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# Syntheses, structure and rare earth metal photoluminescence of new and known isostructural $A_2Mo_4Sb_2O_{18}$ ($A$=Ce, Pr, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu) compounds

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ABSTRACT

Nine new $A_2Mo_4Sb_2O_{18}$ ($A$=Ce, Pr, Eu, Tb, Ho, Er, Tm, Yb, Lu) compounds have been synthesized by solid-state reactions. They are isostructural with six reported analogues of yttrium and other lanthanides and the monoclinic unit cell parameters of all fifteen of them vary linearly with the size of $A^{3+}$ ion. Single crystal X-ray structures of eight $A_2Mo_4Sb_2O_{18}$ ($A$=Ce, Pr, Eu, Gd, Tb, Ho, Er, Tm) compounds have been determined. Neat $A_2Mo_4Sb_2O_{18}$ ($A$=Pr, Sm, Eu, Tb, Dy, Ho, Er, Tm) compounds exhibit characteristic rare earth metal photoluminescence.

## 1. Introduction

Crystalline tellurites containing $d^0$ transition metal ions have been attracting the attention of solid-state chemists from the point of view of both structural diversity and second harmonic generation (SHG) activity [1–4]. $Te^{4+}$ and isoelectronic $Sb^{3+}$ exhibit similar coordination versatility in oxides and exist in three asymmetric coordinations [5,6], namely, pyramidal, disphenoid and square pyramidal. Antimonites containing $d^0$ transition metal ions are rather few and are mostly ternary oxides. Some of these compounds were studied from the point of view of luminescence and ferroelectric properties [6].

We investigated the quaternary $A$/Mo/Sb/O ($A$=rare earth metal) system and reported [5] the synthesis and structural characterization of six isostructural $A_2Mo_4Sb_2O_{18}$ ($A$=Y, La, Nd, Sm, Gd, Dy) compounds, which represent the first examples of rare earth metal molybdoantimonites. They crystallize in $C2/c$ space group with four formula units and contain $A^{3+}$ cations and discrete tetramolybdodiantimonite anionic aggregates $(Mo_4Sb_2O_{18})^{6-}$. In view of the obvious scope for isostructural compounds of the rest of lanthanides and their lanthanide photoluminescence, a continuation of this investigation has been considered worthwhile and, therefore, taken up. The results of these studies, namely, synthesis of nine new isostructural $A_2Mo_4Sb_2O_{18}$ ($A$=Ce, Pr, Eu, Tb, Ho, Er, Tm, Yb, Lu) compounds, X-ray single crystal structures of $A_2Mo_4Sb_2O_{18}$ ($A$=Ce, Pr, Eu, Gd, Tb, Ho, Er, Tm) compounds and the rare earth metal photoluminescence of neat $A_2Mo_4Sb_2O_{18}$ ($A$=Pr, Sm, Eu, Tb, Dy, Ho, Er, Tm) compounds, are presented in this paper.

## 2. Experimental section

### 2.1. Synthesis and crystal growth

$MoO_3$, $MoO_2$, $Sb_2O_3$, $Ce_2(MoO_4)_3$, $CeO_2$, $Pr_6O_{11}$, $Tb_4O_7$ and $A_2O_3$ ($A$=Nd, Sm, Eu, Gd, Dy, Ho, Er, Tm, Yb, Lu) oxides of high purity ($>99.99\%$) were used for the solid-state synthesis and single crystal growth of thirteen $A_2Mo_4Sb_2O_{18}$ ($A$=Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu) compounds, in evacuated sealed quartz tubes of 7 cm length and 1.4 cm diameter. Neodymium, samarium, gadolinium and dysprosium compounds were reported [5], whereas the remaining nine compounds are new. All lanthanide oxides, except $CeO_2$, were dried by heating to 900 °C for 6 h, before use. In the synthesis and crystal growth of all compounds, the reactant mixtures were initially heated at 650 °C for 1 day. Only the details of further heating and subsequent cooling to room temperature are mentioned below.

Polycrystalline samples of $A_2Mo_4Sb_2O_{18}$ compounds were synthesized quantitatively, on a scale of about 0.5 g, by heating

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stoichiometric mixtures of appropriate reactants at 700 °C for 3 days and then cooling over 1 day. $MoO_2$, along with $MoO_3$, was employed in the synthesis of cerium, praseodymium and terbium compounds, when $CeO_2$, $Pr_6O_{11}$, $Tb_4O_7$ were the reactants, respectively.

