Ceramics International 31 (2005) 349–351

CERAMICS INTERNATIONAL

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Short communication

Dielectric properties of LTNO ceramics and LTNO/PVDF composites

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Received 24 November 2003; received in revised form 31 March 2004; accepted 12 May 2004
Available online 10 August 2004

Abstract

The sol–gel method was used to prepare Li and Ti co-doped NiO (LTNO) ceramics with high dielectric constant due to the boundary-layer capacitor (BLC) structure. The dielectric properties of the LTNO/polyvinylidene fluoride (PVDF) composites were also studied along with the change of frequency with the volume fraction of LTNO fillers. The low dielectric constant of the LNTO/PVDF composites is close to the destruction of the BLC microstructure in LTNO ceramics after their grinding into fine powders. Ti content has been found to affect the dielectric properties of LTNO ceramic and LTNO/PVDF composites.

Keywords: B. Composites; C. Dielectric properties; C. Electrical conductivity; LTNO

Much attention has been paid to high dielectric constant materials since they have been used as important devices in microelectrics, such as capacitors and memory devices [1–3]. Zhang et al. [4,5] have recently reported that a flexible polymer composite with high dielectric constant could act as artificial muscles in future medical treatment, 'smart skins' for drag reduction, and in microfluidic systems for drug delivery. The current method for improving the dielectric constant of the polymers is still to disperse some high dielectric constant ceramic powders into the polymer to form 0–3 type composites. Therefore, it is very important to choose high dielectric constant ceramic fillers and suitable processing conditions for polymer composite preparation in order to disperse the ceramic powders into polymer uniformly. In this paper, Li and Ti co-doped NiO ceramics (LTNO) with a giant dielectric constant were prepared using the sol–gel and sintering process as previously reported [1,6]. This material is lead-free compared to perovskite-like ceramics, such as PMN-PT, which might release harmful lead gas during sintering. Indeed, lead-free materials with high dielectric constant values are increasingly attractive [1,2,6]. In addition, the ac dielectric behavior of LTNO/PVDF composites was studied carefully using a HP 4194A impendence analyzer.

Two kinds of LTNO, i.e., $Li_{0.1}(Ti_{0.02}Ni_{0.98})_{0.9}O$ (LTNO-1) and $Li_{0.1}(Ti_{0.05}Ni_{0.95})_{0.9}O$ (LTNO-2), were prepared using the sol–gel and sintering process as reported in references [1,6]. LTNO bulk ceramics obtained by sintering at 1250 °C for 4 h were ground into fine ceramic powders. Then LTNO/PVDF composites were prepared by a simple mixture processing and hot molded at about 200 °C under 10 MPa. The final disk-shaped samples were 12 mm in diameter and about 1 mm in thickness.

Fig. 1 shows the dielectric properties of two kinds of LTNO ceramics as a function of frequency. The dielectric constant values of the LTNO ceramics are extremely high ($\varepsilon \approx 3 \times 10^4$ to 8×10^4) at low frequency. The giant dielectric constant is ascribed to the boundary-layer capacitors (BLC), which is different from ferroelectric relaxor effect. The dielectric constant of the LTNO-2 ceramic is lower than that of LTNO-1, which can be explained due to high Ti content in the LTNO-2.

The dielectric constant of the LTNO/PVDF composites measured at 2 kHz increases with the increase in the LTNO content (Fig. 2). The dielectric constant of the LTNO-1/

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0272-8842/$30.00
doi:10.1016/j.ceramint.2004.05.008

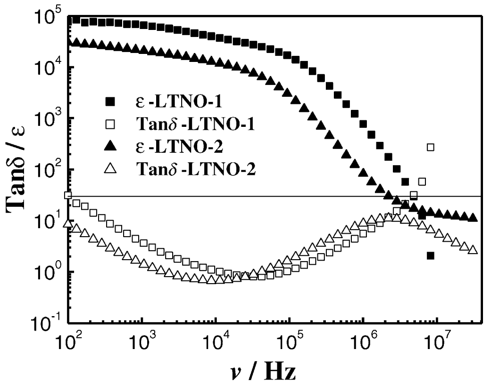

Fig. 1. Dependence of ε (filled symbols) and tan δ (open symbols) of two kinds of LTNO ceramics on frequency.

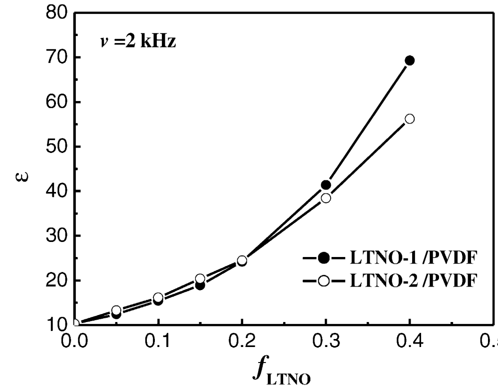

Fig. 2. Dependence of ε of two kinds of LTNO/PVDF composites on the volume fraction of LTNO fillers, f_{LTNO}.

