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Characterization of phase transitions of $[N(CH_3)_4]_2ZnCl_2Br_2$ mixed crystals

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HIGHLIGHTS

- Raman spectroscopy.
- Dielectric proprieties.

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ABSTRACT

The X-ray powder diffraction patterns show that at room temperature $[N(CH_3)_4]_2ZnCl_2Br_2$ crystallizes in the orthorhombic system with Pnma space group. Three endothermic peaks at $T_1 = 251$ K, $T_2 = 276$ K and $T_3 = 283$ K are observed by differential scanning calorimetry technique. In order to characterize these transitions, Raman spectra have been recorded in the wide temperature range (between 170 and 400 K) and the frequency range related to the internal and external vibrations of the cations and anions (3200–20 cm^{-1}). The evolution of Raman spectra against temperature shows that the compound is homogeneous, and singularities occur in the vicinity of 283 K and especially at 251 K. The second goal of the present work was to obtain the T_c temperature transition using the dielectric measurements at different temperatures. Measurements of the dielectric constant ε', ε'' and $\tan\delta$ at several temperatures showed that this compound becomes ferroelectric below 257 K. The impedance spectra and the complex modulus show double relaxation peaks in the paraelectric phase, which suggests the presence of grains and grain boundaries in this sample.

1. Introduction

$[N(CH_3)_4]_2ZnCl_4$, $[N(CH_3)_4]_2ZnBr_4$, $[N(CH_3)_4]_2Zn_{0.5}Cu_{0.5}Cl_4$ and $[N(CH_3)_4][N(C_2H_5)_4]ZnCl_4$ compounds belong to a crystal family with the general formula A_2MX_4 that exhibit many interesting physical properties related to structural phase transitions at low temperatures such as the possibilities of application of the A_2MX_4 crystals as a temperature and humidity sensors [1]. The optical properties of these crystals are dependent on the electron configuration of metal ions, and also on the crystal field associated with the crystal's molecular structure. The spectral investigations of these crystals of the A_2MX_4 family with the Cu^{2+} ion showed that the optical spectra can clearly vary at different temperatures. The result of this, for example, is the thermochromic effect observed in the $[NH_4]_2CuCl_4$ crystal [2]. This effect can have a practical application in wireless temperature sensors [3,4]. The structure of these compounds contains two entities: TetraMethylAmmonium (hereunder denoted TMA) $[N(CH_3)_4]^+$ and $[MX_4]^{2-}$ tetrahedra. The MX_4^{2-} anions in organic inorganic hybrid solids are capable of participating in C–H···Cl hydrogen bonds with organic cations. The importance of this type of hydrogen bonding is now well established in crystal engineering and in the supramolecular architectures of organic species, as well as in bimolecular structures and transition metal complexes [5,6]. The atomic arrangement of $[N(CH_3)_4]_2ZnCl_2Br_2$ can be described by an alternation of organic–inorganic $[(TMA)^+/MX_4^{2-}]$ layers. The transitions, detected in the 160–300 K temperature range, are related to dynamics of the organic or inorganic groups, which may lead to vibrational singularities [7]. It has been shown that aliphatic tetra-ammonium groups are governed by reorientational dynamics [8]. These materials belong to the $(NH_4)_2SO_4$ family that is known to exhibit ferroelectric transition [9–12].

The polar properties in this type of compound are frequently connected with a large electric polarizability of the organic moieties [13].

The present paper is devoted to the preparation and characterization of the phase transitions in $[N(CH_3)_4]_2ZnCl_2Br_2$. It is based on calorimetric studies, Raman scattering investigations and dielectric measurements at different temperatures.

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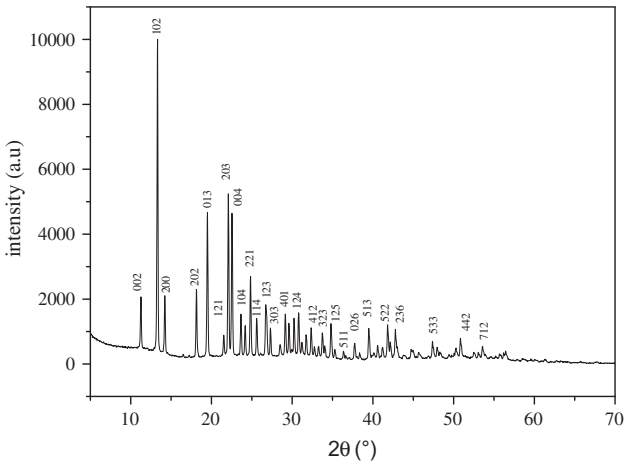

Fig. 1. X-ray diffractogram of the $[N(CH_3)_4]_2ZnCl_2Br_2$ compound.

2. Experimental procedure

The $[N(CH_3)_4]_2ZnBr_2Cl_2$ compound was prepared by reaction with the stoichiometric quantities of (TMA)Cl, (TMA)Br, $ZnBr_2$ and $ZnCl_2$ in an aqueous solution according to the following scheme:

$$2(TMA)Cl + 2(TMA)Br + ZnBr_2 + ZnCl_2 \rightarrow 2[N(CH_3)_4]_2ZnBr_2Cl_2$$

The mixture was slowly evaporated at room temperature. Thus, high-quality transparent crystals of tetrahedral shape were obtained.

