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$MgTa_2O_6$ and $ZnTa_2O_6$ ceramics from oxide precursors

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Abstract

An experimental route from mixed oxides of binary compounds and a solid-state reaction has been established for the synthesis of $MgTa_2O_6$ (MT) and $ZnTa_2O_6$ (ZT) compounds. MT and ZT powders have been prepared in a reproducible manner, with special attention focusing on the correlation of reaction conditions, sintering time, crystalline phase formation, density and microstructural development. The conditions under which a single phase was obtained were mean particle diameter of 0.73 μm for ZT and of 0.83 μm for MT, after 24 hours of milling, and a 12 h reaction temperature of 1250 °C. A highly dense ceramic of up to 98% of the theoretical density was produced by sintering compacted powders at 1400 °C for 8 h.

Keywords: Columbite; Powders-solid state reaction; sintering; tantalates; $MgTa_2O_6$; $ZnTa_2O_6$

1. Introduction

Among the various dielectric compositions, complex perovskite compounds such as $Ba(Mg_{1/3}Ta_{2/3})O_3$ and $Ba(Zn_{1/3}Ta_{2/3})O_3$ are known to possess the best dielectric microwave properties for future applications. Dielectric ceramics for use in resonators with microwave frequencies have received increasing attention due to the fast growth of mobile communication systems such as cellular phones, phasors and personal communication systems.[1,2]

However, active research to identify new compositions is still ongoing, due to the high demand for a variety of dielectric constants, lower costs and low-firing conditions.[1,2] Little attention has focused specifically on binary compounds such as $MgTa_2O_6$ (MT) and $ZnTa_2O_6$ (ZT) and one of the difficulties encountered in the study of these types of material has been the high melting point of Ta_2O_5-based structures.

Lee et al.[1] found that binary compounds, such as AB_2O_6 (A = Ca, Mg, Mn, Co, Ni, Zn, B = Nb, Ta) compounds, are very promising for dielectric resonator applications, and that compounds containing Mg^{+2} and Zn^{+2} elements, in particular, have excellent dielectric properties for such applications. These authors used sintered ceramic MT and ZT samples prepared by solid-state reaction at 1550 and 1350 °C, respectively, for 2 h. However, they offered no information about the optimum experimental conditions required to obtain a single crystalline phase or high-density ceramics.

This work consists of the ceramic processing involved in obtaining single MT and ZT phases through solid-state synthesis from precursor oxides, with the purpose of obtaining a final product with high yield, exact stoichiometry and high density. MT and ZT powders were prepared in a reproducible manner, with special attention focusing on the correlations between reaction conditions, sintering time, crystalline phase formation, density and microstructural development.

2. Experimental

2.1. Preparation of the powder

To synthesize the material by solid-state reaction, appropriate amounts of reagent grade MgO (Merck, P.A.), ZnO (Vetec, P.A.) and Ta_2O_5 (TEP, 99,99%) were mixed for 24 h by ball-milling in isopropyl alcohol, using ZrO_2 balls (0.94×0.96 mm^2 in size) to produce an optimized grain size. The reactions were performed in an open platinum crucible at 1200, 1250 and 1300 °C for

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12 h, resulting consistently in a single crystalline phase for the ZT compound. In contrast, the synthesis of MT required an additional amount of MgO to convert the unreacted (free) Ta_2O_5 phase into $MgTa_2O_6$. The molar ratios used were: 1:1.05, 1:1.1 and 1:1.15 of Ta_2O_5:MgO. A single phase was obtained with the 1:1,15 Ta_2O_5 : MgO ratio.

The ceramic was conformed (10×2 mm) by adding a polyvinyl alcohol (PVA) binder to the reacted powders, which were uniaxially pressed at 64 MPa and sintered at 1400 °C for 4, 6 and 8 h.

