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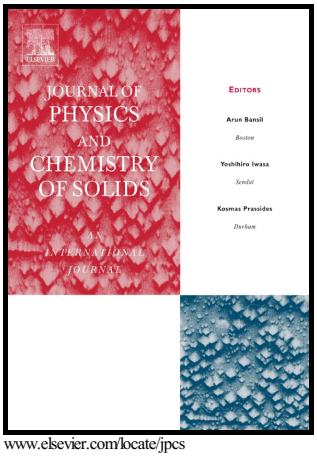

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Abstract

Thermal analysis, X-ray diffraction and vibrational spectroscopy have been used to investigate pyridinium methanesulfonate in order to verify its crystal structure and to have insight into its anomalous dynamical properties. This compound undergoes a solid-solid, reversible phase transition at 255.8/266.8 K (cooling/heating). It crystallizes in non-centrosymmetric $Pna2_1$ space group at the high-temperature phase (**I**) and in centrosymmetric *Pbca* one at the low-temperature phase (**II**). The entropy gain occurred at the **II→I** transition has shown that two independent orientations of ions in the disorder phase (**I**) are allowed. Infrared spectra have confirmed that the pyridinium cation as well as the $–CH_3$ group of the anion exhibit changes in their dynamics when entering the phase **I**. These spectra have also suggested residual disorder of both, the pyridinium cation and the $–CH_3$ group, in the low temperature phase (**II**).

Keywords: pyridinium, methanesulfonate, hydrogen bond, DSC, temperature-dependent IR spectra, phase transition, disorder

1. Introduction

Although plastic crystals have been known for decades [1] they have still attracted tremendous attention and have been studied from different points of view. It is because of their very interesting physical properties and practical applications. Most of them exhibit, among other properties, high conductivities at ambient temperature [2] what makes them promising materials for devices such as fuel cell, batteries and solar cell. Such physical properties have been found, among other things, for the compounds comprising cations such as pyrrolidinium, imidazolium and pyridinium and anions such as BF_4^-, PF_6^-, $CF_3SO_3^-$, $CH_3SO_3^-$ etc [2-7]. Pyridinium methanesulfonate appears to belong to this family.

The crystal structure of the pyridinium methanesulfonate (abbreviated as PyHMS) was determined and two reports of these studies are available in the scientific literature [8, 9]. Although the both structures were determined at the same temperature (173 K) the data reported in refs 8 and 9 differ. According to Bolte et al. [8] the crystal in question crystallizes in non-centosymmetric $Pna2_1$ space group. In turn, according to Lehtonen et al. [9] it crystallizes in centrosymmetric *Pbca* space group. This difference may arise from different ways of the PyHMS crystal preparation. It is also possible that each of these research groups has obtained different polymorphic forms of the PyHMS crystal.

To explain this uncertainty, we have used various methods to investigate properties of the PyHMS compound. First of all, the thermal properties of the crystal in question have been measured. Further, the structural properties have been reexamined at various temperatures. The temperature