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Pressure and magnetic field effects on the crystallographic texture and electrical conductivity of the $Bi_4(V_{0.85}Co_{0.15})_2O_{11-\delta}$ compound

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Abstract. The compound $Bi_4(V_{0.85}Co_{0.15})_2O_{11-\delta}$ figures among the solid electrolyte materials exhibiting a high oxygen ion conduction. It belongs to the well known BIMEVOX family whose structure originates from the aurivillius phase Bi_2MoO_6. The layered structure of these compounds results in a larger bidimensional conductivity in the (a, b) planes than along the c axis. This physical characteristic is clearly observed in a single crystal, whereas it is completely inhibited in misoriented powders. This paper deals with the means to retrieve this anisotropic conduction from free powders. Powder orientations were obtained using a high magnetic field and a uniaxial pressure. The correlation between the crystallographic texture and the electrical conductivity of this compound is reported here for the first time.

1. Introduction

Solid electrolytes exhibiting good ionic conductivity by O^{2-} ions are used in oxygen sensors, oxygen pumps and fuel cells. Their main features are (i) high oxide ion conductivity over a wide range of temperatures and oxygen partial pressures, and (ii) low fabrication cost of tubes and membranes with large surface and low thickness. Therefore, polycrystalline ceramics represent an important economical and technological challenge.

Among compounds showing such properties, the compound discovered in 1985 [1, 2] and formulated as $Bi_4V_2O_{11}$ is of interest. Its structure is close to the aurivillius phase Bi_2MoO_6. This compound may be viewed as an intergrowth, along the c axis, of alternating $(Bi_2O_2)^{2+}$ sheets and $(MoO_4)^{2-}$ perovskite layers. The complete substitution of Mo^{6+} ions by V^{5+} cations induces the creation of oxygen vacancies to conserve the total electroneutrality. Other works have demonstrated that these vacancies are located in the $(VO_{5.5}\square_{0.5})$ perovskite-like layers, conferring a bidimensional behaviour on the conductivity [3–5].

In order to stabilize, at room temperature, the high-temperature γ-phase (one of the best O^{2-} conductors ($\sigma = 10^{-1}$ S cm^{-1} with an activation energy $E_a = 0.17$ eV at 900 K)), the vanadium ions are partially substituted by cobalt cations with a substitution ratio of 0.15. The corresponding compound, called BICOVOX.15%, is formulated as $Bi_4(V_{0.85}Co_{0.15})_2O_{11-\delta}$ and has a $\gamma' \rightarrow \gamma$ phase transition around 780 K. The high-temperature γ-phase is characterized by a quasi-liquid disorder of the O^{2-}-anions improving the conductivity, and the γ'-phase presents modulations due to the splitting of oxygen crystallographic sites [3–5].

Taking into account the high-conductivity performance of these materials, it seemed interesting to try to optimize their use conditions, especially in making use of the bidimensional ionic conductivity. The aim of this paper is to show the relation between the texture and the conductivity of the $Bi_4(V_{0.85}Co_{0.15})_2O_{11-\delta}$ compound. The uniaxal pressure-induced and the magnetic field-induced orientations will be studied.

2. Experimental methods

2.1. Sample preparation

Polycrystalline samples were prepared by solid state reaction, starting from the basic oxides Bi_2O_3, V_2O_5, and CoO. The weighted oxides were ground, and fired in a gold

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crucible for 12 h at the following different temperatures: 900 K, 1000 K, and 1100 K. Between each temperature step, the mixture was quenched in air and ground in an agate mortar to prevent $BiVO_4$ formation. After the last firing, the compound was cooled to room temperature with a cooling rate of -20 K h^{-1}.

To grow single crystals, 'decrescendo' cyclic temperature variations were chosen. This thermal cycle consists of slow thermal oscillations around the melting point. The resulting single crystals are platelet-shaped with largest faces parallel to the $(\boldsymbol{a}, \boldsymbol{b})$ crystallographic plane.

2.2. Orientation processes

To create orientations, two processes based on the application of a uniaxial pressure and/or a magnetic field were used on free powders.

