Studies of concentration dependences in the luminescence of Ti-doped Al$_2$O$_3$

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The variation of luminescence and excitation spectra of titanium doped Al$_2$O$_3$ for the concentration of Ti ranging from 10 to 1000 ppm was investigated using synchrotron radiation. In the lightly doped Al$_2$O$_3$–Ti ($<$100 ppm) samples we identified several emission bands. These are the emission of the excitons localized at Ti (290 nm), the emission due to F$^+$ centers (325 nm), the band around 420 nm traditionally attributed to F center emission, and the luminescence of Ti^{3+} ions at 720 nm. The emphasis in this study is on the clarification of the nature of the blue emission band in the samples with high concentration of Ti ($\geq$100 ppm), where the luminescence and excitation spectra of the blue emission exhibit noticeable variability. This is explained by a model of the luminescence process of Ti^{4+}–F centers that includes the photoionization of Ti^{3+}, the subsequent capture of electrons at F$^+$-centers, formation of excited F-centers and, finally, the emission of a blue photon. The quenching of the blue emission with increasing Ti concentration is interpreted in terms of competition between oxygen vacancies and Ti^{4+} centers in the capture of the electron. © *2011 American Institute of Physics*. [doi:10.1063/1.3552943]

I. INTRODUCTION

A prominent feature of Al$_2$O$_3$ sapphire crystals is the ubiquitous emission spread over a broad spectral range from ultraviolet to near infrared. This emission has received significant attention over decades in view of applications of Al$_2$O$_3$ that rely upon the luminescence performance of the material. The most renowned examples of such applications are Cr- and Ti-doped sapphire lasers that underpinned the development of modern laser technologies. Radiation dosimetry and scintillation detection are two other areas where the use of luminescent Al$_2$O$_3$ facilitated significant improvement and created new opportunities for radiation monitoring.

Because of such practical importance, there have been a large number of comprehensive studies of pure and doped sapphire (see, e.g., Refs. 1–6) that form the basis of our present knowledge of the emission properties of Al$_2$O$_3$. However none of these studies are entirely systematic in their choice of experimental samples. In all cases, the samples used in the experiments studies were either obtained from different suppliers, or they were produced by different methods, or subjected to different thermochemical treatments. Whatever the justification for any particular choice of samples was, this created an inevitable ambiguity in the interpretation of some findings; and the possibilities for comparing results from different studies are limited further due to different experimental techniques used. A prominent example is an ambiguity in the assignment of the blue emission of sapphire.

There have been two major hypotheses on the origin of this emission. Since the blue emission of Ti^{4+} ions is a characteristic emission of wide-gap hosts[7,8] stimulated through charge-transfer transitions, the corresponding assignment of the 420 nm (3 eV) luminescence band of sapphire has been the subject of many publications since the end of the last century.[1,3,4,9–14] Another hypothesis attributes this band to the emission of F$^+$ or F defect centers (an oxygen vacancy occupied by one or two electrons, respectively) ever-present in aluminum oxide.[15–17] The existing ambiguity in the assignment of this luminescence has been acknowledged[2,18] and it has been suggested that there are several clear features permitting to discriminate between the impurity and defect emission, such as band half-width, excitation spectra, lifetimes etc. Nonetheless, it seems that various studies of the blue emission of sapphire report properties that are consistent with either one or the other hypothesis. As the luminescence of Al$_2$O$_3$ can be significantly modified by impurities and thermochemical treatment it is reasonable to assume that the blue emission could be due to more than one cause. Proving this would be the major step toward reconciliation of the existing discrepancy.

Recently we have initiated studies of Ti doped Al$_2$O$_3$ in view of possible application of this material as a scintillation target in cryogenic experiments searching for rare events.[19] The optimization of the scintillation properties of materials for this application requires a detailed understanding of the emission process at high-energy excitation and over a wide

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temperature range. This prompted a systematic investigation of the emission properties of sapphire as a function of temperature, excitation conditions and Ti concentration.[18,20–22] It has been shown that these studies on the concentration dependence can help explain the origin of the ubiquitous emission of Al_2O_3. This motivated further systematic investigations of the emission and excitation spectra of aluminum oxide with different concentration of Ti as well as anion-deficient Al_2O_3 using vacuum ultraviolet (VUV) synchrotron radiation.

