Structure and luminescence properties of some new $AgLnW_2O_8$ compounds

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Three new compounds, $AgLnW_2O_8$ ($Ln^{3+} = Eu$, Gd or Tb), have been prepared by a solid-state reaction and crystallize with a scheelite-related monoclinic symmetry. Their IR spectra show absorption transitions in the region 1000–400 cm^{-1} similar to $KLnW_2O_8$. Broad excitation and emission bands of the tungstate group with a large Stokes shift (12 573 cm^{-1}) are observed in $AgGdW_2O_8$. Excitation and emission spectra of $AgLnW_2O_8$ (Ln = Eu or Tb) show that energy transfer from tungstate to Eu and Tb occurs and that Eu^{3+} ions occupy a unique crystallographic site with C_2 site symmetry.

There are a considerable number of tungstates that have the scheelite ($CaWO_4$) structure. These include compositions of formulae AMO_4 and $A'BM_2O_8$ ($A' = Li^+$, Na^+, K^+, Rb^+ or Cs^+; $A = Ca^{2+}$, Sr^{2+}, Ba^{2+}, Pb^{2+} or Hg^{2+}; B = rare-earth ion; $M = Mo^{6+}$ or W^{6+}).[1–4] The latter compounds with scheelite-related structures are used as hosts for rare-earth ions in luminescence studies. A further composition, of formula Ln_2BMO_8 ($B = Ge^{4+}$, $M = Mo^{6+}$ or W^{6+}), also crystallizes in the scheelite structure and the luminescence properties of these compounds have been reported in ref. 5.

In recent years the crystal structures of the $ALnW_2O_8$ and $ALnMo_2O_8$ series (A = alkali-metal ion; Ln = rare-earth ion) have been determined. The crystal structure and luminescence properties of $CsLnW_2O_8$ ($Ln = Eu^{3+}$ or Tb^{3+}) and $AEuM_2O_8$ ($A = Li^+$, Na^+, K^+, Rb^+ or Cs^+; $M = Mo^{6+}$ or W^{6+}) have recently been studied.[6–9] The structures of $AgLnMo_2O_8$ ($Ln = Eu^{3+}$, Gd^{3+} or Tb^{3+}) and their luminescent properties have been studied by us.[10] Some of these compounds have a scheelite-related crystal structure but others have a completely different structure. A marked property of these systems is the fact that they do not show clear concentration quenching and the WO_6 group may be used as sensitizers.

This paper presents the preparation, structure, and luminescence properties of some new complex oxides, $AgLnW_2O_8$ ($Ln = Eu^{3+}$, Gd^{3+} or Tb^{3+}). The luminescence of $AgGd_{0.96}Eu_{0.04}W_2O_8$ is also reported.

Experimental

The $AgLnW_2O_8$ ($Ln = Eu^{3+}$, Gd^{3+} or Tb^{3+}) compounds were prepared from stoichiometric mixtures of Ag_2O (99.5%), WO_3 (99.5%) and the corresponding rare-earth oxides (99.95%). In the case of Tb, Tb_4O_7 was used directly, no attempt being made to obtain the sesquioxide Tb_2O_3. The samples were mixed with ethanol in an agate mortar, finely ground, placed in alumina crucibles, and fired at 850 °C for 20 h. Then the samples were reground carefully to enhance their reactivity and reheated at the same temperature for 30 h. After heating the samples were cooled slowly to room temperature.

X-Ray powder diffraction analysis was carried out on a Rigaku Denki D/max-IIB diffractometer using Cu-Kα ($\lambda = 0.1542$ nm) radiation with silicon powder used as the internal standard. IR spectra were measured on a FTS–20E IR spectrometer. Luminescence was measured with a SPEX DM3000F fluorescence spectrophotometer with a 45 W xenon lamp as the excitation source (slit: 0.4, filter: 370).