Crystals of $A_2Mo_4Sb_2O_{18}$ ($A$=Ce, Pr, Gd, Tb, Ho, Er, Tm) compounds were obtained from $MoO_3$ flux, by heating at 900 °C for 2 days and then cooling over 3 days. 1:6:1 molar mixtures of $A_2O_3$, $MoO_3$ and $Sb_2O_3$ were used for $A_2Mo_4Sb_2O_{18}$ ($A$=Gd, Ho, Er, Tm) compounds. The crystals of praseodymium and terbium compounds were obtained from 1:2 molar mixtures of polycrystalline sample of $A_2Mo_4Sb_2O_{18}$ ($A$=Pr, Tb) and $MoO_3$, whereas a 1:3:1 molar mixture of $Ce_2(MoO_4)_3$, $MoO_3$ and $Sb_2O_3$ was employed for crystals of cerium compound. In the case of europium compound, a 1:8:1 molar mixture of $Eu_2O_3$, $MoO_3$ and $Sb_2O_3$ was heated at 950 °C for 2 days and cooled over 10 days. All title compounds were obtained as dark yellow block shaped single crystals, along with colourless $MoO_3$ crystals. The crystals of the title compounds were manually separated. It was possible to dissolve the crystals of $MoO_3$ in ~2% $Na_2CO_3$ solution. In the cases of praseodymium and erbium compounds, green crystals of $Pr_2Mo_4O_{15}$ and violet crystals of unidentified composition were obtained, respectively, along with those of the title compounds. Crystal growth attempts for ytterbium and lutetium compounds were not successful.

### 2.2. *X-ray diffraction and crystal structure*

The powder X-ray diffraction (XRD) patterns of the title compounds were recorded on a Bruker D8 Advanced powder X-ray diffractometer using Cu $K\alpha$ ($\lambda$=1.5406 Å) radiation. The monophasic nature of the compounds was verified by comparing their powder XRD patterns with those simulated, using the LAZY-PULVERIX programme [7], on the basis of their single crystal X-ray structures. Single crystals of $A_2Mo_4Sb_2O_{18}$ compounds, suitable for XRD, were selected and mounted on thin glass fibre with epoxy glue and optically aligned on a Bruker APEX II charge coupled device X-ray diffractometer using a digital camera. X-ray data collection, space group determination and structure refinement [8,9] and drawings [10,11] were carried out as reported previously [5]. Structures of eight $A_2Mo_4Sb_2O_{18}$ ($A$=Ce, Pr, Eu, Gd, Tb, Ho, Er, Tm) compounds were modelled, starting with the refined positional parameters of yttrium compound [5], and only yttrium was appropriately replaced. All atoms were refined anisotropically. The final Fourier difference maps did not show any chemically significant feature and the peaks with an electron density of $> 1$ e/Å$^3$ were found to be ghosts of the existing atoms.

### 2.3. *Spectroscopic characterization*

UV/vis absorption and fluorescence spectra were recorded at room temperature on a Cary 5E Varian UV/vis/NIR and Horiba-Jobin Yvon Fluromax-4P spectrophotometers, respectively. Lifetime measurements were carried out on Spectra-physics LAB-150 laser flash photolysis spectrometer.

## 3. Results and discussion

### 3.1. *Synthesis and structure*

Polycrystalline samples of nine new $A_2Mo_4Sb_2O_{18}$ ($A$=Ce, Pr, Eu, Tb, Ho, Er, Tm, Yb, Lu) compounds have been synthesized from stoichiometric mixtures of appropriate reactants by conventional solid-state method. Single crystal X-ray structures have been determined for seven new $A_2Mo_4Sb_2O_{18}$ ($A$=Ce, Pr, Eu, Tb, Ho, Er, Tm) compounds and known [5] $Gd_2Mo_4Sb_2O_{18}$. Pertinent

