Journal of Alloys and Compounds 730 (2018) 417–423

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: http://www.elsevier.com/locate/jalcom

Comparative study of the phase transitions and spectral properties of $NH_2(CH_3)_2Me_{1-x}Cr_x(SO_4)_2\times6H_2O$ (Me = Al, Ga) ferroelectrics

Natalya Ostapenko [a, b, *], Volodymyr Kapustianyk [a, b], Yuriy Eliyashevskyy [a], Victor Rudyk [b], Zbigniew Czapla [c, d], Volodymyr Mokryi [e]

[a] Scientific-Technical and Educational Center of Low-Temperature Studies, Ivan Franko National University of Lviv, Dragomanova str. 50, 79005 Lviv, Ukraine
[b] Department of Physics, Ivan Franko National University of Lviv, Dragomanova str. 50, 79005 Lviv, Ukraine
[c] Department of Physics, Opole University of Technology, Ozimska 75, 45370 Opole, Poland
[d] Institute of Experimental Physics, University of Wrocław, pl. M. Borna 9, 50204 Wroclaw, Poland
[e] Department of Ecological Safety and Nature Protection Activity, Lviv Polytechnic National University, Heneral Chuprynka str. 130, 79057 Lviv, Ukraine

ARTICLE INFO

Article history:
Received 28 April 2017
Received in revised form
29 July 2017
Accepted 28 September 2017
Available online 29 September 2017

Keywords:
Electronic band structure
Crystal and ligand fields
Phase transitions
Optical spectroscopy

ABSTRACT

This article is devoted to study of Cr^{3+} ion complexes in $NH_2(CH_3)_2Me_{1-x}Cr_x(SO_4)_2 \times 6H_2O$, Me = Al, Ga ($DMAMe_{1-x}Cr_xS$) crystals. On the basis of spectroscopic data the energy diagram and the parameters of the crystal field corresponding to the above mentioned complexes were specified. It was shown that isomorphous substitution of the metal ion practically does not affect the temperature of ferroelectric-ferroelastic phase transition in $NH_2(CH_3)_2Ga_{1-x}Cr_x(SO_4)_2 \times 6H_2O$ contrary to the case of $NH_2(CH_3)_2Al_{1-x}Cr_x(SO_4)_2 \times 6H_2O$ crystal. The structure and temperature changes of the absorption spectra of the above mentioned solid solutions are explained in terms of the internal electronic transitions in $[Cr(H_2O)_6]^{3+}$ octahedral complexes. The symmetry and distortion of the complexes within the structure of all investigated crystals were analyzed on the basis of the Raman spectroscopy data.

1. Introduction

The crystals with different alkylammonium cations were widely studied by various experimental methods in order to detect the structural changes associated with a dynamics of organic cations and inorganic anions [1–8]. In particular, they reveal a number of ferroelectric and ferroelastic phase transitions. On the other hand, the compounds with transition metals would manifest also a magnetic ordering. That is why these crystals can be considered as the potential multiferroics [4–8].

The technical application of the considered crystals and solid solutions is restrained because of their hygroscopicity, brittleness and damaging caused by overheating above 100 °C. Nevertheless, it was shown that incorporation of the nanocrystals into a polymer matrix may open a new opportunity for their practical application since such unfavourable properties in this case would be overcame [9,10].

X-ray diffraction study of $NH_2(CH_3)_2Me(SO_4)_2 \times 6H_2O$ (DMAMeS, Me = Al, Ga) crystals [1] showed that the metal ions in their structure is located in the center of symmetry and surrounded by octahedron of water molecules. The same starting octahedral symmetry O_h is adopted for Cr^{3+} ion. Introduction of Cr^{3+} into DMAMeS crystals allows us to study the crystal field parameters reflecting the minimal changes within the metal-hydrate complexes. It is important to note that the energy diagram of Cr^{3+} ion in $DMAMe_{1-x}Cr_xS$ crystals is very similar to the relevant diagram for ruby crystals. Thus, $DMAMe_{1-x}Cr_xS$ crystals would be considered as a convenient model object of the ferroics physics as well as of the quantum electronics.