The polycrystalline ceramics for the conductivity measurements were generally: (i) uniaxially pressed under 1 kbar in order to obtain a cylinder-shaped sample; (ii) isostatically pressed under 2.5 kbar to avoid a preferred orientation; (iii) sintered in air at 1050 K [6]. The isostatical pressure was deliberately omitted in the following sample fabrications, in order to correlate the texture and the uniaxial pressure clearly. The procedure for the synthesis of the sample called P2 (P for pressure dependent (see table 1)) consisted of: (i) application of a uniaxial pressure of 2 kbar on a free powder (several successive pressures with relaxation between each pressure); (ii) firing of the cylinder-shaped sample at 1050 K for 24 h; and (iii) cooling from 1050 K to room temperature with a -20 K h^{-1} cooling rate. In order to appreciate the pressure effect on the texture, another sample (sample P12.5) was fabricated using the same method but with a uniaxial pressure of 12.5 kbar instead of 2 kbar.

A high magnetic field was also used to perform orientations. A $Bi_4(V_{0.85}Co_{0.15})_2O_{11-\delta}$ free powder was mixed with 50% weight of Araldite glue. The resulting mixture was placed, at room temperature, in a 7 T magnetic field $\boldsymbol{H}_a$ generated by a superconducting coil (sample H7, H for magnetic field dependent). To estimate the magnetic field effect, another sample (sample H0.25) was prepared by mixing powder and Araldite glue and oriented under $H_a = 0.25$ T (permanent magnet).

Conductivity measurements cannot be made after processing with Araldite glue for the orientation, since there is no electrical contact between the grains. Thus, an experimental procedure was developed to obtain a textured ceramic by applying successively a magnetic field and a pressure strain. At room temperature, a tube filled with alcohol was placed in a magnetic field $H_a = 7$ T. The free powder, previously ground as fine as possible (grain size <10 μm), was sieved onto the top of it. During the settling of the powder, which was relatively slow owing to the alcohol viscosity and small particle sizes, the crystallites were oriented in the liquid. After alcohol had evaporated, the oriented powder was uniaxially pressed under a pressure of 2 kbar. The $\boldsymbol{P}$ pressure axis was parallel to $\boldsymbol{H}_a$ direction. The resulting cylinder-shaped sample (sample H7P2) was sintered at 1050 K for 24 h, and then cooled to room temperature at a -20 K h^{-1} cooling rate.

2.3. Characterization methods

The magnetic susceptibilities were measured by the axial extraction method. A magnetic field $\boldsymbol{H}_m$ created by a superconductive coil was applied to a sample placed at the centre of a small detection coil B_1. The sample was then shifted to the centre of a second detection coil B_2. Both B_1 and B_2 coils were connected to a detector which measured the magnetic flux variation. This variation was proportional to the magnetization of the sample. The measurements were performed in the temperature range 4.2 K–300 K, with variable magnetic fields (from 0 T to 8 T).

X-ray texture analyses were performed on a four-circle diffractometer in the Schulz reflection geometry [7]. Copper radiation emitted from a rotating target was monochromatized and collimated. Stereographic pole figures were measured by scanning the tilt angle χ between 0 and 72° in steps of 1.8° or 0.9°, and the azimuthal angle ϕ between 0 and 360° in steps of 3.6° or 1.8° depending on the texture strength. These figures are the projection of the diffraction intensity of a given Bragg reflection as the sample is rotated. The experimental data were corrected for background and for defocusing using the standard procedure from a randomly oriented sample and using the program CORTEXG [8, 9]. Normalization of the corrected data into pole densities was realized by integration of the pole figure with the program POFINT. Normalized data were then reduced into a 5×5 grid using a two-dimensional spline interpolation procedure and plotted using the Berkeley Texture Package (BEARTEX) [10].

The {006} pole figures were analysed in order to check $\boldsymbol{c}$ axis orientations, while {113} pole figures showed an eventual in-plane orientation. In order to evaluate the degree of texture, the pole densities $D_{hkl}(\chi, \phi)$ were obtained by normalization of the pole figures [11]. For a standard sample without marked texture, the density is then equal to one for all (χ, ϕ) values, in mrd (multiple of random distribution) unity. The diffracted intensity is then uniformly distributed over the whole pole figure.

The ionic conductivity measurements were carried out by impedance spectroscopy on single crystals and on polycrystalline ceramics. A Hewlett–Packard (HP 4192 A) impedance analyser was used in the frequency range 5 Hz–13 MHz. Both opposite faces of the samples were coated with gold paste. Gold wires connected both the electrodes to gold spots deposited on an alumina plate. The measurements were performed in the temperature range 450 K–1050 K in air using a resistance furnace.

