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HIGH PRESSURE - HIGH TEMPERATURE SYNTHESIS AND PHASE CHARACTERIZATION OF $PbVO_3$ PEROVSKITE COMPOUND

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ABSTRACT. Perovskite compound $PbVO_3$ was synthesized under high-temperature and high-pressure conditions. In this paper we report a new set of milder reaction conditions in which $PbVO_3$ can still be prepared. The effect of the synthesis parameters on phase purity is analysed. The crystalline structure of samples was characterised by X-ray diffraction (XRD) measurements. Rietveld analysis of X-ray powder diffraction pattern revealed that the material stabilized in a tetragonal perovskite phase.

Keywords: *$PbVO_3$, high pressure – high temperature synthesis, XRD*

INTRODUCTION

$PbVO_3$ is a perovskite compound of AVO_3 type (A is a divalent or trivalent cation) that is a strong candidate as a multiferroic compound. It attracts a lot of interest due to its simple structure (tetragonal, space group P4mm [1-8]) which allows a deeper understanding of the connection between the structure and the properties of this material. $PbVO_3$ was first synthesised by Shpanchenko et al in 2004 [1] from stoichiometric mixtures of PbO and VO_2 or PbO, V_2O_3 and V_2O_5. He observed that $PbVO_3$ can only be prepared by solid state reaction under high-pressure high-temperature conditions (HP-HT) [1]. This result has been confirmed in the following years by all authors who prepared bulk $PbVO_3$ samples [1-5]. Shpanchenko's best samples were obtained at HP in the range of 4-6 GPa and HT in the range of 700-750°C [1]. The best samples however contained $Pb_3V_2O_8$ and PbV_6O_{11} as impurities [1]. Nevertheless he was able to describe the structure of $PbVO_3$. Belik prepared better samples one year later from a mixture of PbO, V_2O_3 and V_2O_5 at HP = 6 GPa and HT = 1000°C [2]. He succeeded in reducing the amount of impurities by regrinding the samples and applying a

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second HP-HT treatment in the same conditions as the first one. Unfortunately, his samples still contained enough impurities to hinder measurements of magnetic susceptibility and electric polarization [2]. Tsirlin also prepared $PbVO_3$ samples using as starting products PbO and VO_2 under HP-HT conditions [4] with the best samples obtained at 5 GPa and 950°C maintained for 2 hours [4]. However magnetic impurities were still present [4]. The conditions in which $PbVO_3$ is obtained are too rough for the HP-HT equipments [9]. We present the results of samples synthesis at a relatively low pressure of only 4 GPa and temperatures ranging from 650 to 1000°C,and the investigation of structure and phase purity of $PbVO_3$.

RESULTS AND DISCUSSION

Figure 1 shows XRD patterns recorded for samples S1, S2 and S3, which were obtained by using the following synthesis HT: 650°C, 900°C and 1000°C respectively. For single phase $PbVO_3$, the Miller indices (hkl) were attributed for peaks diffraction as in reference [1].

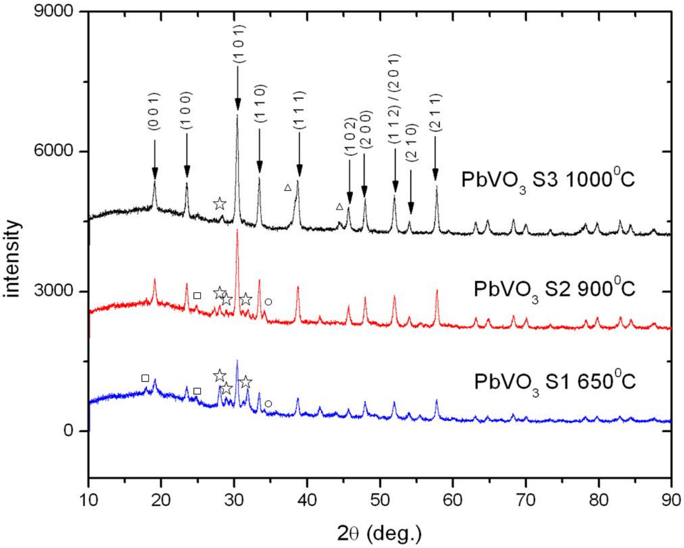

Figure 1. The XRD spectra of samples $PbVO_3$ obtained at the same high pressure (4 GPa) and different temperatures 650°C, 900°C and 1000° C respectively. The impurity phase $Pb_3V_2O_8$ is marked with star, PbV_6O_{11} is marked with circle, $Pb_3\ (C\ O_3)_2\ (O\ H)_2$ is marked with square and Au is marked with triangle.

