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Disappearance and recovery of colossal permittivity in (Nb + Mn) co-doped TiO_2

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ABSTRACT

We investigate the effects of doping and annealing on the dielectric properties of metal ions doped TiO_2 ceramics. Colossal permittivity (CP) above 10^4 was observed in single Nb ion doped TiO_2, which was dominated by electron transport related interfacial polarization. Moreover, the CP can be dropped to 120 when simultaneously introducing Mn ion into the sample. The disappearance of CP behaviors maybe due to the multivalence of Mn which would inhibit the reduction of Ti^{4+} to Ti^{3+}, and thus reduce delocalized electrons. Interestingly, the CP was recovered for the (Nb + Mn) co-doped TiO_2 after post-sintering heat treatment in N_2 atmosphere. The recovery of CP in the sample after annealing can be ascribed to the semiconducting grain and the insulating grain boundary, according to impedance spectroscopy. We therefore believe that this work can help us understand the mechanism of CP from a new perspective.

1. Introduction

Colossal permittivity (CP) ($\varepsilon_r > 10^4$) and low loss (mostly < 0.05) were found in metal ion co-doped rutile TiO_2 ceramics by Liu's group [1]. The dielectric properties are almost independent of frequency and temperature over a wide frequency and temperature range, which is superior to previously studied CP materials, such as ferroelectrics [2], $CaCu_3Ti_4O_{12}$ (CCTO) [3,4], doped NiO [5], and $La_{15/8}Sr_{1/8}NiO_4$ [6]. Therefore, the CP properties based on co-doped TiO_2 have attracted considerable attention due to its potential application in high-performance capacitors, miniature electronics and high-density energy storage. Effects of doped elements on the dielectric properties of TiO_2 and the origin of their CP are the two concerns which would play vital roles in practical application of the CP materials. Generally, donor doping in TiO_2 is considered to raise the permittivity due to the creation of delocalized electrons by reducing Ti^{4+} to Ti^{3+}. Meanwhile, acceptor doping lowers the dielectric losses because it is regarded as providing a local oxygen-deficient environment to hold back the delocalized electrons, according to the formation of electron-pinned defect-dipole (EPDD). Up to now, CP behaviors have been confirmed in TiO_2 ceramics by co-doping acceptor ions (trivalent ions: Al, Ga, In, or rare earth ions; bivalent ions: Zn, or alkaline earth ions) or isovalent ion (Zr) and donor elements (pentavalent ions: Nb or Ta) [7–21]. However, the mechanism is still not fully understood. Other mechanisms have also been presented except for EPDD, including interface effect caused by internal barrier layer capacitor (IBLC) effect [10,22], the electrode effect [11], hopping conductivity [23], surface barrier layer effect [24], as well microscopic inhomogeneities and polaronic relaxation [25]. Those explanations may be relevant to different synthesis processes or combination of co-doped ions.

Manganese (Mn) has been widely used as doping element for the ceramic capacitors. Its doping into perovskite oxide like (Ba, Sr)TiO_3 [26], Ba(Zr, Ti)O_3 [27] has shown positive effects in reducing the dielectric loss, and enhancing the dielectric constant. It could be mainly attributed to the decrease in electron concentration and oxygen vacancies and the reorientation of the defect complex. By contrast, Mn doping can suppress the dielectric permittivity in CCTO by up to two orders of magnitude [28]. The observation was explained by the decrease of potential barrier height at the grain boundary and charge compensation for the conduction electrons caused by the Mn doping [28]. However, Mn-doped CP TiO_2 ceramic has not yet been reported. Therefore, it would be quite intriguing to investigate the Mn doping effect on the dielectric properties of TiO_2 with different possible mechanisms. In this work, the disappearance of the CP is found in the as-fabricated (Nb + Mn) co-doped TiO_2 ceramics. It is intriguing that the CP can be recovered by annealing the ceramics in N_2 atmosphere. The relative mechanisms are discussed based on defect dipole and IBLC effect.

