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Résumé. The synthesis and the thermal stability of the high pressure and high temperature perovskite phase $BiCrO_3$ have been studied. $BiCrO_3$ can be synthesized in a wide range of pressure (1-6GPa) and temperature (690-865°C). The thermal behavior of $BiCrO_3$ depends on the atmosphere : it tends to be stable under inert gas whereas it decomposes at 650°C under O_2. The melting point of $BiCrO_3$ is determined by DTA under argon and a value of 1040°C is proposed. First SEM and TEM observations are also presented.

1. Introduction

Multiferroics are materials which combine two or all three properties of ferroelectricity, ferromagnetism and ferroelasticity in the same phase. For several years, this class of materials arouses increasing interest in solid-state physics as well as in different technological fields. However, although lots of materials are ferroelectric or ferromagnetic, only few of them present both magnetic and electric ordering simultaneously [1] : Ferroelectricity requires structural distorsion to allow electric polarization whereas magnetic ions tend to be stabilized in centrosymmetric structures. $BiFeO_3$ [2] and $BiMnO_3$ [3] have been reported to belong to this class of materials and have been widely investigated in the past few years. In these Bi-containing perovskite-type oxides, the origin of ferroelectricity is thought to be related to a complex distorsion of the Bi-O polyhedra resulting from the stereochemical activity of the Bi^{3+} cation lone pair. Recently, theoretical studies of $BiCrO_3$ have shown the interest of this material as a new multiferroic, which could be an ideal model for studying phase transitions in perovskite-structure ferroelectrics [4, 5]. However, $BiCrO_3$ has still not been extensively investigated. In the work of Sugawara et al. [6], the perovskite phase was synthesized between 3.5 and 5.5GPa and 700 and 800°C. The authors determined a structural phase transition at 137°C and suggested triclinic and monoclinic symmetries for the low and high temperature phases, respectively. As for magnetism, $BiCrO_3$ is inferred to be antiferromagnetic below -150°C. The recent study of Niitaka et al. [7], based on powder synchrotron diffraction patterns, confirms the structural transition temperature between 147 and 167°C but proposes C2 monoclinic and Pnma orthorhombic structures for the low and high temperature phases, respectively. It also shows the existence of a parasitic ferromagnetic ordering at -159°C and of an anomaly in the dielectric permittivity at about 167°C, temperature of the structural phase transition. A few papers also present the thermal behavior of $BiCrO_3$. Sugawara et al [6] reported a decomposition temperature of 400°C in air and 300°C in vacuum. Reznitskii [8] found that $BiCrO_3$ presents a polymorphic transition

temperature at 882°C and melts at 928°C, in accordance with results of Masuno [9]. These latter values, however, have not been confirmed yet and recently, DTA experiments of Chen et al. [10] explain this melting event at 928°C as an eutectic-like behavior of the Bi_2O_3-Cr_2O_3 system rather than the melting point of $BiCrO_3$.

In this study, we firstly propose to determine more precisely the conditions to synthesize $BiCrO_3$. The effect of synthesis parameters, like temperature, pressure and time, are examined to determine optimized conditions. In a second part, we focus our interest on the thermal study of the phase up to the decomposition temperature, under different atmospheres. In a last part, first TEM observations of $BiCrO_3$ are presented.

