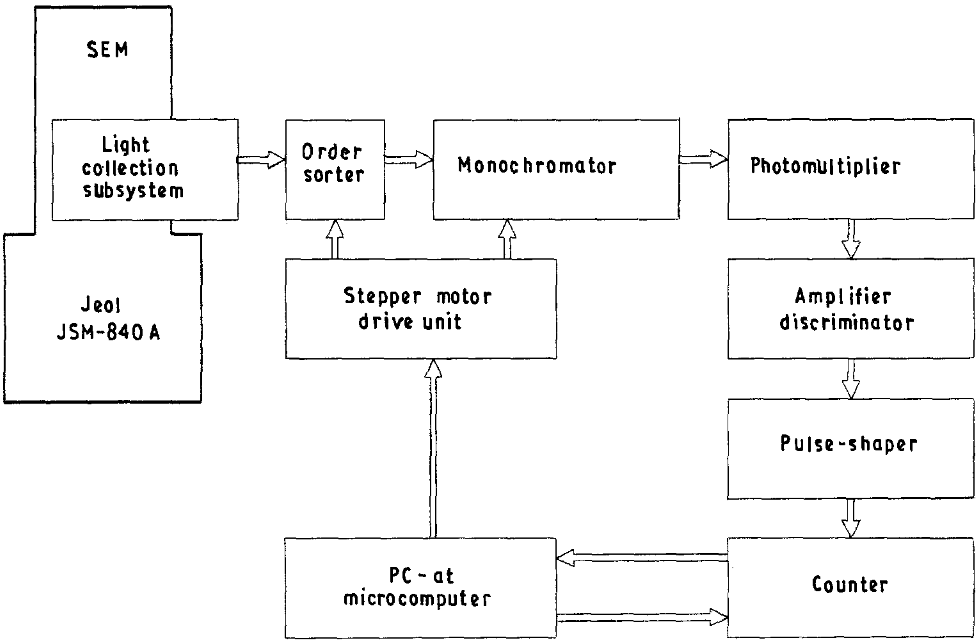


Figure 2 Schematic of the CL detection system.

In the case of zirconia ceramics, it is established that the luminescence properties of the monoclinic phase are much greater than that of the other structures [10], namely the partially stabilized tetragonal phase or the fully stabilized (e.g. by magnesia) cubic phase. These differences in luminescence efficiency have been used to produce panchromatic CL images mapping the distribution of the monoclinic phase, particularly in damaged zirconia ceramics. The problem associated with panchromatic imaging is that it is virtually impossible to differentiate between phases of similar luminescence efficiency without recourse to some other microstructural analysis technique. We show that monochromatic imaging is of immense value in circumventing this problem and in clarifying the spatial distribuiton of such phases.

2. Experimental procedure

The CL investigations in the present work were carried out on a spectroscopic CL analysis system attached to a JSM-840A SEM controlled by a PC 286 microcomputer (Fig. 2). The light collection subsystem used was an Oxford Instruments CL301 collector

