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A Raman spectral characterization of ceramics in the system ZrO_2–TiO_2

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Ceramics of zirconium titanate, $ZrTiO_4$, were prepared by the mixed oxide route, sintered at 1400 °C and cooled at various rates: water quench to 1 °C h^{-1}. Mixed oxide-prepared ceramics of $Zr_5Ti_7O_{24}$ were sintered at 1400 °C and cooled at 6 °C h^{-1}. TEM analysis of the $ZrTiO_4$ ceramics showed the development of an incommensurate superstructure in the more slowly cooled specimens. The $Zr_5Ti_7O_{24}$ ceramics exhibited a commensurate superstructure with a tripled *a*-axis. Raman spectra were obtained from polished ceramic specimens at room temperature. Major differences between spectra for $ZrTiO_4$ ceramics are believed to reflect differences in the degree of cation ordering. The Raman spectrum for $Zr_5Ti_7O_{24}$ is similar to that of slowly cooled $ZrTiO_4$ but there are significant differences.

1. Introduction

Zirconium titanate-based ceramics are of interest for their useful dielectric properties in the microwave regime. The relative permitivity is typically 38 and, depending upon the composition and processing conditions, the dielectric *Q* value can be up to 10 500 at 5 GHz [1–3]. Such materials find application as dielectric resonators [4] and substrates.

The end-member $ZrTiO_4$ has the α-PbO_2 structure type and belongs to the space group *Pbcn* [5]. McHale and Roth [6] demonstrated that zirconium titanate exists in two major forms: a so-called high-temperature form where the length of the unit cell in the *c*-direction is "long" (~0.55 nm), and a low-temperature form, having a shorter cell parameter in the *c*-direction (~0.535 nm). The transition between these variants is believed to occur at approximately 1120–1150 °C, marking the difference between the random distribution of zirconium and titanium cations in the high-temperature form and the ordered distribution in the low-temperature form. Specimens exhibiting different degrees of ordering may be generated by sintering at an elevated temperature and cooling at different rates [7]. It has been suggested that the compound $Zr_5Ti_7O_{24}$ has the structure of the low-temperature form of zirconium titanate in its equilibrium state. This compound also has the α-PbO_2 type structure and a well-defined superstructure with a tripled *a*-axis.

Because the dielectric properties of materials at microwave frequencies depend critically upon ionic polarization caused by lattice vibrations, then high-frequency spectroscopic techniques can, in principle, provide insight into the processes of dielectric loss [8]. Raman spectroscopy, Fourier transform-infrared spectroscopy and dielectric spectroscopy are useful to investigate dielectric ceramics [8, 9].

Krebs and Condrate [10] obtained Raman spectra for powdered specimens in the systems ZrO_2–TiO_2 and HfO_2–TiO_2 and showed that the data could be interpreted in terms of structural differences. In this study we use Raman spectroscopy to explore structural changes in $ZrTiO_4$ ceramics, cooled at different rates after sintering, and the related compound $Zr_5Ti_7O_{24}$. A complementary electron diffraction study has been performed to provide crystallographic information.

2. Experimental procedure

2.1. Materials and preparation

The starting materials were ZrO_2 (Magnesium Elektron MEL E20 grade), TiO_2 (Tioxide A-HR), ZnO (BDH analar grade) and Y_2O_3 (Fluka analar grade). The oxides with the desired compositions were mixed wet for 8 h, calcined at 1100 °C for 4 h and milled again for 12 h. Pellets were pressed at 120 MPa in the shape of discs of 16 mm diameter and 8 mm thickness. Ceramics of zirconium titanate ($ZrTiO_4$) were sintered at 1400 °C for 4 h in air and cooled at various rates: water-quench, air-cooled, 120, 6 and 1 °C h^{-1}. Ceramics of $Zr_5Ti_7O_{24}$ were sintered with the aid of Y_2O_3 [7] at 1400 °C for 4 h and cooled at 6 °C h^{-1}.