2.2. Characterization of the powder and ceramic

After milling, the particle size distribution of the precursor oxides was determined by the sedimentation technique using a Micromeritics Sedigraph 5100 device. The reacted and non-reacted powders were evaluated by differential thermal analysis (DTA) (T.A. Instruments, DTA 2600) in a temperature range of 300 to 1300 °C, at a heating rate of 10 °C/min in air, using an alumina powder as reference. After the DTA evaluation, the calcined powders were examined by X-ray diffraction (XRD) to identify the phase formed. The X-ray diffraction patterns were measured in the continuous scan and step scan modes, using a Rigaku Rotaflex-RU-200B diffractometer and CuKα radiation, with a step width of 0.02° and 3 s per step over a 2θ range of 10 to 80°. The XRD patterns were analyzed by the Rietveld method, using version 0.3 of the Rietveld analysis program Fullproof.[3] A pseudo-Voigt function was chosen to generate the shape of the diffraction peaks. The profile refinements were made in the space group P42/mnm ($a=b=4.719$; $c=9.200$Å)[4] for MT and space group Pbcn ($a=4.702$; $b=17.094$; $c=5.070$)[5] for ZT.

The density of the sintered specimens was determined by the fluid displacement method (Archimedes method) using distilled water. The microstructural evolution was examined by scanning electron microscopy (SEM) of the polished and thermally etched surface (Zeiss-DSM960).

3. Results and discussion

3.1. Analysis of the powder

The particle size distribution and mean particle size values are based on measurements taken from the unmilled precursor powders up to those milled for different lengths of time. These results are summarized in Table 1, which shows a steady decrease in the particle size of both materials as milling time increases, until a mean size of 0.83 μm and 0.73 μm is reached for MT and ZT, respectively, after 24 h. All the milled powders showed a narrow size distribution range. It is a well-known fact that small particle size is a fundamental factor for greater reactivity between oxide compounds.

Table 1
Mean particle size of precursor powders $MgO+Ta_2O_5$ (MT) and $ZnO+Ta_2O_5$ (ZT)

Milling time (h)	MT (μm)	Distribution[a] MT(μm)	ZT (μm)	Distribution∗ ZT (μm)
0	4.64	1.3–10.5	2.30	6.0–1.0
6	0.94	1.9–0.4	0.91	2.0–0.4
12	0.89	2.0–0.3	0.77	1.9–0.4
18	0.86	1.9–0.4	0.77	1.9–0.4
24	0.83	1.9–0.4	0.73	1.9–0.4

[a] Distribution range of particle size.

The reaction temperatures for MT and ZT compounds were determined based on DTA curves. The high exothermic peak in the MT sample, with its maximum centered at 1254 °C, indicated the reaction temperature of the oxide precursors. This phenomenon was absent from the calcined powder curve in this temperature region. The onset temperature was determined as 1200 °C. The onset temperature in the ZT curves was identified at 1200 °C, with the maximum centered at 1259 °C.

3.2. Analysis of the crystalline phase

Fig. 1 depicts the XRD patterns of the MT and ZT with stoichiometric compositions obtained from the calcined powders at various calcination temperatures. The ZT compound consistently formed a single crystalline phase at all the calcination temperatures tested (Fig. 1a). On the other hand, the MT compound that was formed showed some additional X-ray reflections (different from the calculated pattern), which were identified as Ta_2O_5 (Fig. 1b).

Different amounts of MgO were used to obtain a single MT phase, and the results were analyzed by XRD, as shown in Fig. 2. Under our experimental conditions, particularly the open platinum crucible, an excess of 0.15 mol of MgO was required to form the single MT phase.

Fig. 3 shows reacted and refined diffraction patterns for the MT and ZT X-ray data. The XRD patterns were in good agreement with the experimental data, revealing only slight differences between the intensities and only single MT and ZT phases. The same refinement conditions and strategy were employed for the two compounds. The R_{Bragg} index and the crystal parameters calculated for the refinement of both samples were 2.87 and 2.60%, respectively, for MT and ZT. The low Bragg index value, R_{Bragg}, indicates the good correspondence between the refined structural model and the observed data. The unit cell and cell volume values obtained for the MT compound were $a=b=4{,}714$ Å, $c=9.199$ Å and V = 204.4 Å, and are in good agreement

with those reported in the literature.[4] The values obtained for ZT were $a=4.696$ Å, $b=17.065$ Å, $c=5.063$ Å and $V=405.7$ Å for unit cells and cell volume, respectively. These values are comparable those reported by Waburg et al.[5]

