

## Dielectric properties of $\text{Bi}_2\text{O}_3\text{-ZnO-Ta}_2\text{O}_5$ pyrochlore and zirconolite structure ceramics

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This letter reports the dielectric properties of the cubic pyrochlore  $(\text{Bi}_{3/4}\text{Zn}_{1/4})_2(\text{Zn}_{1/4}\text{Ta}_{3/4})_2\text{O}_7$ , monoclinic zirconolite  $\text{Bi}_2(\text{Zn}_{1/3}\text{Ta}_{2/3})_2\text{O}_7$ , and their composites in the temperature range of 10–400 K from  $10^2$  to  $\sim 10^{10}$  Hz. Composites with a near zero temperature coefficient of capacitance (TCC) consisting of the cubic pyrochlore and monoclinic zirconolite phases have been obtained. The observed microwave dielectric properties ( $\epsilon' \sim 60$ ,  $Q \sim 325$ , and  $\text{TCC} \sim 30$  ppm/K at  $\sim 5.1$  GHz) as well as their low sintering temperatures (950–1100 °C) show that the compounds are promising materials for recently developed microwave devices, which demand that dielectric ceramics can be cofired with silver electrodes. © 2003 American Institute of Physics. [DOI: 10.1063/1.1575933]

The compounds in the ternary system  $\text{Bi}_2\text{O}_3\text{-ZnO-Me}_2\text{O}_5$  (Me=Nb) have received much attention since the 1970's due to their low-temperature sintering characteristics.<sup>1–16</sup> At that moment, a main motivation for the study was to apply this type of materials to low sintering temperature multilayer capacitors at radio frequency. With recent developments in microwave devices, the compatibility of the ceramic processing (mainly sintering) with metal electrodes is emphasized, in which a moderate quality factor  $Q$  value is allowed.<sup>17,18</sup> For this application, the compounds in the ternary system  $\text{Bi}_2\text{O}_3\text{-ZnO-Me}_2\text{O}_5$  (Me=Nb and Ta) become promising candidates due to the advantage of the low-temperature sintering characteristic, which allow low temperature cofiring with silver electrodes.<sup>19,20</sup>

The most studied compounds in this ternary system are  $(\text{Bi}_{3/4}\text{Zn}_{1/4})_2(\text{Zn}_{1/4}\text{Me}_{3/4})_2\text{O}_7$  and  $\text{Bi}_2(\text{Zn}_{1/3}\text{Me}_{2/3})_2\text{O}_7$  (Me=Nb and Ta) with a cubic pyrochlore (hereafter denoted as C-BZT for Me=Ta and C-BZN for Me=Nb) and monoclinic zirconolite structure (hereafter denoted as M-BZT for Me=Ta and M-BZN for Me=Nb).<sup>21</sup> In addition, the composites consisting of the cubic pyrochlore and monoclinic zirconolite phases are also studied due to the technical interest that a near zero temperature coefficient (TCC) can be obtained from two-phase composites C-BZT + M-BZT, because of the sign of TCC of the dielectric constant for C-BZT and M-BZT is opposite.

The ternary system  $\text{Bi}_2\text{O}_3\text{-ZnO-Nb}_2\text{O}_5$  has been extensively studied.<sup>7–16</sup> However, less attention was paid to the system  $\text{Bi}_2\text{O}_3\text{-ZnO-Ta}_2\text{O}_5$ . In this letter, we report the dielectric properties of C-BZT, M-BZT, and their composites in the wide temperature and frequency range (450–10 K, 100 Hz– $\sim 8.7$  GHz).

