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Synthesis, structure and dielectric properties of new ordering perovskites $LnPbMgSbO_6$ (Ln = La, Pr, Nd)

Lin Han [a, b], Yijia Bai [c], Xiaojuan Liu [a, *], Chuangang Yao [a, b], Junling Meng [a, b], Qingshuang Liang [a, b], Xiaojie Wu [a], Jian Meng [a, *]

[a] State Key Laboratory of Rare Earth Resources Utilization, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, PR China
[b] University of Chinese Academy of Sciences, Beijing 100049, PR China
[c] Applied Chemistry Department, Chemical Engineering College, Inner Mongolia University of Technology, Huhhot 010051, PR China

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ABSTRACT

The synthesis, crystal structure, and dielectric properties of the titled compounds were described. The structural symmetry was determined to be monoclinic $P2_1/n$ (No. 14) space group. Based on the highly ordered array of alternating MgO_6 and SbO_6 octahedra, these double perovskites exhibited significant octahedral tilting distortion according to the Glazer's notation system $a^-a^-c^+$. As the result of substituting different rare earth ions from La^{3+} to Nd^{3+}, both the tolerance factor (t) and coordination number (CN) were reduced simultaneously and the B-site lattice distorted more heavily with the increase in chemical pressure by adopting smaller Ln^{3+} ion. For the investigation of dielectric properties, all the samples consistently presented weak frequency dependent characteristic with relatively low dielectric constant (ε') and low tangent loss ($\tan\delta$). With the shrinkage of the Ln^{3+} ion size, the corresponding ε' decreased remarkably and the dispersive $\tan\delta$ peaks around 300 K shifted to low temperature, indicating that the space-charge-hopping mechanism dominated permittivity property can be tuned by controlling the degree of lattice distortion via substituting different Ln^{3+} ions.

1. Introduction

Double perovskite oxides with the general formula of $A_2BB'O_6$ or $AA'BB'O_6$, where A and A′ represent rare earth or alkaline earth metals and B and B′ stand for transition metals or main group elements, have been extensively investigated in the recent decades because of their various physical properties and technological application potentials [1–4]. Double perovskites may present different kinds of cationic ordering at the B-site sublattice, and the most common ordering is a rock-salt arrangement of the BO_6 and $B'O_6$ octahedra perfectly alternating along the three dimensions. The ordering of the B-site cations in the double perovskites has profound effects in determining their properties. For example, La_2MnMO_6 (M = Co, Ni) with B-site ordering exhibits rare ferromagnetic insulating behavior with a high Curie temperature (T_C = 270 K) [5]. Many correlated researches have revealed that both the strength of ferromagnetic coupling and the extent of electric insulation are sensitive to the ordering degree of the structure and charge [6,7]. In particular, a pronounced large magnetodielectric coupling of 8%–20% has been discovered over a wide temperature range of 150–300 K in a partially disordered La_2NiMnO_6, and the antisite defects were also found to greatly influence the magnetic and dielectric properties in partially B-site ordered La_2CoMnO_6 [8,9].

Aside from the compounds with two magnetic B-site cations of transition metal, another family of double perovskite exists, where one or both of the B-site cations are nonmagnetic. Among these compounds, some analogues containing p-block B′ ions, such as Sb^{5+} remained to be explored [10–12]. The antimony containing double perovskites have been investigated since 1960s [13]. The different charges and bonding characteristics of transition metals and p-block metals may give rise to high degree of cation order in the B-sublattice, which can further influence the physical properties. A higher degree of order is generally obtained in the Sb-containing double perovskites than that in the B ions occupied by high valence transition metal, such as Nb^{5+} and Ta^{5+}. Woodward et al. [14] contributed this phenomenon to the hybridization effects. In their view, the 180° Sb^{5+}–O–Sb^{5+} linkages are not favorable for

* Corresponding authors. Tel.: +86 431 85262415; fax: +86 431 85698041.
E-mail addresses: hanlin@ciac.ac.cn (L. Han), lxjuan@ciac.ac.cn (X. Liu), jmeng@ciac.ac.cn (J. Meng).