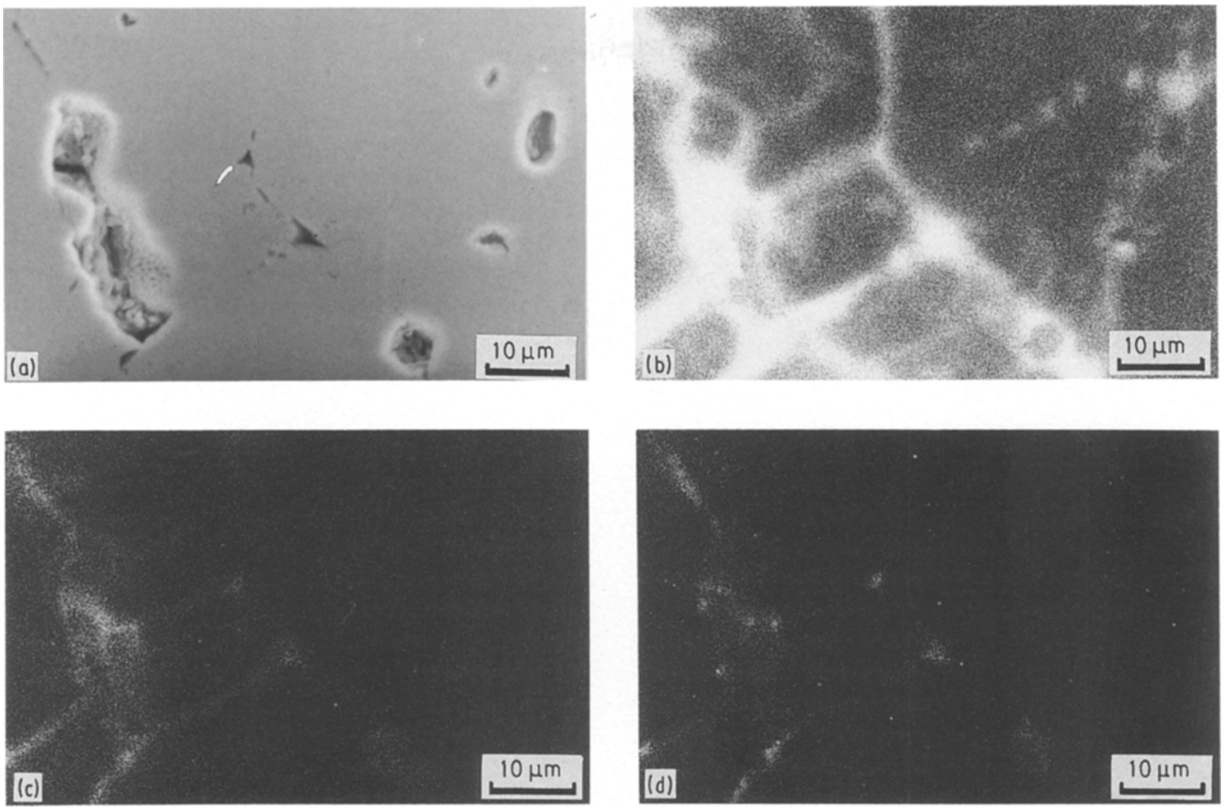


Figure 3 (a) Secondary electron image of the Mg–PSZ studied. (b) Zero-order CL image of the same area. (c) Monochromatic image at 466 nm. (d) monochromatic image at 414 nm.

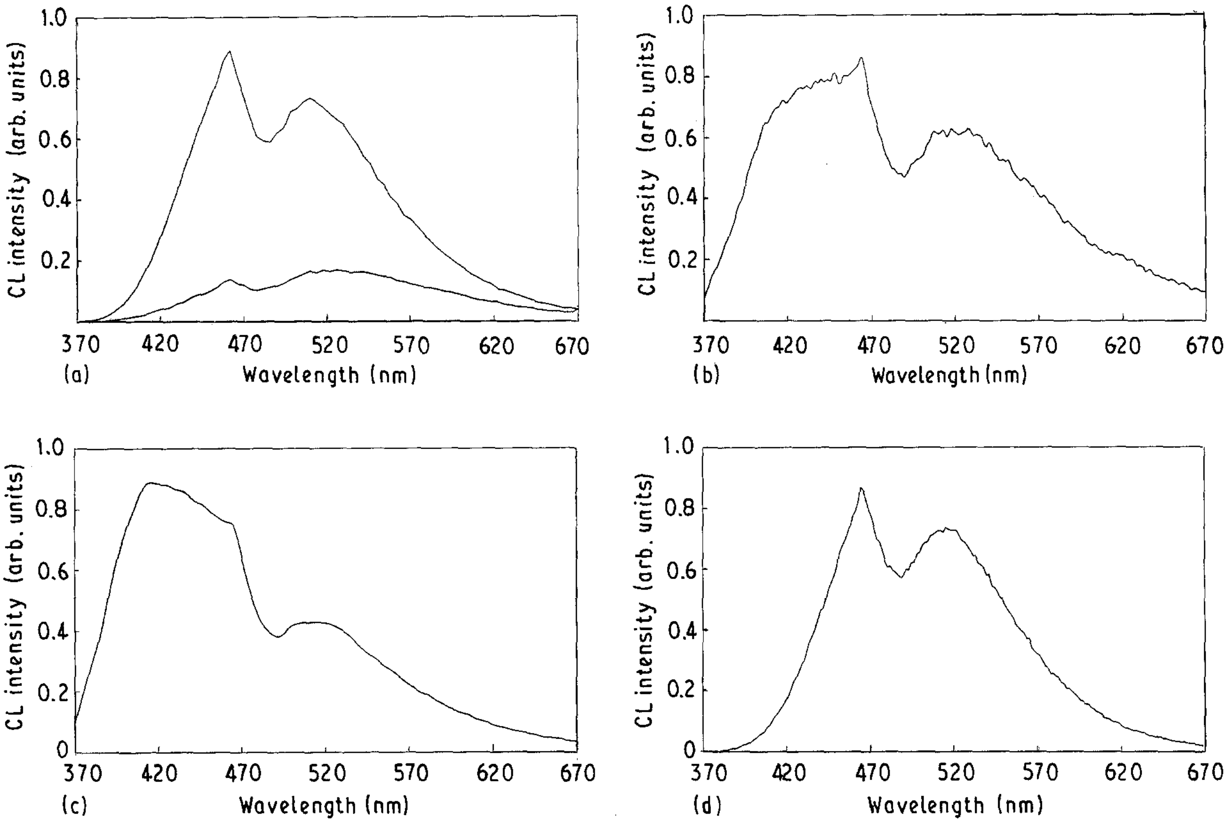
which incorporates a semi-ellipsoidal aluminium mirror positioned approximately 1 mm above the specimen. The Mg–PSZ material used has also been previously extensively characterized [11]. Where necessary, the samples were studied at low temperatures using a variable temperature stage cooled by liquid nitrogen, designed by one of the present authors (C.N.) [12].