The additional peaks, were identified from the impurity phases: $Pb_3V_2O_8$ (marked with star), PbV_6O_{11} (marked with circle), and $Pb_3\ (C\ O_3)_2\ (O\ H)_2$ (marked with square). Sometimes gold dust from the capsule mixed with the sample. Gold diffraction peaks are marked with triangles.

The diffraction peaks for the impurity phases were indexed based on structural data available in literature. Structural information for $Pb_3V_2O_8$ was taken from references [10, 11, 12], for PbV_6O_{11} from [13, 14] and for $Pb_3 (C\ O_3)_2 (O\ H)_2$ from references [15,16], respectively. We found that the quality of the samples, defined by the phase purity, varies with the reaction conditions.

An almost single phase sample was obtained at 4 GPa and 1000° C (the "best" sample, S3) and the "worst" sample was obtained at 4 GPa and 650°C (sample S1). It can be easily observed that the intensities of the diffraction peaks corresponding to the impurity phases are comparable to those of the main phase for the "worst" sample. The same impurity peaks vanish almost completely in the "best" sample. $Pb_3V_2O_8$ is reported to be formed alongside $PbVO_3$ which might suggest that its presence is unavoidable [1, 2]. The presence of PbV_6O_{11} phase causes problems in the acquisition of magnetic measurements since it is antiferromagnetic (with the transition at about 90 K) and the signal produced by PbV_6O_{11} covers the signal of $PbVO_3$. The third identified impurity was the hydrocerussite, $Pb_3 (C\ O_3)_2 (O\ H)_2$, which gives no magnetic signal. Also, it is the least frequently encountered impurity. The mass percentages of the phases present in the sample S3 (the "best" sample) were calculated from FullProf, by assuming the presence of minority phases $Pb_2V_3O_8$ and PbV_6O_{11}, respectively. The results are as follows:

$PbVO_3$	91.6 %
$Pb_2V_3O_8$	5.9 %
PbV_6O_{11}	2.4 %

The amount of PbV_6O_{11} is beyond the detection limit of 5% of typical diffractometers so the presence of this impurity is hard to be confirmed by XRD. In the XRD pattern of S3 an additional impurity can be observed. This is gold that got mixed with the sample during the opening of the capsule. Since gold did not participate in the $PbVO_3$ forming reaction, its percentage was not calculated. The χ^2 value for the Rietveld refinement is 2.45. The X-ray powder peaks of our $PbVO_3$ phase were indexed by assuming a tetragonal structure in the space group P4mm (no. 99) [1]. The following lattice parameters were obtained: a = b = 3.8 Å and c = 4.67 Å, (Table 1). Figure 2 shows the Rietveld refinement for the S3 (the best sample). Table 1 shows that the structural data for $PbVO_3$ is in agreement with the previous results [1,2,3,6]. In figure 2, the experimental peaks of XRD diffraction data is marked with circles. The calculated XRD pattern is shown in a continuous line. The ticks under the diagrams mark the position of the Bragg peaks of each phase taken into the refinement as following. The first row of ticks shows the reflections for the main phase, $PbVO_3$. The second row shows the reflections for $Pb_3V_2O_8$. The third row of ticks shows the peaks of PbV_6O_{11}. Finally, the fourth row shows the Bragg reflections of gold. The difference between the experimental and calculated diagrams is shown by the continuous line located under the rows of ticks.

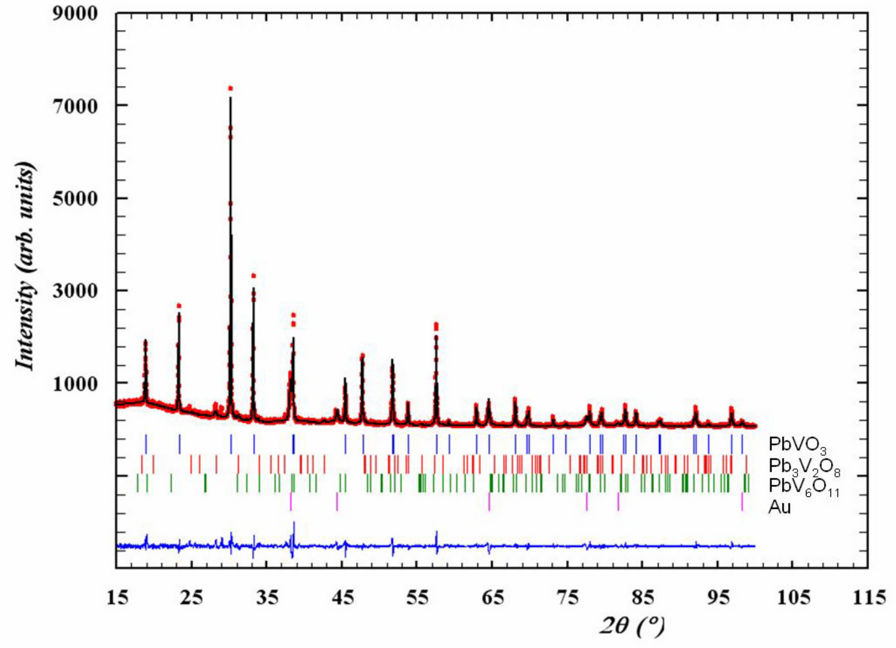

Figure 2. Rietveld refinement for PbVO$_3$. Experimental, calculated, and difference X-ray patterns for PbVO$_3$.