Results and Discussion

Structure and composition

The lattice type, cell parameters, and unit cell volumes of the three new compounds and $AgGd_{0.96}Eu_{0.04}W_2O_8$ are listed in Table 1. The indexing of patterns obtained was examined with the aid of the CELL computer program.[11] The structure of the series $AgLnW_2O_8$ ($Ln = Eu^{3+}$, Gd^{3+} or Tb^{3+}) can be deduced from the scheelite-related $AgLnMo_2O_8$ structure by a monoclinic distortion. The X-ray powder patterns of $AgLnW_2O_8$ ($Ln = Eu^{3+}$, Gd^{3+} or Tb^{3+}) are shown in Fig. 1.

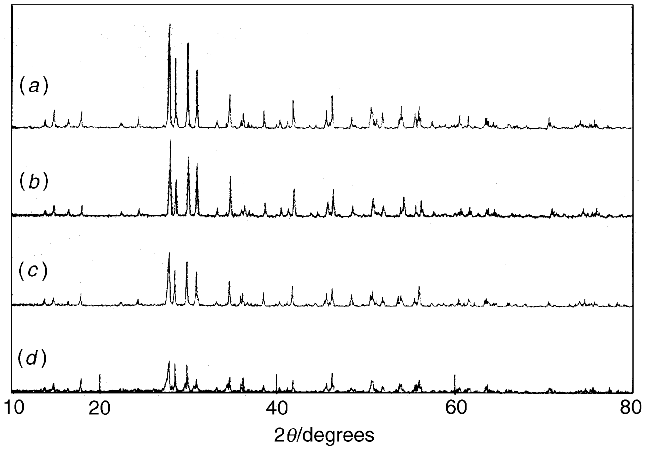

Fig. 1 X-Ray powder diffraction patterns of $AgLnW_2O_8$: (*a*) $AgGd_{0.96}Eu_{0.04}W_2O_8$, (*b*) $AgTbW_2O_8$, (*c*) $AgEuW_2O_8$, (*d*) $AgGdW_2O_8$

Table 1 Cell parameters for $AgLnW_2O_8$ ($Ln = Eu^{3+}$, Gd^{3+} or Tb^{3+})

compound	*a*/Å	*b*/Å	*c*/Å	*β*/degrees	*V*/Å³
$AgEuW_2O_8$	10.796(1)	5.006(8)	13.165(8)	114.1(8)	649.19
$AgGd_{0.96}Eu_{0.04}W_2O_8$	10.796(2)	5.006(7)	13.165(7)	114.1(8)	649.19
$AgGdW_2O_8$	10.775(2)	4.986(5)	13.005(2)	114.0(2)	638.39
$AgTbW_2O_8$	10.774(4)	4.986(1)	13.000(6)	114.0(2)	638.00

Table 2 X-Ray powder diffraction data for $AgEuW_2O_8$

h	*k*	*l*	d_{obs}/Å	d_{calc}/Å	I/I_o	*h*	*k*	*l*	d_{obs}/Å	d_{calc}/Å	I/I_o
1	0	1	6.43	6.4319	9	3	2	−5	1.761	1.7630	24
0	0	2	6.005	6.0050	14	1	1	−7	1.709	1.7114	21
2	0	−1	5.42	5.3981	9	6	1	−3	1.700	1.6933	27
0	1	0	4.973	5.0070	25	0	3	1	1.656	1.6531	22
1	1	−2	3.948	3.9510	5	3	0	−8	1.643	1.6435	41
2	1	−1	3.665	3.6709	13	4	0	−8	1.605	1.6076	9
3	0	0	3.282	3.2827	5	1	0	7	1.584	1.5841	6
2	0	−4	3.211	3.2151	99	4	2	2	1.569	1.5662	6
2	1	1	3.137	3.1323	80	2	1	−8	1.552	1.5542	6
0	0	4	2.995	3.0025	99	6	0	1	1.544	1.5436	4
3	1	−2	2.893	2.9008	81	4	1	−8	1.529	1.5306	20
2	1	−4	2.704	2.7054	9	7	0	−2	1.516	1.5145	7
2	0	−5	2.621	2.6236	5	1	1	−8	1.507	1.5102	17
1	0	4	2.583	2.5910	57	1	3	3	1.49	1.4866	6
0	1	4	2.55	2.5750	3	5	1	−8	1.466	1.4677	18
0	2	0	2.503	2.5035	21	0	3	4	1.459	1.4588	10
3	0	2	2.486	2.4837	27	2	0	−9	1.446	1.4462	7
0	2	1	2.45	2.4508	9	6	0	2	1.441	1.4403	6
1	2	−1	2.426	2.4263	5	0	2	7	1.414	1.4152	9
1	2	1	2.339	2.3330	28	1	3	4	1.403	1.4031	3
2	2	−1	2.257	2.2711	6	5	2	2	1.397	1.3944	5
4	0	−5	2.237	2.2376	10	4	3	−4	1.379	1.3814	6
2	0	−6	2.191	2.1943	8	7	0	1	1.335	1.3355	14
0	1	5	2.161	2.1657	44	2	3	−6	1.325	1.3284	3
5	0	−4	2.071	2.0846	4	8	1	−4	1.304	1.3030	3
4	1	1	2.043	2.0433	6	7	2	−2	1.298	1.2958	5
1	2	3	1.988	1.9879	24	0	1	9	1.288	1.2894	7
1	1	−6	1.961	1.9679	40	0	3	6	1.281	1.2818	14
2	0	5	1.881	1.8769	25	3	1	7	1.272	1.2721	17
4	2	−2	1.836	1.8355	4	7	0	2	1.261	1.2599	7
1	0	−7	1.821	1.8211	3	1	0	9	1.256	1.2557	14
1	2	4	1.804	1.8004	38	5	3	1	1.234	1.2325	7
6	0	−3	1.799	1.7994	24	7	1	2	1.221	1.2218	10
6	0	−2	1.784	1.7796	9	2	4	−2	1.211	1.2132	4