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2. Experimental procedure

(Nb + Mn) co-doped TiO_2 ceramics were prepared by a conventional solid state reaction method. The starting raw materials contain rutile TiO_2 (99.99%), Nb_2O_5 (99.99%) and MnO (99.99%). These powders were weighted according to a composition of $(Nb_{0.5}Mn_{0.5})_xTi_{1-x}O_2$ (x = 0.25%, 0.5%, 1%, 2%) and then milled by ball-milling with ZrO_2 balls for 6 h ~ 8 h in ethanol. The mixed slurry was heated to evaporate ethanol. Then the dried powders were calcined at 1000 °C for 4 h in air with a heating rate of 3 °C/min. After this pre-sintering process, the samples were reground and the dried powders were pressed into pellets by uniaxial compression. These ceramic biscuits with a diameter of 10 mm and a thickness of 1.5 mm were fired at 650 °C for 6 h in air to remove the organic polyvinyl alcohol binder. Finally, the samples were sintered at 1400 °C for 10 h by a heating rate of 3 °C/min and then cooled down to room temperature. In addition, the doping level of x = 2% sample was post-sintered at 1400 °C for 5 h in N_2 atmosphere. The phase of co-doped TiO_2 ceramics was confirmed using an X-ray diffraction technique (XRD, DMAX1400, Rigaku), and Raman spectroscopy (InVia, Renishaw) excited by 514 nm laser line. The microstructures and elemental mapping of the samples were characterized using scanning electron microscopy (SEM, MAIA3, Tescan). X-ray photoelectron spectroscopy (XPS) was used to analyze the valence states of elements in the ceramics. A monochromatic aluminium Kα radiation source with energy of 1486.8 eV was used in Thermo SCIENTIFIC ESCALAB 250Xi system (Escalab 250Xi; Thermo Scientific, Leicestershire, UK). Room temperature dielectric properties and the impedance spectroscopy were measured using a Partulab HDMS-1000 high-temperature dielectric measurement system (Wuhan Partulab Technology Co. Ltd, China) combined with an Agilent 4294A Precision Impedance Analyzer (Agilent Technologies Inc., USA).

3. Results and discussion

Fig. 1 shows the XRD patterns of all sintered $(Nb_{0.5}Mn_{0.5})_xTi_{1-x}O_2$ ceramics in the 2θ range of 20–75°. The diffraction peaks of all samples can be indexed to the rutile TiO_2 (JCPDS 21-1276). No peaks of secondary phases were observed in the XRD patterns and all samples exhibit a rutile phase structure, indicating Nb and Mn elements have incorporated into the TiO_2 lattices to form homogenous solid solutions. Generally, the presence of secondary phases is not beneficial to the dielectric property, which has been confirmed in the (Bi + Nb) co-doped TiO_2 and other microwave dielectric materials system [7,29]. Therefore, a small amount of Mn ions was doped into TiO_2 in order to exclude

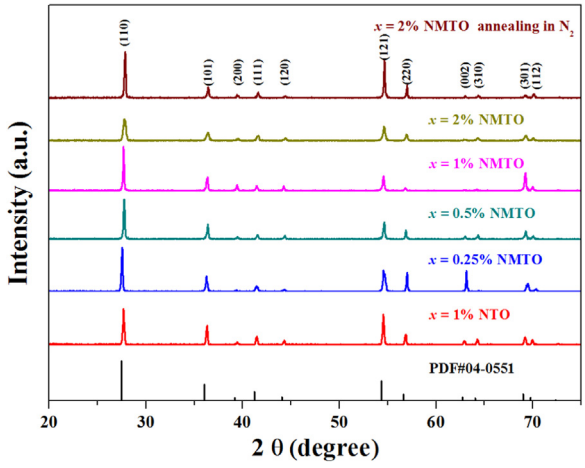

Fig. 1. XRD patterns of 1% only Nb-doped TiO_2(NTO), $(Nb_{0.5}Mn_{0.5})_xTi_{1-x}O_2$ (NMTO, x = 0.25%, 0.5%, 1%, 2%), and x = 2% after post-sintering in N_2 ceramics.

