Journal of Physics and Chemistry of Solids 96-97 (2016) 92–99

Contents lists available at ScienceDirect

Journal of Physics and Chemistry of Solids

journal homepage: www.elsevier.com/locate/jpcs

Review

Vibrational study, phase transitions and electrical properties of 4-benzylpyridinium monohydrogenselenate

Wassim Maalej, Asma Ben Rached, Tahar Mhiri, Abdelaziz Daoud, Nabil Zouari *, Zakaria Elaoud

Laboratoire de Physico-Chimie de l'Etat Solide, Département de Chimie, Faculté des Sciences de Sfax, Université de Sfax, BP 1171, Route de Soukra km 3.5, 3000 Sfax, Tunisia

ARTICLE INFO

Article history:
Received 2 January 2016
Received in revised form
7 May 2016
Accepted 17 May 2016
Available online 18 May 2016

Keywords:
A. Organic-inorganic compound
B. Chemical synthesis
C. Impedance spectroscopy
D. Raman spectroscopy
E. Ionic conductivity

ABSTRACT

The title compound $C_6H_5CH_2C_5H_4NH^+ \cdot HSeO_4^-$ crystallizes in the orthorhombic system with the space group *Pbca* and the following unit cell dimensions: $a=27.449(5)$ Å; $b=10.821(6)$ Å and $c=8.830(1)$ Å.

The structure consists of infinite parallel two-dimensional planes built of $HSeO_4^-$ anions and $C_6H_5CH_2C_5H_4NH^+$ cations mutually.

Differential scanning calorimetry study on 4-benzylpyridinium monohydrogen-selenate was carried out. A high temperature second order phase transition at 363 K was found and characterized by electric measurements. The Raman of polycrystalline sample has been recorded at different temperature between 297 and 373 K.

The conductivity relaxation parameters associated with some H^+ conduction have been determined from an analysis of the M''/M''_{max} spectrum measured in a wide temperature range. An appearance of the superionic phase transition in 4-BSe is closely related to a liberation or even a rotation increase of $HSeO_4^-$ groups with heating.

Contents

1. Introduction . . . 92
2. Experimental . . . 93
3. Results and discussion . . . 95
   3.1. X-ray diffraction study . . . 95
   3.2. Calorimetric study . . . 96
   3.3. Electrical properties . . . 96
   3.4. Raman and IR spectroscopic studies . . . 99
4. Conclusion . . . 99
Acknowledgements . . . 99
References . . . 99

1. Introduction

Proton migration in hydrogen-bonded materials and their electric properties have received considerable attention for a number of years. Knowledge of charge transfer properties in hydrogen-bonded materials is not only of major importance for understanding many biophysical processes in the biological systems [1] but also of great use for their practical applications. In particular, the solid electrolytes exhibiting high proton conductivity are of great interest as the electrolyte for fuel and electrolysis cells [2,3].

The salts of selenic acid are a large family of hydrogen bonded

* Corresponding author.
E-mail address: bizrirl@yahoo.fr (N. Zouari).

