Materials Science-Poland, Vol. 23, No. 4, 2005

Some implications of the nonlinear properties of SASD crystals

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The paper deals with the results of optical and EPR measurements performed on single-crystalline- and powdered samples of sodium ammonium sulphate dihydrate (SASD) and sodium ammonium selenate dihydrate (SASeD) doped with Cr^{3+} and irradiated with X-rays. It is shown that for samples doped with Cr^{3+} one detects in the optical spectrum, apart from the existence of two broad transmission bands, yet another narrow band, corresponding to the $^4A_{2g}(F) \rightarrow {}^4T_{1g}(F)$ transition, which suggests that such samples can potentially exhibit laser action. The EPR spectra of X-ray irradiated pure samples of SASD crystals indicate that a variety of paramagnetic centres (NH_4^-, SO_4^{-n}) are easily induced by irradiation. The concentrations of these centres are in close relation with the dose of irradiation. The observed relation can be used for dosimetry purposes.

Key words: *SASD crystas; optical spectrum; EPR; irradiation induced paramagnetic centre*

1. Introduction

Sodium ammonium sulphate dihydrate (SASD) and sodium ammonium selenate dihydrate (SASeD) belong to the same class of crystallographically isomorphous systems with the space group $P2_12_12_1$ in the paraelectric phase and $P2_1$ in the ferroelectric phase. Details of the structures of these crystals can be found in the literature [1, 2]. For pure (undoped) crystals, the transition temperature is 101 K for SASD and 180 K for SASeD. The introduction of Cr^{3+} (also Mn^{2+} or Fe^{3+}) ions as dopants substituting Na^+ ions can reduce T_C by a few degrees, even at as low concentrations as 0,01 mol % [3].

Over the last few years we have investigated physical properties of the crystals under discussion by using many different experimental and theoretical methods. These include: EPR (e.g. [4]), neutron inelastic scattering [5], optical [6], and hydro-

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static stress [7] methods. The main results of these investigations were: description of the crystal lattice dynamics, the detection of new anomalies yet not reported in literature, and the discovery of the existence of a new “glassy” phase of SASD in the temperature range from 190 to 140 K [8].

A theory explaining the nature of the phase transitions in these crystals and the origin of the newly discovered anomalies was subsequently developed by us on the basis of the modified two-sublattice Mitsui model (e.g. [8–10]). Although the applied methods were meant to shed new light on the still controversial problem of the physical principles ruling the phase transition and newly detected anomalies, we found that some of the results we obtained can have practical value. These results will be discussed in more detail below.

2. Experimental

Large and good quality single crystals of SASD were grown by the evaporation of equimolar water solutions of $(NH_4)_2SO_4$ and Na_2SO_4. During the crystal growth the temperature was lowered from 304 K to 299 K at a rate of 0.4 deg/24 h. An example of the obtained single crystal is shown in Figure 1.

Samples of SASeD doped with Cr^{3+} were kindly supplied by Prof. Z. Czapla from the University of Wrocław. They were grown using the same technique as described above, and Cr^{3+} ions were introduced to the crystal lattice by adding $Cr_2(SO_4)_2{\cdot}18H_2O$ to the saturated solution of $NaNH_4SeO_4{\cdot}2H_2O$ in a molecular ratio of 1:0.02. The obtained single crystals have a light-green colour; a sample is shown in Figure 2.

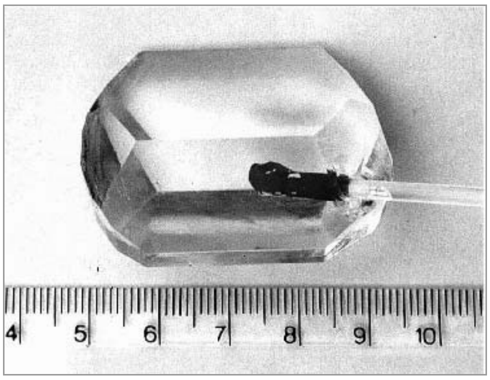

Fig. 1. A photograph of a grown $NaNH_4SO_4{\cdot}2H_2O$ single crystal

Fig. 2. A photograph of a grown $NaNH_4SeO_4{\cdot}2H_2O$ single crystal doped with Cr^{3+}

Optical measurements were done with a SPECORD UV VIS spectrometer working in the UV range of 50 000–28 000 cm^{-1} and VIS range 30 500–12 500 cm^{-1}. The experimental error was 20 cm^{-1}.

X-ray irradiation was carried out using an X-ray Dron-2.0 diffractometer. A wolfram tube was used as the source of X-rays. The applied cathode voltage was 30 kV, with a current of 20 mA. EPR measurements were performed with a standard X-band spectrometer working with a 100 kHz magnetic field modulation.

