Structure and Properties of [4-$NH_2C_5H_4NH$][$BiCl_4$]

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The halogenoantimonates(III) and halogenobismuthates(III) of the general formula $R_aM_bX_{3b+a}$ (where R denotes organic cations, X = Cl, Br, I and M = Sb, Bi) form a large group of ferroelectric crystals [1]. The title crystal [4-$NH_2C_5H_4NH$][$BiCl_4$] (abbreviation – 4APCB) is closely related to the recently found antimonate(III) analog [4-$NH_2C_5H_4NH$][$SbCl_4$] [2] , which reveals interesting ferroelectric properties with intermediate incommensurate phases. 4APCB undergoes at 252 K structural phase transition (PT) of first order. The room temperature structure (phase I) is monoclinic, space group Cc with a = 13.229, b = 13.505 c = 7.350 Å and $\beta = 120.31^o$. The structure is composed of $BiCl_4^-$ ions which form infinite chains through the crystals via chloride linkages. Each bismuth lies in a distorted octahedral environment. The 4-aminopyridinium cation reveals substantial disorder. The low temperature phase (II) is monoclinic, space group $P2_1\backslash c$ with a = 11.1660(7), b = 13.5857(8), c = 7.2750(4) Å and $\beta = 93.777(5)^o$. Over the phase II the organic cations are fully ordered. The structural analysis, calorimetric (DSC) and spectroscopic studies (IR) show that the PT is governed by the dynamics of the 4-aminopyridinium cations.

[1] Sobczyk L., Jakubas R., Zaleski J., *Pol. J. Chem.* 1997, **71,**265. [2] Jakubas R., Ciunik Z., Bator G., *Phys. Rev. B,* 2003, **67**, 024103.

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