2. Experimental

Polycrystalline samples of $BiCrO_3$ were synthesized by a solid state reaction under high pressure in a Conac anvil-type apparatus. Stoichiometric proportions of Bi_2O_3 (Aldrich, 99.9%) and Cr_2O_3 (Prolabo, 99.0%) were mixed, ground and packed into a gold capsule (6mm diameter x 6mm high). A wide range of synthesis conditions was studied : pressure, temperature and time were varied from 1 to 6GPa, 690 to 865°C and 1 to 7h, respectively. The desired pressure was first applied, then the samples were heated to the dwell temperature. After the reaction, they were quenched and the pressure was slowly released. Each obtained sample was characterized by x-ray diffraction (XRD) on a SIEMENS D5000 diffractometer operating in reflection mode and equipped with Co Kα radiation ($\lambda = 1.7890\mathring{A}$). More precise patterns were also collected on a BRUKER D8 diffractometer (Cu Kα1 radiation, $\lambda = 1.5406\mathring{A}$). Differential thermal analyses (DTA) were performed to study the thermal stability of the perovskite phase, either in oxygen or in argon atmosphere, by using a NETZSCH TASC 414/3 analyzer at a heating rate of 10°C/min. High temperature X-ray diffraction was also carried out by using an INEL diffractometer equipped with a home-made furnace and operating with Fe Kα1 radiation ($\lambda = 1.936\mathring{A}$). The experiment was performed in inert gas (He) and the heating rate was 1°C/min, from room temperature up to 850°C. The samples were either quenched or slowly cooled (1°C/min). Synthesized powders were observed by scanning electron microscopy (SEM JEOL 840) at 20kV and analyzed by energy-dispersive x-ray spectrometry (EDS). Transmission electron microscopy (TEM) observations were performed using a Philips CM300ST microscope working at 300kV and powder samples were dispersed on a carbon-coated copper grid.

3. Results and discussion

3.1. Optimization of the synthesis conditions

The different conditions tested for the synthesis of $BiCrO_3$ and the influence of these parameters on grain sizes and impurities are summarized in table 1. $BiCrO_3$ with perovskite-type structure was previously reported to be synthesized in the ranges 3.5-5.5GPa and 700-800°C [7][6]. The experiments of the present study show that the phase has a larger domain of stability and can be synthesized at a pressure "as low as" 1GPa. The diffraction patterns of C28-0, C28-4 and C28-2 samples are shown on Figure 1. At 6GPa (C28-0 sample), the high-pressure polymorph of bismuth oxide with hexagonal structure [11] is detected (peaks with open squares on figure 1). Our experiments therefore agree with an upper limit of ~5.5GPa. Concerning the influence of the temperature at 2GPa, 690°C appears to be the lowest limit of the domain of stability of $BiCrO_3$. Indeed, the monoclinic polymorph α-Bi_2O_3, which is one of the initial powders, is identified in the C28-4 sample (peaks with open triangles on figure 1).

The main impurities detected by XRD analyses (see table 1 and C28-2 diffraction pattern on figure 1) are the bismuth oxycarbonate $Bi_2O_2CO_3$ (or bismutite, open circles) and a phase which may be identified as a cubic bismuth oxide with body-centered symmetry γ-Bi_2O_3 [11], but which could also incorporate chromium cations (filled circles). SEM microanalysis shows an atomic bismuth/chromium ratio of 50/50 in most of the grains, in accordance with the

Tab. 1. Synthesis conditions of BiCrO$_3$.