2.2 Analytical procedures

Raman spectra were obtained from polished ceramic surfaces. The Raman system consisted of a spex 1403

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monochromator, coupled to a modified microscope and an argon ion laser. The 488 nm line was used to excite the Raman spectrum. A spectral bandpass of approximately 10 cm^{-1} was used and spectra, in the backward scattering geometry, were obtained from selected regions of the polished surfaces, typically 1–2 μm in size.

For transmission electron microscopy (TEM), prepared 3.5 mm diameter discs were ground to 200 μm. The centres were reduced to 30 μm thickness by a mechanical dimpling method and then ion-beam thinned. A Philips EM 430 transmission electron microscope was used for microstructure and electron diffraction studies.

3. Results and discussion

All sintered products were approximately 95% theoretical density.

TEM microstructure, and electron diffraction studies confirmed that there were major structural changes between the rapidly cooled and slowly cooled zirconium titanate ceramics. Electron diffraction patterns were obtained at [0 1 1] orientation in order to examine the reflections for the reported superstructure in the *a*-direction [11].

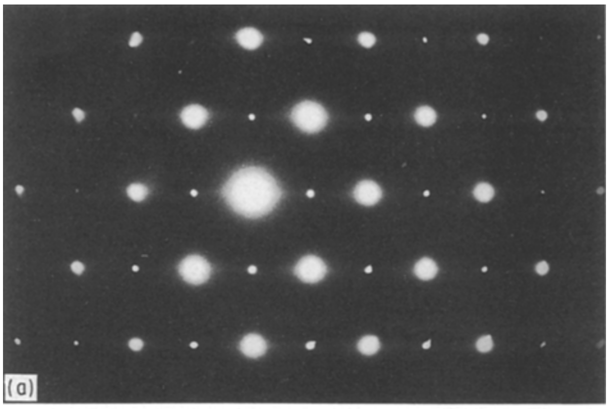
Fig. 1 shows two [0 1 1] electron diffraction patterns of $ZrTiO_4$ specimens cooled at different rates. Fig. 1a shows the [0 1 1] diffraction pattern of an air-quenched sample. This simple pattern indicates a disordered structure for the rapidly cooled $ZrTiO_4$. Fig. 1b shows the [0 1 1] electron diffraction pattern of an ordered sample cooled at 1 °C h^{-1}. Extra reflections, arising from an incommensurate superstructure, can be seen in the diffraction pattern. The modulation wavelength is approximately 0.84 nm. Full details are given elsewhere [7].

In specimens cooled very slowly e.g. 1 °C h^{-1}, small exsolved nodular particles were also observed. Energy dispersive chemical analysis of these particles indicated that such particles are rich in zirconium. Therefore, on slow cooling, there was progressive "ordering" of Zr^{4+} and Ti^{4+}, and the zirconium titanate became deficient in Zr^{4+} because of the exsolution of zirconia.

Fig. 2 is a [0 1 1] electron diffraction pattern of a $Zr_5Ti_7O_{24}$ specimen. The electron diffraction pattern confirms the presence of a superstructure with a tripled *a*-axis [11]. Full details are given elsewhere [7].

In common with the variation in the diffraction patterns for the ceramics, major differences were observed between Raman spectra of the $ZrTiO_4$ samples cooled slowly and cooled rapidly. The number, intensity and location of the Raman bands were found to be dependent on the cooling rate. The Raman spectrum of a rapidly cooled (air-quenched) $ZrTiO_4$ sample (Fig. 3a) showed broadened bands. As the cooling rate decreased to 6 and 1 °C h^{-1}, the Raman bands became sharper and extra peaks appeared in the shoulders of existing peaks (Fig. 3b, c).

The location of Raman bands for $ZrTiO_4$ ceramics cooled at different rates are listed in Table I. The data obtained by Krebs and Condrate [10] are listed for comparison.