The ceramic samples of  $(\text{Bi}_{3/4}\text{Zn}_{1/4})_2(\text{Zn}_{1/4}\text{Ta}_{3/4})_2\text{O}_7$ ,  $\text{Bi}_2(\text{Zn}_{1/3}\text{Ta}_{2/3})_2\text{O}_7$  and their composites,  $(1-x)\%$  C-BZT

+ $x\%$  M-BZT, with  $x=20, 60, 60,$  and  $74$ , respectively, were prepared by solid state reaction. The complex dielectric permittivity was measured using an HP 4284 A meter with an ac field of 1 V/mm. The temperature dependence of the dielectric properties was measured in the temperature range 10–423 K, while the specimen was being cooled or heated at a typical ramp rate of 1–2 K per min. TCC was calculated from the slope of dielectric constant in the temperature range of 120– $-55$  °C. The ring resonator and waveguide transmission techniques were adopted to measure the dielectric properties of the samples at microwave frequencies. The accuracy of the measurements was compared using resonant post and split cavity techniques. The details of sample preparation and measurement were described in Ref. 20.

The temperature dependence of the dielectric constant ( $\epsilon'$ ) and dissipation factor ( $\tan \delta$ ) for C-BZT and M-BZT at radio frequency is shown in Figs. 1(a) and 1(f). For the cubic pyrochlore structure C-BZT, with decreasing temperature,  $\epsilon'$  first increases slightly, then decreases quickly. An obvious dielectric relaxation behavior is observed for both  $\epsilon'$  and  $\tan \delta$ . For monoclinic zirconolite structure M-BZT, with decreasing temperature,  $\epsilon'$  continuously decreases at a slow rate. Neither noticeable drops nor frequency dispersions within the radio frequencies range are observed in  $\epsilon'$  for M-BZT. The temperature dependence of the dielectric constant ( $\epsilon'$ ) and dissipation factor ( $\tan \delta$ ) for C-BZT at a microwave frequency 1.5 GHz is shown in Fig. 2 in the temperature range, which is a most practical application temperature range. It shows that the overall tendency for the temperature coefficient of dielectric constant of C-BZT is negative, and the one for M-BZT is negative. The dielectric loss behaves in the same way.

The dielectric measurement reveals that,  $\epsilon' \sim 73$ , and  $\tan \delta = 0.007$  (quality factor  $Q = 143$ ) at 1 MHz;  $\epsilon' \sim 64$ ,  $\tan \delta = 0.018$  ( $Q = 56$ ) at  $\sim 5.2$  GHz at room temperature, with  $\text{TCC} = -172$  ppm/K (1 MHz) for C-BZT. For M-BZT,  $\epsilon' \sim 61$ , and  $\tan \delta = 0.001$  ( $Q = 1000$ ) at 1 MHz;  $\epsilon' \sim 60.4$ ,

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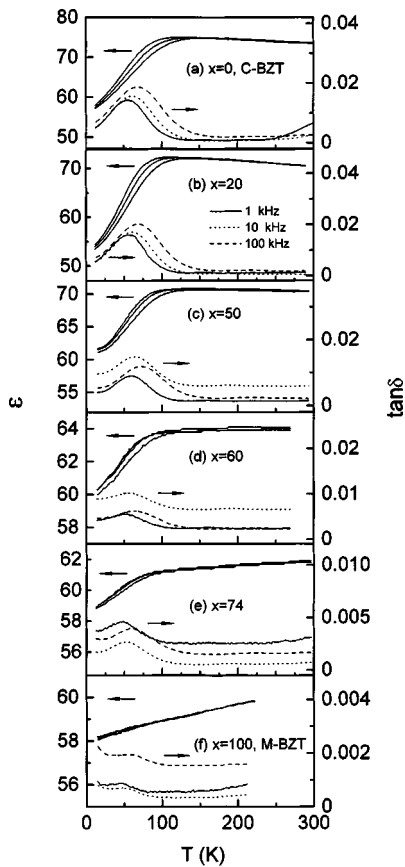


FIG. 1. Temperature dependence of  $\epsilon$  and  $\tan \delta$  for C-BZT ( $x=0$ ), M-BZT ( $x=100$ ), and composites with  $x=20, 50, 60$ , and  $74$ , at  $1, 10$ , and  $100$  kHz.

and  $\tan \delta=0.0014$  ( $Q=710$ ) at  $\sim 6$  GHz with  $TCC=+60$  ppm/K ( $1$  MHz). As the signs of TCC for C-BZT and M-BZT are opposite, it is expected that a near zero TCC can be obtained from a two-phase composite, C-BZT + M-BZT.