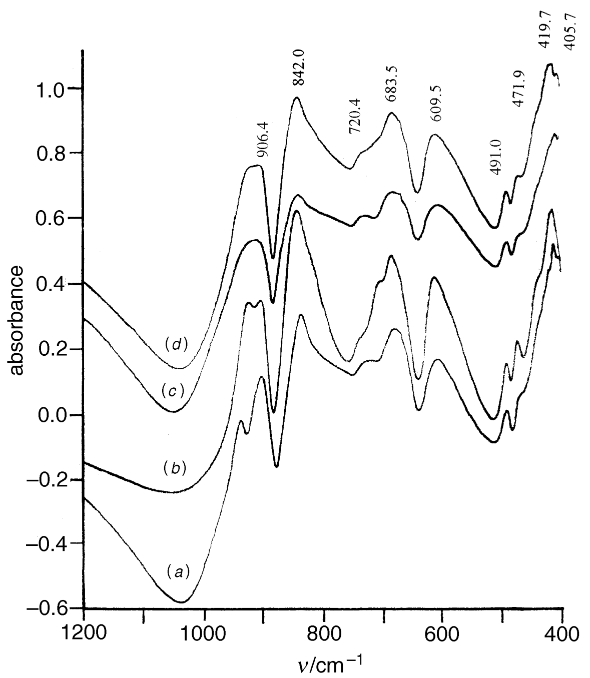

Fig. 2 IR spectra of $AgLnW_2O_8$ compounds: (*a*) $AgEuW_2O_8$, (*b*) $AgGd_{0.96}Eu_{0.04}W_2O_8$, (*c*) $AgTbW_2O_8$, (*d*) $AgGdW_2O_8$