Sample	P(GPa)	T(°C)	Dwell time (h)	Grain sizes (μm)	Impurities
C28-0	6	690	3	?	Hex. Bi$_2$O$_3$, Cr$_2$O$_3$, (Bi$_{1-x}$Cr$_x$)$_2$O$_3$ (cub.)
C28-1	4	750	3	0.5 to 2	(Bi$_{1-x}$Cr$_x$)$_2$O$_3$, Bi$_2$O$_2$CO$_3$
C28-2	2	805	3	2.5 to 5	(Bi$_{1-x}$Cr$_x$)$_2$O$_3$, Bi$_2$O$_2$CO$_3$
C28-3	1	825	3	4.5 to 7	(Bi$_{1-x}$Cr$_x$)$_2$O$_3$, Bi$_2$O$_2$CO$_3$
C28-4	2	690	3	1.5 to 3.5	α-Bi$_2$O$_3$ (mon.), (Bi$_{1-x}$Cr$_x$)$_2$O$_3$
C28-5	2	740	3	1.5 to 3.5	(Bi$_{1-x}$Cr$_x$)$_2$O$_3$, Bi$_2$O$_2$CO$_3$
C28-6	2	865	3	6 to 12	(Bi$_{1-x}$Cr$_x$)$_2$O$_3$, Bi$_2$O$_2$CO$_3$
C28-7	2	805	1	1.5 to 2.5	(Bi$_{1-x}$Cr$_x$)$_2$O$_3$, Bi$_2$O$_2$CO$_3$
C28-8	2	805	5	1.5 to 6.5	(Bi$_{1-x}$Cr$_x$)$_2$O$_3$, Bi$_2$O$_2$CO$_3$
C28-16	2	805	7	1.5 to 6.5	(Bi$_{1-x}$Cr$_x$)$_2$O$_3$, Bi$_2$O$_2$CO$_3$
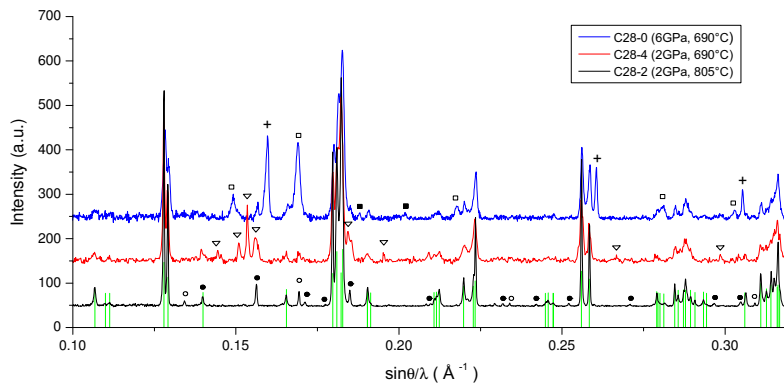
Fig. 1. XRD patterns of the C28-0, C28-2 and C28-4 samples. $\triangledown$ α-Bi$_2$O$_3$, $\square$ hexagonal Bi$_2$O$_3$, $\bullet$ (Bi$_{1-x}$Cr$_x$)$_2$O$_3$, $\circ$ Bi$_2$O$_2$CO$_3$, $\blacksquare$ Cr$_2$O$_3$, + Si (standard reference peak). Diffraction peaks of BiCrO$_3$ are represented by green lines.

composition of BiCrO$_3$. A few analyses however show 80/20 or 90/10 ratios. Locally, by TEM, it was also possible to find Cr-rich zones and particles of chromium oxide. In the following, we will call this cubic phase (Bi$_{1-x}$Cr$_x$)$_2$O$_3$. The quantity of bismutite is similar in all samples (about 2 wt%). Its presence is not surprising, since it has already been observed during previous syntheses of BiCrO$_3$ [7] and BiMnO$_3$ [12] and may be related to the CO$_2$ contamination from the graphite heater [12]. On the contrary, the amount of (Bi$_{1-x}$Cr$_x$)$_2$O$_3$ may depend on the synthesis conditions. At 2GPa, the lowest quantity of this phase is obtained at 805°C (around 3 wt%). We therefore decide that, in our experimental setup, the optimized conditions for the synthesis of BiCrO$_3$ are 2GPa, 805°C and a mean dwell time of 3h (C28-2 sample).

In table 1 are also reported the grain sizes determined by SEM and illustrated by micrographs of the C28-1, C28-5 and C28-6 powders (figure 2). The grains display irregular and angular shapes. Some aggregates are observable although they are not predominant. The comparison of images (a) and (b) suggests a light influence of the pressure : a 2GPa decrease leads to slightly larger grain sizes. The influence of the temperature is stronger and clearly visible on images (b)

