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Phase equilibria and electrical properties of pyrochlore and zirconolite phases in the Bi_2O_3–ZnO–Ta_2O_5 system

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Abstract

The complete subsolidus phase diagram of the system Bi_2O_3–ZnO–Ta_2O_5, including cubic pyrochlore and monoclinic zirconolite phases, has been determined at 950–1050 °C. Through systematic heat treatment and X-ray diffraction of over 100 compositions, the layout of compatibility triangles (both 2-phase and 3-phase) and single phase solid solution areas has been determined. Pyrochlore and zirconolite phases have ideal nominal compositions $Bi_{1.5}Zn_{1.0}Ta_{1.5}O_7$ and $Bi_2(Zn_{1/3}Ta_{2/3})_2O_7$ respectively, but both form solid solution areas. The sintering condition of pyrochlore pellets has been optimised to obtain high density ceramics with minimal weight loss: optimised condition is 1100 °C for pellets covered with sacrificial powder. Permittivity, ε' dielectric loss and temperature coefficient of capacitance, TCC, of single phase materials were measured using impedance spectroscopy; ε' and TCC show little variation with composition but the losses are higher for Zn-deficient compositions.

Keywords: Powder solid-state reaction; Sintering; X-ray methods; Electrical properties; Tantalates

1. Introduction

Pyrochlore phases have many potential application areas due to their wide spectrum of electrical, magnetic, optical and catalytic properties. These properties are normally controlled by ionic size, polarisability and electronic configuration parameters and sometimes by the preparation and fabrication conditions. Pyrochlores can be used as solid electrolytes, oxygen electrodes, and catalysts and in active or passive electronic applications such as high permittivity ceramics, thermistors, gas sensors, switching elements, thick film resistors and materials for screen printing.[1,2] They play a role in nuclear waste disposal and can be used as semiconductor electrodes for solar energy conversion.[3]

Pyrochlore and zirconolite-related phases in the Bi_2O_3–ZnO–Ta_2O_5/Nb_2O_5 (referred to as BZT and BZN) systems have attracted considerable interest recently due to their favourable combination of electrical properties, coupled with low firing temperatures, for capacitor and high-frequency filter applications. Historically, development of microwave dielectrics has focused on materials with high quality factor, Q (defined as the reciprocal of dielectric loss) with $Q > 10{,}000$. However, device manufacturers have more recently emphasised compatibility with low resistivity metals during processing and considered the use of lower Q dielectrics, $Q \approx 200$. This change in material needs has led to the development of several new classes of high frequency dielectric ceramics. Ceramics based on BZN and BZT ternary systems containing pyrochlore and zirconolite two-phase mixtures are promising dielectrics because of their suitable Q values and also their TCC can be compositionally controlled to achieve a low value.[4,5]

BZN pyrochlore has a high permittivity, ε', of ~150 and a low dielectric loss, with $\tan\delta$ ~0.0005 at 1 MHz, but a large negative TCC, ~−500 ppm/°C. BZT pyrochlore has ε' ~71 and $\tan\delta < 0.005$ at 1 MHz.[5–10] In both systems, the pyrochlore phase occupies a solid solution area on the phase diagram,[11–13] but little information is available on possible composition-dependence of the electrical properties. Ling et al.[14] studied the dielectric properties of a series of

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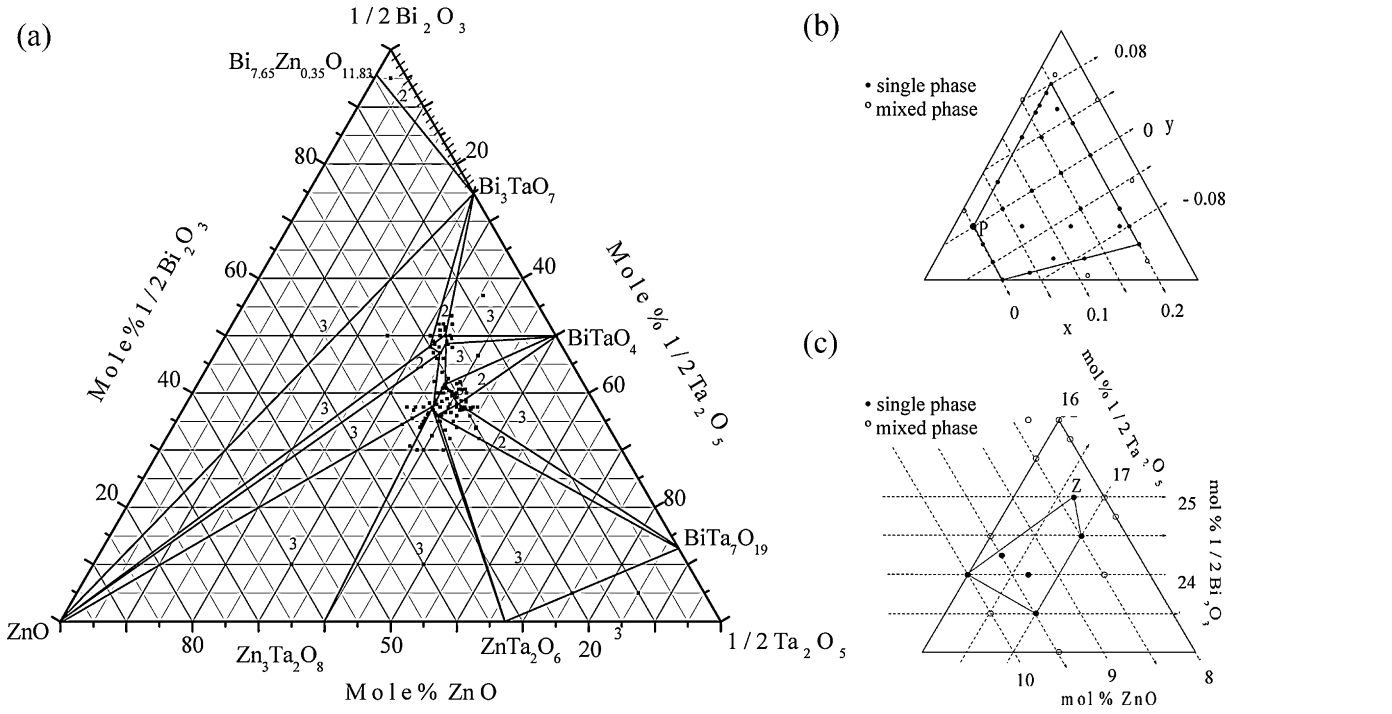