II. EXPERIMENTS

The samples of Al_2O_3 crystals doped with Ti were produced at the Institute for Single Crystals (Kharkiv, Ukraine) by the Czochralski method. The crystals have been annealed in strongly reducing conditions (redox potential −230 kJ/mol) that favors conversion of Ti into its 3 + valence state.[6] It is important to stress that the samples have been produced in the same conditions, providing the necessary benchmark for the comparison and interpretation of the results. The nominal concentrations of Ti in the samples, specified by the manufacturer, were 10, 50, 100, 500, and 1000 ppm.

The sample of anion-deficient Al_2O_3 from the same manufacturer was produced by annealing in a strongly reducing atmosphere that is required for the formation of F^+ or F defect centers. It was supplied as nominally pure, though present studies revealed that it contains inadvertent impurities of Cr^{3+} and Ti^{3+} (see below).

The studies of the luminescence properties have been carried out at the SUPERLUMI station of HASYLAB, which is designed for comprehensive investigations of luminescence materials in the VUV range.[23] The $5 \times 5 \times 1$ mm^3 samples (cut perpendicular to optical axis c) were polished to optical quality and glued to the sample holder of a He-flow cryostat. Different samples were presented to the excitation radiation by translating the holder in a direction orthogonal to the beam. The fixed geometry of the experiment as well as the equal size and the surface finish of the samples allow a direct comparison of the intensity of the light emitted by the crystals.

For the measurements of excitation spectra, the emission band was selected by a SpectraPro308 (Action Research) monochromator and recorded with a Hamamatsu, R6358P Photomultiplier tube (PMT). The excitation spectra were normalized to equal quantum intensity of the synchrotron radiation by dividing for the response of a sample of sodium salicylate that has constant quantum yield over the energy range of interest.

The emission spectra were measured at fixed excitation wavelength using a liquid nitrogen cooled CCD camera (Princeton Instruments), mounted on the second exit arm of the monochromator. To eliminate the second order effect of the grating monochromator, a GG420 cut-off filter was placed in front of the entrance slit for the measurements in the 450–900 nm spectral range. The measurements of the optical absorption spectra were made using a Perkin-Elmer Lambda 9 absorption spectrometer.

III. RESULTS AND DISCUSSION

Three emission bands have been previously detected in the luminescence spectra of Ti-doped Al_2O_3 at high energy excitation (x-ray or VUV), i.e., 290, 425, and near IR bands around 750 nm.[18,20,21] The emission spectra of the studied samples measured at T = 300 and 8 K are shown in Fig. 1. The investigation of concentration dependence at selected excitation revealed additional features of the luminescence spectra of Al_2O_3−Ti that have not been previously reported. There is a noticeable difference in the luminescence of samples with low (< 100 ppm) and high (≥100 ppm) concentration of Ti. At excitation with high energy photons (7.1 eV) the emission spectra of Al_2O_3–Ti with high concentration exhibits two bands at about 300 and 730 nm. Note that the mismatch in the observed position of the near IR band (730 nm against generally quoted value of 750 nm) is due to the difficulties of the correction for the instrumental response of the detection system in this spectral range. The origin of the
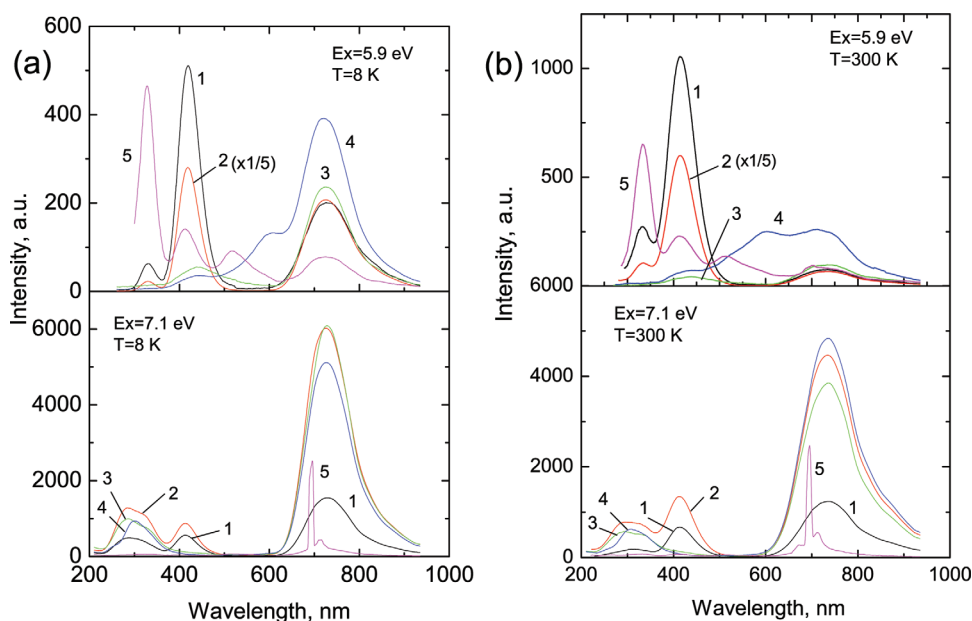

