Report on HE1424
17 May 12:00 to 22 May 6:00

Pentakis-(methylammonium) undecachlorodibismuthate, $(CH_3NH_3)_5Bi_2Cl_{11}$ (PMACB), belongs to a rich family of alkylammonium halogenantominate(III) and bismuthate(III) crystals showing interesting polar properties and a number of structural anomalies. In most cases, these anomalies are related to changes of orientational and/or translational disorder of the alkylammonium cations sublattice. However, it has been shown that in PMACB the Bi_2Cl_{11} anion sublattice also contributes to the structural changes (Carpentier *et al.,* 1995; Carpentier *et al.,* 1997). We report on the measurement of DAFS at the chlorine K-edge (λ_K = 4.4 Å) and at the bismuth M_V edge (λ_{MV} = 4.76 Å) related to structural changes in PMACB.

The ferroelectric phase of PMACB crystals, which is stable at room temperature, changes to a paraelectric phase at a temperature of 34°C. There is a concomitant change of the space group from $Pca2_1$ to Pcab. Hence, diffraction experiments were carried out at room temperature and at a temperature well above 34°C. As X-rays at wavelengths near the absorption edges mentioned above are strongly absorbed in air and as the experiment can't be done in vacuum, a helium atmosphere was preferred. A cylindrically bent image plate of 10 cm radius was used as a detector (maximum scattering angle ±123°).

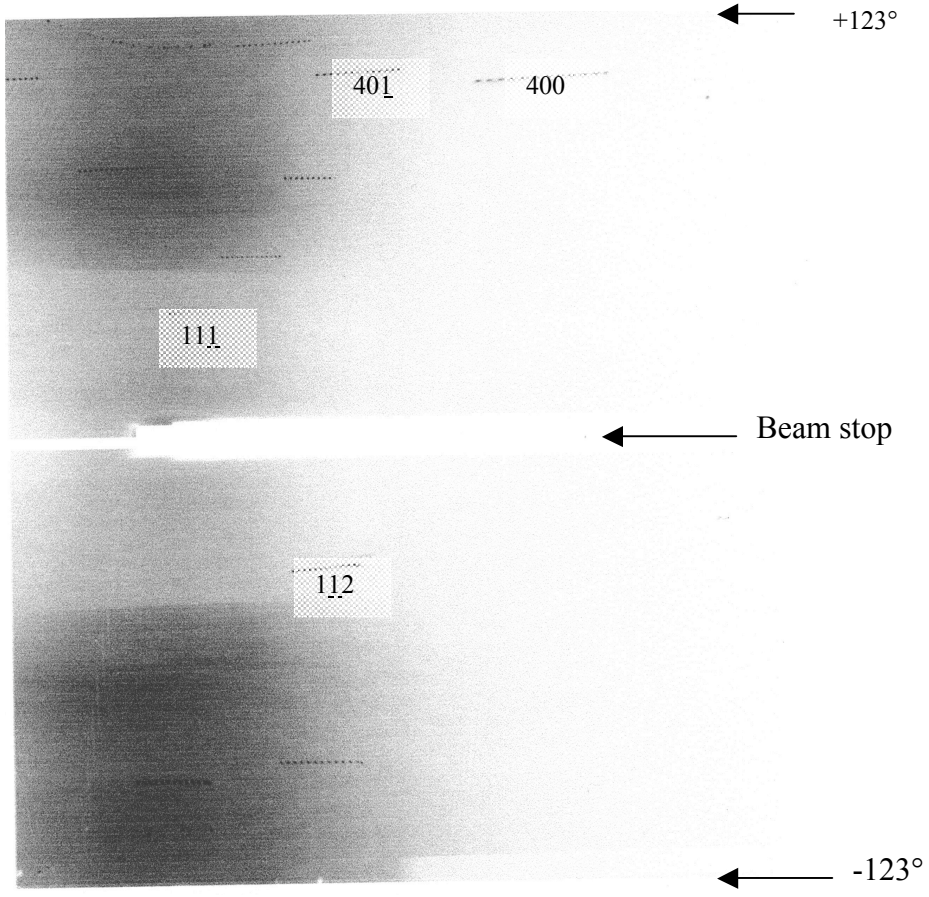

Fig. 1. Raw DAFS data taken at the M_V-edge of bismuth. The energy was changed from 2596 to 2608 eV by steps of 1 eV (wavelengths from 4.776 to 4.754 Å).
For each film the crystal was rotated by 10° with exposure time of 2 minutes at 13 different energies: The 13 spots of a few indexed reflections can be seen on the film.
6 films were necessary for measuring one DAFS spectrum at 78 energies for the same crystal rotation.