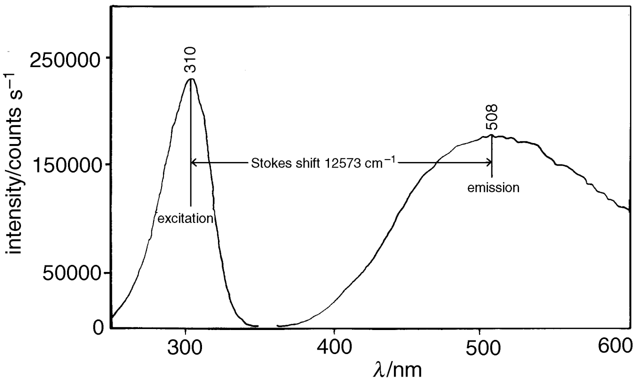

Fig. 3 Excitation and emission spectra of $AgGdW_2O_8$ at room temperature

The X-ray powder diffraction patterns of this series are more complicated than those of $AgLnMo_2O_8$. All reflections can be indexed on a simple monoclinic cell, which is twice as large as that of the scheelite-related $AgLnMo_2O_8$ along the *a* axis. For example: $AgGdMo_2O_8$ has a tetragonal structure with $a_t = b_t = 0.5248$ nm, $c_t = 1.1510$ nm; $AgGdW_2O_8$ is monoclinic with $a_m = 1.0775$ nm, $b_m = 0.4987$ nm, $c_m = 1.3005$ nm and $\beta = 114.00°$. The relationship between the tetragonal and monoclinic cell can be expressed simply as $a_m \approx 2a_t$, $b_m \approx b_t$, $c_m \approx c_t$. $CsLnW_2O_8$ (Ln = Pr, Sm, Eu, Gd, Tb or Lu) prepared by Torardi *et al.*[6] and α-$KLnW_2O_8$ (Ln = Sm–Lu, Y) prepared by Hanuza and Macalik[12] are also monoclinic. The ionic radius of K^+ (1.33 nm) is similar to that of Ag^+ (1.26 nm), which supports our deduction. As a representative example, the X-ray powder diffraction data of $AgEuW_2O_8$ are shown in Table 2.

Although Tb_4O_7 was used as the starting material the colour of the tungstate $AgTbW_2O_8$ obtained was white, and it is isomorphous with the others (Ln = Eu or Gd) where the valence can only be +3 (see Table 1). It is, therefore, very unlikely that the valence of Tb in $AgLnW_2O_8$ is +4. If the cations were present in mixed valence with an average valence between +3 and +4, one would expect deeply coloured

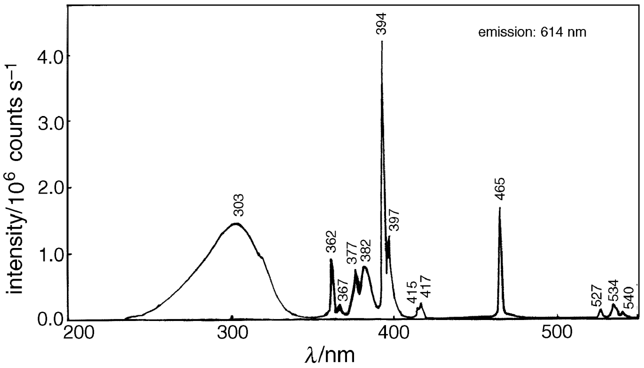

Fig. 4 Excitation spectrum of $AgGd_{0.96}Eu_{0.04}W_2O_8$ at room temperature

materials. It is likely, therefore, that this reaction proceeds according to eqn. (1).

$$1/2Ag_2O_{(s)}+2WO_{3(s)}+1/4Tb_4O_{7(s)}\rightarrow AgTbW_2O_{8(s)}+1/8O_{2(g)} \qquad (1)$$

A similar phenomenon was also seen in the aerial preparation of Pr_2O_3–3WO and Tb_2O_3–$3WO_3$,[13] in which Pr_6O_{11} and Tb_4O_7 were used as starting materials.

IR spectra

The IR spectra of $AgLnW_2O_8$ ($Ln=Eu^{3+}$, Gd^{3+}, Tb^{3+}) are shown in Fig. 2 and are more complicated than those of the scheelite-related $AgLnMo_2O_8$ compounds owing to their lower unit-cell symmetry.[12] Eight absorption peaks with varying intensities are observed in the range 400–1000 cm^{-1} for the samples and are somewhat similar to those of $KLnW_2O_8$.[12] We can thus conclude that the tungstate group is of the octahedral form WO_6 in the $AgLnW_2O_8$ compounds.

Luminescence

It is interesting that $MLnW_2O_8$ compounds with M = Li, Na or K do not luminesce, in contrast to the Ag compounds. Although K^+ and Ag^+ have similar ionic radii, they have different electronic configurations. The excitation and emission spectra of $AgGdW_2O_8$ are shown in Fig. 3. There is an intense excitation band from 250 to 350 nm peaking at 310 nm. At an excitation wavelength of 310 nm, an intense emission band is observed with λ_{max} at *ca.* 508 nm. There is no overlap between the excitation and emission bands and the room-temperature Stokes shift is large (12 573 cm^{-1}).

