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X-RAY-IRRADIATED $KTiOPO_4$: ESR STUDIES

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The study of radiation paramagnetic centres (RPC) arising in flux-grown $KTiOPO_4$ (KTP) single crystals at X-ray-irradiation at 300 K was conducted by the ESR-method in the temperature range of $3.7 \div 300$ K. For the first time in X-ray-irradiated KTP there were found electron and hole RPC stable at room temperature and related to Ti^{3+} and Al^{3+} impurity, respectively.

1. Introduction

Radiation paramagnetic centres (RPC) arising upon γ-irradiation of $KTiOPO_4$ (KTP), were first studied in Ref. 1. In that work, they were identified as hole PO_4^{2-} centres and electron Ti^{3+} centres. In later work,[2] in which X-ray-irradiated crystals were studied, RPC with similar characteristics were identified as hole O^- centres and electron Cr^{5+} centres, localized in the impurity $[SO_4]^{2-}$ and $[CrO_3(OH)]^-$ complexes, respectively, substituting for PO_4 tetrahedrons. On the other hand, in Ref. 3 the ESR-spectra of four Ti^{3+} related centres, arising in KTP under the influence of dc electric fields or as a result of annealing in hydrogen at 800°C were reported to be observed. The ESR-parameters of all these centres were different from those of the Ti^{3+} related RPC described in Ref. 1. The author of Ref. 3 believes that paramagnetic Ti^{3+} centres may also be the colour centres forming the so-called gray tracks in KTP. It should be noted, that the problem of the gray tracks or the darkening of crystals during frequency doubling of Nd:YAG lasers is one of the main problems of KTP as of nonlinear optical material. Therefore, the study of the nature of the laser-induced colour centres in KTP is a matter of acute importance.

Recently, one of us reported in Ref. 4 that in KTP subjected to laser radiation with $\lambda = 0.532$ μm (the average power $400 \div 500$ MW cm^{-2}) at T_{room}, there was observed a new paramagnetic centre — an Al related hole O^--centre. At the same time, no Ti^{3+} related centres were observed in that work.

The present one is a continuation of the study of radiation- and photo-induced colour and paramagnetic centres in KTP and it is concerned with the ESR-studies of X-ray-irradiated crystals.

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2. Experimental Procedure

Undoped KTP single crystals grown by the flux method were studied. The ESR spectra were recorded in the X-band by a THN-251 spectrometer ("Thomson") with a double modulation at the frequency of 4.2 kHz and 10 Hz. A liquid-helium ESR-9 cryostate ("Oxford-Instruments") allowing measurements to be made in the temperature range of $3.7 \div 300$ K with the temperature stabilization accuracy of 0.1 K was used. A BSV-2 (Mo-anticathode) X-ray tube operating at 55 kV and 15 mA during $1 \div 2$ hours at 300 K was used to produce RPC.

3. Results and Discussion

Before irradiation, no signals in the region of g-factors close to 2 were observed in the ESR spectra of the investigated crystals. After irradiation, the crystals became light-pink, and the ESR spectrum recorded at 300 K showed signals of two types — of electron and of hole nature. The electron component may be stipulated by[1] Ti^{3+} and[2] Cr^{5+} related RPCs, as well. Unfortunately, the low intensity of these signals and the absence of a hyperfine structure due to the interaction with the $^{47,49}Ti$ or ^{53}Cr nuclei did not allow us to choose between the models of the electron RPC suggested in Ref. 1 and 2.[a] The hole component of the spectrum resembles the O^--centre described in Ref. 2.