http://dx.doi.org/10.1016/j.jpcs.2016.05.010
0022-3697/

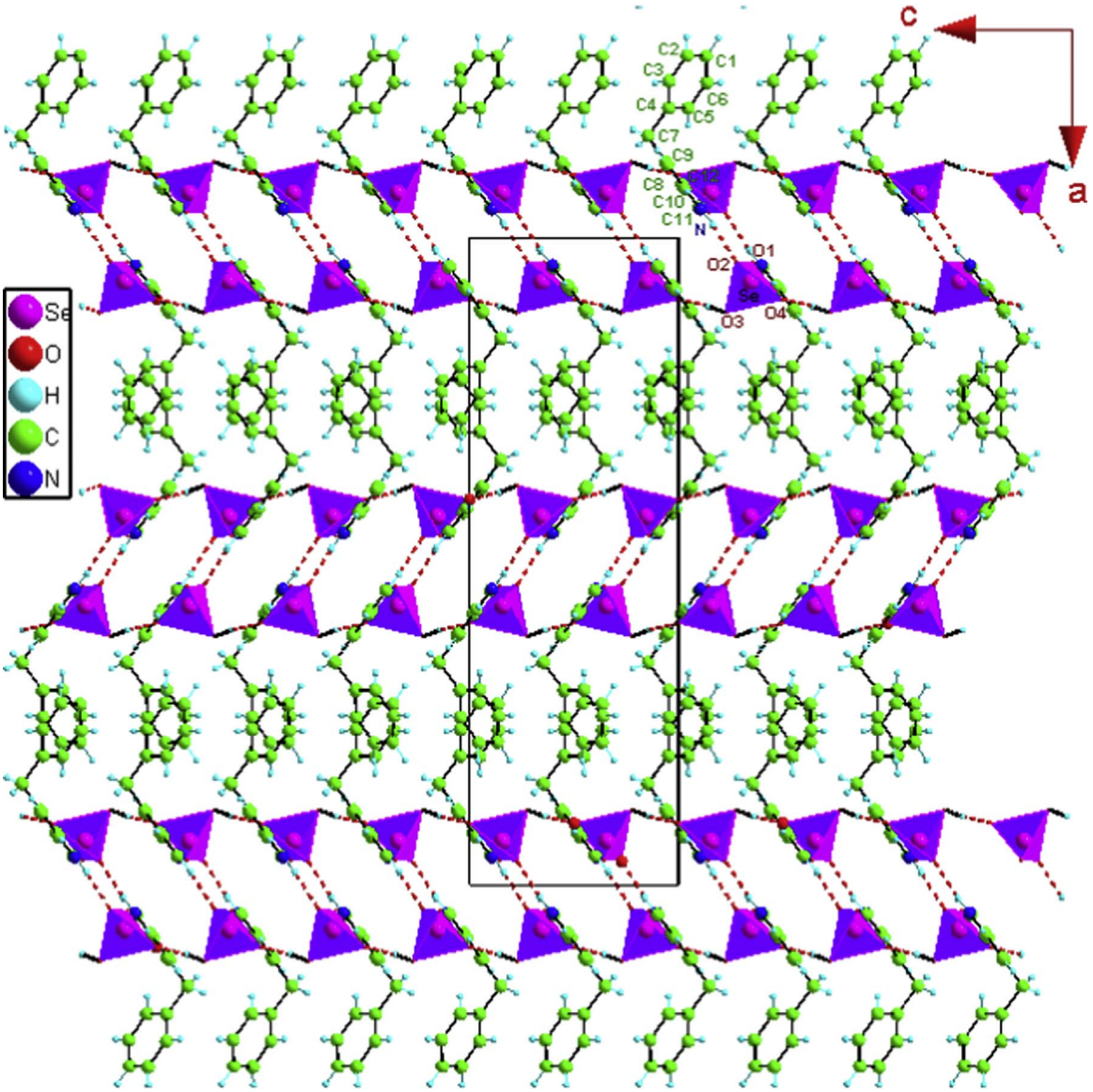

Fig. 1. Projection along the *b* axis of the atomic arrangement of $C_6H_5CH_2C_5H_4NH^+ \cdot HSeO_4^-$.

crystals which were intensively studied [4–7]. During a systematic investigation of interaction between selenic acid and organic molecules numerous structures have been described;

$[(CH_3)_3N^+CH_2COOH\cdots(CH_3)_3N^+CH_2COO^-] \cdot [HSeO_4^-]$ [8],

$(CH_2CH_2NH_2CH_2CH_2NH_2)_2(SeO_4) \cdot H_2O$ [9], $[N(C_2H_5)_4]HSeO_4$ [10],

$(C_3H_7N_6^+)_4$ $(SeO_4^{2-})_2 3H_2O$ [11], $C(NH_2)_3HSeO_4$ [12–14], $(NH_4)_4H_2(SeO_4)_3$ [15,16].

Sondes Hajlaoui et al. show that hybrid compounds offer the opportunity to combine properties of organique and inorganique groups such as electronic, optical and ferroelectric [17].

For most protonic conductors, the coordinating atoms is an oxygen. If the oxygen is well separated from other oxygen atoms, the proton-oxygen pair forms an O–H bond ~1 Å in length. As the distance to other electronegative species lessens, a hydrogen bond, O–H…O, will be formed, with O…O distances in the range of 2.4–3 Å long. As the proton can never be free from the electron density of its neighbours, it must move by a method where it is bonded to at least one atom during the entire process. This restraint leads directly to the two main methods of proton conduction: the vehicle and Grotthus mechanisms [4,5].

In the present work we will not describe the crystal structure of the 4-benzylpyridinium monohydrogen selenate "$C_6H_5CH_2C_5H_4NH \cdot HSeO_4$", (here after abbreviated to 4-BSe), but we will report some results of impedance spectroscopy, calorimetric and Raman measurements. The aim of our work is to prove the phase transition and study the Grotthus mechanism of proton conduction in the title compounds.

We demonstrate here through some results of calorimetric analysis, evolution of the Raman spectra at different temperature and through measurements of conductivity using the complex impedance method, all carried at high temperature, that the transition in 4-BSe at 363 K is superprotonic.

2. Experimental

The crystals of 4-BSe were grown in two stages: first, a bath of seed material was prepared from an aqueous solution containing a stoechiometric mixture of 4-benzylpyridine C_6H_5–CH_2–C_5H_4N and selenic acid H_2SeO_4, second, the growth of nuclei to desired dimensions was carried out by slow evaporation of the solvent at constant temperature (298 K). After some days of evaporation; the pink needle-shaped mono-crystals appear in the solution in molecular ratio 1:1 [18].