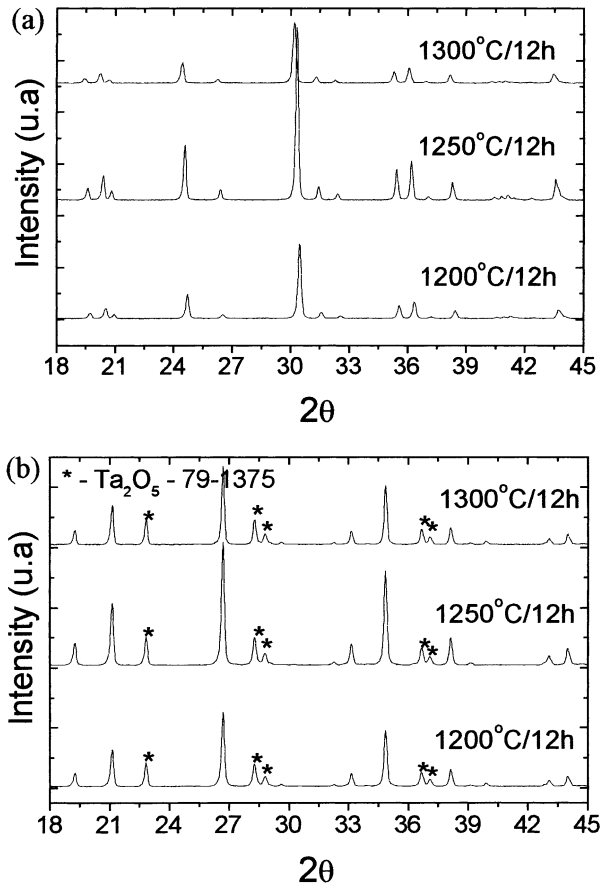

Fig. 1. XRD patterns of the calcined powders at various calcination temperatures with constant time. (a) ZT and (b) MT with Ta_2O_5 phase.

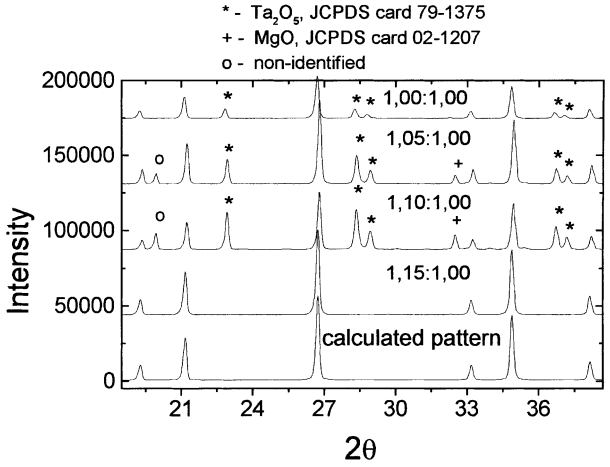

Fig. 2. XRD patterns of MT powders calcined with different amounts of MgO.

3.3. Microstructural and densification analysis

Fig. 4 illustrates the density of sintered specimens versus sintering time, at a temperature of 1400 °C. We found that the pellets density increases with sintering