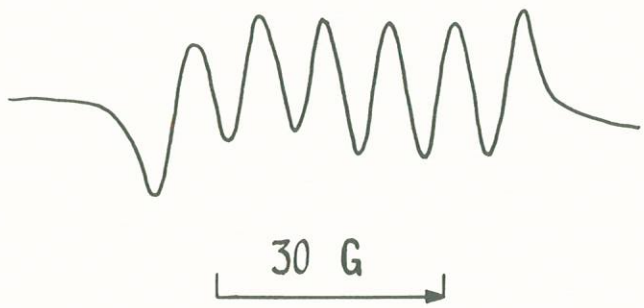

Fig. 1. ESR-spectrum ($H \parallel a$) at 77 K of a new hole O^--centre stabilized by Al^{3+}-impurity in $KTiOPO_4$ (space group $Pna2_1$) X-ray-irradiated at 300 K.

When the temperature is decreased to 77 K, the ESR spectrum of the irradiated samples, shows an additional signal, which represents a set of four groups with six lines of equal intensity in each. When the magnetic field is oriented along the crystallographic axes all the groups become equivalent and only one sixth with the distance between the lines of about 8.5 G is observed (Fig. 1). From the angle dependences of the g-factors the maximum value $g_z = 2.0713$ and the minimum value

[a] It is noteworthy that during the ESR-studies of KTP doped by Cr (0.01 weight % in crystal), we did not find any signals with the parameters of the Cr^{5+}-centre from Ref. 2 in the X-ray-irradiated samples.

$g_x = 2.0036$ were determined. All the values of the g-factor were higher than that of a free electron, which points to a hole-type character of the paramagnetic centre. The six lines structure observed is a characteristic of the hyperfine interaction of the unpaired electron with the nucleus having the spin $I = 5/2$. Such nuclei may be represented by ^{27}Al ($I = 5/2$, natural abundance 100%) and ^{55}Mn ($I = 5/2$, natural abundance 100%) that are present in KTP as uncontrollable impurities. The concentration of Mn in flux grown crystals is known to be by an order of magnitude lower than that of Al.[5] On the other hand, the charge state and the ionic radius of Al are better than those of Mn for entering into KTP lattice to a place of Ti and probably P. As a matter of fact, this property of Al is used when KTP is doped by Al for specific purposes.[6] In addition, the spectroscopic parameters of the observed signal are in agreement with those of the familiar Al related hole centres.[7] All these facts allow us to identify the observed signal as the one which comes from the O^--Al hole centre, arising during the trapping of the hole on O^{2-}, neighboring with Al.

To determine the structure of the centre and the position of Al, it is necessary to carry out an additional study. Obviously, Al may substitute not only for Ti but also for P (at a specific local charge compensation). It is noteworthy that the O^--Al centre is stable at room temperature.

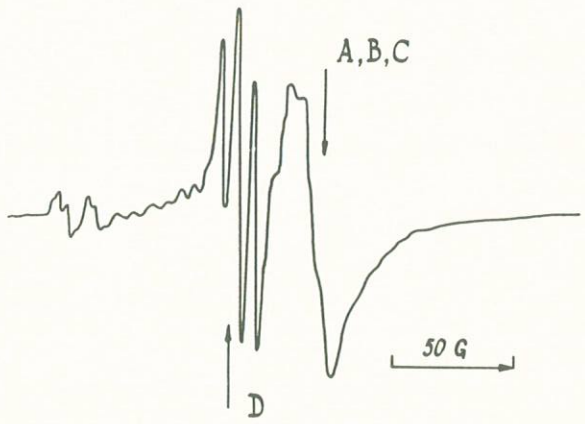

Fig. 2. ESR-spectrum ($H \parallel a$) at 60 K of the four centres related to Ti^{3+} in $KTiOPO_4$ (space group $Pna2_1$) X-ray-irradiated at 300 K. Four types of signals from the four structurally non-equivalent Ti^{3+}-centres are lettered in accordance with Ref. 3 by A, B, C, and D.

