

Structure and Luminescent Properties of Three New Silver Lanthanide Molybdates

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Three new compounds $\text{AgLnMo}_2\text{O}_8$ ($\text{Ln} = \text{Eu, Gd, Tb}$) crystallize with a tetragonal scheelite-type structure characterized by MoO_4 tetrahedra. The IR spectra show three absorption bands, which correspond respectively to the ν_1 , ν_2 , and ν_3 modes of the tetrahedral- MoO_4^{2-} groups. The emission of $\text{AgGdMo}_2\text{O}_8$ shows the band of the MoO_4^{2-} groups around 600 nm wavelength with very weak intensity. Both $\text{AgEuMo}_2\text{O}_8$ and $\text{AgTbMo}_2\text{O}_8$ emit intensely, and the concentration quenchings of both Eu^{3+} and Tb^{3+} luminescences are very weak. For all compounds, Ag^+ luminescence is not observed. © 1996 Academic Press, Inc.

1. INTRODUCTION

There are a considerable number of molybdates that have the scheelite (CaWO_4) structure. These include compositions that fit the formulas AMoO_4 and $\text{A}'\text{BM}_2\text{O}_8$, where $\text{A}' = \text{Li}^+, \text{Na}^+, \text{K}^+, \text{Rb}^+, \text{and Cs}^+$; $\text{A} = \text{Ca}^{2+}, \text{Sr}^{2+}, \text{Ba}^{2+}, \text{Pb}^{2+}, \text{and Hg}^{2+}$; $\text{B} = \text{rare earth ions}$; and $\text{M} = \text{Mo}^{6+}$ or W^{6+} (1–4). The latter compounds with scheelite-related structure have often been used as hosts for rare earth ions, for fundamental studies in the field of fluorescence. Another composition, which has the formula Ln_2BMO_8 ($\text{B} = \text{Ge}^{4+}, \text{M} = \text{Mo}^{6+}, \text{W}^{6+}$), crystallizes also in the scheelite structure. The luminescent properties of these compounds were reported in literature (5).

In recent years the crystal structures of the compounds ALnW_2O_8 and ALnMo_2O_8 ($\text{A} = \text{alkali metal ions}$; $\text{Ln} = \text{rare earth ions}$) have been determined. The crystal structure and luminescent properties of CsLnW_2O_8 ($\text{Ln} = \text{Eu}^{3+}, \text{Tb}^{3+}$) and AEuM_2O_8 ($\text{A} = \text{Li}^+, \text{Na}^+, \text{K}^+, \text{Rb}^+, \text{and Cs}^+$; and $\text{M} = \text{Mo}^{6+}, \text{W}^{6+}$) have recently been studied by researchers (6–8). 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 obvious concentration quenching.

In the present paper the structures, IR spectra, and luminescent properties of some silver rare-earth molybdates are reported.

2. EXPERIMENTAL

$\text{AgLnMo}_2\text{O}_8$ ($\text{Ln} = \text{Eu, Gd, Tb}$) compounds were prepared from stoichiometric mixtures of Ag_2O (AR, 99.9%), MoO_3 (AR, 99.5%), and the corresponding rare earth oxides (99.95%). In the case of Tb, Tb_4O_7 were used directly; no attempt was made to first form the sesquioxide. The samples were mixed with ethanol (AR) in agate mortars, fired at 800°C for 50 hr with an intermediate regrinding to enhance the activity, and then cooled slowly to room temperature.

X-ray powder diffraction analysis was carried out on a Rigaku denki D/max-IIB diffractometer using $\text{CuK}\alpha$ ($\lambda = 0.1542$ nm) radiation. Silicon powder was used as the internal standard. The IR spectra were measured on a FTS-20E IR spectrometer. The excitation and emission spectra were measured with a Hitachi MPF-4 fluorescence spectrophotometer.

3. RESULTS AND DISCUSSION

Structure

Cell parameters, c/a , and volumes of all compounds are listed in Table 1. The c/a values are almost constant indicating that the $\text{AgLnMo}_2\text{O}_8$ compounds all form the same structure with closely scheelite-related tetragonal symmetry. So the conclusion is made that all rare earth ions (Eu, Gd, Tb) are trivalent in the compounds. The X-ray powder diffraction data for the three $\text{AgLnMo}_2\text{O}_8$ which were calculated by us fit the experimental data very well.

