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# Single-crystal growth of transition metal oxides at high pressures of several GPa

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## Abstract

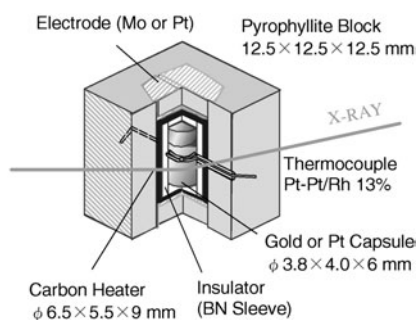
Single-crystal growth of various transition metal oxides exhibiting fascinating physical properties was performed, based on the powder x-ray diffraction studies at high pressures of several GPa. Results on a  $S = \frac{1}{2}$  one-dimensional alternating exchange antiferromagnet  $(\text{VO})_2\text{P}_2\text{O}_7$ , an oxychloride high- $T_c$  superconductor  $\text{Ca}_{2-x}\text{Na}_x\text{Cu}_2\text{Cl}_2$ , and  $\text{CaFeO}_3$  with unusual  $\text{Fe}^{4+}$  ions are reported.

## 1. Introduction

High-pressure (HP) synthesis is a powerful technique in searching for new materials. We have discovered many low-dimensional magnets such as high- $T_c$  superconductors and spin ladder compounds using this technique. Generally speaking, however, it used to be almost impossible to obtain single-crystal samples of these HP phases because of the lack of the information about the HP–HT (high-temperature) reactions. High-energy, high-flux x-rays from synchrotron radiation enabled us to observe such a reaction in a HP cell even if the sample was in a gold or a platinum capsule. The melting points of the samples with various kinds of flux were determined by means of powder x-ray diffraction (XRD) and the information obtained was applied in the single-crystal growth. In this paper, we report the crystal growth of three transition metal oxides which exhibit fascinating physical properties.

## 2. Experimental details

Powder XRD studies were performed using the cubic anvil-type HP apparatuses ‘SMAP-180’ and ‘SMAP-2’ installed at BL14B1 of SPring-8. The data were collected by means of the energy-dispersive method with a SSD detector fixed at  $2\theta \sim 4^\circ$ . The cell assembly used for the XRD study is shown in figure 1. The starting oxides mixed with flux were packed in a gold or a platinum capsule which was placed at the centre of the cell with a carbon heater



**Figure 1.** The cell assembly used for the power XRD study at HP.

and a BN insulator. A thermocouple was threaded through the BN sleeve and was looped around the capsule, both ends touching the faces of WC anvil tops. The thermoelectromotive force was measured through the anvil tops, so the monitored temperature was the temperature difference between the sample and the surface of the anvil top. We put another thermocouple on the surface of one of the remaining anvil tops. The two thermocouples were connected in series such that the total thermoelectromotive force corresponds to the difference between the sample and room temperatures. After the determination of a suitable flux and the melting temperature, crystal growth was performed using an in-house cubic anvil-type HP apparatus. The cell assembly was basically the same as used for the XRD except for the size. The edge of the pyrophyllite block was 30 mm long, and the size of the capsule was  $\varnothing 9.6 \text{ mm} \times 16 \text{ mm}$ .