3. Magnetic measurements

The absence of magnetic order already established by neutron diffraction at low temperature was confirmed by magnetization measurements on a free powder [3]. In the temperature range 4.2 K $\leftrightarrow$ 300 K, the inverse susceptibility versus temperature shows a Curie–Weiss behaviour related to a paramagnetic state [3]. This paramagnetic state is in agreement with the strong dilution of the cobalt atoms in the material preventing long-range magnetic interactions. From the Curie constant ($C_{mol} =$

Table 1. Summary of the orientation densities $D_{006}(0, 0)$ and the conductivities of all the samples.

	Orientation processes		Binders		Conductivities at 870 K (γ-phase)		
	Pressure (kbar)	Magnetic field (T)	Alcohol	Araldite	$\sigma_{\parallel}$ ($\times 10^3$ S cm^{-1})	$\sigma_{\perp}$ ($\times 10^3$ S cm^{-1})	$D_{006}(0, 0)$ (mrd)
Single crystal	—	—	—	—	73.2	2.6	$>$ 4000
Sample P2	2	—	—	—	40.2	20.2	14.8
Sample P12.5	12.5	—	—	—	—	—	22
Sample H7	—	7	—		—	—	430
Sample H0.25	—	0.25	—		—	—	23
Sample H7P2	2	7		—	59.1	13.8	33.5

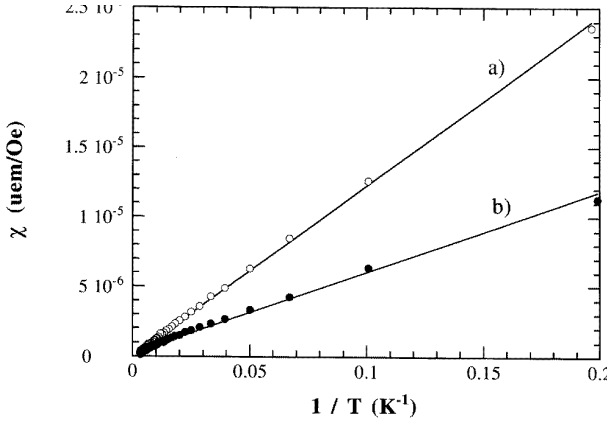

Figure 1. Evidence of the anisotropic magnetic susceptibility for two parts of magnetic field oriented sample H7: (a) $\boldsymbol{H}_m$ parallel to $\boldsymbol{H}_a$; (b) $\boldsymbol{H}_m$ perpendicular to $\boldsymbol{H}_a$.

0.86), an effective magnetic moment μ_{eff} equal to 4.79 μ_B per Co atom has been determined with the hypothesis that only the cobalt atom carried a magnetic moment (only V^{5+} cations). Such a μ_{eff} value can be interpreted either as a $Co^{3+}(\delta = 0.30)$ in a high spin state (spin moment only), or as a $Co^{2+}(\delta = 0.45)$ with an orbital moment not completely quenched.

For the sample H7 previously oriented under a high magnetic field, the magnetization measurements, performed either with the measuring magnetic field $\boldsymbol{H}_m$ parallel or perpendicular to the $\boldsymbol{H}_a$ applied direction exhibited different values for both orientations, the largest one occurring when $\boldsymbol{H}_m$ is parallel to $\boldsymbol{H}_a$ (figure 1). These results suggest a strong preferred orientation associated with anisotropic paramagnetism.

With the assumption that the vanadium atoms carry no magnetic moment, this anisotropic paramagnetic behaviour can be related to the existence of a significant orbital moment on the cobalt atoms. Consequently, the assumption of a Co^{2+} configuration can be preferred to a Co^{3+} one, in agreement with the calculated effective magnetic moment μ_{eff}.

4. Texture analyses

The texture of one plate-shaped single crystal was firstly investigated to test the quality of the crystals. In single crystals, the orientation density reaches high values somehow limited by the experimental resolution. For example, a maximal density near 4000 mrd was estimated using the {006} pole figure (figure 2(a)). This figure showed the perfection of this crystal, together with the {113} pole figure which exhibits four poles corresponding to the (113) reflection and to $(\bar{1}13)$, $(1\bar{1}3)$ and $(\bar{1}\bar{1}3)$ equivalent reflections (figure 3(a)). However these poles indicate a noticeable mosaic spread of 3°–4° at half width of the maximum in the χ direction.

