

Crystal structures and microstructures of $\text{PbV}_{1-x}\text{Fe}_x\text{O}_3$ perovskites with $x \leq 0.3$

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The $\text{PbV}_{1-x}\text{Fe}_x\text{O}_3$ (with $0 \leq x \leq 0.3$) perovskites were synthesized by solid state reaction method under high-temperature and high-pressure conditions. The effects of the synthesis parameters on the structure and phase compositions were analysed by X-ray diffraction. The main phase is tetragonal, of PbVO_3 type, space group $P4mm$. Some impurity phases were also identified and their content estimated.

(Received November 11, 2013; accepted March 13, 2014)

Keywords: PbVO_3 , High pressure – high temperature synthesis, Vanadium substitution with iron, XRD, SEM, EDX

1. Introduction

The PbVO_3 perovskite crystallizes in a tetragonal structure (space group $P4mm$) without a centre of inversion [1-3] and therefore it has attracted considerable attention as a potential multiferroic (MF) material [4-7]. The PbVO_3 perovskite has been predicted to be both antiferromagnetic and ferroelectric with large spontaneous polarization [3,4,7,9]. The lone pair of the divalent Pb^{2+} cation induces polarization while the vanadium ion, V^{4+} , contributes to their magnetic properties. However, up to now the magnetic properties of PbVO_3 have not been unambiguously determined [3, 5-8]. The most pure PbVO_3 samples have been obtained by solid state reaction at $700^\circ\text{C} \leq T \leq 750^\circ\text{C}$, in the pressure range $4 \text{ GPa} \leq p \leq 6 \text{ GPa}$, [8].

The partial substitution of Fe^{3+} for Ti^{4+} , as an acceptor centre in PbTiO_3 , leads to the creation of oxygen vacancies. The above type substitutions are expected to have a strong impact on the physical properties of the system. The $\text{PbV}_{1/2}\text{Fe}_{1/2}\text{O}_3$ sample was previously synthesized at the pressure $p = 7 \text{ GPa}$ and temperature $T = 800\text{-}1000^\circ \text{C}$ [10]. The partial substitution of V up to 50 at% Fe in the PbVO_3 compound maintains the tetragonal symmetry of the unit cell and the pyramidal coordination of vanadium. The Fe moments are antiferromagnetically coupled in the above system [10].

In this note the synthesis, structures and microstructures of the $\text{PbV}_{1-x}\text{Fe}_x\text{O}_3$ perovskites will be presented. The phase compositions of the resultant materials are also analysed in correlation with the synthesis parameters.

2. Experimental

Bulk samples with the starting composition $\text{PbV}_{1-x}\text{Fe}_x\text{O}_3$ ($0 \leq x \leq 0.3$) were synthesised by conventional solid-state reaction method, at pressures of 4 and 6 GPa and temperature ranging from 900 to 1100°C . The reaction for the synthesis of the $\text{PbV}_{1-x}\text{Fe}_x\text{O}_3$ system can be described by: $\text{PbO} + \text{PbO}_2 + (1-x) \text{V}_2\text{O}_3 + x \text{Fe}_2\text{O}_3 \rightarrow \text{PbV}_{1-x}\text{Fe}_x\text{O}_3$. PbO_2 is used to provide the supplementary oxygen required for the oxidation of vanadium from 3+ to 4+. According to the above equation, stoichiometric quantities of high purity PbO , PbO_2 , V_2O_3 and Fe_2O_3 were mixed in an agate mortar for 30 minutes. The powder mixture was sealed in a gold capsule which was mounted in the pressure cell of a BELT type apparatus. The starting iron contents, temperatures and pressures used in the synthesis as well as the sample notation are given in Table 1.

Table 1. Parameters used in the synthesis of $\text{PbV}_{1-x}\text{Fe}_x\text{O}_3$.

| Sample | S0 | Fe01 | Fe03a | Fe03b | Fe03c |
|---------------------------|------|------|-------|-------|-------|
| x | 0.00 | 0.1 | 0.3 | 0.3 | 0.3 |
| T [$^\circ\text{C}$] | 1000 | 1000 | 1000 | 900 | 1100 |
| p [GPa] | 4 | 4 | 4 | 4 | 6 |

XRD patterns were recorded on a Siemens D5000 diffractometer working in Debye-Scherrer geometry, using a Cu anode and a monochromator. Samples were measured in steps of 0.016 degrees and 0.4 seconds counting time per step. The phases were identified using

the EVA software. The crystallographic data were refined using the Rietveld method with the FullProf software.