X-ray powder diffraction pattern was recorded using a Philips PW 1710 diffractometer operating with copper radiation $\lambda_{K\alpha}$ = 1.5418 Å. The differential Scanning Calorimetric investigations have been done using a DSC (Q-100) TA Instrument in the 200–413 K temperature range with scanning rate 5 °C/min and resolution of 0.1 °C [14]. The impedance spectroscopy was performed on pellet disks of about 8 mm diameter and 1.3 mm thickness. A (SOLARTRON SI 1260) impedance coupled to a dielectric interface 1296, in the 200–373 K temperature range and (10^{-1} Hz – 1 MHz) frequency range was used to characterize the dielectric properties. The Raman spectra were recorded using a T-64000 (Horiba–Jobin–Yvon) Raman spectrometer. The wavelength radiation for excitation was 514.5 nm using an Ar/Kr laser. The value of laser power for excitation of Raman was 5Mw of the sample. All measurements were taken under microscope using X50 LF objective in backscattering geometry on transparent single crystal using the parallel polarization. The spectra were collected with 1800 tr/mm grating, from 10 to 3500 cm^{-1}, with 1.5 cm^{-1} typical spectral resolution. The studies as a function of temperature were performed using FDCS196 and TS1000EV stages from Linkam for measurements below and above room temperature, respectively; temperature stability is better than 0.5 K.

3. Results and discussion

3.1. Structural analysis

The X-ray powder diffraction pattern was collected at room temperature on powder finely ground in an agate mortar with Cu Kα1 radiation and 2θ range from 5° to 80°. The diffractogram is presented in Fig. 1. The $[N(CH_3)_4]_2ZnBr_2Cl_2$ crystallizes in the orthorhombic system with Pnma space group, and the unit cell parameters refined by the least square method are: a = 12.491 Å, b = 9.130 Å and c = 15.772 Å. These values are in good agreement with the literature and close to the average value of the parameters obtained for the $[N(CH_3)_4]_2ZnCl_4$ and $[N(CH_3)_4]_2ZnBr_4$ compounds [15–17].

3.2. Calorimetric study

The DSC measurements of $[N(CH_3)_4]_2ZnBr_2Cl_2$ were recorded both on heating and on cooling a sample of 11.2 mg mass in the temperature range 200–413 K in order to characterize the transitions phase where they are observed in the parent compound $[N(CH_3)_4]_2ZnCl_4$ and $[N(CH_3)_4]_2ZnBr_4$ between 160 and 300 K (Table 1). The temperatures of the phase transitions were estimated from the peak positions (Fig. 2). This unambiguously shows the existence of three reversible heat anomalies at T_1 = 251/240 K, T_2 = 276/270 K and T_3 = 283/279 K on heating and cooling, respectively which defines four successive phases. These transitions are characterized by a noticeable temperature hysteresis ΔT = 11, 6 and 4 K respectively. The heats of transitions are 1.092 J/g for the transition at the T_2/T_3 temperature, and 0.287 J/g at the T_1 one. So the entropy variations are ΔS = 3.89 J mol^{-1} K^{-1} and ΔS = 1.15 J mol^{-1} K^{-1}, respectively. The entropy of the formers being higher than 2 J mol^{-1} K^{-1} suggest an order–disorder type [18] whereas the transition at T_1 would be rather related with the "displacive" mechanism [19].

3.3. Temperature evolution of the Raman spectra

The Raman spectra have been collected at different temperatures in the range 170 K to 400 K on cooling and on heating. The temperature evolution of the Raman bands in the low frequency

Table 1
Temperature transitions for the $[N(CH_3)_4]_2ZnCl_{4-x}Br_x$where ($x$ = 0, 2 and 4).

Compounds	Temperature transitions T(K) on heating
$[TMA]_2ZnCl_4$	161 181 276 279 293
$[TMA]_2ZnCl_2Br_2$	251 276 283
$[TMA]_2ZnBr_4$	288

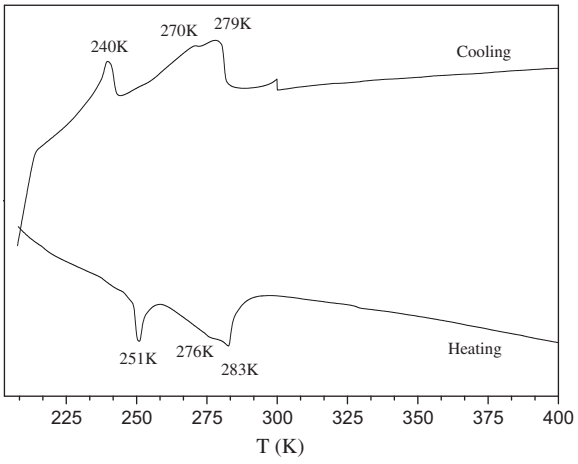

Fig. 2. Differential scanning calorimetry diagram of $[N(CH_3)_4]_2ZnCl_2Br_2$ compound on heating and cooling cycle at 5 °C/min rate.