Considering the single crystal as a reference, a texture analysis was performed on oriented powders under a uniaxial pressure. The texture analysis on the (006) Bragg reflection carried out on the sample P2, has shown a low orientation with a maximal $D_{006}(0, 0)$ density equal to 14.8 mrd (figure 2(b)). The maximum intensity was centred on the pole figure, and the rest of the intensity was spread over a wide angular range. Therefore, the majority of the crystallographic $(\boldsymbol{a}, \boldsymbol{b})$ planes of the grains were parallel to the faces of the cylinder-shaped sample.

For the sample P12.5, the resulting {006} pole figure revealed a better $\boldsymbol{c}$ axis orientation than in the previous case, and the density was slightly greater with $D_{006}(0, 0) =$ 22 mrd. However, the dispersion of the intensity on the pole figure subsisted. Thus, the higher the uniaxial pressure, the better the texture of the compound obtained, but the improvement in the orientation density $D_{006}(0, 0)$ is not proportional to this increase in the applied pressure.

To summarize, a uniaxial pressure induces a non-negligible texture with the crystallite $\boldsymbol{c}$ axes aligned along the pressure axis. However, the large dispersion of the intensity on the {006} pole figures indicates that a large proportion of the grains are not well aligned showing the limited effect of the pressure. Orientation due to the unidirectional pressure results from a mechanical process acting on the platelet-shaped crystallites. The applied pressure is not completely uniaxially transferred to grains, and many remained misoriented.

