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Structure and magnetic properties of the layered perovskite $PbVO_3$

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ABSTRACT

We report synthesis, X-ray diffraction (XRD), magnetic susceptibility, electron paramagnetic resonance (EPR) and Raman studies on the layered perovskite $PbVO_3$. XRD evidenced the tetragonal unit cell. The shape of diffraction peaks of our sample was analysed by using the Thomson–Cox–Hastings (TCH) formulation with an anisotropic broadening model. Anisotropy of strain and of crystallite size along the c^* axis and in the normal plane to this axis was characterised. Magnetic susceptibility function of temperature was analysed by using the frustrated square lattice model (FSL). EPR spectra with a well-resolved hyperfine structure typical for V^{4+} ions were obtained. Raman spectra of the $PbVO_3$ show the specific bands of non-centrosymmetric structure, space group P4/mm.

1. Introduction

Many experimental efforts have been devoted to search for new materials with multiferroic properties and to explore multiferroic properties in known materials [1,2]. The AVO_3 (A = Sr, Ba, and Pb) perovskite-like compounds are considered to possess many potential applications in fields such as multiferroic (MF) devices, high-temperature solid oxide fuel cells and high *Tc* superconductivity [3]. Lead vanadate $PbVO_3$ (PVO) has been predicted to be an antiferromagnetic ferroelectric with large spontaneous polarization [4–9]. The lone pair of the divalent Pb^{2+} cation induces polarization while the transition metal V^{4+} cation gives rise to a magnetic moment. Insulating perovskite PVO has been synthesized by a high-temperature (HT) and high-pressure (HP) technique [4–7]. $PbVO_3$ adopts a layered perovskite-type structure (space group P4/mm, $a = 3.8001$ Å, $c = 4.6703$ Å) and shows a much larger tetragonal distortion ($c/a = 1.229$) than that of $PbTiO_3$ ($c/a = 1.062$). This structure combines the absence of an inversion centre with a magnetic V^{4+} cation, therefore $PbVO_3$ attracts considerable attention as a possible multiferroic [8,9]. The most pure $PbVO_3$ samples with a very large tetragonal distortion were obtained in 40–60 kbar pressure range and at 950 °C [5]. Electron Paramagnetic Resonance (EPR) is a microscopic probe to spin dynamics and gives valuable information concerning the Vanadium (V) local site symmetry, sample inbhomogeneities and the nature of the exchange interaction. Raman spectroscopy is one of the most powerful analytical techniques for studying the lattice vibrations and other elementary excitations in materials providing important information about the structure, composition, strain, defects, phase transitions.

In this work, we report the synthesis of PVO by solid state reaction method at HT–HP, the characterisation of crystalline structure, strain and microstructure from X-ray diffraction measurements, the average magnetic interactions from magnetic susceptibility measurements, the local magnetic interaction from EPR measurements and the lattice vibrations from Raman spectroscopy measurements.

2. Experimental

$PbVO_3$ polycrystalline samples were prepared by solid state reaction under high pressure, high temperature conditions (HP–HT) in a CONAC type apparatus. Appropriate amounts of high purity metal oxides PbO, V_2O_3 and V_2O_5 were selected as starting materials. Almost single phase $PbVO_3$ samples were prepared in a two stage process. In the first stage the powders of starting oxides were mixed in an agate mortar. The mixture thus obtained was placed in a gold (or platinum) capsule to which the first HP–HT treatment was applied (pressures of 6 GPa and temperatures of 950 °C). After this first treatment, XRD shows that the samples contained $PbVO_3$ as the main phase and presented small amounts of secondary phases, namely $Pb_3V_2O_8$ and $Pb_3(CO_3)_2(OH)_2$. In the second stage the samples were ground to a fine powder and underwent a second HP–HT treatment in the same conditions as the first treatment (HP = 6 GPa, HT = 950 °C). After the second HP–HT treatment the

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amounts of secondary phases decreased significantly, under the detection limit of XRD. The necessity of a two stage (or annealing) process was first reported by Belik et al. [5].

X-ray powder diffraction data (XRD) were collected at room temperature using a Siemens D5000 diffractometer (transmission geometry, Cu Kα radiation, 2θ range of 10–90°, step size of 0.016° and 10 s counting time/step).

Low temperature XRD data were collected with a D8 diffractometer equipped with a cryostat in the temperature range of 10–290 K. For the determination of the instrumental contribution to linewidth, a LaB_6 standard sample was investigated by means of XRD using the same scan parameters in which the $PbVO_3$ samples were analyzed. The FullProf software was used to perform Rietveld refinements on the XRD data.

Magnetic susceptibility measurements function of temperature were conducted on a Quantum Design MPMS SQUID magnetometer at temperatures ranging from 350 K to 2 K. Zero field cooling (ZFC) and field cooling (FC) measurements were performed at magnetic field intensities of 0.1 T and 1 T. Raman spectroscopy is complementary to XRD methods as it is a local probe and is sensitive to even subtle changes of symmetry. The Raman spectra were recorded using a Renishaw inVia Raman Microscope. The HeNe laser emitting at 633 nm with a power of 50 mW was used. The spectral resolution of the recorded spectra was ~4 cm^{-1}. For all normal Raman measurements a 40× objective and the 10% neutral density filter was used. The registered spectra are the average of 9 accumulations with 10 s integration time.

Electron Paramagnetic Resonance (EPR) measurements were carried out on a Bruker Elexsys E500 spectrometer in X band (at 9.4 GHz) and in function of temperature.

3. Results and discussion

Fig. 1 shows the experimental, calculated, and difference between the observed and calculated patterns of X-ray for $PbVO_3$ at room temperature.