The crystal structure of DMAAlS [1,2] is built up of Al cations coordinated by six water molecules, regular SO_4 tetrahedra and $[NH_2(CH_3)_2]^+$ (DMA) cations, all hydrogen bonded to a three-dimensional framework. It has been found that this crystal possesses a second order phase transition at temperature $T_{c1} = 152$ K [11] from ferroelastic ($T > T_{c1}$) to ferroelectric ($T < T_{c1}$) phases. This phase transition is of the order-disorder type with a symmetry change $2/m \rightarrow m$. The transition is connected with ordering of the polar DMA cations which execute hindered rotations around their C-C direction in the paraelectric phase and order only in the spatio-

* Corresponding author. Scientific-Technical and Educational Center of Low-Temperature Studies, Ivan Franko National University of Lviv, Dragomanova str. 50, 79005 Lviv, Ukraine.
E-mail address: natalost2011@ukr.net (N. Ostapenko).

https://doi.org/10.1016/j.jallcom.2017.09.319
0925-8388/

temporal average in the ferroelectric phase [12]. The question concerning the low temperature limit of the ferroelectric phase is still discussed [2,13–15].

The ferroelectric phase in $NH_2(CH_3)_2Ga(SO_4)_2 \times 6H_2O$ (DMAGaS) lies within the temperature range from $T_{c1} = 136$ K to $T_{c2} = 119$ K (in a heating run), whereas the antiferroelectric phase was found to be below T_{c2} [2,3].

Previous studies showed that partial substitution of aluminium with chromium affects the phase transition temperature of DMAAlS crystals. In particular, in comparison with the initial DMAAlS the phase transition temperature T_{c1} in the crystal doped with Cr^{3+} (6.5%) is shifted toward higher temperatures by 2.6 K [16]. Otherwise, increase of chromium concentration to $x = 0.2$ leads to the shift of this temperature toward lower temperatures. The temperature of phase transition in $DMAAl_{1-x}Cr_xS$ with $x = 0.2$ is very close to those in the "initial" crystal [17].

The nontrivial dependence of the ferroelectric phase transitions temperatures on the chromium concentration for $DMAAl_{1-x}Cr_xS$ crystal was explained by formation of the massive dipole clusters in vicinity of the ferroelectric phase transition at the lower values of chromium concentration ($x = 0.065$) [16,17]. The higher concentration of chromium ($x = 0.2$) causes fragmentation of clusters and reverse decrease of the phase transition temperature. This effect has an impact not only on the phase transition temperature but also on the fundamental ferroelectric dispersion and, besides, on the thickness of domain walls and hence on their dynamics [17].

One can also expect that the partial isomorphous substitution of the metal ion would considerably affect the structure and spectral properties of $DMAMe_{1-x}Cr_xS$ solid solution. In order to clarify this question we investigated in detail the Raman and absorption spectra of the above mentioned solid solutions.

Taking into account that the partial isomorphous substitution of the metal ion was already investigated on the samples of $DMAAl_{1-x}Cr_xS$ with $x = 0.065$, this paper will be mostly devoted to study of $DMAAl_{0.8}Cr_{0.2}S$ and $DMAGa_{0.935}Cr_{0.065}S$ crystal and comparison of the obtained data with those obtained previously for $DMAAl_{0.935}Cr_{0.065}S$ [16–18].

2. Experiment

Single crystals of $DMAMe_{1-x}Cr_xS$ (Me = Al, Ga) were grown from the water solution containing the metal sulfate in a stoichiometric ratio and excess of dimethylammonium sulfate at a constant temperature of 303 K by slow evaporation method. The samples with $x = 0.065$ for Me = Al, Ga and 0.2 for Me = Al were grown. The concentration of chromium in each sample was additionally estimated using energy dispersive *X*-ray analyzer available in REMMA 102-02 electronic scanning microscope. To avoid the influence of absorption water the samples were annealed before the experiments at the temperatures higher than 320 K.