and (c) : the higher the temperature, the larger the grain sizes. More generally, the evolution of grain sizes for all samples shows that at 2GPa, an increase of the grain size from $1.5\mu m$ up to $12\mu m$ is observed when the temperature is increased from $690°C$ to $865°C$ (table 1). It is also noticeable that longer dwell times tend to involve larger grain sizes, both observations being in accordance with diffusion laws.
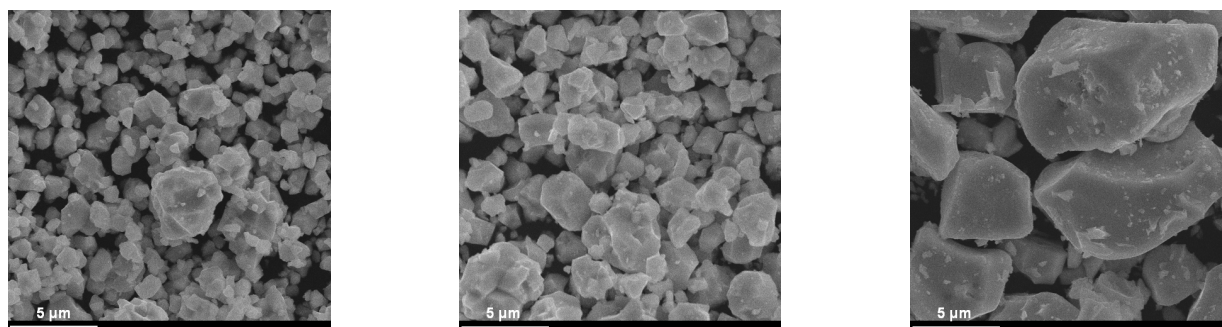
(a) C28-1 : 4GPa, 750°C.   (b) C28-5 : 2GPa, 740°C.   (c) C28-6 : 2GPa, 865°C.

Fig. 2. SEM micrographs of (a) C28-1, (b) C28-5 and (c) C28-6 samples (3h of dwell time).

3.2. Structural transitions and thermal stability

The DTA of $BiCrO_3$ powders is illustrated on figure 3. The thermal behavior of the powders clearly depends on the atmosphere. Under O_2, three endothermic peaks and an exothermic one are observed, with onset temperatures of about $165°C$, $900°C$, $922°C$ and $650°C$, respectively. XRD analyses, performed after heating of the powder at $850°C$, showed that $BiCrO_3$ is decomposed. These measurements suggest that the exothermic peak at $650°C$ is related to the decomposition of $BiCrO_3$ under O_2. This temperature is slightly higher than the temperature proposed by Sugawara et al. [6]. The presence of peaks at $900°C$ and $922°C$ could be attributed to the melting temperatures of the decomposition products of $BiCrO_3$ in O_2. However, the behavior of $BiCrO_3$ under Ar is quite different. Although the drift of the baseline makes the graph less readable, three endothermic peaks are detected at about $160°C$, $870°C$ and $1040°C$. In this case, XRD analyses, performed after heating of the powder at $850°C$, proved that $BiCrO_3$ is stable. Since $870°C$ is close to the melting temperature of Bi_2O_3 ($825°C$), the small endothermic peak detected at this temperature may be associated with the melting of the cubic $(Bi_{1-x}Cr_x)_2O_3$ phase, which is formed during the synthesis of $BiCrO_3$ in our experiments. Optical inspection of the sample after DTA indicated that it has molten during the experiment. The temperature of $1040°C$ can therefore be interpreted as the melting temperature of $BiCrO_3$.

High temperature XRD measurements, performed up to $850°C$ under helium atmosphere, also reveal four noticeable temperatures : $165°C$ and $560°C$ during the heating, $825°C$ and $610°C$ during the slow cooling. For each temperature segment, diffraction patterns were summed and are shown on figure 4. The change at $165°C$, detected by DTA as well as by HT-XRD, is in agreement with the structural phase transition observed by Niitaka et al. [7] and therefore confirms the existence of a high temperature polymorph of $BiCrO_3$. We also verify the reversibility of this transition by both methods (DTA and HT-XRD), as can be seen by comparing diffraction patterns 1 and 3 on figure 4. At $560°C$, the peak at $34.9°$ (identified as the major peak of the cubic $(Bi_{1-x}Cr_x)_2O_3$ phase) is shifted toward lower angles ($34.6°$), as indicated by the pink filled circle on figure 4 (diffraction pattern 4). This shift is combined with a slight decrease of the peak intensities of $BiCrO_3$ and could be associated with the incorporation of chromium cations in $(Bi_{1-x}Cr_x)_2O_3$. Three other new peaks also appear at $36.5°$, $37.5°$ and $38.3°$ (see pink

crosses on diffraction pattern 4, figure 4). Thus, it appears that, on heating under helium, a progressive decomposition of $BiCrO_3$ starts around 560°C. On cooling, two different behaviors are noteworthy :