The XRD patterns were indexed in a tetragonal structure with $a \approx 3.8$ Å and $c \approx 4.67$ Å and the space group P4mm as in Refs. [4–7]. The initial structural parameters were taken from Refs. [4,5], respectively. The lead atom was placed in the origin of the structure with the vanadium atom occupying an off-centre position. The lattice parameters of the tetragonal structure and the widths of the XRD peaks were obtained in the first stage by using a LeBail refinement. The structure was refined in the second stage by using the Rietveld method. Table 1 presents the refined structure (atom coordinates) of the $PbVO_3$ unit cell.

The presence of line width anisotropy of peaks was evidenced in Ref. [4]. The shape of diffraction peaks of our sample was refined using the Thomson–Cox–Hastings (TCH) formulation [10] with an anisotropic broadening model. This model contained a size dependent part and a strain dependent part. The evaluation of strain is important because it is related to the presence of ferroelectric domains. In order to correct the isotropic size widening (described by the TCH function), the size dependent part was modelled by using a uniaxial Lorentzian size parameter. The strain part was modelled by using the formulation of Stephens [11], taking into account the tetragonal symmetry. Since the peaks associated with the $(h\,k\,1)$ Miller indices are much wider than the peaks associated with the $(h\,k\,0)$ indices, the c^* axis is chosen as the direction of the anisotropy. Taking into account the instrumental contribution to the linewidth, the average crystallite size and amount of strain were calculated.

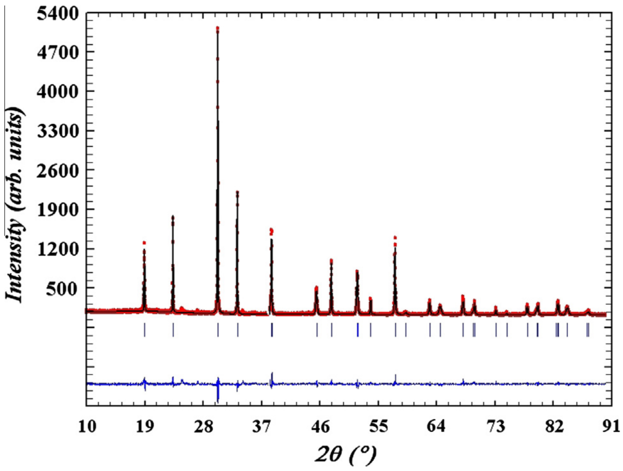

Fig. 1. Observed (dots) and calculated (continuous line) of XRD pattern for $PbVO_3$ sample. The difference between the observed and calculated patterns is shown in the line under the XRD diagram proper. The positions of the reflections are marked by ticks.

Table 1
Wyckoff positions and atom coordinates in the structure of the $PbVO_3$ unit cell.

Atom	Wyckoff	x	y	z
Pb	1a	0	0	0
V	1b	0.5	0.5	0.44
O1	1b	0.5	0.5	0.72
O2	2c	0.5	0	0.31

The average crystallite size in the direction of the *c* axis is approximately 9.7 μm where the size along the *a* or *b* direction is above 10 μm. The mechanical strain is expressed (by FullProf) as double percentage (1/10000). These results suggest that the strain anisotropy has a pronounced effect on the peak broadening comparatively with the size anisotropy.

XRD measurements performed from room temperature to low temperature ($T = 10$ K) have not evidenced any structural phase transition. Fig. 2 shows the dependence of the tetragonal unit cell parameters function of temperature. With decreasing temperature, a small decrease of the height *c* of unit cell with is observed, but the unit cell parameter *a* remains almost unchanged. This behaviour is in agreement with the results reported in Ref. [5].

Fig. 3 shows the temperature dependence of magnetic susceptibility, $\chi(T)$, of $PbVO_3$ sample in zero field cooled (ZFC) and field cooled (FC), respectively. The $\chi(T)$ curve, with a board maximum at about 180 K and the splitting of the ZFC–FC measurements, shows the features typical for $PbVO_3$ previously reported [6,7]. The broad maximum is typical for 2D spin systems while the upturn at low temperatures is usually ascribed to the paramagnetic contribution of impurities and defects. The broad peak of the susceptibility curve for $PbVO_3$ at about 180 K was explained in literature by the Heisenberg square lattice model (SQL), or by the frustrated square lattice model (FSL) [6,7]. We tested both models and we observed that only FSL gives acceptable results (Fig. 3). Because the low-temperature part of the $\chi(T)$ curve (see Fig. 3) is affected by impurity contributions, the FSL fit was performed on the temperature range between 200 K and 300 K.

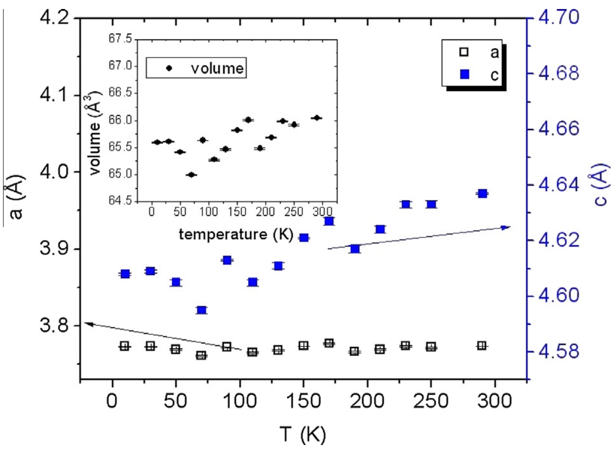

Fig. 2. Temperature dependence of unit cell parameters *c* and *a* of $PbVO_3$ sample function of temperature. The insert shows the variation of the unit cell volume.