IR Spectra

The IR spectra of $\text{AgLnMo}_2\text{O}_8$ ($\text{Ln} = \text{Eu, Gd, and Tb}$) in the region 400–1000 cm^{-1} were recorded (Fig. 1). The $\text{A}^{\text{II}+}\text{Mo}^{\text{VI}+}\text{O}_4$ scheelite oxides, having S_4 site symmetry for the MoO_4^{2-} group, show three absorption bands in this region, around 890, 820, and 420 cm^{-1} , which correspond respectively to the ν_1 , ν_3 , and ν_2 modes of the tetrahedral MoO_4^{2-} group (9). As shown in Fig. 1, all of $\text{AgLnMo}_2\text{O}_8$

TABLE 1
Unit Cell Parameters for the $\text{AgLnMo}_2\text{O}_8$
($\text{Ln} = \text{Eu, Gd, Tb}$) Oxide

Compounds	System	a (nm)	c (nm)	c/a	V (nm ³)
$\text{AgEuMo}_2\text{O}_8$	tetra.	0.5267	1.1552	2.193	0.320
$\text{AgGdMo}_2\text{O}_8$	tetra.	0.5248	1.1510	2.193	0.317
$\text{AgTbMo}_2\text{O}_8$	tetra.	0.5224	1.1456	2.193	0.313

have the same IR spectral pattern. The ν_3 mode has three components around 830, 790, and 700 cm^{-1} , respectively; the ν_2 has only one sharp peak at 420 cm^{-1} ; the ν_1 mode has one peak at 890 cm^{-1} in $\text{AgLnMo}_2\text{O}_8$. This confirms that the $\text{AgLnMo}_2\text{O}_8$ ($\text{Ln} = \text{Eu, Gd, Tb}$) oxides crystallize with scheelite-related structure with MoO_4^{2-} tetrahedra other than those of CsLnW_2O_8 with WO_6 polyhedra (9, 10).

Fluorescent Behavior

The excitation and emission spectra of $\text{AgEuMo}_2\text{O}_8$ are shown in Fig. 2. In spite of the high Eu^{3+} concentration

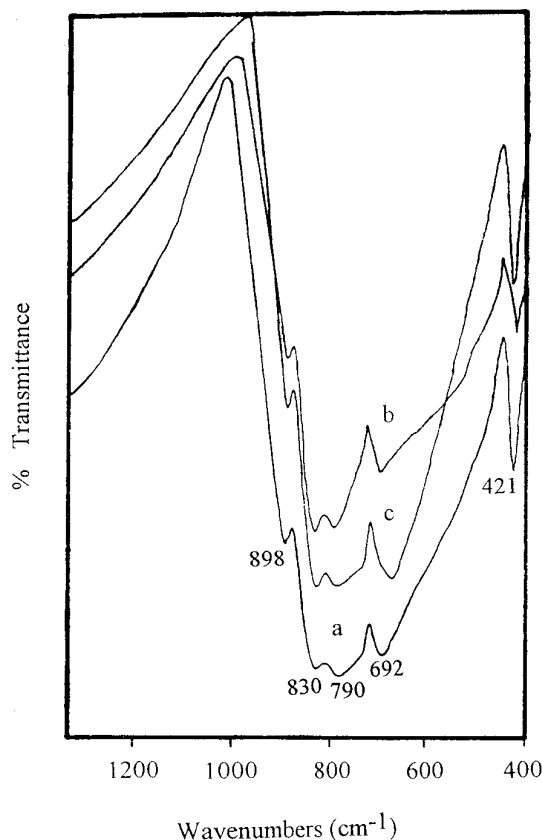


FIG. 1. IR spectra for $\text{AgLnMo}_2\text{O}_8$ oxides. (a) $\text{AgEuMo}_2\text{O}_8$, (b) $\text{AgGdMo}_2\text{O}_8$, (c) $\text{AgTbMo}_2\text{O}_8$.

TABLE 2
Luminescence Data of Double Molybdates at
Room Temperature

Compound	Luminescent center	Excitation max (nm)	Emission max (nm)	Stokes shift (10^3 cm^{-1})
$\text{AgEuMo}_2\text{O}_8$	Eu^{3+}	465	611	5.1
$\text{AgGdMo}_2\text{O}_8$	MoO_4^{2-}	330	597	13.6
$\text{AgTbMo}_2\text{O}_8$	Tb^{3+}	486	537	2.0

the Eu^{3+} emission is very efficient. Under any excitation wavelength, the emission is very efficient. Under any excitation wavelength, the emission consists of Eu^{3+} emission only. The 7F_2 transition of Eu^{3+} dominates the emission and is evidence of the noncentrosymmetric geometry of the Eu^{3+} site in these scheelite compounds. The excitation spectrum of the Eu^{3+} emission consists of the characteristic Eu^{3+} lines and the weak band corresponding with the molybdate group absorption band (Fig. 2).

