Luminescence of U^{6+}-Activated Al_2TeO_6

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The luminescence of U^{6+}-activated Al_2TeO_6 is reported. Some remarks are made on assigning a U^{6+} emission spectrum to an octahedral uranate group or to a linear uranyl group.

Introduction

The influence of crystal structure and chemical composition on the emission spectrum of U^{6+}-activated oxides has been studied intensively in this laboratory *(1, 2)*. Up till now we investigated oxides containing uranate centres with the following constitution: octahedral UO_6^{6-}, distorted UO_6^{6-}, $(UWO_{10})^{8-}$ and U^{6+}-doped zig-zag chains $(WO_4^{2-})_n$. This paper reports on the luminescence of U^{6+}-doped Al_2TeO_6 which seems interesting for two reasons: (a) Al_2TeO_6 has the trirutile structure containing linear chains of edge-sharing octahedra with compositional sequence Al–Al–Te *(3)*. The Te^{6+} ion site symmetry is D_{2h}. This site symmetry has not been investigated before for U^{6+} luminescence. (b) It cannot be excluded that, upon introduction of the U^{6+} ion in Al_2TeO_6, UO_2^{2+} groups are formed if the expansion due to substitution of the smaller Te^{6+} by the U^{6+} ion would be anisotropic. In that case U^{6+} in Al_2TeO_6 would present a situation in between the octahedral UO_6^{6-} and the linear UO_2^{2+} group.

Experimental

Samples were prepared as described in Ref. *3*. Optical measurements were performed as described in Ref. *1*.

Results

Unfortunately our samples Al_2TeO_6–U (0.3 m/o) showed only a weak green luminescence far below room temperature. Samples $Al_2Te_{0.8}W_{0.2}O_6$–U, also with tri-rutile structure *(3)*, show a somewhat stronger emission with $T_{1/2} = 160°K$ and $T_q = 225°K$. Samples without tungsten show in addition a broad emission band peaking at about 480 nm under short-wavelength ultraviolet excitation, those with tungsten a band peaking at 380 nm. These are also present in the absence of uranium. They are ascribed to defect emission in the tellurate host lattice *(4)* and to tungstate charge-transfer emission *(5)*, respectively.

The diffuse reflection spectra of all samples show long absorption tails into the visible instead of steep absorption edges in the ultraviolet. The infrared spectra contain

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broad absorption bands (see also (3)). We selected for optical measurements the samples which were single-phase according to X-ray analysis and showed the smallest absorption tails and narrowest infrared bands. The emission spectrum of the U^{6+} ion in the trirutiles $Al_2(Te, W)O_6$ is given in Fig. 1. It consists of a number of bands forming a progression in ν_s (the symmetrical stretching frequency of the uranate group). Its frequency amounts to $740\ cm^{-1}$. It can be excited in a broad band in the ultraviolet peaking at about 320 nm. The decay time of this emission amounts to 160 μs.

Discussion

In view of earlier results the low luminescence efficiency is surprising. The position of the excitation band implies efficient luminescence with high quenching temperature (2). Further the decay time should be
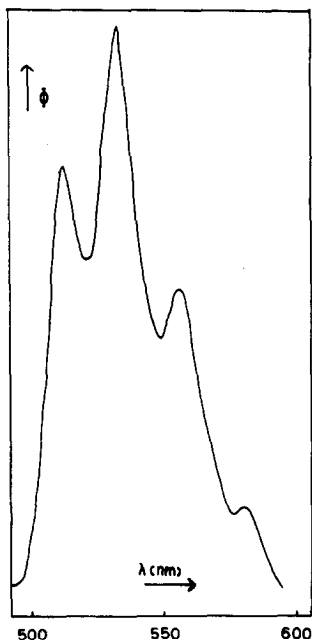

FIG. 1. Spectral energy distribution of the emission of $Al_2Te_{0.997}U_{0.003}O_6$ at 4.2°K under 330 nm excitation. Φ gives the radiant power in arbitrary units per wavelength interval.

some 300 μs for a site with inversion symmetry (1, 2). From the diffuse reflection and infrared spectra we conclude that Al_2TeO_6 shows deviations from the ideal trirutile structure. These may be due either to Al–Te disorder and/or to oxygen deficiency. This offers several possibilities to explain the low efficiency, namely, the absorption tail competes with the luminescent centres for the excitation energy, uranium may be present in the pentavalent state which may in addition act as a killer centre (6), centres due to the oxygen deficiency may act as killer sites.