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the perovskite structure because no impetus for the sp hybridization of oxygen, which would be required for a 180° angle unless the π bonding stabilizes. Both Nb^{5+} and Ta^{5+} have empty d orbital that may be used for π bonding and stabilize the 180° bond angle. However, Sb^{5+} has no d orbital to stabilize a 180° Sb^{5+}–O–Sb^{5+} linkage. Instead, they are favorable to form the pyrochlore structure, where the angle is far from 180°. On the contrary, if the perovskite structure forms, a long-range ordering of Sb^{5+}–O–B–O–Sb^{5+} will be stable and perform high degree of order.

Lead-based perovskites have attracted numerous interests in the recent decades, primarily due to their fascinating physical properties, such as ferroelectricity, piezoelectricity, and dielectricity [15–17]. Given the existence of Pb^{2+} ion with lone-pair $6s^2$ electrons, second-order Jahn–Teller (SOJT) distortions occurred in the perovskites where the lone-pair cations on the A-site intensively hybridize with the 2p-orbital of O^{2-} and shifted out of the center of their coordination polyhedral to form non-centrosymmetric distortion. This result may favor the realization of ferroelectricity.

Considering the aforementioned study, we have explored the double perovskites containing p-block element at the B-site with an electron lone-pair at the A-position. In our previous work, the structure, and the magnetic and dielectric properties of $LaPbMSbO_6$ (M = Co, Ni) have been well studied. These compounds exhibit distinct dielectric properties determined by different 3d-electron configurations of Co^{2+} and Ni^{2+}. In order to further reduce the space electron hopping and improve dielectric performance, we substitute the closed-shell p-block ion Mg^{2+} for 3d transition metal ion Co^{2+}/Ni^{2+} to investigate the influence on dielectric property. In particular, lattice distortions of the double perovskite structure may significantly affect the physical properties. Octahedral tilting distortion presented in the majority of the double perovskites occurs when the A-site cations are too small for the cubo-octahedral cativities [18–20]. Thus, the substitution of different rare earth ions from La^{3+} to Nd^{3+} was performed in our work. This study describes the synthesis, structural characterization, and dielectric properties of a series of novel double perovskites $LnPbMgSbO_6$ (Ln = La, Pr, Nd), and focuses on the influence on crystal structure and dielectric property controlling by the change of Ln^{3+} ions.

2. Experimental section

2.1. Synthesis

Polycrystalline samples of $LnPbMgSbO_6$ (Ln = La, Pr, Nd) were prepared by a two-step semi-chemical method. The B-site precursors were firstly prepared by a sol–gel method, and the target samples were synthesized by solid-state reactions. Stoichiometric amounts of La_2O_3 (99.99%), Pr_6O_{11} (99.9%), Nd_2O_3 (99.9%), PbO (99.99%), $Mg(CH_3COO)_2{\cdot}4H_2O$ (≥99.0%) and Sb_2O_3 (99.99%) were used as starting materials. La_2O_3, Pr_6O_{11} and Nd_2O_3 were precalcined at 950 °C for 12 h to completely eliminate the carbonate and water. Firstly, the citrate was dissolved in deionized water. Then, stoichiometric quantities of Sb_2O_3 and $Mg(CH_3COO)_2{\cdot}4H_2O$ were put into the citrate solution with heating and stirring until the samples were dissolved and the sol was obtained. The obtained sol was dried at 90 °C to get the precursor powder. Subsequently, the precursor was treated at 550 °C for 10 h to oxidize Sb^{3+} to Sb^{5+} [21] and then heated at 1000 °C for 4 h with intermediate grinding in an agate mortar. Finally, the precursor and Ln_2O_3, PbO in stoichiometric ratios were mixed and intimately ground, pressed into pellets and

