Yellow zirconate luminescence in $Ca_3ZrSi_2O_9$

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Abstract

The compound $Ca_3ZrSi_2O_9$ which contains edge-sharing pairs of zirconate octahedra shows a luminescence emission with an unusually long wavelength (maximum 540 nm).

1. Introduction

The number of luminescent zirconates is relatively small. There is no reason to assume that this should be due to fundamental reasons. The Zr(IV)–O(II) charge transfer transition should be able to show efficient luminescence [1]. However, the number of zirconates which can be excited by conventional UV excitation ($\lambda > 240$ nm) is small, so that zirconate emission is easily overlooked. Compounds which absorb conventional UV radiation, e.g. ZrO_2 and $BaZrO_3$ (240 nm), do not luminesce owing to energy migration [2]. However, ZrP_2O_7 [3], $BaZrSi_3O_9$ [4] and $SrZrSi_2O_7$ [5] show efficient UV zirconate emission (around 300 nm) for excitation wavelengths close to 200 nm.

In this paper we report on the zirconate luminescence of $Ca_3ZrSi_2O_9$, the crystal structure of which has been reported recently [6]. This crystal structure is uncommon, since it contains pairs of edge-sharing zirconate octahedra which are an uncommon entity. Also the luminescence is uncommon: it can be excited by conventional UV and its emission colour is yellow, which has not been observed before as far as we are aware.

2. Experimental details

Powder samples were prepared by the usual solid state techniques as described before [6]. The quality of ZrO_2 is Koch–Light (99.8%). They were checked by X-ray diffraction (CuKα radiation). $Ca_3ZrSi_2O_9$ is

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monoclinic with space group $P2_1/c$ and parameters $a = 7.3603(1)$, $b = 10.1766(3)$, $c = 10.4514(3)$ Å and $\beta = 90.875(2)°$.

The luminescence measurements were performed using a Perkin–Elmer spectrofluorometer 44B equipped with an Oxford liquid helium cryostat.

3. Results

Under short wavelength UV excitation $Ca_3ZrSi_2O_9$ shows a yellow photoluminescence at room temperature. Its emission intensity increases considerably upon cooling to liquid helium temperature. Fig. 1 shows the emission and excitation spectra of this luminescence at liquid helium temperature. At room temperature they have hardly changed. There is an emission band
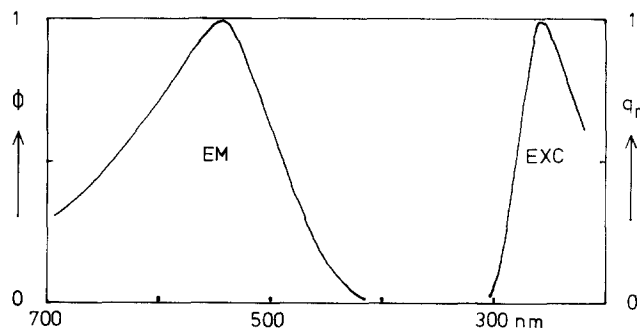

Fig. 1. Emission and excitation spectra of the luminescence of $Ca_3ZrSi_2O_9$ at 4.2 K. Excitation wavelength 255 nm; emission wavelength monitored at 550 nm. The quantity q_r gives the relative quantum output, whereas Φ gives the radiant power per constant wavelength interval in arbitrary units.
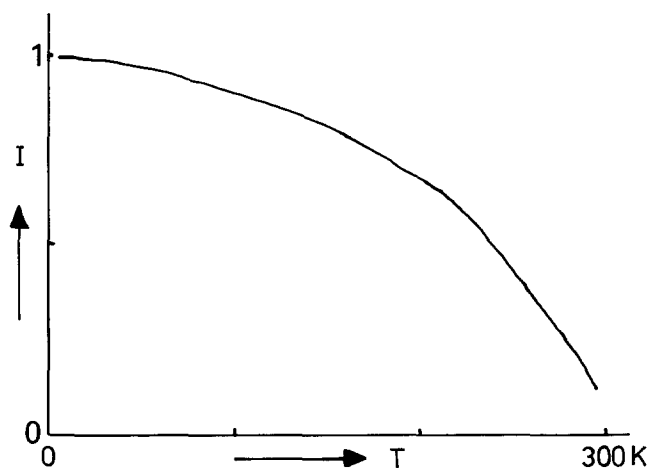
Fig. 2. Temperature dependence of the emission intensity of $Ca_3ZrSi_2O_9$. Excitation wavelength 255 nm.

with a maximum at 540 nm. The corresponding excitation band peaks at 260 nm. This yields a very large Stokes shift of about 20 000 cm^{-1}. Fig. 2 shows the temperature dependence of the luminescence intensity. It is clear that thermal quenching starts at a temperature far below room temperature.

4. Discussion

In order to interpret the results, the Zr_2O_{10} group consisting of two edge-sharing zirconate octahedra should be considered in more detail. Of the six oxygen atoms coordinating one zirconium atom, only three belong to silicate groups. The other three are coordinated by calcium and zirconium only. Two of these form the common edge (O(8)); the other (O(9)) is surrounded by three calcium atoms and one zirconium atom and is therefore unsaturated according to Pauling's electrostatic valence rule [7]. In fact the Zr–O(9) distance (1.989 Å) is shorter than the other Zr–O distances (2.106–2.224 Å).

The lowest optical absorption transition is expected to be the zirconate charge transfer transition involving the most unsaturated oxygen ion, which is O(9). This reasoning is based on earlier arguments which were recently put on quantitative ground [8]. The energy of such a charge transfer transition will be lower than for oxygen ions connected to silicon.

Therefore the relatively low first absorption transition of $Ca_3ZrSi_2O_9$ is ascribed to a charge transfer transition involving O(9) and O(8) on one hand and Zr(IV) on the other. Actually the formula can be written as $Ca_3ZrO_2Si_2O_7$, indicating that some of the oxygen atoms are not bonded to silicon. In this way it is understood why $Ca_3ZrSi_2O_9$ can be excited with conventional UV.

In the same way the emission can be expected at longer wavelengths than usual. However, the fact that the emission colour becomes even yellow must also be ascribed to the very large value of the Stokes shift. Clearly there occurs a large reorganization in the excited state after absorption. It has been shown by van Tol et al. [9] that this is to be expected. In the present case the clustering of two zirconate groups and the presence of chemically inequivalent oxygen ions around Zr(IV) will also contribute to the necessity of a large reorganization. The long wavelength emission of $Ca_3ZrSi_2O_9$ can therefore be considered as a straight consequence of an uncommon aspect of the crystal structure. The large Stokes shift resulting from the large reorganization is in turn responsible for the relatively low thermal quenching region of the luminescence [10].

In conclusion, the uncommon character of the $Ca_3ZrSi_2O_9$ crystal structure results in an uncommon zirconate luminescence.

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