PVDF composites is larger than that of LTNO-2/PVDF composites at high LTNO contents, which can be explained due to a relatively high dielectric constant in the LTNO-1 ceramic itself. The dielectric constant of the LNTO/PVDF composites decreases slowly at low frequencies and drops rapidly after 10^5 Hz, as shown in Fig. 3 The effective dielectric constants of two kinds of composites, i.e., LTNO-1/PVDF and LTNO-2/PVDF with 0.4 volume fraction of LTNO fillers are 80 and 70 at 100 Hz, respectively. The dielectric constant values are still low at such a high LTNO content. In the LTNO [1,6], the introduction of Ni^{2+} vacancies and/or doping with monovalent cations Li^+ can cause considerable increase in the conductivity. Ti dopant is rich on the grain boundaries but low within the grains. Thus the interiors of the grains are semiconducting (i.e., Li-doped NiO), while the shells of the grains are Ti-rich insulating boundaries, which is the feature of the BLC. Therefore, the effective dielectric constants of two kinds of LTNO ceramics are very high as shown in Fig. 1. However, such a giant dielectric constant disappears due to the destruction of the

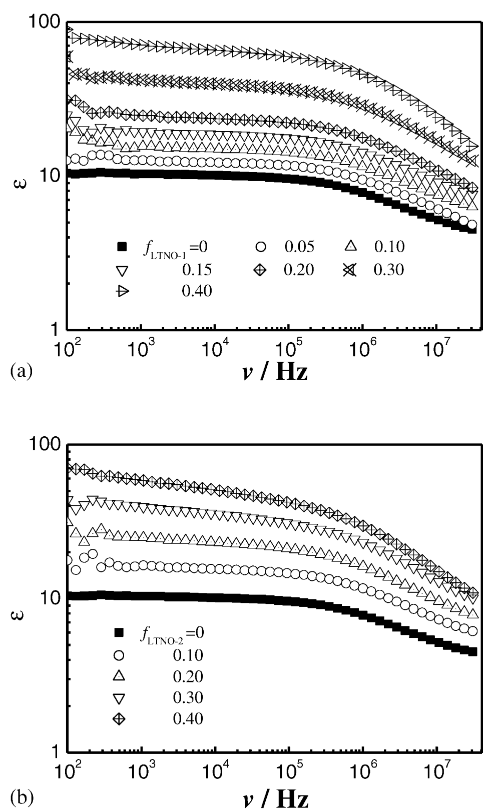

Fig. 3. Dependence of ε of the LTNO-1/PVDF (a) and LTNO-2/PVDF (b) composites on frequency.

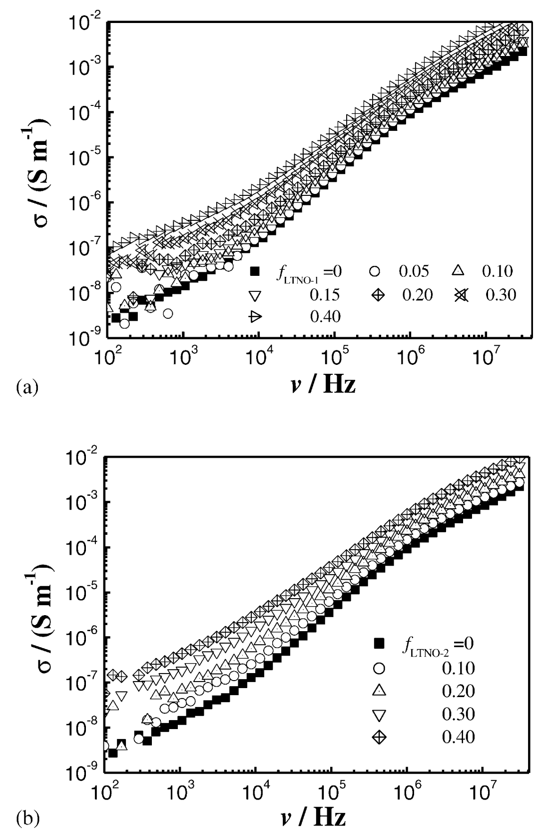

Fig. 4. Dependence of σ of the LTNO-1/PVDF (a) and LTNO-2/PVDF (b) composites on frequency.

BLC microstructure after grinding the sintered LTNO bulk ceramics into fine powders. So the effective dielectric constants of the LTNO/PVDF composites are low as shown in Figs. 2 and 3.

The conductivity of LTNO/PVDF composites increases with increasing frequency and the LTNO content, Fig. 4. However, no obvious change in conductivity was seen with an increase in the LTNO content. The results show that the percolation does not appear even if the volume fraction of the LTNO filler is up to 0.4, which might be ascribed to the poor conductivity of the LTNO fillers.

In conclusion, LTNO ceramics with high dielectric constant were prepared using the sol–gel and sintering processes. The low dielectric constant of the LNTO/PVDF composites is due to the destruction of the BLC microstructure in LTNO ceramics after grinding the sintered LTNO bulk ceramics into fine powders. Ti content was found to affect the dielectric constant of LTNO ceramic and LTNO/PVDF composites.

Acknowledgements

This work was financially supported by the NSF of China (grant 50373024) and the Ministry of Science and Technology of China through 973-Project under 2002CB613303.

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