The measurements of the real part of dielectric permittivity and conductivity were carried out using traditional method of capacitor capacitance measurement. The samples were cut as a plate perpendicular to the ferroelectric direction. The conducting silver paste electrodes were applied on the previously polished samples. The capacitance was measured using automated setup based on LCR-meter HIOKI 3522-50 LCF HiTester in a wide frequency range with an amplitude of 10 V m^{-1}. The dielectric parameters were measured with an accuracy of nearly 1%. The nitrogen vapor flow cryostat with UNIPAN 680 temperature control system was used for the dielectric measurements. The temperature was stabilized with an accuracy not worse than 5×10^{-3} K.

The polarised absorption spectra were measured using computerized site based on ZMR-3 monochromator at the thin (0.05÷1 mm) crystalline platelets. The absorption coefficients were calculated by the traditional method of the two thicknesses.

The Raman scattering spectra were measured using computerized DFS-52 M spectrometer employing a phonon counting system. As the source of excitation the He–Ne-laser radiation was used. The spectral resolutions of the spectrometer was 1–2 cm^{-1}.

In the spectroscopic study the molecular symmetry axes *X, Y, Z* were chosen to be along the crystallographic *a, b* and *c* directions respectively.

3. Results and discussion

The temperature dependences of the dielectric permittivity ε' and tangent of dielectric losses tgδ are very useful for the precise determination of the phase transition temperatures in the samples with different chromium concentration (Fig. 1). Indeed, both these parameters for $DMAAl_{1-x}Cr_xS$ crystals manifest the sharp anomalies at the temperature T_{c1} characteristic of a proper ferroelectric phase transition [16,17]. Very similar situation was observed for $DMAGa_{1-x}Cr_xS$ crystals. As it is clearly seen from Fig. 1, the temperature of the ferroelectric phase transition T_{c1} for them practically is not changed at partial substitution of gallium with chromium. In both cases it was found to be equal 136 K. A similar situation is characteristic of the first order low temperature phase transition from the antiferroelectric into the ferroelectric phase observed for both crystals at 119 K at heating run.

Hence, contrary to the case of $DMAAl_{1-x}Cr_xS$ solid solution, the phase transition temperatures in $DMAGa_{1-x}Cr_xS$ crystals appeared to be not sensitive to the partial substitution of gallium ions with chromium. This is explained by a more close sizes of Cr^{3+} and Ga^{3+} ions contrary to the case of Cr^{3+} and Al^{3+} pair. The latter ion is much smaller in comparison with chromium and partial substitution is followed by the noticeable change of the phase transition temperature.

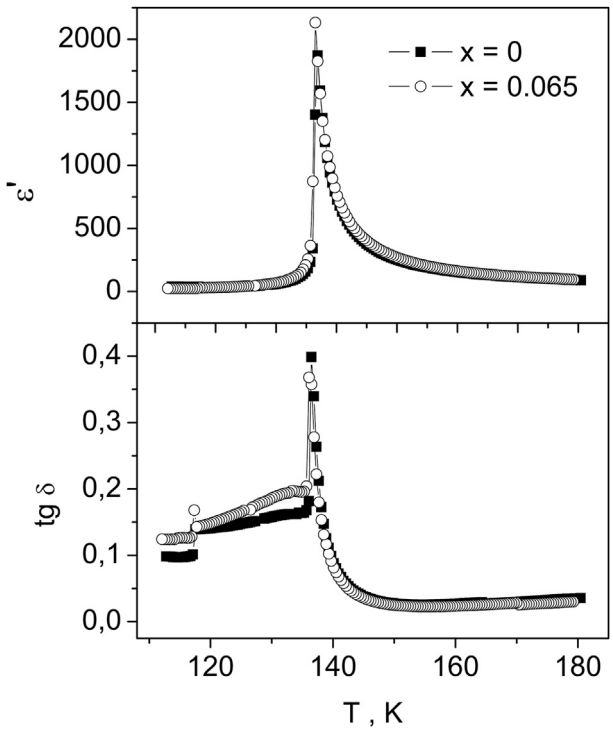

Fig. 1. Temperature dependences of the dielectric permittivity ε' and tangent of dielectric losses tgδ for $DMAGa_{1-x}Cr_xS$ (a) with different Cr concentration measured along the ferroelectric axis in a heating mode at 10 kHz.