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Improve the dielectric properties of $PrSrNi_{0.8}Mn_{0.2}O_4$ compounds by longer mechanical milling

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ABSTRACT

Structural and dielectric properties of $PrSrNi_{0.8}Mn_{0.2}O_4$ ceramics elaborated by a rapid method combining mechanical milling and heat treatment were studied for the first time. The raw materials are milled at different times ($t_{mil} = 0$, 5, 10, 20 and 30 h) and annealed at 1300 °C for 8 h to produce a revealed $PrSrNi_{0.8}Mn_{0.2}O_4$ single phase, exhibiting tetragonal structure with space group *I4/mmm*. This result was confirmed by using the TEM/ED pattern for sample milled at 30 h using the [001] orientation. The corresponding lattice images show a well-ordered compound, indicating the absence of stacking faults and the growth of the crystallites. Giant dielectric response was observed in these ceramics, and only one dielectric relaxation was found on the curve of a dielectric constant as a function of the temperature. The dielectric loss drops with increasing milling time. For 30 h milling it is divided by 100 at room temperature for low frequencies compared with 5 h milling. An equivalent circuit [R-C][R-CPE] was used to fit the experimental data and provide the activation energy of the thermally activated relaxation. Using the same nominal composition, the milling time has a major effect on the dielectric constant by significantly reducing the losses.

1. Introduction

After the discovery of temperature-stable giant dielectric constant in $CaCu_3Ti_4O_{12}$ (CCTO), compounds with giant dielectric constants (GDC) received scientific attention for their potential application in the field of microelectronics [1–6]. The electrode/ceramic interface and grain boundary play a major role in the giant dielectric response of $CaCu_3Ti_4O_{12}$. The value of the dielectric constant measured in mono-crystalline $CaCu_3Ti_4O_{12}$, which is close to the poly-crystalline ceramics value, shows that the giant dielectric response should also have other origins [7,8]. Among these materials, the nickelates with K_2NiF_4 structures are highlighted because of their temperature-stable giant dielectric responses at high frequencies. Considerable dielectric response can be measured up to gigahertzes at room temperature [9,10]. In the particular case of $Ln_{1.5}Sr_{0.5}NiO_4$ceramic (Ln = La, Nd and Sm) authors [11,12] have measured GDR up to high frequencies. The most promising dielectric properties were observed in $Sm_{1.5}Sr_{0.5}NiO_4$ ceramics, where the dielectric constant is about 10^5 at high frequency (5 MHz) and the dielectric loss about 10^{-1}. The Nickelates system has been well received by industry in recent years. This is due to their enormous dielectric permittivity. These compounds are used worldwide in advanced technology. The observation of unusual, high dielectric loss ($\tan\delta$) at room temperature has focused attention on the possible reasons for this behavior, with the objective to understand the mechanism and, ultimately, to reduce that loss. A large effort was devoted to the suppression of electrical conductivity induced by using Mn-substitution in transition-metal oxides. Li et al. [13] have reported the decrease of bulk conductivity in Mn-doped CCTO. Qin et al. [14] have reported that the introduction of Mn ions into $Lu_2Fe_2Fe_{1-x}Mn_xO_7$ can efficiently suppress the electrical conducting leakage. After analysing the relationship between the electrical resistivity and Mn^{3+} content in $La_{0.7}Ca_{0.3}MnO_{3-\delta}$ thin films, Teresa et al. [15] found that the polaron binding-energy is proportional to the Mn-O octahedral distortion.

There are several preparation methods for obtaining the compounds that interest us. However, the condition and the preparation method are closely associated with the extrinsic properties of materials and can greatly affect their physical properties, especially

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the character of the electrical transport. In recent years, the mechanical alloying method has been used for various kinds of materials, such as alloys or mixed oxides (ABO_3). To the best of our knowledge, we are the first authors to use this method to elaborate oxides derived from K_2NiF_4 perovskite-type. High-energy ball milling [16,17] is a very popular technique thanks to the low-cost, high efficiency and low temperature synthesis it offers. This method was extensively used for the synthesis of rare-earth permanent magnets and intermetallic compounds [18,19]. Also, the mechanical ball milling technique is an important method in powder metallurgy because of its high flexibility, simple control of process parameters, and ability to produce a wide range of materials with fine particles. Moreover, mechanical ball milling technique has also been used to produce commercially important alloys, particularly those with a very high melting point [20]. Synthesis of these materials has been extensively studied using different routes, but the mechano-chemical method itself (used not only as activation technique) is not yet common [21]. Mechanochemistry is a relative simple process that uses high-energy ball mills and permits production of nanostructured mixed oxides [22]. The mechanical energy coming from impact and shear forces by application of a high frequency movement is transferred to the powder, inducing solid state chemical reactions. One of the most important advantages of mechano-chemistry is its ability to produce large quantities of material at room temperature and in a relatively short time. Previously, we worked on dielectric and microstructure characterization on $LaSrNi_{1-x}Mn_xO_4$ ceramics obtained by high-energy mechanical milling method [23,24]. We revealed a large dielectric constant ~10^5 at room temperature but a modest dielectric loss, showing that for potential applications this compound has to be modified in order to optimize its properties. In a previous work [25] we substitute Ni by Al in $La_{1.6}Sr_{0.4}NiO_4$ compound elaborated by the Pechini method and then generate a remarkable variation of the dielectric properties. However, the measured dielectric losses show that this compound still needs to be optimized. These promising results encouraged us to continue the optimisation of the dielectric properties of this family of compounds by taking advantage of the super-exchange and double-exchange interactions between Ni^{2+}/Ni^{3+} and Mn^{3+}/Mn^{4+} ions when the material is synthesized by high-energy ball milling. In order to understand the effect of milling time on the structural and physical properties, as well as on the dielectric properties, the compound $PrSrNi_{0.8}Mn_{0.2}O_4$ was prepared using various process durations.