When the temperature is decreased below 60 K the above mentioned signals disappear owing to the saturation of the microwave power. However, a new intensive multiline spectrum appears, which in turn loses intensity and disappears at $T < 15$ K. Figure 2 shows a typical shape of the spectrum for the orientation $H \parallel a$ (space group $Pna2_1$). According to the angle dependences one may find four structurally nonequivalent centres with the signals of different intensity, designated A, B, C, and D in compliance with Ref. 3. Each of the ESR spectra from

those centres (A, B, C, and D) represents a superposition of the signals from four magnetically nonequivalent centres which merge when the magnetic field is oriented along the crystallographic axes. For the most abundant signal, the main values of the g-tensor were determined: $g_x = 1.7704$, $g_y = 1.8718$ and $g_z = 1.9466$. (In Ref. 3 the most abundant signal designated as A, has the following values of g-factors: $g_x = 1.7709$, $g_y = 1.8723$ and $g_z = 1.9462$). All the four signals from the structurally non-equivalent centres (A, B, C, and D) are split into triplets with the intensity ratio 1 : 2 : 1 which should arise at a hyperfine interaction with two equivalent nuclei with the spin $I = 1/2$. The same triplet splitting of the lines in the spectrum of Ti^{3+} centres was observed in Ref. 3 and it was induced by the hyperfine coupling with two ^{31}P nuclei (natural abundance 100%). Comparison of the obtained results with the data from Ref. 3 shows that the signals observed at low temperature in X-ray-irradiated KTP have the parameters similar to those of the four related Ti^{3+} centres. Such centres in X-ray-irradiated KTP are stable at room temperature.

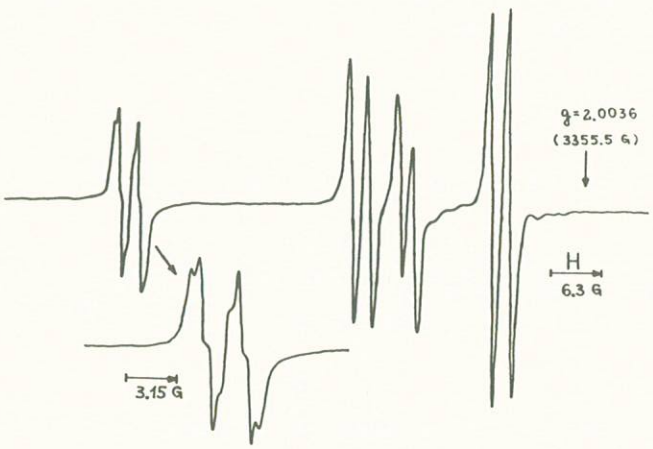

Fig. 3. ESR-spectrum ($H \perp c$) at 77 K of hole PO_4^{2-}-centres in flux grown $KTiOPO_4$ (space group $Pna2_1$) γ-irradiated up to the dose of about 1×10^4 Gy at 77 K (Data from the unpublished work by Andreev of 1986).

It should be noted that results of the recent work,[8] in which point defects in X-ray-irradiated at 77 K hydrotermally grown KTP were also studied by ESR-method are familiar to us. Low-temperature hole PO_4^{2-} centre (which is annealed at 160 K[8]) described by the authors has been observed by one of us in γ-irradiated at 77 K flux-grown KTP earlier (Fig. 3). Hole PO_4^{2-} centres with close ESR parameters were also inspected in X-ray-irradiated at 77 K flux-grown KTP. In Ref. 8, the signal with a complex hyperfine structure was observed at $T < 60$ K too. And it was identified as an electron Ti^{3+} centre. About 85% of such Ti^{3+} centres were

discovered to be annealed at 160 K. That is why, as was to be expected, we did not observe a signal with such parameters in crystals X-ray-irradiated at 300 K.

Thus, in the present work we have first established experimentally the formation in flux-grown KTP under X-ray irradiation at 300 K of stable RPC connected with Ti^{3+} and Al^{3+}. Al^{3+} related RPC is a new variety of a hole O^- centre.

In our opinion, these paramagnetic centres are also the colour centres in KTP. However this supposition requires further evidence. We also believe that these centres may be formed in KTP under radiation of Nd:YAG lasers (that is fair at least to O^--Al centre[4]) and may serve as one of the reasons for the darkening of the KTP crystals during their application in power laser systems. The studies in this direction will be continued.

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