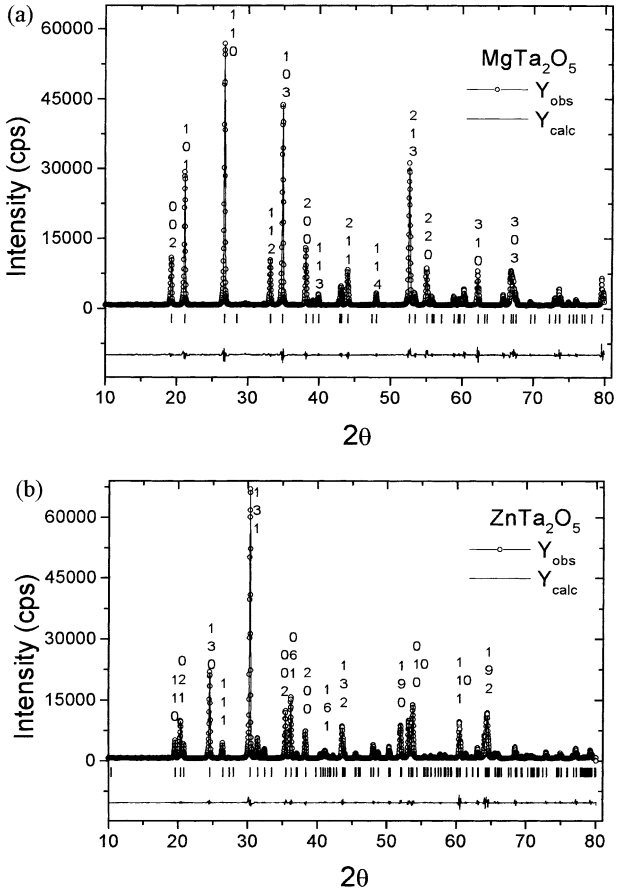

Fig. 3. Plot output from the Rietveld refinements of samples (a) MT and (b) ZT. The dots represent the XRD data while the solid line represents the calculated pattern. The difference plot is shown at the bottom of the graph. Some crystalline planes are indexed.

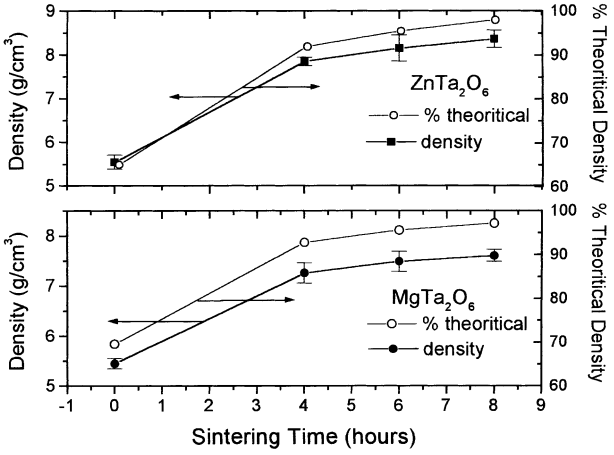

Fig. 4. Density versus sintering time of MT and ZT samples, at temperature of 1400 °C. The line serve to guide for eyes.

time, reaching 98% of the theoretical density after 8 h. Ceramic bodies with this amount of sintering can be used to prepare dielectric resonators. The theoretical value was 8.53 g/cm^3 for ZT and 7.83 gcm^3 for MT compounds.

The microstructural development after sintering was investigated by scanning electron microscopy (SEM), and the micrographs of MT and ZT sintered for 4, 6 and 8 h at 1400 °C are shown in Fig. 5. The results indicated that the grain size tended to increase with