In this work, we introduce the high-energy ball milling method to synthesize the $PrSrNi_{0.8}Mn_{0.2}O_4$ layered perovskite and then discuss optimal milling efficiency. We also investigate the structural properties of the as-milled powders. The structural and dielectric characteristics of the samples were studied after high-temperature sintering.

2. Experimental procedures

MnO_2 (purity >99.9%, Particle size <10 μm), Pr_6O_{11} (purity >99.9%, Particle size <0.2 μm) NiO (purity >99.9%, particle size <44 μm) and SrO powders were used as raw materials. The last one was obtained from calcination of $SrCO_3$ (Aldrich 98%, Particle size 1–2 μm)) at 1200 °C for 12 h. The possible chemical reaction is given by Eq [1].:

$$1/6Pr_6O_{11} + SrO + 0.8NiO + 0.2MnO_2 \rightarrow PrSrNi_{0.8}Mn_{0.2}O_{4\pm\delta} \quad (1)$$

These oxides were mixed with respect to the molar ratio of cations. The powder mixture was mechanically activated using a planetary ball mill (model Micro-Mill Pulverisette 7, Fritsch). The powder-to ball weight ratio and the rotational speed were 5:1 and 600 rpm, respectively. To prevent the heating and sticking of the powder to the container walls and balls, as well as powder agglomeration during the process, the milling sequence was 10 min of milling followed by a 5 min stop period. Milling was conducted in the ambient atmosphere for 5, 10, 20 and 30 h milling. 1 g of each milled sample was then uniaxially pressed into pellets of 12 × 5 mm at room temperature and sintered in air at 1300 °C for 8 h with a heating rate of 10 °C min^{-1} and free cooling. The structural changes of the milled samples were investigated by X-ray diffraction (XRD) by means of a Bruker D8 Advance diffractometer in a (2θ) geometry using CuK_α radiation ($\lambda = 0.15406$ nm). The microstructural parameters were taken out from the refinement of the XRD patterns by using the MAUD program [26], which is based on the Rietveld method.

The phase purity of the samples after sintering was confirmed by X-ray powder diffraction. The XRD patterns were collected in the range of 10–90° with a step size of 0.05°. The structure was analysed by Rietveld method using the FullProf program, and a pseudo-Voigt profile function with preferred orientation correction [27,28]. X-Ray photoelectron spectroscopy analysis was done using PHI Versaprobe 5000 apparatus with $AlK_{\alpha1}$ monochromated line (energy of 1486.7 eV, power of 50 W and X-Ray spot diameter of 200 μm). The C1s peak from pollution (at 284.8 eV) was considered for the energy calibration. During measurements, the residual pressure of the analysis chamber was maintained below 10^{-7} Pa. Spectra were treated with the Casa software package. The microstructure was studied by transmission electron microscope (TEM) at room temperature and the stochiometric ratio was detected by energy dispersive X-ray spectroscopy (EDS). The dielectric properties of these ceramics were investigated with a dielectric spectrometer (HP 4284) over a wide range of temperatures (80–450 K) and frequencies (100 Hz–1 MHz) with a heating rate of 1 K min^{-1}. Sputtered platinum was used as electrodes.

3. Results and discussion

3.1. Milled powder before sintering

Fig. 1 presents the XRD patterns showing the evolution of the crystalline structure of the powder for 5, 10, 20 and 30 h milling. The X-ray pattern of the unmilled powder mixture is also presented in the same figure for comparison. Before milling, the recorded peaks correspond to the free oxides Pr_6O_{11} [29], SrO [30], MnO_2 [31] and NiO [32]. The vanishing and/or the appearance of some peaks can be assigned to the mixing of the elemental powders and, therefore, to the formation of new solid solutions [33]. After 5 h of milling, the peaks corresponding to the initial oxides became

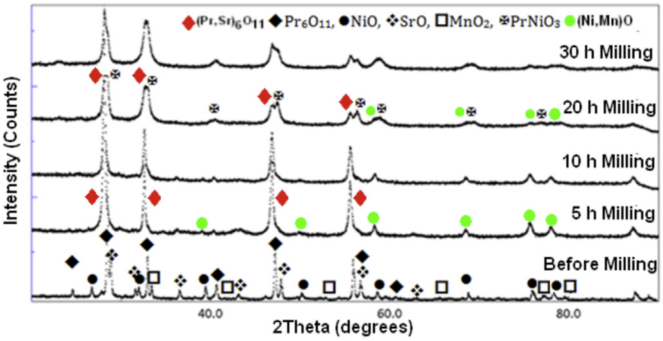

Fig. 1. XRD of powders milled at different times (0 h, 5 h, 10 h, 20 h and 30 h), before sintering.