The temperature dependence of the dielectric behavior for the composites,  $(1-x)\%$  C-BZT +  $x\%$  M-BZT, with  $x=20, 40, 50, 74$ , was also measured and is shown in Figs. 1(b)–1(e). It can be clearly seen with increasing content  $x$  of the monoclinic zirconolite M-BZT, the dielectric step ( $\Delta\epsilon$ ) decreases, from  $\Delta\epsilon=18$  for pure cubic pyrochlore C-BZT ( $x=0$ ) to  $\Delta\epsilon\sim 2.5$  for  $x=74$ , and  $\Delta\epsilon\sim 0$  for pure monoclinic zirconolite M-BZT ( $x=100$ ). TCC of the samples

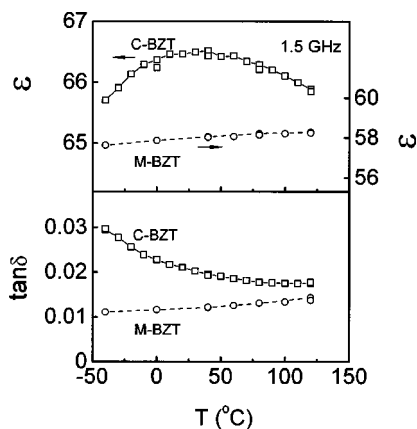


FIG. 2. Temperature dependence of  $\epsilon$  and  $\tan \delta$  for C-BZT ( $x=0$ ) and M-BZT ( $x=100$ ) at  $1.5$  GHz.

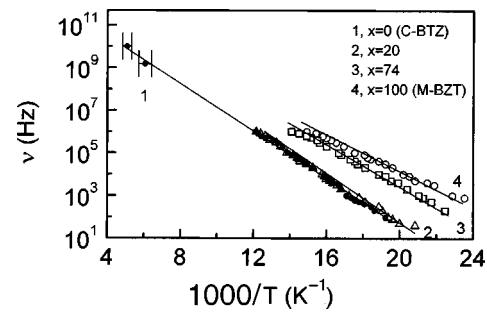


FIG. 3. Relaxation rate  $\nu$  vs  $1/T$  curve of the samples. Open circles: experimental data; Lines: fitting to the Arrhenius law.

increases from  $-172$  ppm/K at  $x=0$ , to  $TCC\sim +20$  ppm/K at  $x=74$ , and to  $TCC=+60$  ppm/K at  $x=100$ . In addition, the quality factor  $Q$  is reasonably high, which is  $\sim 500$  at  $1$  MHz, and  $\sim 325$  at  $\sim 5.1$  GHz. These results indicate that the composites C-BZT and M-BZT indeed provide a technical advantage for obtaining a near zero TCC.

The relaxation rate  $\nu$  as a function of the inverse temperature ( $1/T$ ) for C-BZT is plotted in Fig. 3. The data can be well fitted to the Arrhenius law

$$\nu = \nu_0 \exp(U/k_B T), \tag{1}$$

where  $\nu_0$  is the attempt frequency,  $U$  is the activation energy for relaxation, and  $T$  is the temperature. The fit parameters are  $U=0.11\pm 0.004$  eV and  $\nu_0\sim 4\times 10^{12}$  Hz.