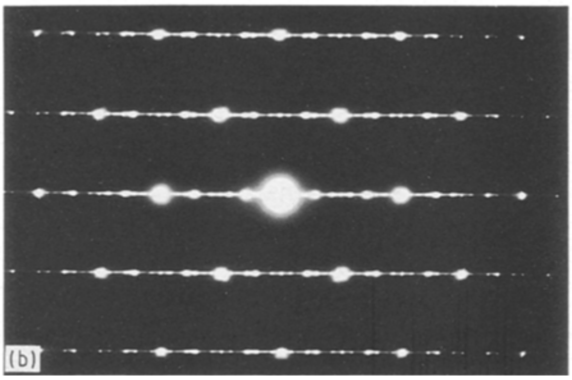


Figure 1 [0 1 1] electron diffraction patterns for $ZrTiO_4$ ceramics: (a) quenched in air; (b) cooled at 1 °C h^{-1}.

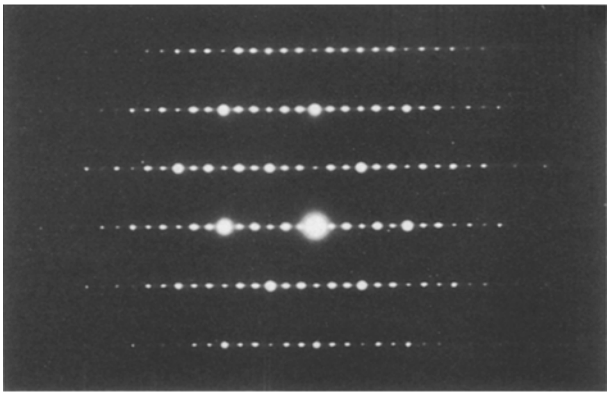


Figure 2 [0 1 1] electron diffraction pattern for $Zr_5Ti_7O_{24}$ ceramic.

Using the factor group analysis, Krebs and Condrate predicted the following optical phonon modes for $ZrTiO_4$ with a random distribution of zirconium and titanium ions (taking zirconium and titanium ions as one type of averaged ion)

$$4A_g + 5B_{1g} + 4B_{2g} + 5B_{3g} + 4A_u + 4B_{1u} + 3B_{2u} + 4B_{3u}$$

giving 18 Raman active and 11 infrared active modes by this model. Krebs and Condrate observed only 12 Raman bands (Table I) for their air-quenched specimen and inferred that others either occurred at lower wave number, were too weak to be observed or were hidden due to overlap by other bands. Our spectrum

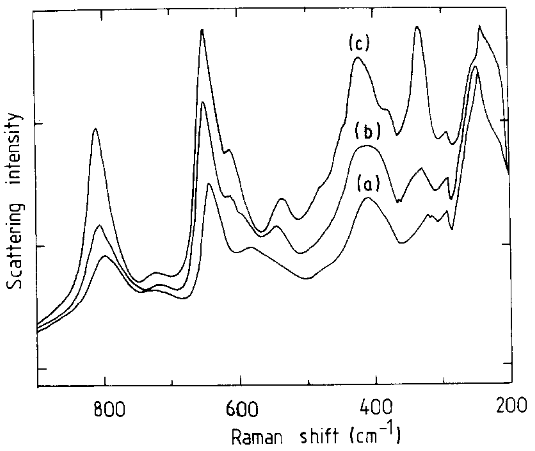


Figure 3 Raman spectra of $ZrTiO_4$ ceramics cooled at various rates: (a) quenched in air, (b) cooled at 6 °C h^{-1}, (c) cooled at 1 °C h^{-1}.

TABLE I Location of Raman bands in $ZrTiO_4$ (cm^{-1})

Band number	$ZrTiO_4$ ceramics (air-quenched), this study	$ZrTiO_4$ ceramics, (cooled at 1 °C h^{-1}), this study	$ZrTiO_4$ powder, air quenched [10]
1	260	248	124
2	290	290	158
3	320	331	258
4	400	277	269
5	465	409	331
6	580	421	394
7	640	444	415
8	705	479	537
9	800	538	590
10		612	625
11		650	646
12		724	795
13		810	

for rapidly cooled $ZrTiO_4$ (Fig. 3a) is similar to that reported by Krebs and Condrate for the 200–800 cm^{-1} region, although there are differences between the location of some bands. The broadness of the bands in the spectrum for the rapidly cooled zirconium titanate is probably mainly due to the random distribution of Zr^{4+} and Ti^{4+} between equivalent sites, although Krebs and Condrate noted that variations in cation stoichiometry and oxygen defects may also be responsible for the peak broadening in such specimens.

