

Structural, Electrical and Magnetic Properties of Perovskite Ceramics
Colin Greaves

Special Safety Precautions

Barium salts are very toxic. Due to the involatile nature of the barium compounds studied in this experiment, the use of a fume cupboard is unnecessary, but care should be taken to avoid ingestion during all handling operations.

The perovskite structure (Fig. 1), which is adopted by many oxides with formula ABO_3 , is very versatile, and many perovskites have useful technological applications (*e. g.* as ferroelectrics, catalysts, sensors and superconductors). In this structure, the A and O ions together form a cubic close-packed array, and the B ions occupy 1/4 of the octahedral holes. This experiment involves the synthesis of four compounds which are structurally closely related to perovskite, but have very different physical properties. Control of the types of cations in the large sites (A) allows some variation of the oxidation state of the smaller octahedral cations (B), and this confers the variable physical characteristics.

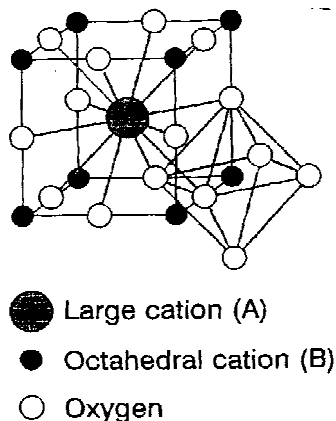


Figure 1. The perovskite structure adopted by many ABO_3 compounds.

Transition-metal ions with unpaired electrons are paramagnetic, provided interactions between neighbouring ions are weak; this "magnetically dilute" situation occurs in solutions and many solids. The perovskite structure allows quite strong interactions to occur *via* covalence in the M - O - M bonds, and this may result in ordering of the magnetic moments to give "ferromagnetic" or "antiferromagnetic" materials. At elevated temperatures, both classes are paramagnetic (random arrangement of magnetic moments), but below a critical temperature, the moments order in a parallel (ferromagnetic) or anti-parallel (antiferromagnetic) fashion. This temperature is known as the Curie temperature (T_C) for ferromagnets and the Néel temperature (T_N) for antiferromagnets.

The synthesis of solid state ceramic samples may be achieved by a variety of techniques. The simplest exploits the finite ionic or atomic diffusion processes which occur in mechanically mixed reactants at elevated temperatures and, in general, this allows precise control of the product's stoichiometry. An alternative approach involves the precipitation of a precursor, which can easily be converted to the final product by heating. This method assures intimate cation mixing prior to heating such that lower temperature may often be used for the final heating stage. In this experiment, both methods are used.

CaMnO_3 , $\text{La}_{0.85}\text{Sr}_{0.15}\text{MnO}_3$ and $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ are prepared from precipitated precursors, whereas $\text{YBa}_2\text{Cu}_3\text{O}_7$ is prepared from a mechanical mixture of Y_2O_3 , BaCO_3 and CuO . For $\text{YBa}_2\text{Cu}_3\text{O}_7$, it is not easy to ensure the correct cation ratio by simple precipitation methods, and a ceramic grinding and sintering technique is preferred. CaMnO_3 is a paramagnetic insulator at room temperature, whereas $\text{La}_{0.85}\text{Sr}_{0.15}\text{MnO}_3$ is paramagnetic but electrically conducting, and $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ is both electrically conducting and ferromagnetic. $\text{YBa}_2\text{Cu}_3\text{O}_7$ is metallic at room temperature, but becomes a superconductor with zero resistance to d. c. currents below 93K. Superconductors are perfectly diamagnetic, and it is this property which is examined in this experiment.

Experimental

a) $\text{YBa}_2\text{Cu}_3\text{O}_7$

It is preferable to use reagents (Y_2O_3 , CuO , BaCO_3) which have been dried (*e.g.* 2 hours at 400 °C in a muffle furnace). Accurately weigh out about 0.5 g of BaCO_3 and the corresponding amounts of Y_2O_3 and CuO to give a Y :Ba :Cu ratio of 1:2:3 (0.1430 g and 0.3023 g respectively for 0.5000 g of BaCO_3). Grind the materials together in a clean pestle and mortar until no white streaks are observed on grinding (*ca.* 10 min). Press 1 or 2 pellets (1-2 mm thick, 13 mm diameter) of the mixture at *ca.* 5000 kg and place the pellets in an alumina boat. Using a furnace with a programmable controller, subject the pellets to the following thermal program in air:

- 1) Heat to 930 °C and hold for 12 h
- 2) Cool to 500 °C and hold for 1 h
- 3) Cool to 400 °C at 50°C h⁻¹
- 4) Cool to room temperature

When the furnace temperature is below 400 °C, the samples may be removed using tongs and placed on an insulating board until cold.

