Experimental techniques

The work presented in this thesis is based on experimental results. Obtaining samples of very good quality is of prime importance, as is proper preparation of the sample with respect to each characterization technique. All of the compounds presented in this work were prepared in our laboratory. Except when otherwise mentioned, all the measurements were also performed in our laboratory.

2.1 Sample preparation

All of the samples investigated in this thesis are perovskites that can be prepared by means of solid state reaction, as is common for such compounds. This method often requires high temperatures and controlled atmosphere, for which we use an Entech alumina-tube furnace. The basic principle of a solid state reaction is to mix the correct quantities of starting materials whose atoms will diffuse at a sufficiently high temperature. The chemical phase that minimizes the free energy will nucleate and grow. It is extremely important not only to mix the starting materials but to grind them thoroughly in order to obtain a better diffusion and increase, if possible, the rate of the reaction. It is also very common to press the ground powders into a pellet before putting them in the oven. In practice, the process of grinding and pelletization should be repeated several times until the result is a single phase material. At every step the powder should be analyzed by
means of X-ray powder diffraction for example in order to verify the crystallinity as well as check for possible impurities. For the synthesis of the rare-earth vanadates, the rare-earth oxides were pre-dried overnight and typically a 2% excess of the vanadium oxide (V$_2$O$_5$) was usually necessary in order to compensate for the V-volatility. The following rare-earth oxides were used in stoichiometric amounts: Y$_2$O$_3$, Tb$_4$O$_7$, Gd$_2$O$_3$, Eu$_2$O$_3$, Sm$_2$O$_3$, Nd$_2$O$_3$, Pr$_6$O$_{11}$. In the case of calcium-doped rare-earth vanadates, stoichiometric amounts of CaCO$_3$ were also used. A first step (typically repeated 3 times) led to the synthesis of RVO$_4$ which was later reduced at 1200°C then 1400°C under a H$_2$/N$_2$ atmosphere in order to obtain the RVO$_3$. These two steps of the synthesis were also on average repeated 3 to 4 times each, with intermediate regrinding and pressing of the powder until the reaction was complete. The obtained powder is black. The oxygen content of the samples was checked with a TA-instruments SDT2960 Simultaneous DSC-TGA, which was also used before the first synthesis to determine the particular temperatures of the reaction. All of the samples proved to be stoichiometric.

Some characterization techniques require the sample to be pressed into a very compact pellet. For this purpose, the powder was put into molds in order to produce the desired shape (typically a disk or a bar). The obtained pellet needed to undergo a sintering process. This consists in heating the pellet to interdiffuse the surfaces and obtain a dense solid.

Crystal growth of these perovskite RVO$_3$ compounds was also attempted by using a floating zone furnace. Unfortunately, the mirror furnace available in our laboratory possesses halogen lamps which are not powerful enough to properly melt the RVO$_3$ as required for the growth. Concerning the calcium-doped compounds, we only attempted to grow a crystal of (Y,Ca)VO$_3$ and the operation was only successful at low doping concentrations, because of incongruent melting for higher doping concentrations.

### 2.2 Structural characterization

X-ray diffraction is used to investigate the atomic scale structure of solids. Two different X-ray sources were used: a laboratory X-ray source with a Bruker-D8 Advance diffractometer using Cu-K$_\alpha$ radiation in Bragg-Brentano geometry and a synchrotron X-ray source ($\lambda$=0.4Å) at the High-Resolution Powder Diffraction Beamline (ID31) at the European Synchrotron Radiation Facility in Grenoble (France). The powder diffraction patterns were analyzed by the Rietveld method [1] using the refinement program GSAS [2] as implemented in the EXPGUI package [3]. On the laboratory diffractometer, the size of the slits
was chosen in order to maximize the signal-to-noise ratio while retaining a good resolution. A Ni filter was sometimes used to reduce fluorescence but resulted in much lower peak intensities. The laboratory diffractometer was useful for initial characterization of the samples regarding crystallinity, purity, and lattice parameters. However, the available temperature controller reached a minimum of 100K and the resolution was too poor to probe the structural changes related to the orbital ordering. One of the difficulties is that the lowering of the symmetry from orthorhombic to monoclinic below the orbital ordering temperature is difficult to probe because of the extremely small deviation of the monoclinic angle from 90°. The resulting splitting of diffraction peaks can only be detected on an extremely high resolution instrument, such as the ID31 synchrotron beamline described below. Whether we use the laboratory or the synchrotron diffractometer, the resolution (defined as $\delta d/d$) decreases almost linearly with increasing d-spacing. On the laboratory diffractometer the decrease of resolution is steeper than that at ID31. By comparison, at 1Å the resolution is 0.06% and 0.035% for the laboratory and ID31 diffractometers, respectively. At 3Å, the corresponding values increase to 0.24% and 0.07%. The resolution is thus better on ID31 and over a wider range than on the laboratory diffractometer. At very high angles the laboratory diffractometer approaches synchrotron resolution but in this range the signal of the D8 is extremely weak. Together with a much higher resolution, the synchrotron diffractometer available at ID31 also provides control of the temperature down to at least 5K and provides a better signal to noise ratio due to the high flux. This allows a very high quality pattern recorded in a few hours. It is thus possible to collect quickly data from a polycrystalline powder in order to detect subtle structural changes involving shifts of oxygen atoms such as those induced by ordering of the $t_{2g}$ orbitals in the RVO$_3$ series.