### 3. Results

#### 3.1. The HP phase of $(\text{VO})_2\text{P}_2\text{O}_7$

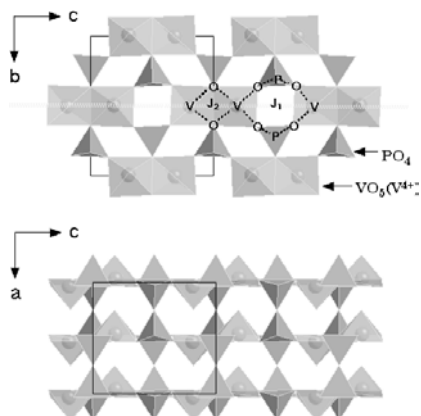
$(\text{VO})_2\text{P}_2\text{O}_7$  (HP phase) is an  $S = \frac{1}{2}$  one-dimensional alternating exchange antiferromagnet with a spin gap [1]. This compound comprises vanadium ions in the 4+ oxidation state with spin  $\frac{1}{2}$ . In the crystal structure shown in figure 2, it has two major AF interactions along the  $c$ -axis, one mediated by the two V–O–(P)–O–V paths ( $J_1$ ) and the other through the almost orthogonal V–O–V paths ( $J_2$ ). The alternation of these interactions along the  $c$ -axis leads to a spin- $\frac{1}{2}$  alternating chain. Therefore, the ground state of this compound is a spin singlet one with a spin gap below the triplet excitation state.

Figure 2 shows the XRD patterns taken at various conditions. The starting material was the ambient pressure polymorph. When the pressure was applied, the peak shifted in the higher-energy direction indicating shrinkage of the lattice. The peak broadening was due to the strain in the particles. The peaks sharpened again with increasing temperature and new peaks corresponding to (221), (113) and (231) reflections of the HP phase appeared at 500 °C. This clearly showed that the transition to the HP phase took place between 400 and 500 °C. Fortunately, this compound melted congruently at 1150 °C and all the peaks disappeared except for those of the characteristic x-rays of lead.

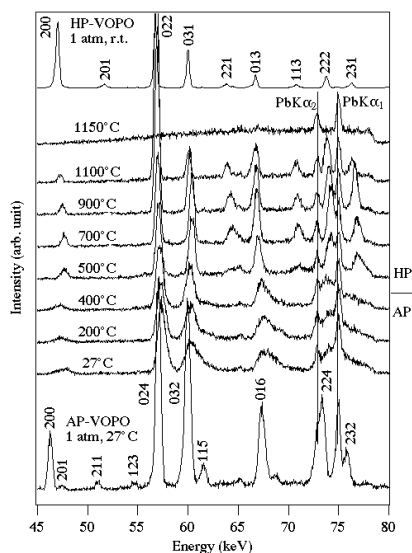
Single crystals were obtained by slowly cooling the melt from 1300 to 700 °C over 60 h at 3 GPa using an in-house HP apparatus [2]. A magnified view of the crystals grown is shown in figure 4.

#### 3.2. $\text{Ca}_{2-x}\text{Na}_x\text{CuO}_2\text{Cl}_2$

This compound is a high- $T_c$  superconductor with chlorine instead of apical oxygen [3] as shown in figure 5. It is an ideal substance for photoemission and STM measurements because



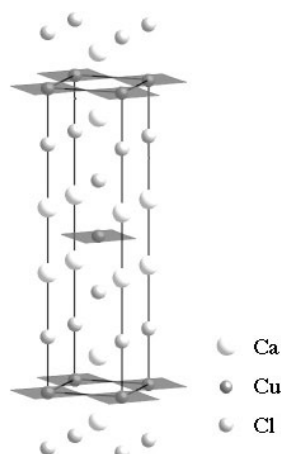
**Figure 2.** Crystal structures of HP  $(VO)_2P_2O_7$  illustrated along the  $a$ -axis and the  $b$ -axis. The spheres represent V ions. P ions are at the centres of tetrahedra.