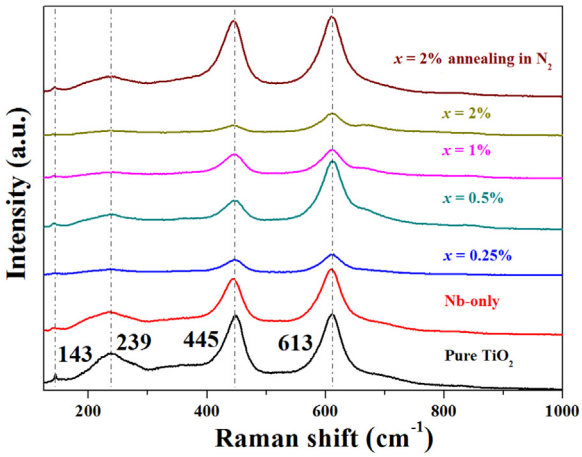

Fig. 2. Raman spectra of pure TiO_2, 1% only Nb-doped TiO_2, $(Mn_{0.5}Nb_{0.5})_xTi_{1-x}O_2$ (x = 0.25%, 0.5%, 1%, 2%), and x = 2% after post-sintering in N_2 ceramics.

the impact of secondary phase in colossal permittivity. The Raman spectra of the sintered (Nb + Mn) co-doped TiO_2 ceramics were recorded in the range of 100–1000 cm^{-1}, as shown in Fig. 2. Four Raman active fundamentals were found in these samples, corresponding to B_{1g} (143 cm^{-1}), E_g (447 cm^{-1}), A_{1g} (612 cm^{-1}), and B_{2g} (826 cm^{-1}), respectively [7]. It is further confirmed that the existence of the rutile phase because of the appearance of B_{1g}, E_g and A_{1g} modes in all compositions. Besides, the 239 cm^{-1} peak is obviously visible in the samples, which is a multi-phonon peak for second-order effect [30]. The 239 cm^{-1} peak is closely related to the internal stress and partial reduction in the TiO_2 grains caused by doping elements with different radii into the host lattice. Thus, the results from Raman spectra suggest the pure rutile TiO_2 of the doped ceramics, which is compatible with the analysis of XRD patterns.

The SEM micrographs of our sintered ceramic samples are shown in Fig. 3(a) ~ (f). For the ceramics of (Nb + Mn) co-doping, the grains with an obvious bimodal distribution are tightly arranged. Both larger coarse grains and smaller ones exhibit a gradual decrease with the increasing doping constants from 0.25% to 2%. However, the grains grow significantly after re-sintering them in N_2 atmosphere. Typically, for the doping level of 2%, the size of larger coarse grains is doubled to around 40 μm while that of smaller ones is almost tripled to about 20 μm. Normally, the grain growth is related to the liquid phase sintering mechanism, which means the mass transport across the grain boundary by diffusion of ions or atoms [9,31]. For the co-doped TiO_2 ceramics herein, the doping Mn elements may inhibit the grain boundary movement, and resulting in the decrease of grain size [32]. However, the different sintering atmosphere can give rise to the disparity of grain size at the same temperature [33]. The grain for the sample grows larger after sintering in N_2, which is similar to the Ba doped $Sr_{0.97}Sm_{0.02}TiO_3$ ceramics [33]. To further characterize the elemental composition and distributions, the element mapping of (Nb + Mn) co-doped TiO_2 is conducted, as presented in Fig. 4. It can be seen that the elements of Nb, Mn, Ti, and O are homogeneously distributed across the grains and grain boundaries before and after annealing in N_2 atmosphere. This result indicates no second phase in our co-doped TiO_2 ceramics, which is coincident with the XRD and Raman results.

As shown in the Fig. 5, the dielectric properties of (Nb + Mn) co-doped TiO_2 ceramics with different compositions are measured at frequencies ranging from 100 Hz to 1 MHz. It is widely accepted that TiO_2 have the largest dielectric constant among the single oxides and it can also improve the permittivity by adding it into other dielectric ceramics [1,34]. Singly doping Nb can significantly increase the permittivity (beyond 10^4) of the host TiO_2. It can be attributed to a typical interfacial polarization effect that space charges are accumulated at grain