b) CaMnO_3

Dissolve 2.36 g of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and 2.87 g of $\text{Mn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in 50 cm³ of distilled

water. Whilst stirring the solution (magnetic stirrer), slowly add 100 cm³ of 1 M KOH using

a separating funnel (about 3 min). After standing for 15 minutes, the brown precipitate should be filtered using a large Buchner funnel and washed thoroughly with distilled water (to remove excess KOH and KNO_3). Pump the sample as dry as possible, transfer to a watch glass and dry at 200 °C in a drying oven (*ca.* 1 h). Grind the sample and press two pellets 1-2 mm thick. The pellets should be placed in a porcelain or alumina boat and heated at 1000°C for about 12 h. When the furnace has cooled to below 400 °C, the boat may be removed using tongs and placed on an insulating board until cold.

c) $\text{La}_{0.85}\text{Sr}_{0.15}\text{MnO}_3$ and $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$

Repeat the procedure described for CaMnO_3 , but use the following reagents:

$\text{La}_{0.85}\text{Sr}_{0.15}\text{MnO}_3$: 3.68 g of $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$; 0.32 g of $\text{Sr}(\text{NO}_3)_2$; 2.87 g of $\text{Mn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$; $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$: 3.03 g of $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$; 0.63 g of $\text{Sr}(\text{NO}_3)_2$; 2.87 g of $\text{Mn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$.

d) Physical Properties

Place one of the pellets of each oxide in turn on a piece of paper and note its behaviour when a bar magnet is placed under the paper. Cool the pellet of $\text{La}_{0.85}\text{Sr}_{0.15}\text{MnO}_3$ in liquid nitrogen using nylon forceps and re-examine its response to the magnet. If necessary, the pellets may be ground in order to examine the magnetic properties. Grind one of the pellets of CaMnO_3 using a clean pestle and mortar. Determine the magnetic susceptibility and effective magnetic moment of Mn^{4+} using any suitable method (*e. g.* a Johnson Matthey magnetic balance).

Cool one of the pellets of $\text{YBa}_2\text{Cu}_3\text{O}_7$ in liquid nitrogen, and quickly place a small magnet (Nd-Fe-B or Sm-Co) above it. The diamagnetic properties of a superconductor should allow you to float the magnet above the sample.

For each sample, measure the electrical resistance of one of the pellets using a suitable method (qualitatively, differences should be observable using a simple DVM in resistance mode, but quantitative measurements will require the use of a conventional 4-probe dc method, if available).

CaMnO_3 gives an X-ray powder diffraction trace with the first six reflections at 2θ values of 23.85°, 34.00°, 41.93°, 48.83°, 55.06° and 60.82° (wavelength 1.542 Å). If X-ray diffraction facilities are available, the pattern can be recorded for the CaMnO_3 sample prepared. Confirm the primitive cubic structure of perovskite and determine the unit cell size.

Exercises

The structures of all four compounds are related to perovskite (Fig. 1). If available, a model of the structure should be examined. There are two independent cation arrays: the first consists of octahedrally coordinated ions, which are Ti^{4+} in the parent CaTiO_3 and Mn/Cu ions in the compounds synthesised; the second array has 12-coordinate ions which are Ca^{2+} in CaTiO_3 , La/Sr in $\text{La}_{0.85}\text{Sr}_{0.15}\text{MnO}_3$, etc. In fact, the Mn perovskites prepared all show minor deviations from the ideal cubic structure, due to size and electronic effects.

For an ideal, undistorted perovskite ABO_3 in which each cation (ionic radii r_A and r_B) contacts the coordinating O^{2-} ions (radius r_O), show that

$$r_A + r = \sqrt{2}(r_B + r_O)$$

Generally, some tolerance is allowed such that

$$r_A + r_B = t\sqrt{2}(r_B + r_O)$$

where the tolerance factor t is 0.8-1.0. For undistorted perovskites, t is high, e.g. 0.99 for SrTiO_3 . From a table of ionic radii, determine t for CaMnO_3 .

Mn^{3+} has the electron configuration $t_{2g}^3 e_g^1$ and is therefore likely to show a substantial Jahn Teller distortion. In fact, the distortion is cooperative as shown in Figure 2. In the layer shown, for example, each Mn has 2 short Mn - O bonds and 2 long bonds. If the O ions above and below the Mn ions have short bonds, all the Mn ions can achieve a similar distorted stereochemistry. Explain why the distortion shown in Figure 4.23-2 should stabilise the structure.