The emission spectrum of $\text{AgTbMo}_2\text{O}_8$ shows the well-known ${}^5D_4-{}^7F_J$ transitions of the Tb^{3+} ion (Fig. 3), of which display an uncommon feature that a single emission line of the ${}^5D_4-{}^7F_2$ transition is by far stronger than any other line in the visible region.

For molybdate excitation (Fig. 3, left) the Tb^{3+} shows its most intense peak at 486 nm; the broad band of the MoO_4^{2-} group is relatively much stronger than that in $\text{AgEuMo}_2\text{O}_8$. However, no molybdate group emission could be observed at room temperature in either the Tb^{3+} or Eu^{3+} compounds.

The broad band in the UV region of the excitation spectra of the Eu^{3+} and Tb^{3+} emission indicates efficient energy transfer from the molybdate group to Eu^{3+} and Tb^{3+} , as discussed in literature (6). The luminescent intensity remains strong for the Eu^{3+} and Tb^{3+} end member compounds by the way of diluting the Eu^{3+} and Tb^{3+} sublattice with a nonluminescent ion Gd^{3+} . This indicates that energy migration in the concentrated compounds over the Eu^{3+} and Tb^{3+} sublattice to acceptor sites is an inefficient process.

The excitation spectrum of $\text{AgGdMo}_2\text{O}_8$ shows only a broad band around 350 nm with very poor intensity and its emission spectrum also shows a broad band of the MoO_4^{2-} group around 600 nm with weak intensity too. However, the emissions of Gd^{3+} and Ag^+ are not observed in the region.

Luminescence data are given in Table 2.

ACKNOWLEDGMENTS

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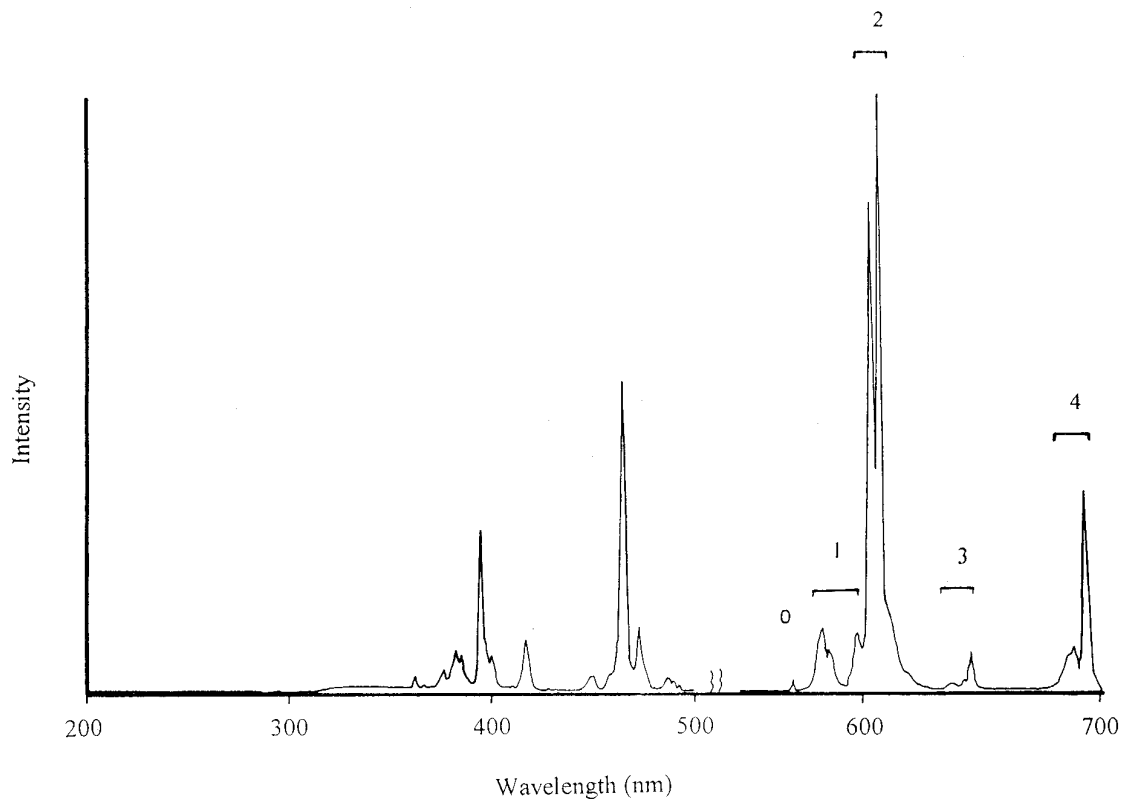