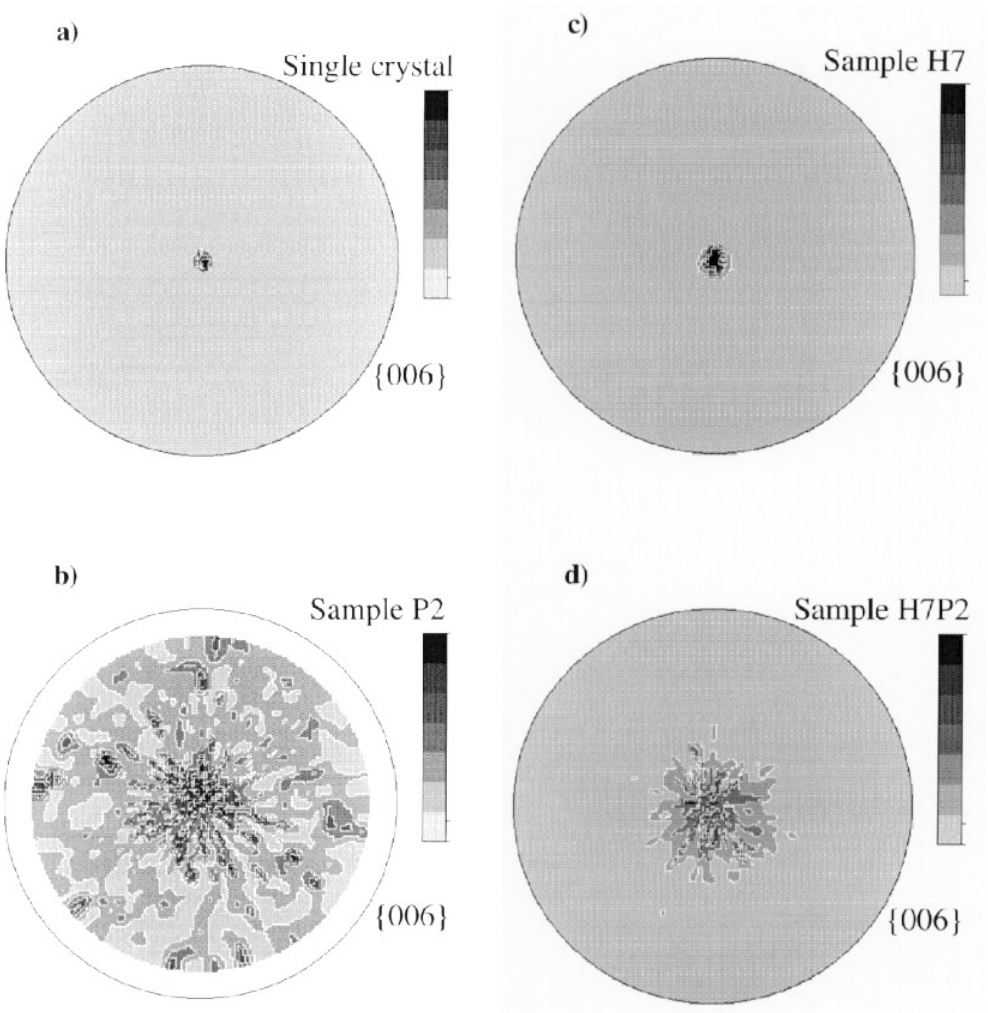

Figure 2. {006} pole figures for several samples: (a) single crystal; (b) sample P2; (c) sample H7; and (d) sample H7P2 (linear intensity scales, minimum is equal to 0, maximum is given in text).

Other measurements were performed on oriented powders under a magnetic field, and the first study concerned the sample H7. An x-ray diffraction diagram was collected, the diffracting plane being a face of the cylinder perpendicular to the applied magnetic field $\boldsymbol{H}_a$, using a conventional θ–2θ diffractometer (D5000 Siemens diffractometer configured in the Bragg–Brentano geometry). The diffraction pattern showed only the $(00l)$ reflections (figure 4), revealing a strong preferred orientation. The magnetic field induces an alignment of the $\boldsymbol{c}$ axes with the direction of $\boldsymbol{H}_a$.

The {006} pole figure (figure 2(c)) gives a quantitative description of this orientation. The $\boldsymbol{c}$ axes are dispersed in a revolution cone centred on the $\boldsymbol{H}_a$ direction and with no more than 5° of full width at half maximum. An orientation density $D_{006}(0, 0)$ of 430 mrd has been calculated. The {113} pole figure shows a ring of 5° of radial half width and centred at $\chi = 53°$ in agreement with the {006} distribution (figure 3(b)). This figure exhibits a random orientation of the $\boldsymbol{a}$ and $\boldsymbol{b}$ axes around the $\boldsymbol{H}_a$ direction. Thus, both pole figures indicate a [001] fibre texture. The $\boldsymbol{c}$ axis alignment is greatly enhanced by the presence of the magnetic field, even if the density value of 430 mrd remains lower than that obtained on the single crystal, and the dispersion of the $[00l]$ directions around $\boldsymbol{H}_a$ as high as 5°.

Following the magnetic characterization results, it is emphasised that the anisotropy in the paramagnetic susceptibility due to the Co atoms is maximum along the $\boldsymbol{c}$ axis and thus the grains align their $\boldsymbol{c}$ axes parallel to the applied magnetic field $\boldsymbol{H}_a$.

On the sample H0.25, the texture analysis also reveals an alignment of the $\boldsymbol{c}$ axes along $\boldsymbol{H}_a$. The density $D_{006}(0, 0)$ equal to 23 mrd (lower than for $H_a = 7$ T) indicates a greater dispersion of the intensity over the pole figure. This relatively lower degree of orientation could be explained by the low magnitude of H_a combined with the strong curvature of the field lines outside the permanent magnet axis.

Thus, the best orientation of the grains is obtained under a magnetic field, which uses the anisotropy of the paramagnetic susceptibility.

Orientation tests were performed on several compounds where V^{5+} ions are partially substituted by transition metals such as Cu^{2+}, Mn^{2+}, Ni^{2+}, and Fe^{3+} cations with equivalent substitution ratios. These tests were carried out with $H_a = 0.25$ T. The resulting diffraction diagrams

