Heat Capacity of Tricyclohexylmethanol

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Tricyclohexylmethanol (TCHM) is a tertiary alcohol with three cyclohexyl groups, i.e. methanol substituted by three cyclohexyl groups. The crystal structure is triclinic P-1 with two molecules in a unit cell at room temperature [1]. The two TCHM molecules face each other and form a dimer through a hydrogen bond. Each hydroxyl group of the two molecules lies at the center of the dimer. The hydroxyl group of TCHM is not able to build a network structure, because of large steric hindrance of three cyclohexyl group. Crystalline TCHM undergoes a phase transition at 103 K and has a spontaneous polarization at low temperature phase [2]. The previous spectroscopic study suggested that the crystal structure changes from P-1 to P1 on cooling at the phase transition temperature [3]. However, detail of the phase transition is not clear. To investigate TCHM from a thermodynamic point of view, we carried out heat capacity measurement in this study. An anomaly was detected at 103 K in the heat capacity of TCHM. This anomaly is due to the paraelectric-ferroelectric phase transition of TCHM. The excess entropy estimated is about 1.3 J K^{-1} mol^{-1}. Our x-ray experiment on a single crystal suggests that the direction of tandem hydroxyl groups with hydrogen bond (O-H···O-H) in dimer is disordered in two possible orientations at room temperature. The expected entropy of transition is 1/2 Rln2 (= 2.9 J K^{-1} mol^{-1}), because of the two orientations per one dimer. The obtained entropy of transition is however smaller than the expected one (about 1/4 Rln2). This small entropy of transition suggests that the strong correlation exists between dimers in TCHM crystal, though TCHM has no hydrogen bond network. We will discuss the mechanism of paraelectric-ferroelectric phase transition of TCHM.

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