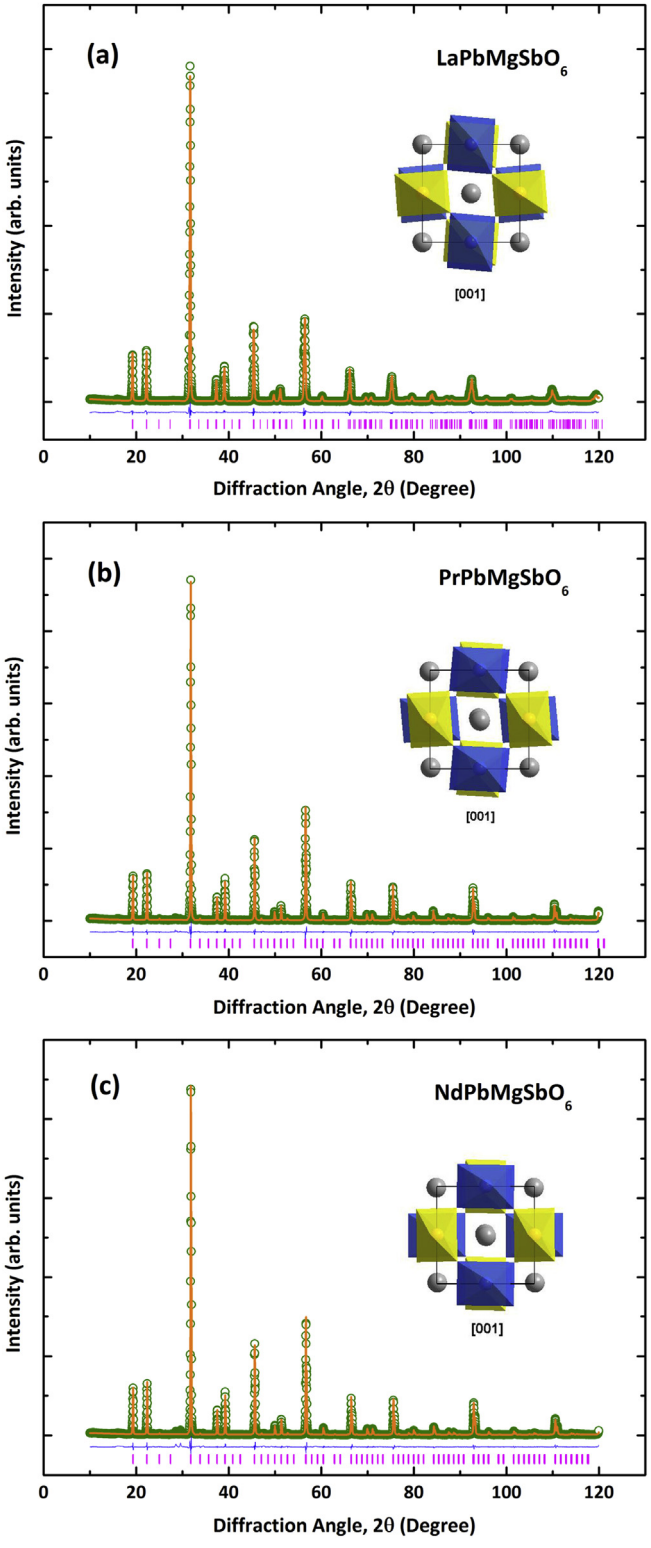

Fig. 1. Rietveld refinements of (a) $LaPbMgSbO_6$, (b) $PrPbMgSbO_6$ and (c) $NdPbMgSbO_6$ from powder XRD data at room temperature. Observed (green circle), calculated (orange line) and difference (bottom) profiles are shown, and the expected Bragg reflection positions are marked with vertical bars (pink). The structure views along the [001] direction are shown for all the compounds. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)