The excitation spectrum of the Eu^{3+} emission ($\lambda_{em}=614$ nm) of $AgGd_{0.96}Eu_{0.04}W_2O_8$ consists of a number of sharp lines of Eu^{3+} absorption and a broad band (250–350 nm). This broad band with λ_{max} at *ca.* 303 nm arises from the tungstate and overlaps with the charge-transfer band of Eu^{3+} (Fig. 4).

The emission spectrum of the Eu^{3+} ion in $AgGd_{0.96}Eu_{0.04}W_2O_8$ is shown in Fig. 5. The electronic $^5D_{3,2,1,0}\rightarrow{}^7F_J$ transitions are observable and a weak and broad tungstate emission is also observed while at high concentrations of Eu^{3+} (*e.g.* in $AgEuW_2O_8$), the tungstate emission disappears, and only the Eu^{3+} emission lines mentioned above are observed. This suggests that the tungstate groups transfer energy efficiently to Eu^{3+}.

It is interesting that the $^5D_0\rightarrow{}^7F_0$ transition at 578 nm is extremely weak, the $^5D_0\rightarrow{}^7F_1$ transition contains three lines (590, 593 and 598 nm) and the $^5D_0\rightarrow{}^7F_2$ contains five lines (603, 609, 614, 619 and 622 nm). This suggests a unique crystallographic site for Eu^{3+} with site symmetry C_2 yielding one line for 0–0, three lines for 0–1 and five lines for 0–2 transitions. This result is in accord with the site symmetry of the Ln^{3+} ions in $KLnW_2O_8$[12] as determined by IR and Raman spectroscopy.

From the $^5D_0\rightarrow{}^7F_0$, $^5D_0\rightarrow{}^7F_1$ and $^5D_0\rightarrow{}^7F_2$ emission transitions shown in Fig. 5 and the $^7F_0\rightarrow{}^5D_3$ (415, 417 nm), $^7F_0\rightarrow{}^5D_2$ (465 nm) and $^7F_0\rightarrow{}^5D_1$ (527 nm) excitation