DAFS requires the measurement of well-resolved energy spectra emitted at different wave vectors corresponding to different reflections. Typically, intensities at a hundred energies or more are measured. For technical reasons outlined below we have chosen 78 energies at both the K-edge of chlorine and the M_V edge of bismuth.

The image plate was readout off-line. As the readout time of 12 minutes was much longer than the measuring time of 2 minutes for a 10° rotation of the crystal, 13 crystal rotations through the same phi-interval but at different energies were recorded on each film. In order to separate spots of the same reflection, the image plate was shifted by 2 mm along the spindle after each change of the energy. Thus 13 peaks of a given hkl reflection are lying in a row (Fig. 1). By this way synchrotron radiation could be used most efficiently.

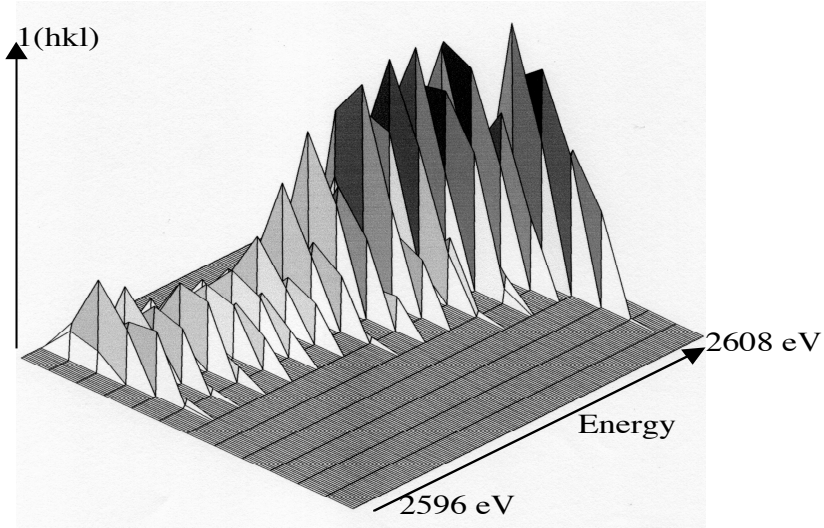

Fig. 2. A row of 13 spots from Fig. 1 (background corrected), obtained in the energy range 2596-2608 eV.
The variation in intensity is dominated by the absorption at the M_V edge of bismuth.

Fig. 2 shows the third energy interval (2596 to 2608 eV) out of six that correspond to a total energy range extending from 2570 to 2647 eV (4.824 to 4.683 Å). Two rotations of 10° (i.e. 20° in total) of the crystal were performed at temperatures on both side of the crystal transition. A similar procedure was used at the K absorption edge of chlorine in the energy range 2808-2846 eV (4.415-4.356 Å) by steps of 0.5 eV. Data are presently indexed and analysed using special programs written by one of us (HS).

These studies will help to understand the relationship between the changes of electron-density of Bi and Cl atoms of the compounds and the structural changes from one to the other phase of PMACB.

P. Carpentier, J. Lefebvre & R. Jakubas (1995) *Structure of Pentakis(methylammonium) Undecachlorodibismuthate(III) [$NH_3(CH_3)]_5Bi_2Cl_{11}$, at 130 K and Mechanism of the Phase Transition*, Acta Cryst. B51, 167-174

P. Carpentier, P. Zielinski, J. Lefebvre, R. Jakubas (1997) Phenomenological analysis of the phase transitions sequence in the ferroelectric crystal $(CH_3NH_3)_5Bi_2Cl_{11}$ (PMACB), Z. Phys. B 102, 403-414