The emission spectrum (Fig. 1) shows that at least part of the uranium is present in the hexavalent, luminescent state. There is a clear progression in the symmetric U–O stretching vibration, ν_s. The second term of the progression has the highest intensity. The terms of the progression are rather broad and do not show further fine structure. Due to the defect character of the samples it is easy to imagine that the samples contain a large number of U^{6+} centres which have slightly different energy level schemes due to differences in their surroundings. This accounts for the broadness of the spectra.

It is tempting to conclude from the emission spectrum that the emitting centre is a uranyl group, especially because the crystal structure offers a possibility for such a configuration. The value of τ is of no use in a discussion on the character of the luminescence centre due to the fact that the efficiency is low, so that τ does not necessarily correspond to a radiative decay time. The value of ν_s seems to be a little low for a uranyl group, but this is not necessarily a serious objection.

The most serious objection against such an assignment is the fact that $LaAlTeO_6$–U shows a strikingly similar emission spectrum (7). This was verified during our study. The tellurate group in $LaAlTeO_6$, however, has a strong trigonal field along one of the threefold axes. This makes distortion of an

octahedral uranate group to a uranyl group in this crystal structure improbable. The same can be said of $SrLaNaTeO_6$–U (*1*). This composition with ordered perovskite structure has a similar emission pattern, although in this case the first term in the progression is the most intense one. The site symmetry of the Te^{6+} ion does also not favour a distortion to linear uranyl groups. Note that $LaAlTeO_6$ as well as $SrLaNaTeO_6$ both have a superstructure, so that disorder is possible. In addition oxygen deficiency is probable also for these tellurates. This may explain the broadness in the emission spectra of the uranium luminescence in these two compounds.

From the experimental data available at the moment we come to the following conclusions: (a) It is easy to decide from the uranium emission spectrum between purely octahedral uranate centres and pronounced uranyl groups (i.e. U–O in the uranyl group considerably shorter than U–O in the plane perpendicular to the uranyl group) (*2*). (b) It is not possible to deduce from emission spectra like those in Fig. 1 the nature of the emitting uranate centre. Spectra of this type are to be expected for strongly distorted uranate octahedra, especially if the crystal field varies from site to site. As a consequence the fine structure in the terms of the progression cannot be resolved. Under certain conditions, however, the uranyl group can also give a spectrum of this kind. In some cases a distinction between the two kinds of centres is useless, because it is a matter of taste whether a tetragonally elongated uranate octahedron is considered as a UO_6^{6-} or as a UO_2^{2+} group (compare the discussion on $MgUO_4$ in Ref. *6*).

Finally we note that the strength of the second term in the progression of the emission spectrum of Al_2TeO_6–U has been explained before in terms of stiffness of the surroundings of the luminescent centre (*2*). In the case of $LaAlTeO_6$–U a similar intensity distribution has been found in the emission spectrum. In fact the oxygen ions surrounding the U^{6+} ion in Al_2TeO_6 and $LaAlTeO_6$ have similar other cation neighbours, namely, two Al^{3+} ions and one Al^{3+} + one La^{3+} ion under comparable angles, respectively. In $SrLaNaTeO_6$–U, however, the cations behind the oxygen ions surrounding the U^{6+} ions are the Na^+ ions. Expansion of the uranate group is easier than in the other two tellurates. As a consequence the first term is the strongest one in the progression (*2*).

References

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