The microstructure was analysed by using a Zeiss SEM. The chemical composition and chemical homogeneity of the samples were analysed by EDX spectrometry. The acceleration voltage was set at 20 kV and the working distance was set at 8 mm. The PB-ZAF correction method was used in the quantitative analysis of the chemical composition.

3. Results and discussion

The XRD patterns recorded for samples S0, Fe01, Fe03a, Fe03b and Fe03c are presented in Fig. 1. For all the samples the main phase is tetragonal, having the P4mm space group.

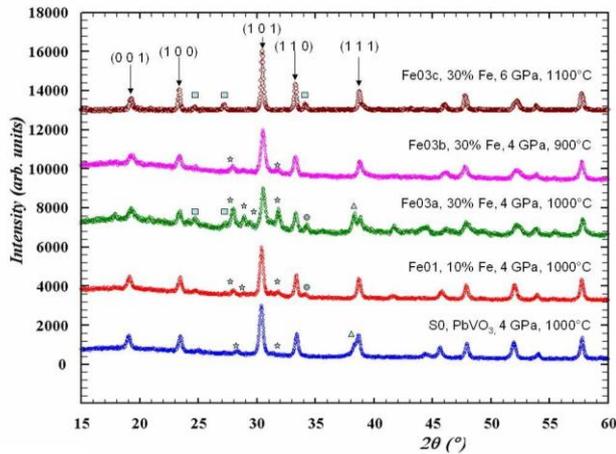


Fig. 1. The XRD patterns of $\text{PbV}_{1-x}\text{Fe}_x\text{O}_3$ perovskites. The impurity phase $\text{Pb}_3\text{V}_2\text{O}_8$ is marked with star, $\text{PbV}_6\text{O}_{11}$ with circle, $\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$ with square and Au, resulting from the diffusion from the capsule, with triangle.

In addition to the pattern characteristic for the tetragonal structure, some additional peaks were observed. These evidence the presence of phases having $\text{Pb}_3\text{V}_2\text{O}_8$ [11-13], $\text{PbV}_6\text{O}_{11}$ [14,15] or $\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$ [16,17] type structures. The types and concentrations of impurity phases depend on the starting composition and the synthesis parameters. As example, the refined pattern for the Fe03b sample is presented in Fig. 2. The red dots denote the experimental diffraction pattern, the continuous black line is the calculated pattern and the blue line is the difference between observed and calculated patterns. The rows of ticks show the Bragg reflections corresponding to the phases entered in the calculation. In addition to the main tetragonal phase, there are contributions from $\text{Pb}_3\text{V}_2\text{O}_8$ and $\text{PbFe}_{12}\text{O}_{19}$ type structures, whose characteristic lines are given in the second and third rows of ticks, respectively (Fig. 2).

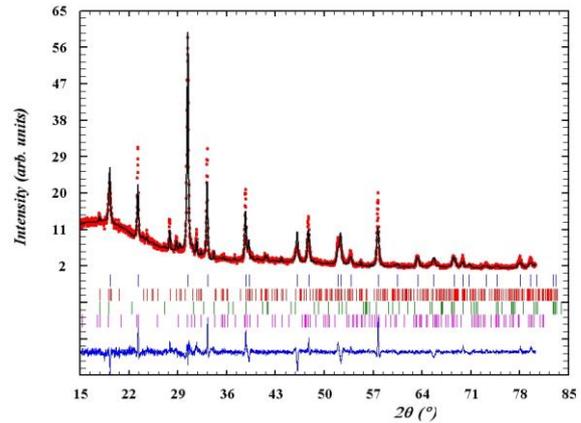


Fig. 2. Rietveld refinement for the Fe03b sample. The hump at low scattering angles is the contribution of the amorphous sample holder (scotch tape).

Small deviations from the values of lattice parameters given, in literature, suggested that the above phases contained also iron or vanadium respectively. The experimental XRD pattern is well described considering the above phases whose content is given in Table 2.

The amount of the PbVO_3 phase in the yield was of 91.62 wt%. The highest content of tetragonal P4mm phase having the starting composition $x=0.3$ was obtained when the sample was sintered at $T = 1100^\circ\text{C}$ and $p = 6 \text{ GPa}$.

