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Application of the infrared spectroscopy to the structural study of Prussian blue analogues

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ABSTRACT

Prussian blue analogues (PBAs) form a versatile family of inorganic polymers that may exhibit promising electronic and magnetic properties. Owing to the partially disordered structure of these systems, a comprehensive characterization of PBAs is often tricky and requires the use of numerous complementary techniques. We present herein an original use of infrared (IR) spectroscopy in the characterization of PBAs. Based on a detailed assignment of both the far- and mid-IR spectra of PBAs, including the description of the metal–ligand bonds and the water molecules in PBAs, we demonstrate that IR spectroscopy allows investigating the electronic and structural properties of PBAs.

RÉSUMÉ

Les analogues du bleu de Prusse (ABP) constituent une famille de polymères inorganiques particulièrement versatiles, pouvant présenter des propriétés électroniques et magnétiques prometteuses. En raison de la nature partiellement désordonnée de ces systèmes, une caractérisation complète des ABP est la plupart du temps difficile et nécessite la mise en jeu de nombreuses techniques complémentaires. Nous présentons dans cet article une approche originale de la caractérisation des ABP par spectroscopie infrarouge (IR). Grâce à l'attribution détaillée des spectres des ABP dans les lointain et moyen IR, incluant une description des bandes de vibration métal–ligand et des molécules d'eau au sein des ABP, nous démontrons ici la pertinence de la spectroscopie IR dans l'étude des propriétés électroniques et structurales des ABP.

1. Introduction

Prussian blue analogues (PBAs) form a wide class of inorganic polymers exhibiting numerous appealing electronic and chemical properties, including room-temperature magnetic properties [1,2], large porous volumes (suitable for gas storage applications) [3–5], electrochemical properties for alkali cation-based batteries [6,7], and electronically switchable properties [8–10]. The understanding of the physical and chemical phenomena occurring at the atomic scale in PBAs is needed to finely tune up these promising properties. Infrared (IR) spectroscopy has recently been evidenced as a well-adapted probe of the electronic and structural properties of PBAs at the molecular level [11]. However, no comprehensive assignment of the IR spectrum of PBAs was available—to date—in the literature.

We demonstrate herein the relevance of the IR approach to the probing of the electronic and structural properties of PBAs. A comprehensive assignment of the IR spectrum of PBAs is performed based on the electronically switchable

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series of cobalt–iron PBAs [12,13]. Both the far-IR region and the spectral range associated with the $\nu\{O–H\}$ of the water molecules of PBAs are discussed. Using these assignments, examples of the use of IR spectroscopy as an accurate tool to investigate PBAs are proposed, including monitoring of the electronic transition, discussion of the chemical disorder, or probing of the interaction between the alkali cations and the bimetallic network.

2. Experimental

The syntheses of K_0CoFe, $Cs_{0.7}CoFe$, Na_2CoFe, Rb_2CoFe and Cs_2CoFe have been already described elsewhere [12,14]. IR/THz measurements were carried out at the AILES beamline at synchrotron SOLEIL (France). The synchrotron was operating in the equal filling mode with 416 approximately equally filled and spaced electron bunches. The average storage beam electron current for the present result was 400 mA. The IR/THz experimental set-up has already been described elsewhere [15,16]. All THz measurements were performed in the transmission mode using a Bruker IFS 125 Fourier transform interferometer fitted with 6 μm Mylar/Si multilayer beam splitter and a liquid-helium-cooled Si bolometer detector, and operated at 1-cm^{-1} resolution. The MIR measurements exploited the interferometer fitted with a KBr beamsplitter combined with a MCT detector. The Fourier transform spectrometer was evacuated down to a 2×10^{-5} mbar pressure (to minimize residual H_2O and CO_2 absorption in the spectrometer). The liquid absorption cell used for these experiments was filled with sample powder dispersed in Nujol and held between two diamond windows. For the FIR spectra, the detector was fitted with a 200–600-cm^{-1} cold optical filter and the spectrometer with a 12.5-mm entrance aperture, but the SR effective source diameter results in beam diameter that fulfills the resolution criterion. All spectra result from the averaging of 400 scans measured with a mobile mirror speed of 2.5 cm·s^{-1}. In order to measure the absorption spectra at well-controlled temperatures, the liquid cell was mounted on a cold head controller by a close cycle cryostat (pulse tube from CryoMech). This set-up allowed the sample temperature to be controlled within 1 K. The transmission spectra were obtained by dividing the signal (I) by the signal transmitted through pure Nujol (I_0). All IR spectra are presented in absorbance ($A = \ln(I/I_0)$) as a function of the incident wavenumbers ω.