The electrical and magnetic properties of Mn perovskites are critically dependent on the Mn oxidation state. What is the formal oxidation state of Mn in CaMnO_3 , $\text{La}_{0.85}\text{Sr}_{0.15}\text{MnO}_3$, and $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$? The conductivity of many transition-metal oxides may be related to a simple mechanism involving the hopping of electrons between two transition-metal ions. Using such a mechanism and considering the energy involved when an electron hops from one Mn ion to a neighbouring Mn ion, explain the difference in conductivity between CaMnO_3 , and $\text{La}_{0.85}\text{Sr}_{0.15}\text{MnO}_3$ and $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$. In the determination of the effective magnetic moment, μ_{eff} , for Mn^{4+} , the Curie Law is used:

$$\chi_a = \mu^2/8T$$

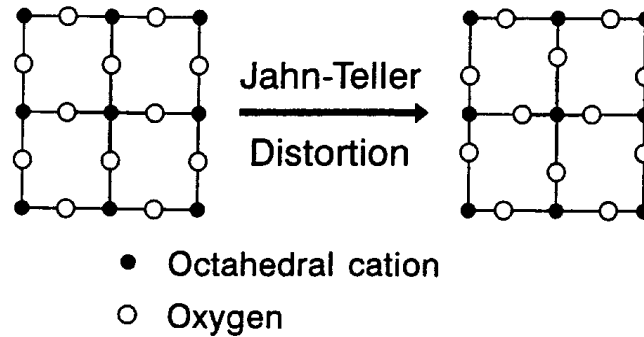


Figure 4.23-2. Cooperative Jahn-Teller distortions in a layer of the perovskite structure.

Compare your value μ_{eff} with μ_{so} , the spin-only moment, which is the magnetic moment expected if only electron spins contribute to μ_{eff} . The main reason for the disagreement is that CaMnO_3 is antiferromagnetic at low temperatures (T_N ca. 120 K). Interactions between magnetic moments are still apparent at higher temperatures and result in an apparent reduction in μ_{eff} due to a deviation from the Curie Law:

$$\chi_a = \mu_{\text{so}}^2 / 8(T + \theta)$$

Using your value of χ_a and the formula above, determine a value for θ .

Notice that whereas CaMnO_3 is antiferromagnetic, $\text{La}_{0.85}\text{Sr}_{0.15}\text{MnO}_3$ and $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ are ferromagnetic. What do your measurements on $\text{La}_{0.85}\text{Sr}_{0.15}\text{MnO}_3$ and $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ tell you about the change in Curie temperature (associated with the onset of ferromagnetic behaviour) with Mn oxidation state in this system?

Superconductors are materials which lose all electrical resistivity below a certain temperature, the critical temperature, T_c ; above T_c , they are generally metallic in nature. Until 1986, when "high temperature superconductors" were discovered, the highest T_c was 23 K for Nb_3Ge . $\text{YBa}_2\text{Cu}_3\text{O}_7$ was the first material discovered with T_c above the temperature of liquid nitrogen, 77 K. When pure, and having its maximum possible oxygen content, this material becomes superconducting at 93 K. An important property of superconductors is that below T_c ,

magnetic fields are expelled from within the material - it becomes a perfect diamagnet. This is achieved by setting up currents on the surface of the bulk material to oppose the applied magnetic field. In this way, it is possible to float a superconductor above strong magnets, using the induced opposing field for levitation.

The structure of $\text{YBa}_2\text{Cu}_3\text{O}_7$ (Fig. 3 and model if available) comprises three perovskite-like unit cells in a row; the Y and Ba ions occupy the large cation positions but in this material, not all the oxygen sites are occupied, which reduces the coordination numbers for all the cations. Layers of 5-coordinate (square pyramidal) and chains of 4-coordinate (coplanar) Cu ions are formed. What is the ratio of 5-coordinate Cu to 4-coordinate Cu in the structure (remember that certain sites in the unit cell are shared with other unit cells)? What is the ratio of Cu^{2+} to Cu^{3+} ions in $\text{YBa}_2\text{Cu}_3\text{O}_7$? A square pyramidal crystal field influences the d -orbital energies of a transition-metal ion in the same way as an elongated octahedral (tetragonal) field, which is common for Jahn-Teller distorted ions. On the basis of Crystal Field Theory, discuss the preferred distribution of the Cu^{2+} and Cu^{3+} ions between the available sites in $\text{YBa}_2\text{Cu}_3\text{O}_7$.

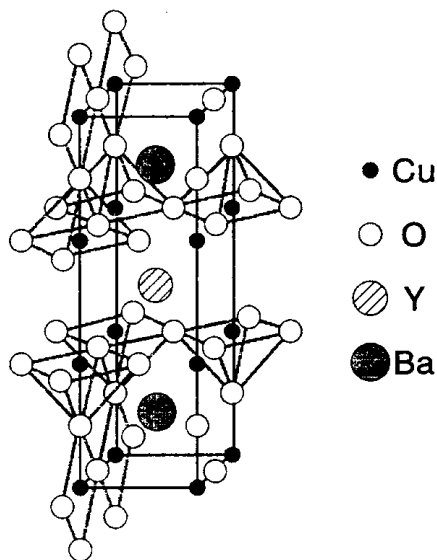


Figure 3. The unit cell of $\text{YBa}_2\text{Cu}_3\text{O}_7$ highlighting the Cu stereochemistry.