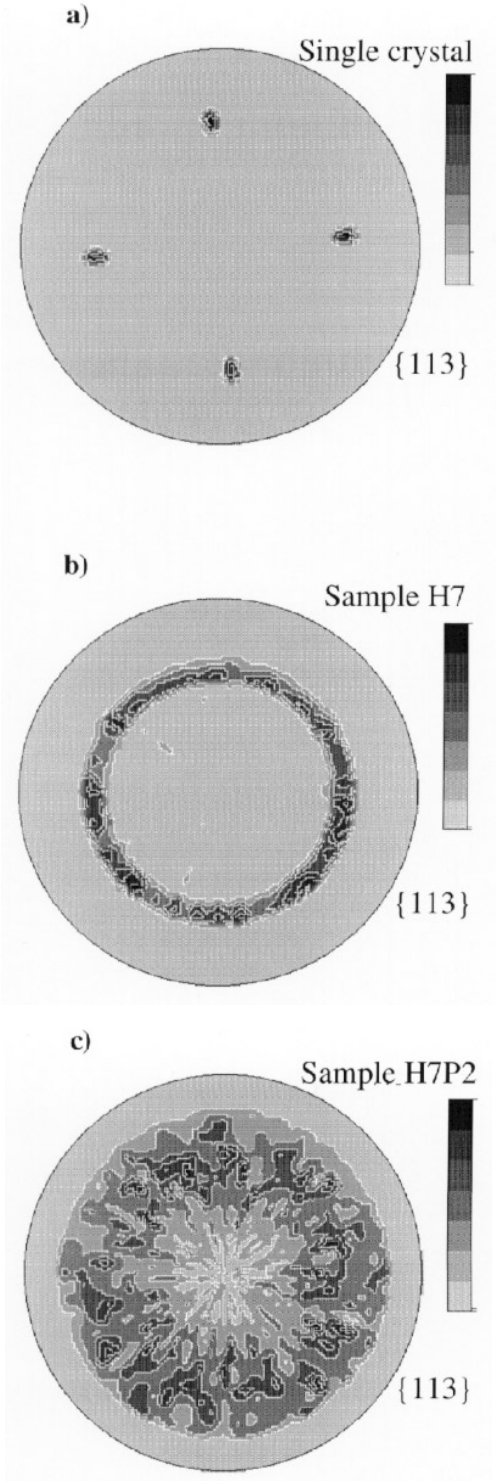

Figure 3. {113} pole figures for several samples: (a) single crystal; (b) sample H7; and (c) sample H7P2 (linear intensity scales, minimum is equal to 0, maximum is given in text).

showed no orientation at all, and only the BICOVOX.15% compound exhibits a particular magnetic behaviour.

On the sample H7P2, for which a magnetic field and a uniaxial pressure were combined, the {006} pole figure showed a $\boldsymbol{c}$ axis parallel to $\boldsymbol{H}_a$ texture of the ceramic with an orientation density $D_{006}(0, 0)$ up to 33.5 mrd

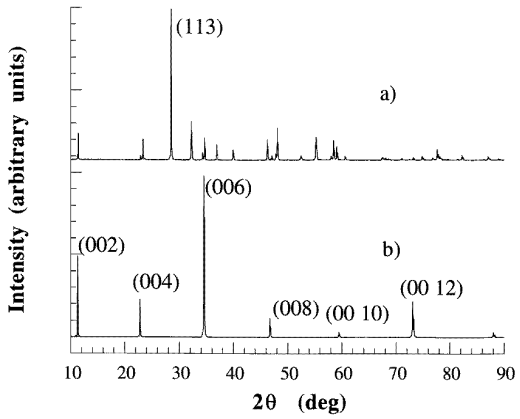

Figure 4. Conventional θ–2θ x-ray diffraction diagrams performed (a) on a free powder and (b) on the sample H7, the diffracting plane perpendicular to the applied magnetic field.

(figure 2(d)). The {113} pole figure exhibited a diffuse ring centred at $\chi = 53^\circ$ associated to a random orientation of the $(\boldsymbol{a}, \boldsymbol{b})$ planes (figure 3(c)). For the same applied pressure, the different densities D_{006} obtained on the samples P2 and H7P2 showed that the magnetic field significantly improved the texture. Then, for the sample oriented without Araldite glue, the combination of both texturation processes improves the overall orientation, since the magnetic field orientates, in a first step, the grains of the powder, and then the uniaxial pressure allows conservation of this orientation since $\boldsymbol{P}$ and $\boldsymbol{H}_a$ were parallel.

In conclusion, whatever the orientation process, all the texture analyses performed have revealed a [001] fibre texture with different orders of magnitude. The quality of the orientation is given by: (i) the orientation density $D_{006}(0, 0)$; (ii) the angular distribution of the maximal intensity; and (iii) the dispersion of the residual intensity over the pole figure.

5. Conductivity measurements

The sample characteristics and the values of the orientation densities $D_{006}(0, 0)$ are summarized in table 1.