3. Results

In Figure 3, the optical spectrum of Cr^{3+} ions in SASeD is presented. As indicated by the arrows, three absorption bands are clearly seen. Two of them are very broad, which is usually observed for transition metal ions subject to the action of a crystal field. These bands were identified to belong to the $^4A_{2g}(F) \rightarrow {}^4T_{1g}(F)$ and $^4A_{2g}(F) \rightarrow {}^4T_{2g}(F)$ transitions, and the respective maxima (of absorption) are observed at 14 300(50) and 16 300(13) cm^{-1}. There exists yet another very narrow transition at 23 700(13) cm^{-1}, identified to correspond to the $^4A_{2g}(F) \rightarrow {}^4T_{1g}(F)$ transition. The Racah parameter B was estimated to be 774.05 cm^{-1}, while the Dq parameter (obtained from the energy diagram) was 1630 cm^{-1}.

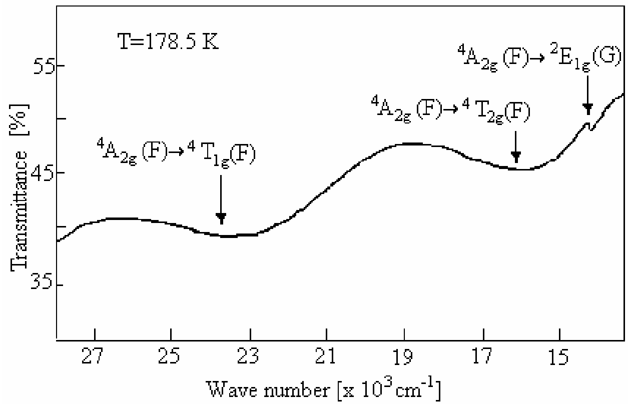

Fig. 3. The optical spectrum of SASeD doped with Cr^{3+}

The narrow band corresponding to the $^4A_{2g}(F) \rightarrow {}^4T_{1g}(F)$ transition, although of rather low quantum efficiency, indicates that relaxation times for this transition are much larger than for the remaining two transitions, and therefore the system investigated here can potentially exhibit laser action.

The EPR spectrum of the X-ray irradiated single crystal, taken at room temperature and with $\vec{B}$ parallel to one of the principal directions, is shown in Figure 4. The analysis of the angular dependence of the spectrum indicated that the it is due to a superposition of a variety of paramagnetic centres induced by the irradiation. Some of the identified centres are: SO_4^{-n} (central part of the spectrum), NH_3^-, and NH radicals.

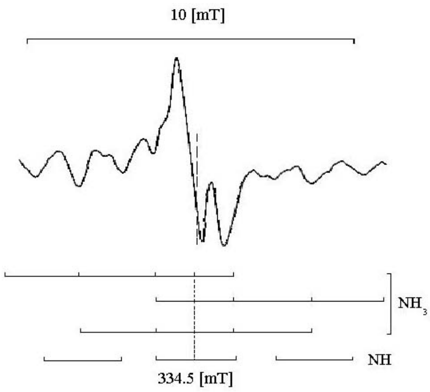

Fig. 4. The EPR spectrum of an X-ray irradiated SASD crystal (above) and the best fit of a “stick-like” spectrum for NH_3^- and NH radicals (below)

The spectra were analysed as a function of the irradiation dose, which was proportional to the time of irradiation. For this purpose, in order to avoid any influence of crystal sample misorientations on the EPR line intensity, the samples were powdered. An example of a powder EPR spectrum is shown in Figure 5.

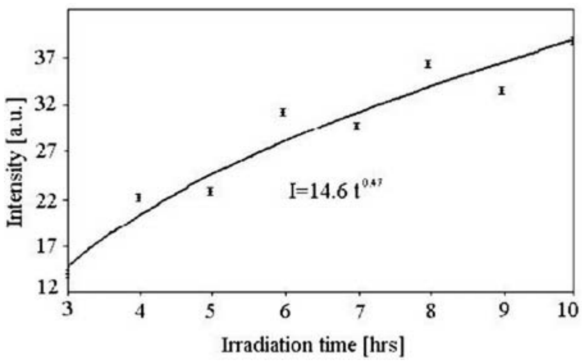

Fig. 5. The intensity of the central line vs. the time of irradiation

Two facts were found. The first is rather obvious – the intensity of the EPR lines is in strict relation with the dose of irradiation. This relation is shown in Figure 5. The experimental error seen in this figure is mainly caused by the error of measuring the exact mass of small powder samples. This can be improved by introducing a more careful procedure. The second fact is that the induced radicals are very stable, at least over a period of one month, which means that SASD and SASeD crystals can be efficiently used for dosimetric purposes.

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Received 12 October 2004
Revised 19 April 2005