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The magnetic and electric properties of PZT-PFW-PFN ceramics

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ABSTRACT

The ceramic samples of solid solution (1-*x*)[0.5($PbZr_{0.53}Ti_{0.47}O_3$)-0.5($PbFe_{2/3}W_{1/3}O_3$)]-*x*($PbFe_{1/2}Nb_{1/2}O_3$) [i.e. (1-*x*)[0.5(PZT-PFW)]-*x*PFN with $x = 0$; 0.1; 0.2 have been obtained by conventional ceramic technology with calcination procedure and free final sintering (FS). This work presents SEM, XRD, dielectric, ferroelectric, magnetic and electric conductivity measurements. The magnetic properties and electric conductivity were investigated at low temperatures, whereas the dielectric properties – at higher temperatures and various frequencies.

XRD study confirmed that the obtained solid solutions have a perovskite structure without foreign phases. The magnetic tests show that at temperature 2 K weak ferromagnetism is observed in all samples, while at higher temperatures all samples of the investigated solid solutions exhibit $M(H)$ dependencies typical for paramagnetic materials. The analysis of the results of measurements of d.c. electrical conductivity, as well as dielectric permittivity at low temperatures, confirmed the presence of characteristic anomalies on the temperature curves.

1. Introduction

The obtained and described in this paper solid solutions belong to the group of materials known as multiferroics. The name multiferroic denotes a material possessing ferromagnetic and ferroelectric properties in the same phase (but obviously not at the same temperature range). Such materials are known as single phase multiferroics (in opposite to multiphase multiferroics, for instance composite materials). Single phase multiferroics are usually solid solutions in chemical sense and can be divided into two groups i.e.: type–I and type–II multiferroics [1], depending on the connection between magnetism and ferroelectricity. The obtained and investigated in this paper materials belong to type I multiferroics with perovskite structure and the general formula of $Pb(B_{1/2}B'_{1/2})O_3$ (B=Nb, W, Ta; B' = Fe, Mn, Ni, Co). B ions are inducting ferroelectricity, while B′ ions are inducting magnetism. Type I multiferroics with perovskite structure can also be obtained without Pb in A position, for example $BiFeO_3$ and solid solution (1-*x*)$BiFeO_3$–*x*$BaTiO_3$ [2]. In general, in such types of materials the significant difference between temperatures of ferroelectric and magnetic phase transitions takes place and, as a result, at room temperature polarization cannot be controlled by magnetic field. In recent years, described have been materials in which electric and magnetic properties are connected by the rotations of common microscopic polar regions. It gives new possibilities of controlling polarization by magnetic field and magnetization by electric field. For such materials, the name birelaxors has been proposed [3]. Some compositions of solid solutions PZT-PFW are suspected to be such type of materials.

Obtained by us and described below solid solution PZT-PFW-PFN consists of three components. The first component is a well-known and widely used ferro- and piezoelectric material PZT. The second component, i.e. $PbFe_{2/3}W_{1/3}O_3$ (PFW), has been described in the early years of the investigations of ferroelectrics [4]. More detailed studies of PFW are presented in Refs. [5–7]. The temperature T_m associated with the maximum of the dielectric permittivity increases with the increase of frequency from 185 K at 1 kHz to 200 K at 1 MHz. The third component $PbFe_{1/2}Nb_{1/2}O_3$ (PFN) is a multiferroic with perovskite structure, and was first synthesized in 1958 [8]. In the PFN, phase transitions from ferroelectric to paraelectric phase (385 K) are observed, as well as transitions from paramagnetic to antiferromagnetic phase (143 K) [9–11]. Recently,

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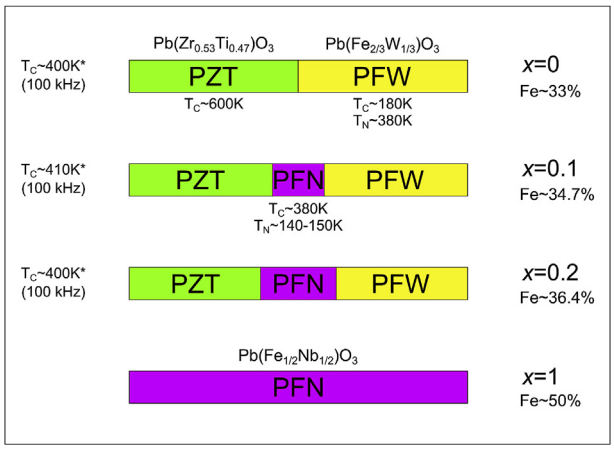

Fig. 1. The schematic diagram illustrating the main motivation of the work. * - data from work [26].

a weak ferromagnetism at room-temperature has been observed in bulk. More detailed studies of the structure, phase transitions and electric conductivity in PFN and PFN:Li are described, for example, in works [12–17].

Very interesting are the properties of solid solution (1-x)($PbZr_{0.53}Ti_{0.47}O_3$)-x($PbFe_{2/3}W_{1/3}O_3$) (PZT-PFW) [18–25]. Pajic et al. described competing antiferromagnetism and local magnetic order in the bulk ceramics PZT–PFW [23]. It has been stated that the most promising ratios between PZT and PFW are from 0.20PZT-0.80PFW to 0.37PZT-0.63PFW. In our previous works [24,25] we have obtained and described ceramic samples PZT-PFW with compositions between 0.75PZT-0.25PFW and 0.45PZT-0.55PFW. In our previous work [26], using solid solution 0.5PZT-0.5PFW as a starting composition, we obtained a new solid solution (1-x) [0.5($PbZr_{0.53}Ti_{0.47}O_3$)-0.5($PbFe_{2/3}W_{1/3}O_3$)]-x($PbFe_{1/2}Nb_{1/2}O_3$) with $x = 0$; 0.1 and 0.2.