3. Results and discussion

3.1. Description of PBAs

PBAs are coordination polymers obtained in aqueous solution from the substitution of the water molecules in $[M(OH_2)_6]^{k+}$ complexes by the isocyanide ligands from $[M'(CN)_6]^{j-}$ complexes (where M and M′ are transition metal ions). The resulting M–N≡C–M′ linkages form a face-centered cubic lattice [17] that may exhibit vacancies in $M'(CN)_6$ units (Fig. 1). In the vicinity of these vacancies, water molecules are coordinated to the M cations. Additional alkali cations and zeolite water molecules can be inserted into the structure. The general formula of PBAs is $A_xM_4[M'(CN)_6]_{\alpha\square 4-\alpha}\cdot nH_2O$ (where A^+ is an alkali cation and $\square$ is a $M'(CN)_6$ vacancy; $\alpha = 4(k + (x/4))/j$), called A_xMM' in the following. Depending on the nature of the A, M and M′ cations, the formers are known to interact with the bimetallic network in some PBAs [13].

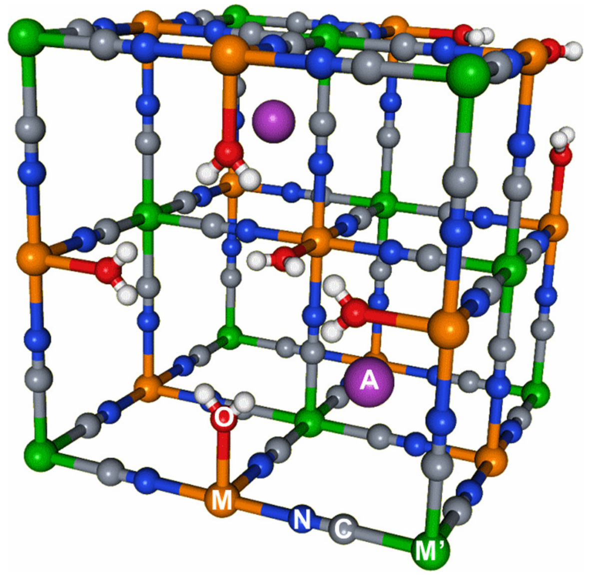

Fig. 1. Scheme of the unit cell of a Prussian blue analogue. Colors: M (orange), M′ (green), C (grey), N (blue), O (red), H (white), A (purple). For interpretation of references to color, see the online version of this article.

The assignment of the IR vibration bands of PBAs has been performed thanks to a series of cobalt–iron PBAs (A_xCoFe) where $k = 2$ and $j = 3$. The general formula of A_xCoFe is therefore given by $A_xCo_4[Fe(CN)_6]_{(8+x)/4\square(4-x)/3}\cdot nH_2O$. Thus, the stoichiometry of A_xCoFe is completely defined by the amount x of alkali cations inserted in the structure. The A_xCoFe PBAs can exhibit two different $Co^{II}(HS)Fe^{III}(LS)$ and $Co^{III}(LS)Fe^{II}(LS)$ (HS: high spin; LS: low spin) electronic states [18] (called $Co^{II}Fe^{III}$ and $Co^{III}Fe^{II}$ in the following). However, as the amounts of cobalt and iron cations per unit cell are not the same, part of cobalt cations cannot undergo the $Co^{II}Fe^{III} \leftrightarrow Co^{III}Fe^{II}$ electronic transition. Consequently, the chemical formula of A_xCoFe PBAs can be rephrased as $A_xCo^{II}_4[Fe^{III}(CN)_6]_{(8+x)/3\square(4-x)/3}\cdot nH_2O$ (in the $Co^{II}Fe^{III}$ state) and $A_xCo^{III}_{(8+x)/3}Co^{II}_{(4-x)/3}[Fe^{II}(CN)_6]_{(8+x)/3\square(4-x)/3}\cdot nH_2O$ (in the $Co^{III}Fe^{II}$ state), taking into account the small amount of residual Co^{II} cations in the $Co^{III}Fe^{II}$ state.

According to the chemical composition and the structure of PBAs, their IR spectrum is expected to exhibit the following vibration bands:

- the $\nu\{C{\equiv}N\}$ vibration band, related to the cyanide bridges;
- the $\nu\{M–N\}$, $\nu\{M–O\}$ and $\nu\{M'–C\}$ vibration bands, related to the metal-to-ligand bonds;
- the $\nu\{O–H\}$ vibration band, related to the water molecules of the system (both zeolite water molecules and water molecules bound to the M cations at the $M'(CN)_6$ vacancies).