Synchrotron radiation was first considered an unwanted product when it was first detected in 1947 in a new kind of particle accelerator (the synchrotron). It was not before the 1960s that it was recognized as light with exceptional properties. For our purposes, the advantage of using the synchrotron light at the ESRF is its very high intensity beam. The X-ray beam is focused to obtain extremely high resolution but with an intensity still several orders of magnitude above that available on a lab diffractometer. The information that can be extracted thanks to the use of this synchrotron light is invaluable. This gives a pattern with narrow peaks, accurate peak positions (reproducible to a few tenths of a millidegree [4]) and high intensities (when a spinning capillary of appropriate size is used) which is a great advantage for crystallographic measurements and accurate structural information.
The beam is monochromated by a water-cooled double-crystal monochromator using Si 111 reflections. The incident beam size is typically 5 mm x 1 mm. A bank of nine scintillation detectors is scanned vertically to measure the diffracted intensity as a function of $2\theta$. The detectors are $\approx 2^\circ$ apart, and each is preceded by a Ge 111 analyzer crystal. This increases the efficiency of detecting the diffracted radiation [4]. The powder was placed in capillaries of 0.4 mm diameter. The capillary size and X-ray energy were chosen to minimize absorption ($\mu r < 1.5$). One must pay attention not to choose an energy near the K-edge of one of the elements. The spinning capillary reduces the effects of preferred orientation. It is generally better than the use of the static or spinning flat-plates used in our laboratory diffractometer. Low temperatures were achieved using a liquid helium cooled cryostat for spinning capillaries.

2.3 Bulk characterization techniques

2.3.1 Magnetization

The magnetic properties were measured using a Quantum Design Magnetic Property Measurement System (MPMS). This apparatus is known as a SQUID magnetometer (Superconducting QUantum Interference Device). Measurements are performed at stable temperatures and magnetic fields. The system can reach magnetic fields up to 7 Tesla and has a temperature range from 1.8K to 300K. We used the DC magnetization technique which measures the magnetic moment of a sample. An external magnetic field is applied to induce a magnetic moment if the sample does not have a permanent magnetic moment. The sample moves through a superconducting second-order gradiometer (over a length of 6.3cm) and the SQUID’s output voltage (data at 64 positions are collected) is then processed in order to compute the sample moment. The system can be used to investigate hysteresis loops, relaxation times, and the magnetic field and temperature dependence of the magnetic moment.

The samples are usually pellets of polycrystalline powder inserted in a gelatin capsule appropriately mounted in a transparent plastic straw (typical diamagnetic contribution: $10^{-5}$ emu in 1T). We measured the sample in an external magnetic field after cooling it either without applying an external magnetic field (zero-field cooled, ZFC), or in an external magnetic field (field-cooled, FC). We also performed some remanent field measurements which consist of cooling the sample in an externally applied magnetic field, then releasing the field and measuring the magnetization.
2.3.2 Specific Heat

Measuring the heat capacity gives information on structural, electronic and magnetic properties of a given sample. The specific heat was measured between 2 and 300K at constant pressure using a relaxation method in a commercial Quantum Design Physical Properties Measurement System (PPMS). The experiments were performed at the University of Leiden by Dr. G.J. Nieuwenhuys and Prof. Dr. J. Aarts. For the measurement, a sample-puck is used; it contains a sample platform below which a platform heater and a platform thermometer are attached. First of all an empty sample-puck with a certain amount of grease (Apiezon) is inserted in the device and the temperature dependence is measured, which represents the addenda specific heat signal. The sample is then mounted on the puck thanks to the grease and its specific heat is measured. The addenda specific heat is automatically subtracted from the obtained data.

2.3.3 Transport

Transport measurements were performed using a commercial Quantum Design Physical Properties Measurement System (PPMS). Temperatures can be varied from 2 to 340K and a magnetic field up to 9 Tesla can be applied by a superconducting magnet.