FIG. 1. (Color online) Luminescence spectra of Al_2O_3 doped with 10 (1), 50 (2), 100 (3), and 500 ppm of Ti (4) and anion-deficient Al_2O_3 (5). Spectra are monitored at excitation with 5.9 and 7.1 eV photons. T = 8 (left) and 300 K (right).
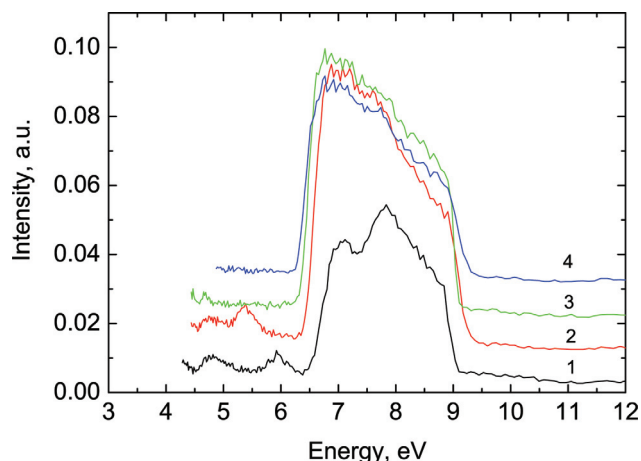
FIG. 2. (Color online) Excitation spectra monitored at 290 nm in Al_2O_3 doped with 10 (1), 50 (2), 100 (3), and 500 ppm of Ti (4). T = 8 K. Spectra are vertically shifted.

near IR emission band has been long agreed as being due to the $^2E \rightarrow \, ^2T_2$ radiative transition of Ti^{3+} ions. The luminescence spectra of the samples with low Ti concentration clearly show that the emission in ultraviolet region is composed of two bands peaking at 290 and 325 nm. Recent studies of the 290 nm band have assigned this emission to the radiative decay of excitons localized at activator ions.[18,20] The prominent feature of the emission spectra at excitation with 7.1 eV photons is the characteristic blue band at 420 nm in lightly doped Al_2O_3−Ti, which is absent in the samples with Ti concentration ≥100 ppm.

At the excitation with 5.9 eV photons the 325 and 420 nm bands observed in lightly doped Al_2O_3−Ti are more distinctive; they also exhibit a conspicuous decrease with cooling. The comparison of these emissions with the luminescence spectra of anion-deficient Al_2O_3 suggests straightforward assignment for the 325 nm and 420 nm bands. It is well established that excitation at 5.9 eV results in the emission of F^+ and F centers in Al_2O_3, peaked at 325 and 420 nm respectively.[2,24,25] The similarity of these two bands with the emission observed in the samples with low Ti concentration, supports the notion that they are of the same origin in undoped and doped samples of Al_2O_3. Further evidence is obtained from the analysis of the excitation spectra and kinetic characteristics of emission bands.