Taking into account the platelet shape of the single crystals, the conductivity measurements were performed either parallel to the $(\boldsymbol{a}, \boldsymbol{b})$ plane (referred to as $\sigma_\parallel$), or perpendicularly (referred to as $\sigma_\perp$). Both curves (figure 5) show the same behaviour: for a temperature around 780 K, a discontinuity appears corresponding to the $\gamma \leftrightarrow \gamma'$ phase transition. The classical Arrhenius law $\sigma = \sigma_0 \exp -(E_a/k_B T)$ is not respected over the whole temperature range. Between parallel and perpendicular directions, a large conductivity difference of about one or two orders of magnitude is observed. These measurements confirm the bidimensionality of the conduction already observed in previous work [2–4].

The conductivities $\sigma_\parallel$ and $\sigma_\perp$ measured on a single crystal can be considered as the upper and lower limits which can be attained on a perfect tridimensionally oriented material.

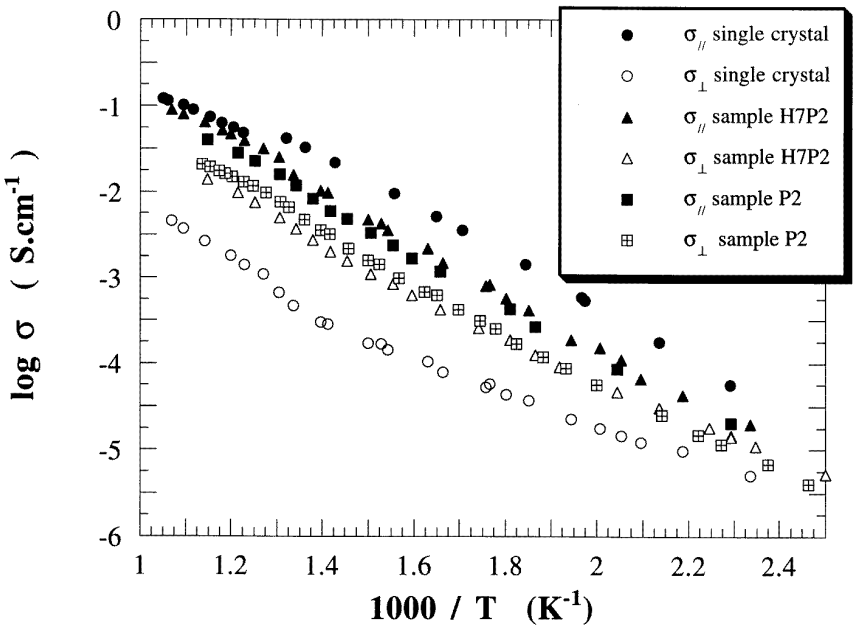

Figure 5. Conductivity measurements on a single crystal, and on the samples P2 and H7P2.

In contrast, on free powders, the absence of preferred orientation averages out the parallel and perpendicular conduction effects. The conduction curves [12] exhibit an intermediate behaviour between the $\sigma_{\parallel}$ and $\sigma_{\perp}$ values measured on a single crystal, and a smoother discontinuity at the $\gamma \rightarrow \gamma'$ phase transition.

The conductivity measurements were also performed on two parts of the uniaxial pressure textured sample P2. On the first piece, the measurements were carried out parallel to the cylinder faces, while on the second, along the cylinder axis. The conductivity curves show an obvious anisotropy which corroborates the texture analysis previously reported (figure 5).

On the other hand, the effect on the electrical conductivity of the texture resulting in the combination of magnetic field and uniaxial pressure could be shown by measurements on two parts of the sample H7P2. As previously, the first textured piece was measured parallel to the $(\boldsymbol{a}, \boldsymbol{b})$ plane, the second along the $\boldsymbol{c}$ axis. The curves exhibit a strong anisotropy closer to the single crystal behaviour than to that observed on the sample P2 (figure 5).

In table 1, the conductivity values of $\sigma_{\parallel}$ and $\sigma_{\perp}$ are given at 870 K (in the γ-phase): the values obtained on the sample H7P2 are close to the values measured on the single crystal. The difference between $\sigma_{\parallel}$ and $\sigma_{\perp}$ is around 70×10^{-3} S cm^{-1} for the single crystal, 50×10^{-3} S cm^{-1} for the sample H7P2, and around 20×10^{-3} S cm^{-1} for the sample P2. The difference is greater for the sample H7P2 than for the sample P2, and shows the effect of the magnetic field on the macroscopic conductivity anisotropy, in relation to the degree of texture.