- if a slow cooling is imposed, the decomposition of $BiCrO_3$ continues. At 825°C, which is the melting (and crystallization) temperature of Bi_2O_3, the intensity of the peak at 34.6° suddenly increases (orange arrow on figure 4, diffraction pattern 6), while the $BiCrO_3$ peaks are dramatically reduced. The intensities of the peaks at 36.5°, 37.5° and 38.3° progressively increase (purple arrows on diffraction pattern 7). At 610°C, two other new peaks are detected at 21.2° and 21.6°, as shown by the black arrows on figure 4 (diffraction pattern 7). $BiCrO_3$ is therefore almost entirely decomposed and the main product of decomposition is the $(Bi_{1-x}Cr_x)_2O_3$ phase. A small amount of α-Bi_2O_3 (monoclinic) and Cr_2O_3, the initial phases, are also identified. A few diffraction peaks remained not identified.
- if the sample is quenched, the phase decomposition is stopped and the $BiCrO_3$ phase is mainly recovered, with $(Bi_{1-x}Cr_x)_2O_3$ and a small amount of Cr_2O_3.
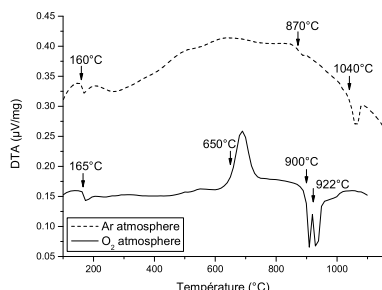

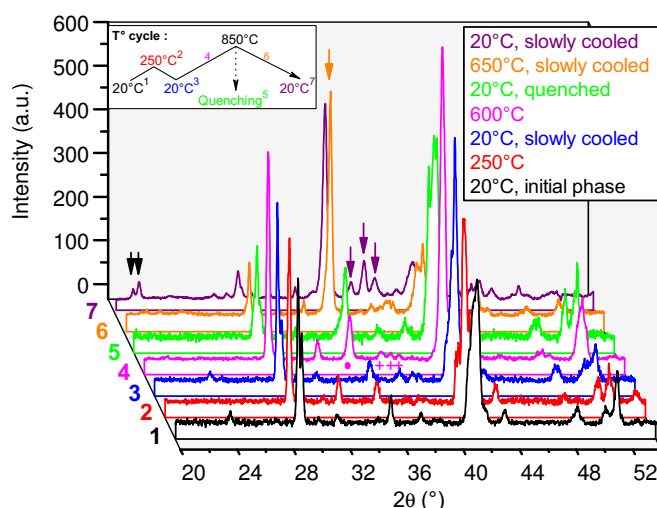**Fig. 3.** DTA of $BiCrO_3$ powders under O_2 or Ar atmosphere.

Fig. 4. High temperature XRD of $BiCrO_3$ powders in inert gas (He), presented in a 3D-plot. The inset shows the temperature profile used. ● major peak of the cubic $(Bi_{1-x}Cr_x)_2O_3$ phase; + new peaks at 36.5°, 37.5° and 38.3°; ↓ sudden increase of the major peak of the cubic $(Bi_{1-x}Cr_x)_2O_3$ phase; ↓ increase of the peaks at 36.5°, 37.5° and 38.3°; ↓ new peaks at 21.2° and 21.6°

3.3. TEM characterization

TEM observations were performed on samples synthesized in optimal conditions (2GPa, 805°C, 3h (C28-2 sample)). Electron diffraction patterns of the $BiCrO_3$ phase indicate a twinning of the monoclinic unit cell. Fig. 5(a) shows a diffraction pattern obtained in the [1 3 1] zone axis. The vertical rows of diffraction spots next to the central row show a systematic alternation of strong and weak spots (families A and B, respectively). These two families of spots belong to two orientations of a twinned crystal. In the second row from the center, the diffraction spots of the two orientations coincide. The common plane in real space of the twin domains is (1 0