Fig. 1. (a) Overall phase diagram of the Bi_2O_3–ZnO–Ta_2O_5 ternary system; numbers in each compatibility triangle refer to the number of phases. (b) Expanded pyrochlore area with x and y as variables in the formula, $Bi_{1.5+y/2}Zn_{1.0-x/2}Ta_{1.5-y/2}O_{7-x/2-y/2}$. (c) Expanded zirconolite area with mol% of Bi_2O_3, ZnO and Ta_2O_5 shown.

compositions in the Bi_2O_3–NiO–ZnO–Nb_2O_5 system consisting of $xBi_3(Ni_2Nb)O_9 + (1-x)Bi_2(ZnNb_{2(1+\delta)})_yO_{3+6y+5\delta y}$ and found that compositional changes significantly alter the dielectric properties. Several approaches were used in their study: (1) with fixed $x = 0.265$, varying y ($0.8 \le y \le 1.1$) and δ ($-0.05 \le \delta \le 0.05$), ε' increased and TCC decreased with increase of y and δ while there was little variation of dielectric loss with $\tan\delta < 0.005$ for most compositions; (2) with fixed $x = 0.265$, $y = 0.8$ and varying δ ($-0.05 \le \delta \le 0.05$), ε' increased and TCC decreased with increase of δ whereas dielectric losses were almost constant; (3) with fixed $y = 0.8$, $\delta = 0$ and varying x ($0 \le x \le 1$), ε' and $\tan\delta$ decreased initially and then increased when $x = 0.5$ and 0.265, respectively, but no systematic variation of TCC with x was found. Wang et al.[15] showed that for $xBi_{1.5}Zn_{0.5}(Zn_{0.5}Nb_{1.5})O_7 + (1-x)Bi_{3/4}Nb_{1/4}O_{7/4}$ ($0.05 \le x \le 0.35$) ceramics biphasic mixtures of $Bi_2(Zn_{1/3}Nb_{2/3})_2O_7$ (β phase) and $Bi_{3/4}Nb_{1/4}O_{7/4}$, a distorted cubic fluorite (F), were obtained for $x = 0.05$–0.3. The permittivity and dielectric loss of β–F ceramics decreased with x whereas TCC values appeared to increase with x.[7,14] The zirconolite phases of nominal stoichiometry, $Bi_2Zn_{2/3}Nb_{4/3}O_7$ and $Bi_2(Zn_{1/3}Ta_{2/3})_2O_7$, appear to have variable composition that, as yet, has not been well characterised. BZT zirconolite has $\varepsilon' = \sim 61$, $\tan\delta < 0.001$ and TCC = +60 ppm/°C at 1 MHz.[6,12] BZN zirconolite has, $\varepsilon' = \sim 80$, $\tan\delta = 0.0001$ and TCC ~+200 ppm/°C.[7,15,16] Of particular interest for applications requiring temperature stability of electrical characteristics is to make composites of the pyrochlore and zirconolite phases and adjust their relative amounts so that the net TCC is close to zero.

The components of the Bi_2O_3–ZnO–Ta_2O_5/Nb_2O_5 systems are two unreactive oxides, Ta_2O_5/Nb_2O_5 and ZnO, together with one volatile, reactive oxide Bi_2O_3. In order to prepare samples and obtain phases or phase mixtures that represent thermodynamic equilibrium, it is necessary to find appropriate heat treatment conditions such that the temperature is high enough for Ta_2O_5/Nb_2O_5 and ZnO to react, but not too high that volatilisation of Bi_2O_3 occurs before it can be combined chemically.

The subsolidus phase diagram of the system Bi_2O_3–ZnO–Ta_2O_5 in the region of the cubic pyrochlore phase has been reported previously.[13] The pyrochlore forms a compositional or solid solution area in the phase diagram, rather similar in size and location to that in the Nb_2O_5 system,[11] but in this case including the ideal composition $Bi_{1.5}Zn_{1.0}Ta_{1.5}O_7$, marked as point 'P' in Fig. 1(b). A phase diagram containing pyrochlore and zirconolite, $Bi_2Zn_{2/3}Nb_{4/3}O_7$, phases in the BZN system was presented previously by ourselves[11,17,18] and Vanderah et al.,[12] and the two diagrams showed reasonably good agreement.

The only previous attempt to investigate the phase diagram for the BZT system was a detailed study of the join between the stoichiometric compositions of pyrochlore (α) and zirconolite (β).[8] This join was represented by the general formula $(Bi_{3x}Zn_{2-3x})(Zn_xTa_{2-x})O_7$ ($0.5 \le x \le 0.67$). The crystal structure gradually transformed from β to α with decreasing x. There was a (α + β) coexisting two phase region between the two single phase end-member regions. Clear evidence was obtained for a limited range of cubic pyrochlore solid solutions[8]; however, since there was also evidence that Bi_2O_3 volatilisation