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Fluorescence of Europium Tungstate

We have prepared a new compound, europium tungstate, which exhibits fluorescence of good intensity in a relatively narrow spectral range. The material is easily prepared without the addition of fluxing agents, and the resulting peak-fluorescence intensity is comparable to that reported[1] for europium in calcium tungstate.

This compound belongs to a family of rare-earth tungstates which can be described by the generic formula $R_2(WO_4)_3$, where R stands for rare earth. Some other members of this group, particularly terbium tungstate, also fluoresce strongly. While some tungstates of this group have been investigated by others,[2,3] their fluorescent properties have not been reported previously.

Europium oxide (99.9 %) from Research Chemicals, Inc. and reagent-grade tungstic acid, in the proportion of one mole of oxide to three moles of acid, were mechanically mixed by grinding with a glass pestle and mortar. About 11 g of the mixture were placed in a 50 cc crucible (of Morganite, Vitreosil or platinum), fired for one hour at 1000°C, and slowly cooled at a linear rate of 16°C/hr to room temperature. The resulting material was a highly crystalline white powder with a pinkish cast and a density of 7.44 g/cm³. The melting point of the fired material is 1130°C, as determined from a temperature-time cooling plot.

Single crystals suitable for x-ray diffraction studies were produced by firing the material at 1150°C and oscillating the temperature of the furnace by ±30°C. New material was added as required to build up the crystals and the whole crucible was then slowly cooled to room temperature. The results of the single-crystal analysis[4] and some other measured properties are tabulated in Table 1.

Powder diffraction patterns have also been recorded and indexed on the basis of the results of the single-crystal analysis. These patterns show that the powdered samples and cerium tungstate, the only rare-earth tungstate for which previous x-ray data[2] are available, are isomorphous.
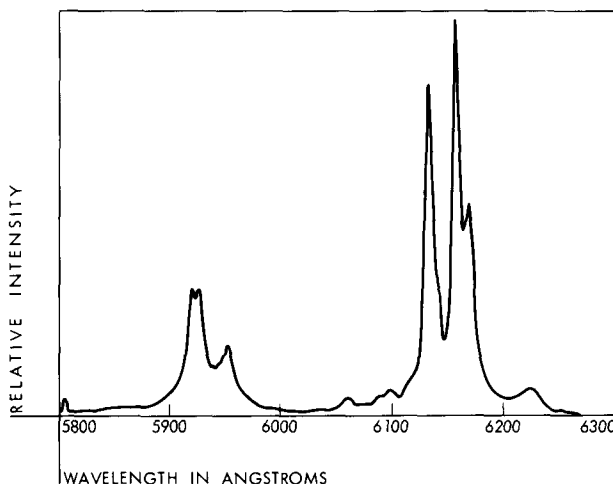
A number of wavelengths in the range of 2537 to 5300 A are effective in exciting the fluorescence. A sharp excitation doublet occurs at 5260 A, four sharp lines at 4665 A, and five sharp lines at 4110 A, consistent with the visible absorption spectrum of europium compounds.[5,6]

Figure 1 shows the fluorescence spectrum of a sample of powdered europium tungstate at room temperature, as recorded by a Carey Model 14 spectrophotometer. The stronger lines of the spectrum occur in the 5800 to 6300 A range, with the strongest emission in the 6150 A region. Weaker fluorescence (not shown in Fig. 1) is found at longer and shorter wavelengths, but the strongest fluorescence outside the range indicated is only 0.5 % of the peak at 6150 A. At liquid helium temperature, traces obtained are similar to those at room temperature, except for an increase in peak intensity by a factor of five and a narrowing of the halfwidths of the stronger lines from 6 to 3 A. In contrast to calcium tungstate phosphors, this compound does not show broad-band fluorescence under short-wave excitation.

It seems likely that in the regions of 5928 and 6150 A we are dealing with transitions from the upper $^5D_0$ to the lower $^7F_1$ and $^7F_2$ levels, respectively. A very weak line at 5810 A could be the normally forbidden $^5D_0$ to $^7F_0$ transition. These transitions are compatible with the published[6,7] energy levels of Eu^{3+}, but confirmation must await the results obtained with single crystals.

Rare-earth tungstates have been prepared of all the

Figure 1 **Fluorescence of europium tungstate at room temperature.**

Crystal system	Monoclinic
Unit cell dimensions*	$a = 7.676 \pm 0.003A$
	$b = 11.463 \pm 0.003A$
	$c = 11.396 \pm 0.005A$
	$\beta = 109.63 \pm 0.04°$
Probable space group	$C_{2h}^6 - C2/c$
Density	7.44 g/cm³ (exptl.), 7.29 (theor.)
Formula weights/unit cell	4
Melting point	$1130 \pm 15°C$
Fluorescence decay (1/e)	150×10^{-6} sec
Magnetic susceptibility	8.36×10^{-6} emu/g (294°K)
Effective number of Bohr magnetons Eu^{3+}	3.28 (exptl.)
Effective number of Bohr magnetons Eu^{3+}	3.4 (theor.)
Refractive index, approx.	2.1
Dielectric constant (1 kc)	4.1

* The lattice can also be described by a face-centered cell with $a = 7.676$, $b = 11.463$, $c = 21.467$, $\beta = 90°$, which is more convenient for indexing of the powder pattern. The symmetry is not orthorhombic, however.

members of this lanthanide series with the exception of promethium and thulium. To the best of our knowledge, these compounds represent a new family of fluorescent materials, some of which (e.g., europium and terbium tungstate) have not been previously reported as compounds.

Acknowledgments

References

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