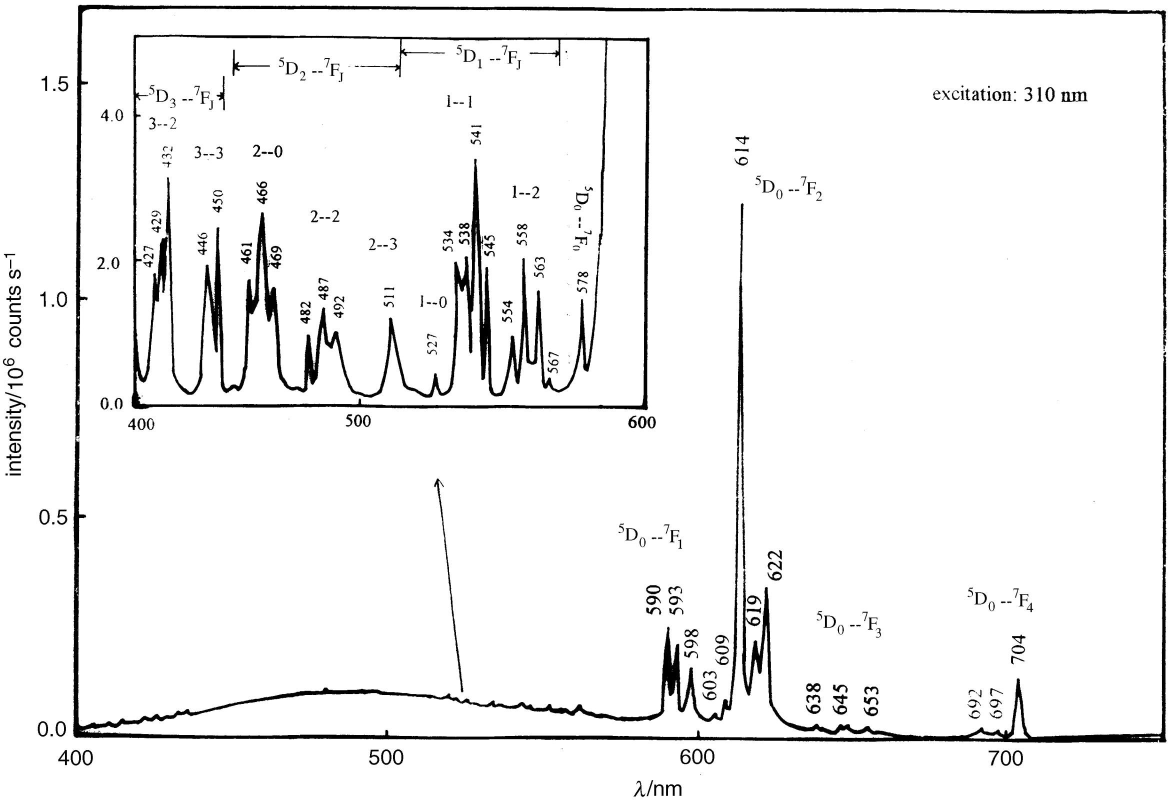

Fig. 5 Emission spectrum of $AgGd_{0.96}Eu_{0.04}W_2O_8$ at room temperature

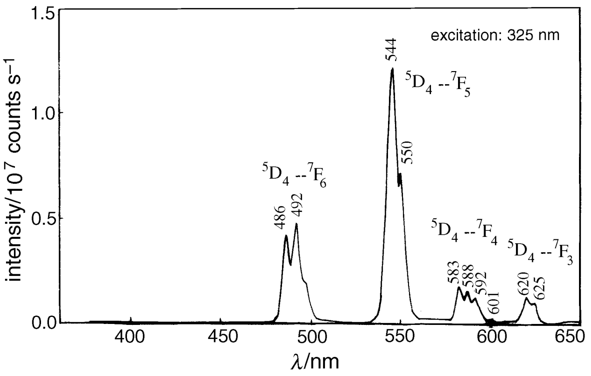

Fig. 6 Emission spectrum of $AgTbW_2O_8$ at room temperature

transitions shown in Fig. 4, the energy levels of the $^5D_0$, $^5D_1$, $^5D_2$, $^5D_3$ and $^7F_0$, $^7F_1$, $^7F_2$ states can be determined.

From these levels the position of the emission lines for $^5D_3 \rightarrow {}^7F_{2,3}$, $^5D_2 \rightarrow {}^7F_{0,2,3}$ and $^5D_1 \rightarrow {}^7F_{0,1,2}$ can be calculated and are found to be in agreement with the experimental values shown in the emission spectrum, Fig. 5. Torardi *et al.*[6] also observed weak $^5D_3$ and $^5D_2$ emissions from Eu^{3+} doped in $CsLuW_2O_8$, but they postulated that only the $^5D_0 \rightarrow {}^7F_J$ emission transitions appear in $CsEuW_2O_8$, the high-level emissions being quenched by cross-relaxation. Nevertheless, in $AgEuW_2O_8$, even though the concentration of Eu^{3+} is high, the emissions from $^5D_3$, $^5D_2$ and $^5D_1$ still appear and non-radiative transitions between the ^5D_J levels of Eu^{3+} have therefore only a low probability. This excludes coupling to the tungstate stretching vibrations.

The emission spectrum of Tb^{3+} in $AgTbW_2O_8$ is shown in Fig. 6 and shows the well known $^5D_4 \rightarrow {}^7F_J$ emission transitions of Tb^{3+}. Emission from the WO_6 group is at best very weak, suggesting that WO_6 groups transfer energy efficiently to Tb^{3+} in $AgTbW_2O_8$.

Conclusion

The new monoclinic compounds $AgLnW_2O_8$ (Ln = Eu, Gd or Tb) show strong luminescence. The large Stokes shift (12573 cm^{-1} in the Gd compound) reveals that the tungstate is involved in the luminescence and energy transfer occurs from the tungstate to Ln^{3+} which lie on a C_2 crystallographic symmetry site.

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