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Neutron powder diffraction and magnetic study of perovskites $Pb(Mn_{1/2}Nb_{1/2})O_3$ and $Pb(Mn_{1/4}Fe_{1/4}Nb_{1/2})O_3$

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Abstract

The structural and magnetic properties of the complex metal oxides $Pb(Mn_{1/2}Nb_{1/2})O_3$ (PMNO) and $Pb(Mn_{1/4}Fe_{1/4}Nb_{1/2})O_3$ (PMFNO), which belong to a class of disordered perovskites have been studied. The magnetic susceptibilities of PMNO showed hysteresis between field cooled and zero-field cooled conditions below the transition of 15 K, suggesting that the material has a spin-glass feature. Neutron diffraction patterns of PMNO showed no evidence of a long-range magnetic ordering at 1.5 K, which is consistent with spin-glass behavior. Rietveld refinements of neutron powder diffraction data collected at different temperatures between 1.5 and 700 K have been carried out in order to extract structural information. The crystal structure of this compound is cubic (space group $Pm\bar{3}m$) within the whole temperature interval. The Mn and Nb ions were found to be disordered over the perovskite B-sites. The main feature of this structure is the positional disorder at the Pb site, the importance of which in connection with the ferroic transitions is briefly discussed. The Pb cations show a positional disorder shifting from their high-symmetry positions along the [1 1 1] direction. The effect of Fe-doping on PMNO has been studied. The substitution of Fe at the Mn site in PMFNO results in a small changes of the magnetic properties without significant differences in the crystal structures. The factors governing the observed structural and magnetic properties of PMNO and PMFNO are discussed and compared with those of other quaternary Mn-containing perovskites. For the $PbB^{3+}{}_{1/2}Nb_{1/2}O_3$ series with the isomorphous substitution B^{3+}, graphs of average lattice parameters of the perovskite phase and the temperatures of ferroelectric and magnetic phase transitions as functions of the B^{3+} cation radius were constructed and are discussed. Influence of A-cation sublattice on magnetic properties is also considered.

Keywords: A. Electronic materials; C. Neutron scattering; D. Crystal structure; D. Magnetic properties; D. Ferroelectricity

1. Introduction

Materials known as magnetoelectrics, which are simultaneously ferroelectric and ferromagnetic (or at least show some type of magnetic ordering), have recently become the focus of much research [1–4]. These compounds present

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opportunities for a wide range of potential applications [5,6] in addition to that the fundamental physics of multiferroic materials is rich and fascinating [1–4].

The coexistence of ferromagnetism and ferroelectricity is difficult to achieve for many reasons [7] and only very few multiferroic materials are known [8]. First, and most fundamentally, the cations, which are responsible for the electric polarization in conventional ferroelectrics, have a formally empty d-electron configuration. In contrast, ferromagnetism requires unpaired electrons, which in many materials are provided by d electrons of transition metal ions. Therefore the coexistence of the two phenomena, although not prohibited by any physical law or symmetry consideration, is discouraged by the local chemistry that favors one or the other but not both. In practice, alternative mechanisms for introducing the polar ion displacements other than the magnetic transition metal ions, such as stereochemically active lone pairs of Bi^{3+} and Pb^{2+} cations can be used to circumvent this restriction. Because all well-known single-phase multiferroics are mainly Mn- or Fe-based oxides, perovskite oxides containing Bi and Pb cations in the A-sublattice and Mn and Fe cations in the B-sublattice are particularly promising candidates of multiferroic materials.

The capability of perovskite-structured oxides to substitute one ion with another (or a set of ions) without remarkable structural distortion provides a way of obtaining new magnetoelectric perovskites. Studies of the series of complex perovskite-structured oxides, which give insight into the regularities of the structural changes and physical properties (with no allowances for complexity added to the compound composition), are of particular interest. A broad range of ferroelectric and magnetic properties determined by structure peculiarities of the compounds has been investigated in one of the most complete series of isomorphous substitution, $PbB^{3+}{}_{1/2}Nb_{1/2}O_3$ [9–12] in order to understand the nature of magnetoelectric interactions in these compounds. It is known that the B site can accommodate several kinds of metal ions while the cation arrangement on this sublattice is controlled primarily by the charge difference between the B cations and secondarily by the ionic size difference between them. Depending on the valencies and the ionic radii, the B cations settle either in an orderly or in a random fashion in the lattice. The literature data on the $Pb(Mn_{1/2}Nb_{1/2})O_3$ are very scarce. The complex perovskite PMNO was first prepared as a ceramic in Refs. [13,14]. However, the specimens obtained were not single-phase, for which reason it was not possible to reliably investigate the properties of the new compound. Later, the synthesis in N_2 atmosphere gave a single-phase ceramic PMNO and it was concluded that this compound was ferroelectric with $T_c = 293$ K and antiferromagnetic below 77 K [15]. No distortion of the perovskite cell in which the two kinds of cations (Mn^{3+} and Nb^{5+}) are randomly distributed at the octahedral B-site positions, was observed at room temperature and the phase was assigned to cubic symmetry (space group $Pm\bar{3}m$) with $a = 4.004$ Å. More extensive studies of the magnetic properties of PMNO was made in [16,17] and the paramagnetic Curie temperature $\Theta = 40$ K was found.

However, numerous discrepant results appeared after single crystals were synthesized [18–20]. In one study it was found a small monoclinic distortion at room temperature ($a \sim b \sim c = 4.006$ Å, $\beta = 90^\circ 5'$). The temperature dependence of the reciprocal magnetic susceptibility obtained in these studies shows anomalies at 135, 73 and 11 K. Below 11 K PMNO was considered as antiferroelectric and antiferromagnetic accompanied by a weak ferromagnetic moment.

A magnetoelectric effect was also found below 11 K [18,19] where the spontaneous magnetic moment could be induced whose magnitude and direction were determined by the magnetic and electric fields imposed on the single crystal during cooling.

The dielectric measurements performed on PbMNO ceramics, do not show the typical broad diffuse phase transition known for Pb-based perovskite relaxors. However, an anomalous increase of the permittivity with clear maximum can be observed at 165 K [15], 400 K [24] and 420 K [16]. The understanding of these anomalies is still a matter of debate and the real magnetic and dielectric properties are much more complicated than originally anticipated.

In the same time, an X-ray study of PMNO single crystal, which was obtained from a high-temperature solution growth [22] showed that the average lattice symmetry is cubic.

In the light of the above considerations, a detailed further characterisation of crystal structure and magnetic properties is still needed.

In the perovskite manganese oxide, the introduction of other transition metal elements, which exhibit dissimilar electronic configuration to Mn, should lead to dramatic effects associated with the electronic configuration mismatch between Mn and the other substituted magnetic ions. In this sense, and in order to avoid the lattice distortion, the Fe atom has been selected regarding the identical ionic radii of Fe^{3+} and Mn^{3+}. At high Fe-doping level, the strong competition between the Mn—O—Mn and the Mn—O—Fe superexchange interactions might also result in spin-glass behavior [23].