Table 1. Structural data for PbVO$_3$.

Space group/ Lattice parameters	Atom types / positions / occupancy					
P 4 m m	Type	Wyckoff	x	y	z	occ.
a = 3.80 b = 3.80 c = 4.67	Pb	1b	0.5	0.5	0.56	1
	V	1a	0	0	0	1
	O1	1a	0	0	0.3	1
	O2	2c	0.5	0	-0.14	2

CONCLUSIONS

Samples with majority of phase PbVO$_3$ were obtained by solid state reaction method, using a new set of milder reaction conditions at HP = 4 GPa and HT in the range of 650°C to 1000°C. XRD shows that along with the majority PbVO$_3$ phase some minority phases are present. By increasing HT from 650°C to 1000°C, the intensity of the Bragg peaks for the minority phases decreases, and the impurity phases were diminished. PbVO$_3$ samples prepared by using HP = 4 GPa only, show a tetragonal structure with unit cell parameters in good agreement with previously reported results [1, 2, 3, 4].

EXPERIMENTAL SECTION

Bulk samples of $PbVO_3$ were synthesised by solid-state reaction method under high pressure (HP) and high temperature (HT). It is known that bulk $PbVO_3$ can only be synthesised under HP-HT conditions [1-6] at pressures as high as 8 GPa and temperatures over 1000° C. The typical reaction conditions are at the very limits of endurance for the machines and considering the high cost of the parts (pistons and cambers) and the fact that their lifespan is inversely proportional to the applied pressure we decided to search for other, milder, conditions at which we would still obtain the same product.

Samples were prepared at the Néel Institute, Grenoble, France (Laboratory of Structure and Properties of Materials - Extreme Conditions, SPMCE). We used a route for the synthesis of $PbVO_3$ at a relatively low pressure of only 4 GPa and temperatures ranging from 650 to 1000° C.

The chemical equation for the $PbVO_3$ synthesis is the following:

$$PbO + PbO_2 + V_2O_3 \rightarrow 2PbVO_3$$

PbO_2 is used to provide the “additional” oxygen required for the oxidation of vanadium from 3+ to 4+.

Stoichiometric ratios of high purity PbO, PbO_2, V_2O_3 were mixed in an agate mortar for 30 minutes. The powder mixture obtained was sealed in a gold capsule which was mounted in the pressure cell of a BELT type apparatus. The applied HP-HT treatment consisted in submission for 30 min to a pressure of 4 GPa and a temperature between 650 and 1000° C.

The diagram of the HP-HT treatment is shown in figure 3.

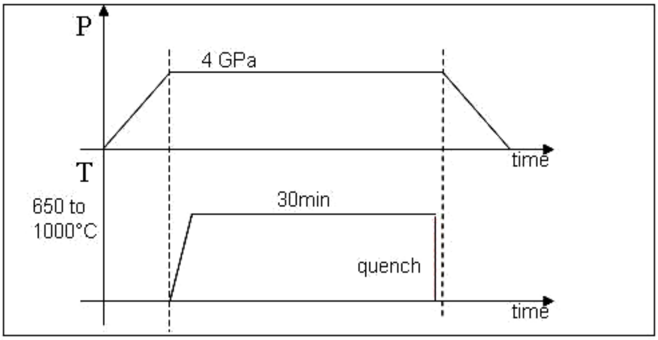

Figure 3. The diagram of HT-HP treatment program.

The following samples were obtained: S1 (T=650°C), S2 (T=900°C), S3 (T=1000°C). X-Ray diffraction was used for phases analysis and to characterise samples crystalline structure. XRD patterns were recorded with a Siemens D5000 diffractometer equipped with a Cu anode and a monochromator filtering the Cu Kα1 radiation.

Samples were measured in transmission (Stoe) geometry, with a step size of 0.016 degrees and 0.4 seconds counting time / step. In order to reduce the noise and for a better resolution, the representative samples were analysed by using a Bruker D8 diffractometer, also working in transmission geometry.

The phases were identified using the EVA software, by comparison to the database. The crystallographic data were refined using the Rietveld code with the FullProf software.

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