3. Results

A secondary electron image of a typical Mg–PSZ is shown in Fig. 3a. Grain boundaries, pores showing some internal structure and a triple point are visible. The panchromatic, or zero order, CL image shows bright contrast close to some of the grain boundaries and at the triple point (Fig. 3b). It should be noted that the amplitude of these spectra is modulated by the response characteristics of the CL detection system used. Point CL spectra, collected at room temperature, were taken from the grain interior where dark contrast was observed (Fig. 4a), a grain-boundary region where bright contrast was observed (Fig. 4a), and from the triple point (Fig. 4b). Each spectrum consists of a sharp peak at around 460 nm and a broader peak at around 530 nm. The positions of the two peaks, common to all the spectra, vary in their relative intensities and apparently shift slightly between spectra. Between the grain boundaries (predominantly monoclinic) and the grain interiors (predominantly a mix of tetragonal and cubic) the luminescent efficiency changes, but not the general shape of the spectrum. In the case of the spectrum collected from the triple point, an additional, broad maximum occurs, peaking at around 440 nm. This "shoulder" is most prominent in the spectrum collected at low temperature (Fig. 4c). Reference spectra from undoped zirconia and a synthetic sample of forsterite, generally thought to be the grain-boundary phase, are shown in Fig. 4d and e, respectively. Using the room-temperature spectral information it was possible to select appropriate wavelengths for monochromatic CL imaging which highlighted the monoclinic zirconia (466 nm, Fig. 3c) or the triple point phase (414 nm, Fig. 3d).

4. Discussion

These observations clearly demonstrate the benefit of selected wavelength CL imaging techniques in establishing the distribution of phases in ceramic and other materials. However, the low Q of the (two) peaks observable in the zirconia spectrum means that a high level of phase discrimination is not possible in this system. Thus monoclinic is primarily distinguished from the other zirconia phases by luminescent efficiency; the grain-boundary silicate by wavelength. The use of the cold stage, operating at near liquid nitrogen temperatures, was seen to sharpen the silicate peak. Although the major element chemical analysis of the silicate corresponds to forsterite (as is generally the case in this type of material), the CL spectrum does not correlate well with that obtained from a pure sample of synthetic forsterite implying some form of



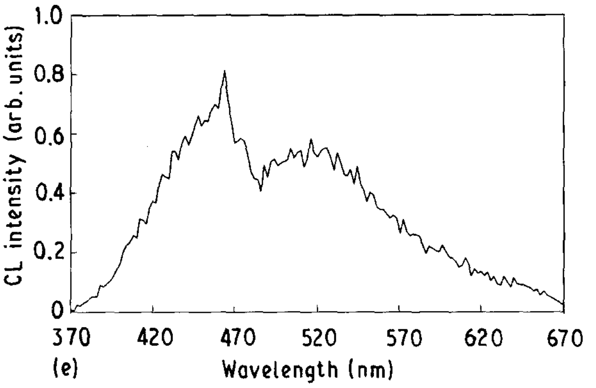


Figure 4 CL spectra collected from (a) a grain interior and a grain boundary, (b) a triple point containing a silicate phase, (c) as (b) but at low temperature (160 K), (d) undoped zirconia, and (e) pure synthetic forsterite.

structural modification. The precise nature of this difference is currently under investigation.

Similarly, useful information is obtainable in certain other ceramic systems, e.g. the well-resolved ruby red line in chromium-doped alumina [9], contrast due to dislocations in ZnO [13] and distinct red and blue emissions associated with different dislocation types in MgO [14].

It is believed that the CL technique, with its ability to map out phase distributions and damage in a wide range of materials, will make a significant contribution to the development of non-destructive testing techniques in the near future.

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Received 23 April
and accepted 1 May 1991