**Figure 3.** XRD patterns of  $(VO)_2P_2O_7$  at 3 GPa and various temperatures.

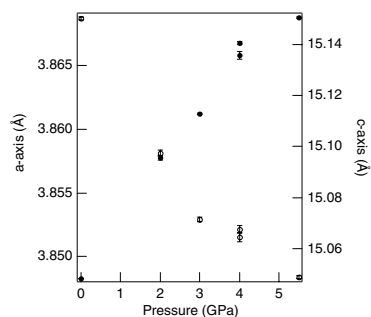


**Figure 4.** Single crystals of the HP VOPO obtained by cooling the melt from 1200 to 600° over 60 h at 3 GPa.

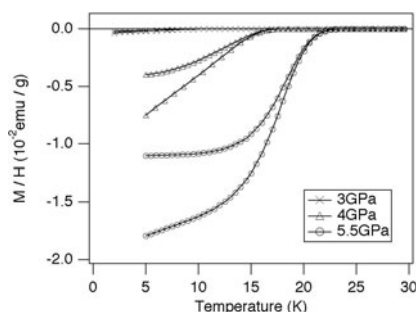


**Figure 5.** The crystal structure of  $Ca_{2-x}Na_xCuO_2Cl_2$ .

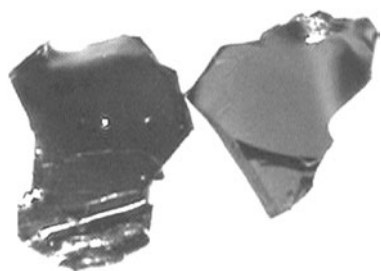
(a) it is easy to cleave (a fresh  $CuO_2$  plane is readily available), (b) samples from insulator to doped superconductor are available, (c) there is no orthorhombic distortion at low temperature, (d) it has no modulation. The last two points are of advantage to the popular HTS compounds  $La_{2-x}Sr_xCuO_4$  and Bi-2212 phases, respectively. Mixtures of  $Ca_2CuO_2Cl_2$ ,  $NaClO_4$  and  $NaCl$  in the ratio 1:0.2:0.2 were slowly cooled from 1250 to 1050 °C at various pressures to obtain plate-like crystals [4].  $NaClO_4$  operated as the flux, Na source and oxygen generator. The Na content ( $x$ -value) was controlled by changing the pressure during the crystal growth.



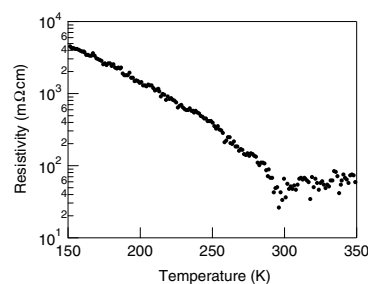
**Figure 6.** Lattice constants of  $\text{Ca}_{2-x}\text{Na}_x\text{CuO}_2\text{Cl}_2$ . Open circles represent the  $a$ -axis while filled circles represent the  $c$ -axis.



**Figure 7.** Susceptibility data for the single crystals grown at various pressures.



**Figure 8.** Cleaved surfaces of  $\text{Ca}_{2-x}\text{Na}_x\text{CuO}_2\text{Cl}_2$  single crystals.



**Figure 9.** The resistivity of a single crystal of  $\text{CaFeO}_3$ .

Consequently, the lattice parameters and  $T_c$  changed systematically. As seen in figure 6, the  $a$ -axis shrank while the  $c$ -axis expanded with increasing pressure. These features are characteristic of a  $p$ -type superconductor. From the comparison with the powder sample data, the maximum Na content was estimated to be  $x = 0.13$  for the sample grown at 5.5 GPa. Figure 7 shows the susceptibility of the crystals grown at various pressures. Both  $T_c$  and the volume fraction increased monotonically with increasing Na content, indicating that the samples are in the underdoped region. The crystals were cleaved to obtain smooth surfaces as shown in figure 8 for various measurements such as resistance, optical conductivity, angle-resolved photoemission and STM.

### 3.3. $\text{CaFeO}_3$

This is a distorted perovskite ( $\text{GdFeO}_3$  type) with unusual  $\text{Fe}^{4+}$  ions which show charge disproportionation to  $\text{Fe}^{3+}$  and  $\text{Fe}^{5+}$  below room temperature. Single-crystal samples were grown from a mixture of  $\text{CaFeO}_{2.5}$ ,  $\text{KClO}_4$ ,  $\text{NaCl}$  and  $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$  in the ratio 1:0.25:0.25:0.25 by slowly cooling the melt from 1300 to 900 °C at 4 GPa [5]. Figure 9 shows the resistivity measured for a crystal thus obtained. A metal–insulator transition owing to the charge disproportionation was clearly observed at 295 K.

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