Fig. 1 presents a schematic diagram illustrating the main motivation of this work. PFN substitutes partially PZT and partially PFW. As a result, we have a slight increase of the content of Fe-ions in B-positions of perovskite structure. The main goal was to investigate how it influences the magnetic and dielectric properties, as well as electric conductivity, especially at low temperatures.

On the other hand, in such kind of materials the addition of PFN improves sintering conditions of ceramics and causes some changes in the parameters which may be relevant for applications, nonetheless at the same time changes magnetic and electric parameters. SEM investigations presented in Ref. [26] show that the microstructure of the obtained samples is rather fine-grained with average grain sizes below 1.0 μm (from 0.74 μm to 0.84 μm). The obtained in Ref. [26] XRD patterns of final ceramics after sintering show that only the maxima related to the perovskite phase were observed, i.e. there were no lines related to another unwanted phases. No splits of lines suggested that the samples are in a cubic or pseudocubic phase were observed. The temperature dependence of dielectric permittivity has been investigated in Ref. [26], however at temperatures higher than room temperature only. Having analysed the obtained results, we concluded that the position of the maximum of dielectric permittivity does not depend on the content of PFN (i.e. x). In Ref. [26], also the investigations of electric conductivity have been done, however also at temperatures higher than room temperature, with a conclusion that the lowest electric conductivity takes place at a sample with $x = 0$ (i.e. 0.5PZT-0.5PFW).

In this paper, for the same samples as in the case of [26], we describe and analyse the results of investigations of magnetic properties (at the temperature range from 2 K to 273 K), d.c. electrical conductivity calculated from impedance measurements (within the range of 5 K–273 K) i.e. below room temperature. We try to answer the following questions:

- if these solutions can be classified as multiferroics;
- what are the magnetic properties at low temperatures, and to determine whether there is a ferromagnetic phase;
- check whether there are any anomalies of magnetic susceptibility vs. temperature and at what temperature range;
- whether and how electric conductivity depends on magnetic field;
- specify what anomalies of electric conductivity occurs below room temperature.

Hereinunder, we describe the results of investigations of magnetic properties (in the temperature range from 2 K to 273 K) and electrical conductivity calculated from impedance measurements (within the range from 5 K to 273 K) for the same samples as in Ref. [26].

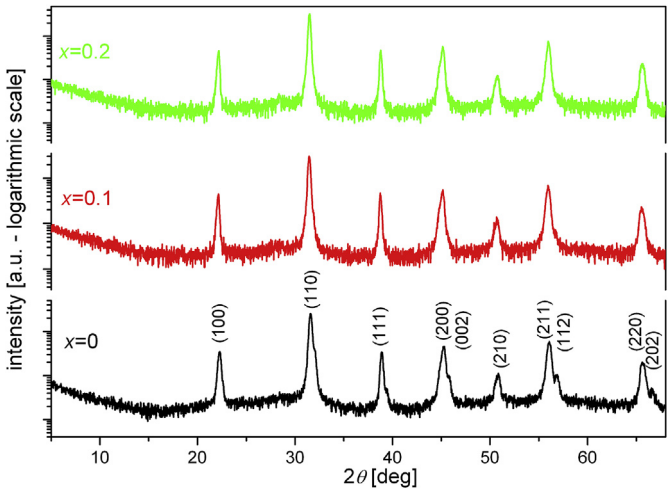

Fig. 2. X-ray patterns of the PPP powders.

2. Material and methods

The ceramic samples of solid solutions (1-x) [0.5($PbZr_{0.53}Ti_{0.47}O_3$)-0.5($PbFe_{2/3}W_{1/3}O_3$)]-x($PbFe_{1/2}Nb_{1/2}O_3$) with $x = 0$; 0.1; 0.2 were prepared using the conventional solid-state reaction method. High purity powders PbO (99.99% purity, POCH), ZrO_2 (99.00% purity, Merck), TiO_2 (99.99% purity, Merck), Fe_2O_3 (99.98% purity, Sigma-Aldrich), WO_3 (99.9% purity, Fluka) and Nb_2O_5 (99,9% purity, Sigma-Aldrich) have been used as starting materials. To compensate lead evaporation during sintering, 10% weight of PbO lead oxide has been added. The mixtures of oxides were ball-milled using wet technique, in a Fritch planetary mill (in ethyl alcohol and using zirconia balls) for the period of 12 h. The powders were successively dried, pressed into discs and then sintered at 1173 K/2 h. In the next step, the obtained pellets have been crushed and milled in a mortar. The obtained powders were uniaxially pressed into discs with a diameter of 10 mm and the thickness of about 3 mm, using polyvinyl alcohol as a binder. Such prepared discs have been sintered in alumina crucibles at 1273 K for 3 h, with the heating rate of about 2.5 K/min. Finally, the obtained ceramic samples were grinded, polished and annealed at temperature 973 K (in order to removing mechanical stresses), whereas for