$\bar{1}$). Dark field images taken close to the [1 3 1] zone axis and selecting a spot from one or the other family show complementary contrast corroborating the twinning of the crystal (fig. 5(b) and (c)). The mean size of the twin domains can be estimated from these images to be less than 10 nm. In the diffraction pattern, streaky features of the spots in the [2 0 $\bar{2}$] direction can be interpreted as a consequence of the small domain size of the twins.
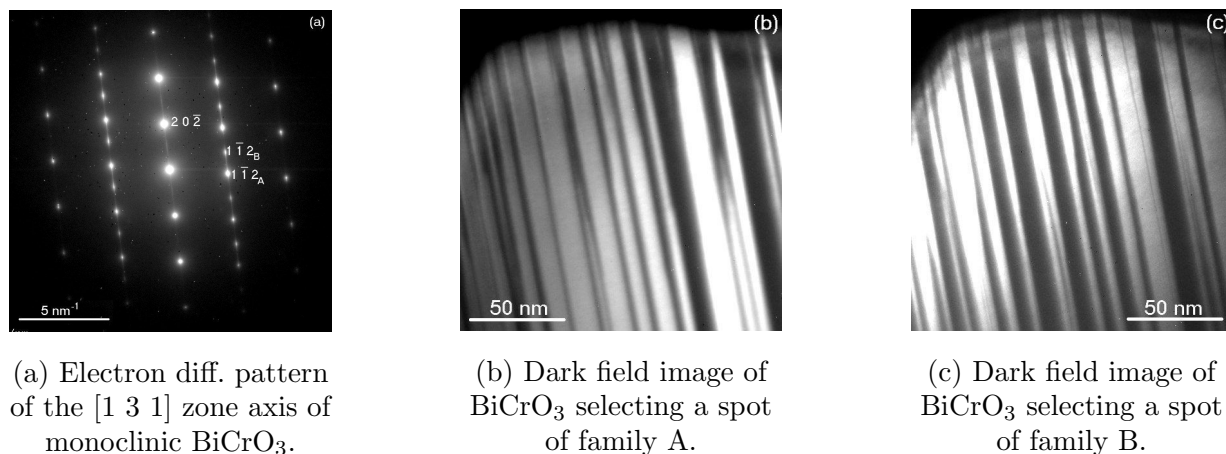

(a) Electron diff. pattern of the [1 3 1] zone axis of monoclinic BiCrO$_3$.

(b) Dark field image of BiCrO$_3$ selecting a spot of family A.

(c) Dark field image of BiCrO$_3$ selecting a spot of family B.

Fig. 5. TEM observations of BiCrO$_3$ (C28-2 sample).

4. Conclusion

Powder samples of BiCrO$_3$ have been obtained by a solid state reaction under high pressure and high temperature of the stoichiometric mixture of Bi$_2$O$_3$ and Cr$_2$O$_3$. The synthesis domain is large, from 1 to 6GPa and 690 to 865°C, at least. It is interesting to note that, very recently, Belik et al. [13] reported a single-phased BiCrO$_3$ synthesis at 6 GPa and higher temperature (1380°C). In our optimized conditions (2GPa, 805°C, 3h), the main impurities are the bismuth oxycarbonate Bi$_2$O$_2$CO$_3$ and a cubic bismuth oxide, of type (Bi$_{1-x}$Cr$_x$)$_2$O$_3$. The thermal stability of BiCrO$_3$ has been studied under O$_2$ and inert gas. In the first case (O$_2$), the phase is entirely decomposed at 650°C. In the second case (inert gas), BiCrO$_3$ is still present at 850°C and is preserved after a quenching. The melting of BiCrO$_3$ at ambient pressure has been observed by DTA and occurs at 1040°C. First TEM observations of BiCrO$_3$ indicate a twinning of the monoclinic unit cell, characterized by twin domains of about 10 nm and a common plane in real space of (1 0 $\bar{1}$).

5. References

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