FIG. 2. Excitation (left, emission wavelength 611 nm) and emission (right, excitation wavelength 465 nm) spectra of $\text{AgEuMo}_2\text{O}_8$ at room temperature. The figures denote the value of J in the transitions ${}^5D_0-{}^7F_J$.

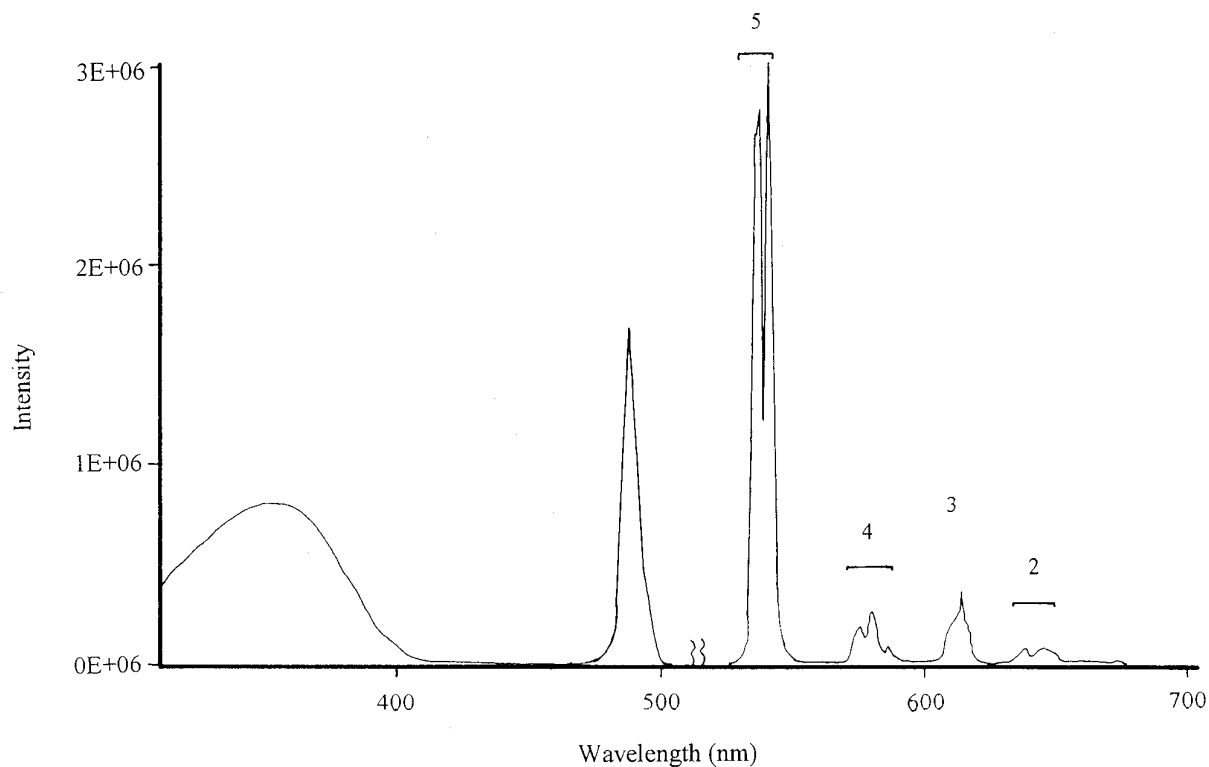


FIG. 3. Excitation (left, emission wavelength 537 nm) and emission (right, excitation wavelength 486 nm) spectra of $\text{AgTbMo}_2\text{O}_8$ at room temperature. The figures denote the value of J in the transitions ${}^5D_4-{}^7F_J$.

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