The activation energies E_a, given in table 2, corresponding to the slope of the curve $\log \sigma = f(10^3/T)$, have been calculated for both the high-temperature γ-phase and the lower temperature γ'-phase. In the γ-phase, the values of $\sigma_{\parallel}$ and E_a for the ceramic H7P2 are close to those of the single crystal. These characteristics confirm the quasi-liquid disorder of the oxygen anions at high temperature. Indeed, the tridimensional orientation of the single crystal or the random in-plane orientation of the ceramics do not modify the electrical properties, i.e. in this phase there are no privileged conduction pathways.

Table 2. Activation energies E_a of the samples measured by impedance spectroscopy.

	Single crystal		Sample P2		Sample H7P2	
	$\sigma_{\parallel}$	$\sigma_{\perp}$	$\sigma_{\parallel}$	$\sigma_{\perp}$	$\sigma_{\parallel}$	$\sigma_{\perp}$
γ-phase E_a(eV)	0.45	0.61	0.46	0.52	0.45	0.55
γ'-phase E_a(eV)	0.60	0.37	0.52	0.52	0.58	0.44

In contrast, in the γ'-phase, the $\sigma_{\parallel}$ conductivity curves of the single crystal and the ceramic H7P2 are clearly separated. Because of the modulations exhibited in this crystallographic phase (in the reciprocal space, the satellite reflections are visible along the $\boldsymbol{a}^*$ and $\boldsymbol{b}^*$ axes) [3–5], the O^{2-} ions probably have preferred passageways in the $(\boldsymbol{a}, \boldsymbol{b})$ plane. In ceramics, a [001] fibre texture has been shown. Therefore, the crystallites are in-plane randomly oriented, and the conductivity is averaged out.

All the conductivity measurements have corroborated the results of the texture analyses, giving all indication of a strong correlation between physical properties and crystallographic texture.

6. Conclusion

The aim of this paper was to correlate the crystallographic texture and the conductivity of the BICOVOX.15%

compound. The orientation induced by a uniaxial pressure and/or by a magnetic field has been studied by texture analyses which have revealed, in all cases, a [001] fibre texture with a random in-plane orientation.

A uniaxial pressure creates an alignment of the $\boldsymbol{c}$ axes of most of the grains along the pressure axis, but the texture analysis has shown that many grains remained misoriented.

A magnetic field orientates powders using the anisotropy of the paramagnetic susceptibility: the grains aligned their $\boldsymbol{c}$ axes with the direction of the applied magnetic field $\boldsymbol{H}_a$. The resulting orientation is very strong and most of the grains follow the field effect. Furthermore, we have shown the interesting results of applying a magnetic field before the pressure.

Conductivity measurements were performed to assess the effect of the orientation on the electrical properties. The sample aligned under combined $\boldsymbol{H}_a$ and $\boldsymbol{P}$ presents physical properties close to those obtained on the single crystal, taken as reference. Investigations are now under way in order to improve the texture of the samples.

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References

[1] Bush A A, Koshelayeva V G and Venevstev Yu N 1985 *Japan. J. Appl. Phys.* **24** 625
[2] Abraham F, Debreuille-Gresse M F, Mairesse G, Nowogrocki G 1988 *Solid State Ionics* **28–30** 529
[3] Muller C 1996 *Thesis* Université J Fourier, Grenoble, France
[4] Pernot E 1994 *Thesis* Université J Fourier, Grenoble-France
[5] Pernot E, Anne M, Bacmann M, Strobel P, Fouletier J, Vannier R N, Mairesse G, Abraham F and Nowogrocki G 1994 *Solid State Ionics* **70/71** 259
[6] Iharada T, Hammouche A, Fouletier J, Kleitz M, Boivin J C and Mairesse G 1988 *Solid State Ionics* **48** 257
[7] Schulz L G 1949 *J. Appl. Phys.* **20** 1030
[8] Feng C 1965 *J. Appl. Phys.* **36** 3432
[9] Chateigner D 1994 *Thesis* Université J Fourier, Grenoble-France
[10] Wenk H R, Matthies S and Donovan J 1996 *Proc. ICOTOM 11 (X'iang, China) 24–27 September 1996* to be published
[11] Wenk H R (ed) 1985 *Preferred Orientation in Deformed Metals and Rocks: an Introduction to Modern Texture Analysis* (New York: Academic) p 39
[12] Lazure S, Vannier R N, Nowogrocki G, Mairesse G, Muller C, Anne M and Strobel P 1995 *J. Mater. Chem.* **5** 1351