When the concentration of titanium in the sample reaches ca. 100 ppm the 325 nm band vanishes, while the appearance of the blue emission changes: the maximum shifts to 425 nm, and becomes noticeably broader and less sensitive to the change of temperature. This indicates a change in the emission mechanism that is further supported by analysis of the excitation spectra. The intensity of the 425 nm band in Al_2O_3 with 100 ppm Ti is comparable with that of the 730 nm band at excitation with 5.9 eV (T = 300 K). In the sample with even higher Ti concentration (500 ppm) the blue emission of Al_2O_3 decreases, whereas a new luminescence band emerges at 600 nm. The intensity of this band increases with the concentration of titanium, so that in the sample with the 1000 ppm it dominates the luminescence at room temperature and low energy excitation (5.9 eV).

The anion-deficient Al_2O_3 sample exhibits a narrow line at 693 nm at excitation with 7.1 eV photons that is a distinctive feature of Cr^{3+} emission ($^2E \rightarrow \, ^4A_2$ transitions). Excitation with 5.9 eV photons results in a broad emission band at 730 nm. This indicates that the sample contains impurities of chromium and titanium. The presence of these impurities in nominally pure samples is a fairly common feature for Al_2O_3.[2,26–28] The luminescence band at 510 nm observed in anion-deficient Al_2O_3 has been attributed to donor centers like interstitial aluminum ions[29] and this assignment prevailed for long.[5,27] However the authors of Ref. 29 also mentioned that F_2 centers can yield emission in this region and latest studies provided comprehensive support for such divacancy model of the emission center.[25,30]

The next step is to establish the changes in the excitation spectra with the titanium concentration. Figure 2 shows that the excitation spectra of the 290 nm band in Al_2O_3−Ti are very similar for all concentrations. The broad band of asymmetrical shape exhibits a steep onset at 6.2 eV and vanishes above 9 eV. This reproduces well the excitation spectrum of ultraviolet emission in Al_2O_3−Ti reported earlier.[18,20]

The excitation spectra of the 325 nm band measured in Ti-doped and anion-deficient crystals of Al_2O_3 are displayed in Fig. 3. The low energy part of the spectra is fitted by Gaussians revealing three individual bands with their maxima at 4.85, 5.37, and 5.92 eV, which is an unmistakable signature of F^+ centers.[26,31–33] The excitation spectrum of the Ti-doped sample exhibits an additional broad band between 6.5 and 9 eV that is very similar to the excitation spectrum of the 290 nm band. The appearance of this additional band in the excitation spectrum under discussion can be readily explained by spectral overlap of the 290 and 325 nm emission bands. It is also found that these overlapping emission bands in the Ti-doped samples exhibit distinctively different kinetics characteristics. The decay time constants of the 290 and 325 nm emission bands at 300 K are 140 and 2 ns, respectively. The first value agrees very well with the decay time constant measured by us earlier for the 290 nm band in
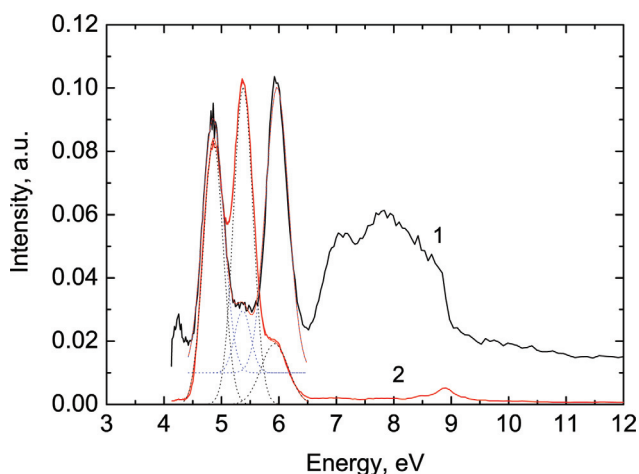

