THERMAL BEHAVIOUR AND VIBRATIONAL CHARACTERIZATION OF MH$_2$(IO$_3$)$_3$ PHASES ($M = K$, Rb and NH$_4$)

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The thermal behaviour of the MH$_2$(IO$_3$)$_3$ ($M = K$, Rb and NH$_4$) isomorphous compounds, as well as the IR and Raman spectra have been investigated as part of a study of the properties of solid protonic conductors. Detailed stoichiometries, sustained by TG, DTA, XRD and IR analysis, have been developed into the three phases. There were also evidences of the formation of the [I$_3$O$_8$]$^-$ polymeric phases. Their stabilities were associated to the different polarizing power of the H, K and Rb cations.

Keywords: isomorphous compounds, solid protonic conductors, TG, DTA, XRD, IR

Introduction

The solid protonic conductors, which are materials used for electrode and fuel cells, have lately led to a lot of investigations. The structural, thermal and spectroscopic characterization of these phases are undoubtedly related to the protonic mobility.

The ammonium diacid iodate (NH$_4$)H$_2$(IO$_3$)$_3$ has been found to exhibit protonic conductivity [1]. Although the literature provides general information about the MH$_2$(IO$_3$)$_3$ phases ($M = K$, Rb and NH$_4$) this is not clear enough [2–9] and the crystal structure of the ammonium and potassium isomorphous salts have been recently analyzed and compared [10]. The present inform attempts to clarify some aspects of these systems. Thus, the thermal and vibrational behaviour of this series have been reported.

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Experimental

The monovalent (ammonium, potassium and rubidium) diacid iodates were obtained by evaporating aqueous solution of I₂O₅ and respective MHCO₃ in dilute sulfuric acid. Small crystals were used as seeds to obtain large crystals by evaporating the solutions.

Powder diffraction data were obtained with a Philips PW 1730 diffractometer, using CuKα radiation (nickel filter).

IR spectra were recorded with a Perkin Elmer 580–B Spectrophotometer using the CsCl-pellet as well as the nujol technique.

Raman spectra were obtained with a Spex-Ramalog 1403 double monochromator spectrometer, equipped with a SCAMP data processor. The 514.5 nm line of an Ar-ion laser was used for exciting the samples.

The TG and DTA thermal analysis were carried out using a Rigaku CN 8002 L2 thermoanalyzer. The measurements were performed under a N₂ stream (0.4 l.min⁻¹). The temperature was raised up to 700°C (heating rate 10 deg.min⁻¹). The specimens were analyzed against α-Al₂O₃ as reference. Additional thermal studies were carried out in a crucible furnace. The samples were investigated by X-ray diffractometry and IR spectroscopy.

Results and discussion

According to the X-ray and neutronic diffraction studies, the potassium, rubidium and ammonium diacid iodates are isomorphous phases. They belong to the triclinic system, space group P1 and Z = 2. More recent cell parameters data are shown in Table 1. Although the literature data are not entirely consistent [10], these lattices are structurally built up by a framework of strongly distorted IO₆ octahedra (three I–O bonds are close to 1.8 Å while the other three are farther away at 2.7 Å) [7, 10]. The polyhedra are linked together by corner sharing and by H–bonds in the ammonium compounds. On the other hand, three are I–O...(H) and I–O...(M) bonds in the remaining K- and Rb-isomorphous phases. The NH₄ and K cations should be considered in a ten coordination [10]. On the other hand, there are three types of slightly different IO₆ polyhedra in the lattice with one common corner and a very complex and highly condensed structural group. Two of these groups are linked in a block of six octahedra, repeated along the three crystallographic axis. This type of framework generates cavities (occupied by the M ions) and also channels running along the three axis of the triclinic lattice, in which the acids protons are located [10]. These H-atoms can easily be removed when an electric field is applied and their migration is responsible for the ionic conductivity. The transversal dimensions of the channels are shorter in KH₂(IO₃)₃ than in the ammonium compound. So, the movement of the protons in-