When the Raman data for zirconium titanate specimens cooled at 6 and 1 °C h^{-1} (Fig. 3 and Table I) are compared with those for the rapidly cooled zirconium titanate, it may be seen that the peaks become sharper and more bands can be resolved as the specimens are cooled more slowly. Hence, Fig. 3, Spectrum C (specimen cooled at 1 °C h^{-1}) exhibits 13 Raman bands within the 200–800 cm^{-1} range compared to 9 for the rapidly cooled specimen. The increase in the number and improved resolution of the peaks is believed to reflect the increased degree of ordering as the specimens were cooled more slowly.

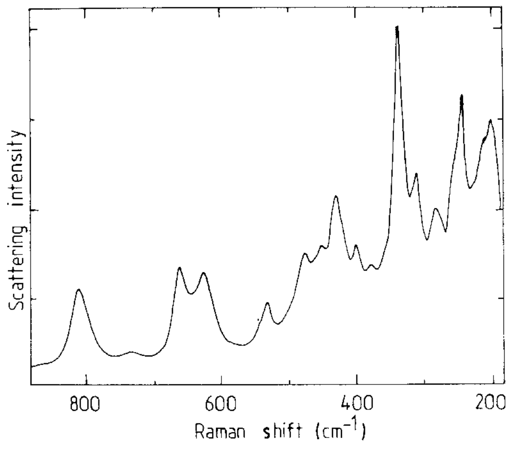


Figure 4 Raman spectrum for $Zr_5Ti_7O_{24}$.

TABLE II Locations of Raman bands in $Zr_5Ti_7O_{24}$

Band number	Wave number (cm^{-1})
1	210
2	215
3	245
4	282
5	310
6	340
7	380
8	400
9	430
10	450
11	475
12	535
13	625
14	650
15	730
16	800

The basic pattern of the Raman spectrum of $Zr_5Ti_7O_{24}$ (Fig. 4) is similar to that for $ZrTiO_4$ cooled very slowly, but there are distinct differences. The factor group analysis of the $Zr_5Ti_7O_{24}$ structure can be based on the structural model from a neutron diffraction study [12] which suggests the AB_2O_4 structural type (space group $Pbcn$, $Z = 4$) with statistical occupation of A sites (symmetry $4c$ (2)) by 0.968 Zr and 0.032 Ti ions and B sites (symmetry $8d$ (1)) by 0.889 Ti and 0.111 Zr ions. The oxygen atoms are at general $8d$ (1) sites, as well. Taking (as in the case of $ZrTiO_4$) the A and B sites occupation by zirconium and titanium ions as an occupation by averaged ions, the classification of long-wavelength optical phonons is

$$13A_g + 13A_u + 14B_{1g} + 13B_{1u} + 13B_{2g} + 12B_{2u} + 14B_{3g} + 13B_{3u}$$

which yields 54 Raman and 38 infrared active modes. As anticipated, the number of observed bands (Table II) is much smaller (16) for the reasons discussed above for $ZrTiO_4$. Unfortunately, it is not easy to assign the bands for such a complex structure, and either calculations on the basis of some microscopic model or comparison of isostructural substances with different ions would be necessary.

Hence both electron diffraction and Raman spectra data of zirconium titanate reflect progressive differences in the state of ordering of the ceramics. Whilst selected peaks can be identified in the Raman spectra for both $Zr_5Ti_7O_{24}$ and slowly cooled $ZrTiO_4$, there are major differences and it is not possible to confirm that the spectrum for $Zr_5Ti_7O_{24}$ represents the ultimate development of the spectra for $ZrTiO_4$ ceramics. However, this study has shown the benefit of performing complementary TEM and Raman spectroscopy studies.

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