2.3.3.1 Resistivity

Samples with a large resistivity were measured using an Agilent 3458a multimeter and samples with a low resistivity were measured with a Linear Research AC Bridge resistance model LR700. Bar-shaped polycrystalline samples were prepared as described in Section 2.1. Although various methods exist to measure resistivity [5, 6], we chose to use a four-wire setup. In this setup, a current is passed through the sample by two outer leads, while the potential drop across the sample is measured using two inner leads (Fig. 2.1a). The electrical contacts were made using Pt wire (0.05mm diameter) connected to the sample using either silver paint or a two-component silver epoxy. The resistivity was calculated as follows:

$$\rho = \frac{V}{I} \frac{S}{d}$$  \hspace{1cm} (2.1)

We typically measured the resistivity from 5 to 300K with steps of 5K while warming the sample at a heating rate of 5K/min.
2.3.3.2 Magnetoresistance

The sample geometry and four-wire setup mentioned in the previous paragraph was also used to measure magnetoresistance. We typically performed a temperature dependent measurement of the magnetoresistance under a field of 5 T. Magnetoresistance could only be observed for two samples (see Chapter 5) for which more precise measurements were carried out.

2.3.3.3 Hall effect

E.H. Hall discovered in 1879 that a small transverse voltage appeared across a current-carrying thin metal strip in an applied magnetic field [7]. The technique has since then also been widely developed for semiconducting materials.

The Lorentz force is the physical principle underlying the Hall effect [9, 10]. The so-called Hall effect is important because it allows the carrier density, electrical resistivity and mobility of carriers to be determined. The Hall coefficient
2.3. Bulk characterization techniques

(also called Hall resistance) is defined as:

\[ R_H = \frac{E_y}{j_x H} = -\frac{1}{ne} \]  \hspace{1cm} (2.2)

We used two different geometries to measure the Hall effect. The first one is represented in Figure 2.1c and the contacts were connected to the samples as mentioned in the previous paragraph. We put the sample on a special sample-puck and placed it on a rotator so that the sample can be rotated around the current direction with \( j_x \perp H \). The Hall resistance was then measured at various temperatures in a fixed magnetic field using the ability of the rotator to measure the resistance at all angles. The second geometry was similar to that used for the resistivity and magnetoresistance measurements except that the leads to probe the potential are arranged perpendicular to the current axis as can be seen in Figure 2.1b. The resistance was measured in +5T then in -5T and the Hall voltage was taken as half of the difference of the two measurements.

2.3.3.4 Thermopower

T.J. Seebeck observed in 1821 that if two dissimilar materials are joined together and the junctions are held at different temperatures (\( T \) and \( T+\Delta T \)) a voltage difference (\( \Delta V \)) proportional to the temperature difference (\( \Delta T \)) develops [9]. The ratio of the voltage developed to the temperature gradient is related to intrinsic properties of the materials. A home-made Seebeck platform using a MMR Seebeck stage (MMR Technologies, Inc.) was connected to a standard sample-puck in order to measure the thermopower of the sample. The MMR Seebeck stage includes two pairs of thermocouples. One pair is formed from junctions of copper and a reference material of known Seebeck emf (in our case Constantan wire). The other pair is formed from junctions of copper and the material whose Seebeck emf is to be determined. A reference made of Constantan wire is also glued to copper leads. Two Agilent 3458a multimeters were used, one to measure a Constantan wire reference and one to measure the actual sample and the heater was connected to a HP 6625a power supply. The bar-shaped samples were prepared as described in Section 2.1.

2.3.4 Thermal expansion

The thermal expansion was measured at the ICMA at the University of Zaragoza. For these experiments, a sintered bar (as described in Section 2.1) is used. The surface of the sample is cleaned and polished, then a strain gauge (SG) is glued
to it. The glue is cured under a pressure of 0.25 N.m for about two hours. The sample is inserted in a cryostat. When the length of the sample \((l)\) varies, the strain gauge resistance \((r)\) will vary as follows:

\[
\frac{\delta r}{r} = g \frac{\delta l}{l}
\]  

(2.3)

where \(g\) is the gauge factor which depends on the geometry and alloy of the gauge. We used strain gauges SK-09-031DE350 from Micro Measurements with \(r=350\Omega\). A similar gauge is glued to a quartz crystal whose thermal expansion can be neglected in our temperature range. The two gauges are connected to a DC Wheatstone bridge [11], which results in a compensation of the thermal expansion of the gauge. The output voltage of the bridge is proportional to the thermal expansion of the sample.
References