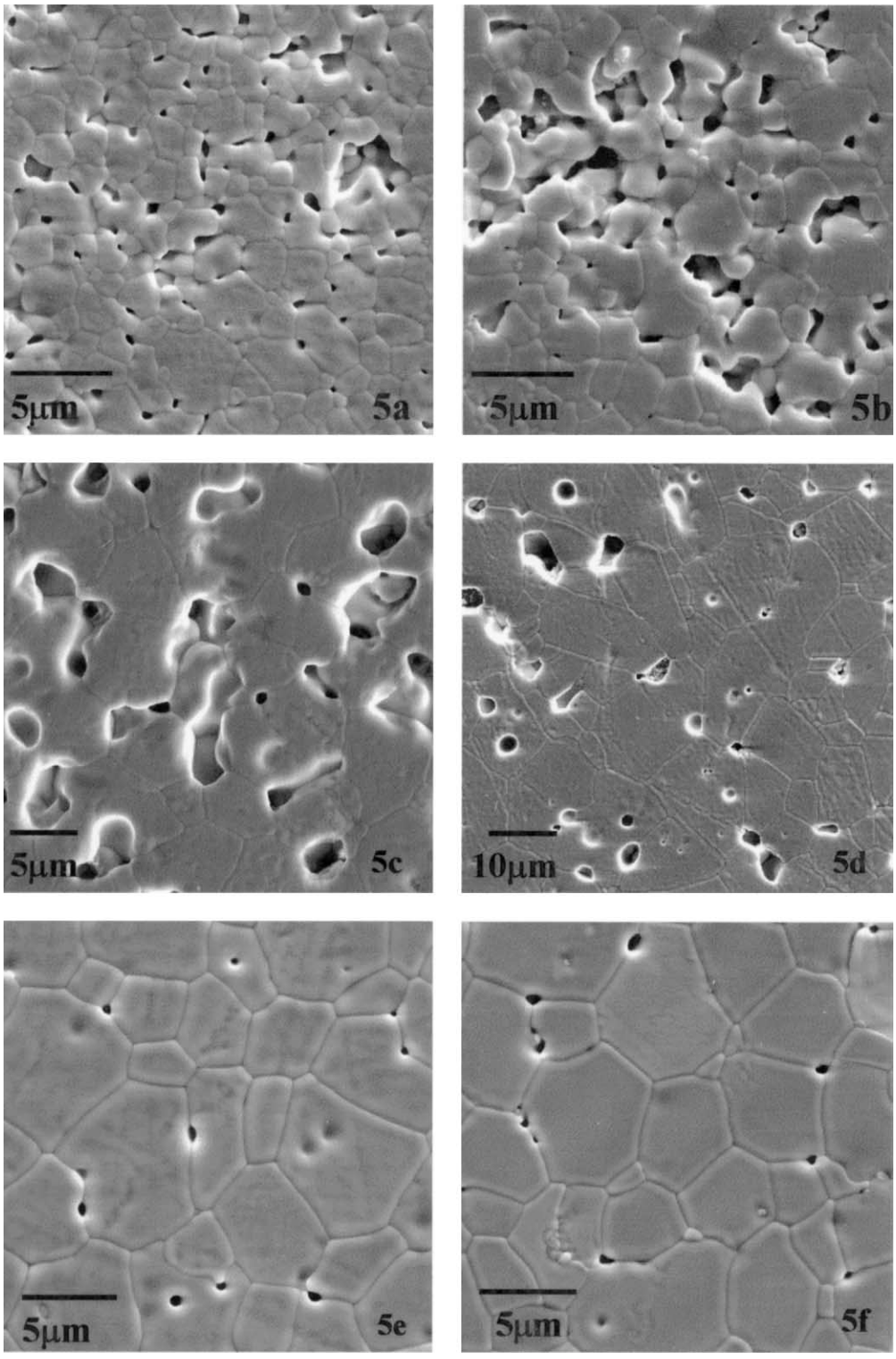

Fig. 5. SEM micrographs of specimens sintered at 1400°C (a) MT for 4 h, (b) ZT for 4 h, (c) MT for 6 h, (d) ZT for 6 h, (e) MT for 8 hours and (f) ZT for 8 h.

sintering time, increasing the samples' density, as was expected. As these micrographs reveal, the samples already presented well-defined grain boundaries, with a grain size of almost 10 μm after 8 h of sintering.

4. Conclusions

The solid-state reaction and sintering conditions of MT and ZT ceramics were developed, resulting in a straightforward method of preparing high density and single crystalline phase ceramics with a high level of reproducibility and yield. The mean particle diameter reached 0.73 μm for the ZT sample and 0.83 μm for the MT sample after 24 h of milling. Using the DTA technique, the reaction temperature was determined as 1250 °C. Single MT and ZT phases, confirmed by XRD, were obtained at 1200, 1250 and 1300 °C with 12h sintering. However, an excess of 0.15 mol of MgO precursor powder was required for the MT compound during solid-state synthesis in an open platinum crucible to produce the single phase. Sintering at 1400 °C for 8 h provided highly dense ceramic bodies with a relative density of 98%. This is a time saving route offering significant gains in productivity in comparison to the synthetic procedures via chemical routes currently in use.

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