The $a = b$ lattice parameters of $\text{PbV}_{1-x}\text{Fe}_x\text{O}_3$ perovskites remained unchanged while the c ones decreased when the iron content was higher.

The microstructures and phases contents were also analysed. Some SEM images are given in Fig. 3 for the sample Fe03b.

The compositions of the main tetragonal phase were determined. The data show relatively small deviations from the compositions of the starting mixtures. As example, $\text{Pb}_{1.01}\text{V}_{0.94}\text{Fe}_{0.06}\text{O}_3$ has been obtained for the sample Fe01 ($x=0.1$) and $\text{Pb}_{1.03}\text{V}_{0.76}\text{Fe}_{0.20}\text{O}_3$ for the Fe03b ($x=0.3$) one. We mention that oxygen contents were not determined.

Table 2. Lattice parameters and phase contents of the $\text{PbV}_{1-x}\text{Fe}_x\text{O}_3$ samples.

| sample (x) | S0 (x=0) | Fe01 (x=0.1) | Fe03b (x=0.3) | Fe03c (x=0.3) |
|---|----------|--------------|---------------|---------------|
| a (Å) | 3.8 | 3.8 | 3.8 | 3.8 |
| c (Å) | 4.67 | 4.64 | 4.59 | 4.60 |
| $\text{PbV}_{1-x}\text{Fe}_x\text{O}_3$ [wt%] | 91.62 | 74.82 | 84.39 | 89.05 |
| $\text{Pb}_3\text{V}_2\text{O}_8$ [wt%] | 5.92 | 14.9 | 8.64 | - |
| $\text{PbV}_6\text{O}_{11}$ [wt%] | 2.46 | 10.28 | 3.43 | - |
| $\text{PbFe}_{12}\text{O}_{19}$ [wt%] | - | - | 3.54 | 7.75 |
| $\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$ [wt%] | - | - | - | 3.21 |

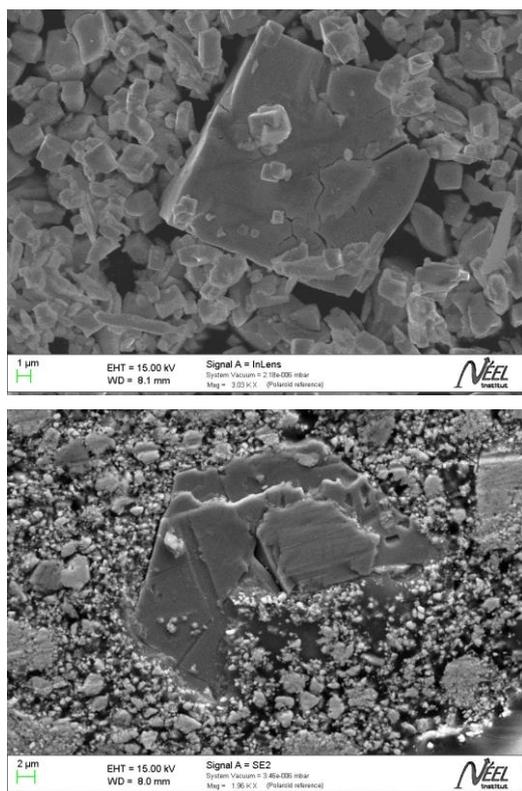


Fig. 3. The microstructures of the Fe03b sample at different enlargements.

As suggested by XRD the additional phases also formed solid solutions. As example the magnetoplumbite component was shown to be doped with vanadium and having a composition of $\text{PbFe}_{0.1}\text{V}_{2.7}\text{O}_{19}$.

4. Conclusions

By using the solid state reaction method the $\text{PbV}_{1-x}\text{Fe}_x\text{O}_3$ compounds with $x \leq 0.3$ were obtained. The amounts and types of impurity phases were found to be strongly dependent on the composition and the preparation conditions. XRD diffraction peaks of the main phase in all samples were indexed assuming a tetragonal structure in the space group $P4mm$. The $a = b$ lattice constants do not depend on the composition. The c parameters of the tetragonal unit cell decreased with increasing iron content. The compositions of the prevailing tetragonal phases were little different from those expected from starting compositions, as determined by EDX analysis.

Acknowledgements

This work was possible with the financial support of the Sectoral Operational Programme for Human Resources Development 2007-2013, co-financed by the European Social Fund, under the project number POSDRU/

107/1.5/S/76841 with the title „Modern Doctoral Studies: Internationalization and Interdisciplinarity”.

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