The dielectric relaxation rate versus  $1/T$  for the composites  $(1-x)\%$  C-BZT +  $x\%$  M-BZT, with  $x=20, 50, 60$ , and  $74$ , respectively, is also shown in Fig. 3, which fits well to the Arrhenius law. The activation energy  $U$  varies within  $0.1\pm 0.015$  eV for all samples. This implies that the dielectric relaxation has the same physical origin for all samples, that is, it comes from the dielectric relaxation of C-BZT, which is attributed to the reorientation of the “seventh” oxygen with Bi and/or Zn cations dipoles of cubic pyrochlore  $(\text{Bi}_{3/4}\text{Zn}_{1/4})_2(\text{Zn}_{1/4}\text{Me}_{3/4})_2\text{O}_7$  under external ac fields in our previous work.<sup>22</sup>

From the results of the phase assemblages and crystal-line structure analyses of the samples,  $(1-x)\%$  C-BZT(N) +  $x\%$  M-BZT(N), with  $x=0, 20, 50, 60, 74$ , and  $100$ , respectively, by x-ray diffraction,<sup>20</sup> we know that between the two end compositions, i.e., as  $20\leq x\leq 74$ , the compositions belong to diphasic composites including C-BZT phase and M-BZT phase.

In addition, an interesting phenomenon we observed in M-BZT is that, although no visible drop in  $\epsilon$  can be seen, a slight but visible relaxation process can be observed in  $\tan \delta$ , as shown in Fig. 1(f). The result means that  $\tan \delta$  is a more sensitive parameter reflecting the dielectric polarization responses. A similar phenomenon has been observed in  $\text{SrTiO}_3$  thin films.<sup>23</sup> Currently, the physical nature of the  $\tan \delta$  peak is uncertain. An explanation is, although M-BZT is a nominally pure single phase examined by x-ray diffraction, it may include a small amount of C-BZT phase, which leads to the appearance of a slight dielectric relaxation in  $\tan \delta$ . Indeed, with careful inspection in  $\tan \delta$  for other compositions, as shown in Fig. 1(f), it can be seen that the  $\tan \delta$  peak, for example at  $10$  kHz, occurs at almost the same temperature for all samples, with increasing  $x$  from  $0$  to  $100$ . This implies

that  $\tan \delta$  peaks may be caused by C-BZT phase, which is small in quantity but exists even in nominally pure monoclinic phase as  $x=100$ .

However, a possibility that the dielectric relaxation does occur in the zirconolite structure M-BZT (i.e., Me=Ta) cannot be excluded at this moment. In fact, in addition to the  $\tan \delta$  peak at  $\sim 70$  K, a quick increase in  $\tan \delta$  below  $\sim 50$  K in M-BZT is also visible. A similar decrease (increase) in  $\epsilon$  ( $\tan \delta$ ) below 50 K in the zirconolite structure M-BZN (i.e., Me=Nb)<sup>24</sup> has been also observed. This implies that an additional polarization mechanism might exist at even lower temperatures. It is an interesting subject to study in detail the dielectric polarization mechanism in the zirconolite structure system.

In conclusion, we have reported the microwave frequency dielectric properties and the dielectric relaxation process in C-BZT and M-BZT ceramics. The observed microwave dielectric properties are,  $\epsilon' \sim 61.4$  and  $Q \sim 56$  at  $\sim 5.2$  GHz with TCC =  $-172$  ppm/K (1 MHz) for C-BZT;  $\epsilon' \sim 60.4$  and  $Q = 710$  at  $\sim 6$  GHz with TCC =  $+60$  ppm/K (1 MHz) for M-BZT and  $\epsilon' \sim 60$  and  $Q \sim 325$ , at  $\sim 5.1$  GHz with TCC =  $\sim 30$  ppm/K (1 MHz) for the composite. The microwave dielectric properties, along with low sintering temperatures (950–1100 °C) show that the compounds and their composites are promising materials for recently developed microwave devices. Low temperature dielectric relaxation behavior for cubic C-BZT was observed, whose relaxation rate follows well the Arrhenius law in the wide frequency range  $10^2 - \sim 10^{10}$  Hz, and is tentatively attributed to the reorientation of dipoles formed by the seventh oxygen with the A-site cations (i.e., Bi and/or Zn) of pyrochlore C-BZT.

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