FIG. 3. (Color online) Excitation spectra monitored at 325 nm in Al_2O_3 doped with 10 ppm of Ti (1) and anion-deficient Al_2O_3 (2). T = 8 K. The low energy part of the spectra is fitted by three Gaussians. Spectra are vertically shifted.
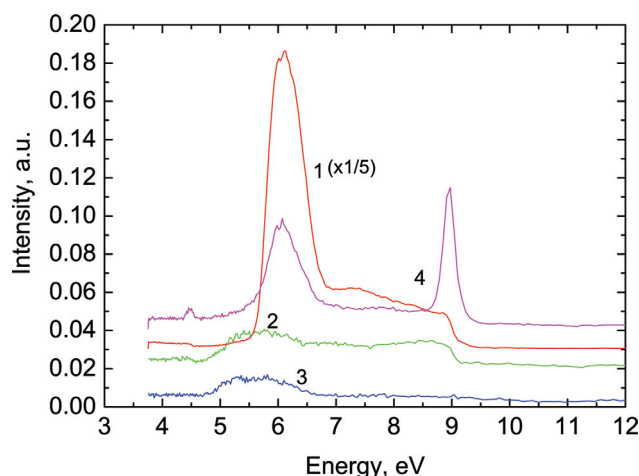
FIG. 4. (Color online) Excitation spectra monitored at 420 nm in Al_2O_3 doped with 50 (1), 100 (2), 500 ppm of Ti (3) and anion-deficient Al_2O_3 (4). T = 8 K. Spectra are vertically shifted.

Al_2O_3-Ti (Ref. [18]) whereas the second matches the decay time constant of F^+ centers emission.[5,26,31]

The excitation spectra of the blue 420 nm luminescence band show the most noticeable changes with concentration (Fig. 4). In the samples with a low Ti content (<100 ppm) the main excitation band starts at 5.5 eV, exhibits a distinctive peak at 6.1 eV that is followed by a plateau region throughout the 7–9 eV region (Fig. 4, curve 1). This makes the excitation spectrum of the blue emission in Ti-doped aluminum oxide look like the excitation spectrum of F-centers in anion-deficient Al_2O_3 (compare Fig. 4, curves 1 and 4). The only difference is the sharp peak at 8.96 eV. However, it should be noted that this peak is detected in lightly doped Al_2O_3-Ti samples at room temperature. This observation provides a sensible argument supporting the idea that in this case the blue emission is due to the radiative decay of F-centers.

As the titanium concentration reaches 100 ppm the excitation spectra show substantial changes: a new band appears in the low-energy part that shifts the excitation threshold to 4.7 eV. This fact indicates that when the concentration of impurity ions of titanium is about 100 ppm the excitation mechanism becomes more complicated and the blue emission can no longer be explained by radiative transitions of F-centers alone. There is yet another excitation process that contributes to the blue emission. This is consistent with the change in position and shape of this band with the concentration of Ti mentioned above.

Figure 5 shows the excitation spectra of Ti^{3+} emission monitored at 680 nm. In the 6.2–9.2 eV range these excitation spectra are very similar to the excitation spectra monitored at 290 nm, which is consistent with the results of our earlier measurements.[18,20] However in the 5.0–6.2 eV range there is noticeable difference in their appearance. The excitation spectra of lightly doped samples exhibit a steplike bump peaking at ∼6.1 eV, while those with titanium concentration ≥100 ppm show a gradual rise of intensity from 5.0 to 6.2 eV. This difference can be readily understood as being caused by coherent changes in the excitation spectra of the blue emission. Indeed, the spectral overlap between

the blue emission and the d-d absorption band of Ti^{3+} in Al_2O_3-Ti favors the energy transfer between the emission centers associated with these bands. Therefore the shape of the excitation spectra of Ti^{3+} over the 5.0–6.2 eV range should reproduce the features of the excitation spectra of the blue emission. Comparison with the spectra in Fig. 4 reveals that this is indeed the case: the correlation of such features in the excitation spectra of the Ti^{3+} band with the shape of the excitation spectra of the 420 nm band as well as their regular change with the titanium concentration is fairly obvious.

Analysis of these new experimental observations suggests that the blue emission band of Ti-doped Al_2O_3 is most likely due to two different, though complementary, emission processes. The excitation features of the 420 nm emission band detected in undoped and lightly doped crystals shows that this luminescence stems from the radiative recombination of F-centers. On the other hand both the emission and excitation spectra show a change when the concentration of Ti exceeds ∼100 ppm. Apparently at this concentration the Ti ions start to contribute to the excitation and emission process, leading to the luminescence in this spectral domain.

The most popular scenario that has been discussed over decades attributes this emission to the charge-transfer transition of Ti^{4+}.[1,3,4,9–14] The luminescence is excited when an electron from the valence band is transferred to Ti^{4+} with creation of Ti^{3+} and a hole in the valence band. The de-excitation of these states results in the luminescence, following the scheme:

$$Ti^{4+} + h\nu_{ex} \rightarrow Ti^{3+} + h^+ \rightarrow (Ti^{4+})^* \rightarrow Ti^{4+} + h\nu_{lum}(420\,nm).$$
(1)
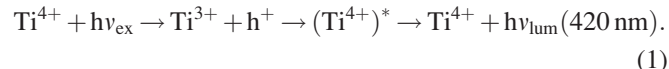
Let us verify whether present experimental results are consistent with this model. Given that the samples are prepared in identical conditions one can expect that the intensity of Ti^{4+} emission should increase with the concentration of titanium. Here, we exclude the possibility of concentration quenching since for both Ti^{4+} and Ti^{3+} emissions such an effect is only observed at concentrations that exceed the maximal doping level, i.e., 1000 ppm, in the Al_2O_3-Ti
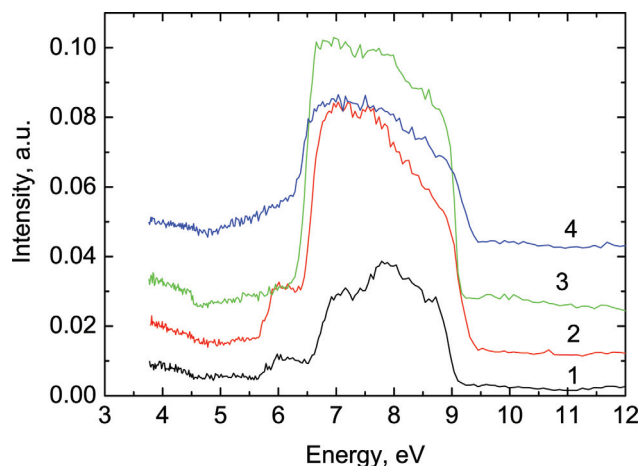

FIG. 5. (Color online) Excitation spectra monitored at 680 nm in Al_2O_3 doped with 10 (1), 50 (2), 100 (3), and 500 ppm of Ti (4). T = 8 K. Spectra are vertically shifted.

samples under test (see Refs. 8 and 34, respectively). The experimental results though show that the intensity of the blue emission decreases; it totally vanishes at 1000 ppm titanium concentration, in disagreement with the behavior expected from this model.

Another model has been put forward very recently, suggesting that the emission may be initiated by the photoionization of Ti^{3+} that promotes an electron to the conduction band:[18,20]

$$Ti^{3+} + h\nu_{ex} \rightarrow Ti^{4+} + e^-, \qquad (2)$$
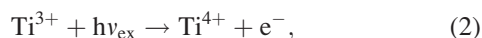
The electron can then trigger the recombination luminescence of F-center according to the scheme:

$$F^+ + e^- \rightarrow (F)^* \rightarrow F + h\nu_{lum}(420 \text{ nm}). \qquad (3)$$
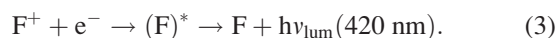
where F* stands for excited F center. The model implies that the recombination occurs at the defect center while the Ti^{3+} ion serves merely as a donor of electrons. Therefore the intensity of the emission will be controlled by the number of F^+ centers and the probability of the electron capture. The increase of the total amount of titanium results in the concomitant rise of the concentration of tetravalent Ti^{4+} ions, which creates an excess of local positive charge. Taking as reference that 2% of titanium ions reside in the tetravalent state[2] one can estimate that the Al_2O_3-Ti (500 ppm) sample contains 5×10^{17} cm^{-3} of Ti^{4+}, while the typical concentration of oxygen vacancies in Al_2O_3 is 10^{16}–10^{17} cm^{-3}.[2,25] Therefore, at these concentrations, Ti^{4+} starts to compete with the oxygen vacancy in the capture of free electrons according to the following reaction:

$$Ti^{4+} + e^- \rightarrow (Ti^{3+})^* \rightarrow Ti^{3+} + h\nu_{lum}(730 \text{ nm}), \qquad (4)$$
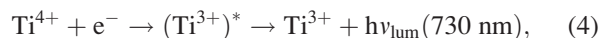
thus reducing the numbers of carriers which are available for recombination with the F^+-centers through the luminescence process (3).

This model can also account qualitatively for the small changes in the shape of the emission spectrum (broadening and redshift) as being due to the deformation of the lattice in the vicinity of the oxygen defect induced by Ti^{3+} when it looses an electron, in line with the discussion in Ref. 35. This, as well as the proximity of the excitation and photoionization thresholds,[18] adds more confidence to the statement that the blue emission of Ti-doped aluminum oxide is due to the radiative decay of a defect F-center, stimulated by the capture of an electron, supplied by Ti^{3+}. The involvement of the titanium ion in this emission process suggests calling the center "Ti^{4+}-F-center."

Finally, it is worth remarking that the luminescence band at 600 nm manifests the type of concentration dependence which is expected for the emission of Ti^{4+}. The intensity of this band increases with the concentration of dopant while the centroid of the excitation spectrum is positioned in the energy range of the O-Ti^{4+} charge transfer transitions. These transitions exhibit a threshold at 4.17 eV and are located around 5.4–6.8 eV,[3] which is consistent with the luminescence excitation spectra (see Fig. 6). Such tentative assignment could reconcile the exciting experimental results
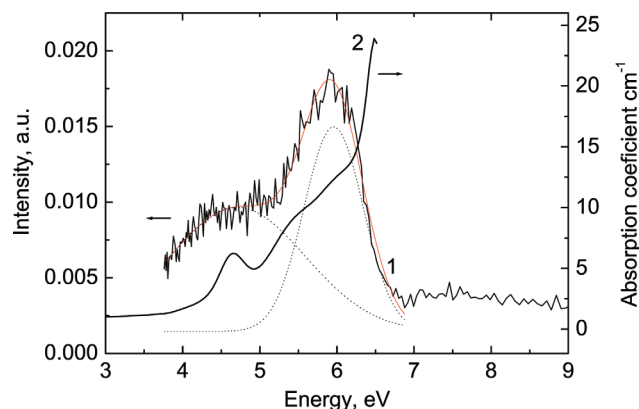

FIG. 6. (Color online) Excitation spectrum monitored at 600 nm in heavily doped Al_2O_3 (1000 ppm of Ti). 2-absorption spectrum of the sample. T = 300 K.

and complete the model of radiative decay of high energy excitation in Ti-doped Al_2O_3.

IV. CONCLUSION

In this work we investigated the significance of the Ti concentration on the luminescence of Ti-doped Al_2O_3 under excitation over a wide energy range, using synchrotron radiation. In the lightly doped Al_2O_3-Ti (<100 ppm) samples we detected and identified a number of previously observed emission bands, i.e., the band at 290 nm due to exciton localized at Ti, the band at 325 nm band due to F^+ centers, the band at 420 nm due to F centers and the band at 730 nm due to emission of Ti^{3+}. The studies of the samples with higher concentration of Ti allowed us to distinguish the alteration of the emission around 420 nm that is accompanied by related changes in the excitation spectra of this band. The appearance of the low energy band in the excitation spectra of Al_2O_3–Ti at higher concentration ($\geq$100 ppm) is explained as involvement of Ti^{3+} ions in the excitation of the F^+-centers. Photoionization of Ti^{3+} is followed by capture of electrons at an F^+-center, formation of an excited F-center and subsequent emission of a blue photon. Therefore the emission is assigned to the luminescence of Ti^{4+}–F centers. The quenching of the emission intensity with the increase of Ti concentration is explained by competition between oxygen vacancies and Ti^{4+} centers in the capture of the electron. Finally, we put forward the hypothesis that the emission band at 600 nm emerging in the samples with high concentration of titanium may be due to the charge-transfer luminescence transitions of Ti^{4+}.

ACKNOWLEDGMENTS

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