**Table 1**
Pertinent crystallographic data for $A_2Mo_4Sb_2O_{18}$ ($A$=Ce, Pr, Eu, Gd, Tb, Ho, Er, and Tm) compounds.

| $A$ | Ce | Pr | Eu | Gd | Tb | Ho | Er | Tm |
|---|---|---|---|---|---|---|---|---|
| Formula | $Ce_2MO_4Sb_2O_{18}$ | $Pr_2Mo_4Sb_2O_{18}$ | $Eu_2Mo_4Sb_2O_{18}$ | $Gd_2Mo_4Sb_2O_{18}$ | $Tb_2Mo_4Sb_2O_{18}$ | $Ho_2Mo_4Sb_2O_{18}$ | $Er_2Mo_4Sb_2O_{18}$ | $Tm_2Mo_4Sb_2O_{18}$ |
| Formula weight | 1195.50 | 1197.06 | 1219.18 | 1229.76 | 1233.10 | 1245.12 | 1249.78 | 1253.12 |
| Crystal system | Monoclinic | Monoclinic | Monoclinic | Monoclinic | Monoclinic | Monoclinic | Monoclinic | Monoclinic |
| Space group (no.) | $C2/c$ (15) | $C2/c$ (15) | $C2/c$ (15) | $C2/c$ (15) | $C2/c$ (15) | $C2/c$ (15) | $C2/c$ (15) | $C2/c$ (15) |
| $a$ (Å) | 13.1279(4) | 13.0849(4) | 12.984(3) | 12.9457(2) | 12.9398(4) | 12.8906(3) | 12.8501(3) | 12.837(3) |
| $b$ (Å) | 14.4996(4) | 14.4275(4) | 14.249(3) | 14.1971(3) | 14.1335(4) | 14.0629(3) | 14.0361(4) | 14.010(3) |
| $c$ (Å) | 10.9059(3) | 10.8695(6) | 10.770(2) | 10.7399(3) | 10.7178(5) | 10.6696(2) | 10.6372(2) | 10.626(4) |
| $\beta$ (°) | 123.515(10) | 123.544(10) | 123.64(3) | 123.696(10) | 123.755(10) | 123.751(10) | 123.783(10) | 123.847(7) |
| $V$ (Å$^3$) | 1730.79(9) | 1710.24(12) | 1658.9(8) | 1642.27(6) | 1629.69(10) | 1608.19(6) | 1594.63(7) | 1587.3(8) |
| $Z$ | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 |
| $\rho_{calcd}$ (g/cm$^3$) | 4.588 | 4.649 | 4.881 | 4.974 | 5.026 | 5.143 | 5.206 | 5.244 |
| $\mu$(Mo $K\alpha$) (mm$^{-1}$) | 11.099 | 11.607 | 13.653 | 14.230 | 14.880 | 16.124 | 16.863 | 17.546 |
| Crystal size (mm$^3$) | 0.35 × 0.25 × 0.22 | 0.38 × 0.25 × 0.20 | 0.25 × 0.22 × 0.17 | 0.22 × 0.20 × 0.18 | 0.19 × 0.15 × 0.11 | 0.26 × 0.21 × 0.18 | 0.20 × 0.18 × 0.15 | 0.22 × 0.20 × 0.20 |
| $\lambda$(Mo $K\alpha$) (Å) | 0.71073 | 0.71073 | 0.71073 | 0.71073 | 0.71073 | 0.71073 | 0.71073 | 0.71073 |
| Temperature (K) | 298 | 298 | 298 | 298 | 298 | 298 | 298 | 298 |
| $\theta$ range (°) | 2.24–28.29 | 2.82–28.27 | 2.45–28.29 | 2.28–28.33 | 2.29–28.32 | 2.39–24.98 | 2.30–28.34 | 2.31 to 28.27 |
| Total/independent reflections | 6066/2060 | 5559/1713 | 5998/1999 | 5879/1911 | 5703/1970 | 4737/1398 | 5621/1876 | 5213/1824 |
| Reflections with $I > 2\sigma$ ($I$) | 2028 | 1693 | 1948 | 1878 | 1925 | 1393 | 1804 | 1730 |
| Parameters refined | 120 | 120 | 120 | 120 | 120 | 120 | 120 | 120 |
| $R1^a/wR2^b$ | 0.0178/0.0402 | 0.0227/0.0622 | 0.0181/0.0394 | 0.0216/0.0504 | 0.0215/0.0571 | 0.0226/0.0525 | 0.0220/0.0530 | 0.0303/0.0781 |
| Goodness of fit | 1.204 | 1.305 | 1.232 | 1.213 | 1.073 | 1.346 | 1.178 | 1.174 |

[a] $R1=\Sigma||F_o|-|F_c||/\Sigma|F_o|$.
[b] $wR2=[\Sigma w(|F_o|^2-|F_c|^2)^2/\Sigma w(|F_o|^2)^2]^{1/2}$.

**Table 2**
Bond lengths (Å) for $A_2Mo_4Sb_2O_{18}$ ($A$=Ce, Pr, Eu, Gd, Tb, Ho, Er, Tm) compounds.

| $A$ | Ce | Pr | Eu | Gd | Tb | Ho | Er | Tm |
|---|---|---|---|---|---|---|---|---|
| Sb–O(4) | 2.328(3) | 2.322(3) | 2.299(3) | 2.294(3) | 2.283(4) | 2.268(5) | 2.275(5) | 2.281(5) |
| Sb–O(8) | 1.975(3) | 1.985(4) | 1.983(3) | 1.979(3) | 1.978(4) | 1.980(5) | 1.976(6) | 1.986(5) |
| Sb–O(9) | 2.066(3) | 2.065(3) | 2.068(3) | 2.067(3) | 2.070(4) | 2.072(5) | 2.068(5) | 2.070(5) |
| Sb–O(9)′ | 1.992(3) | 1.995(4) | 1.995(3) | 1.992(3) | 1.993(4) | 1.992(5) | 1.994(5) | 1.992(5) |
| Mo(1)–O(1) | 1.719(3) | 1.719(4) | 1.728(3) | 1.726(4) | 1.726(4) | 1.726(6) | 1.738(6) | 1.733(5) |
| Mo(1)–O(2) | 1.747(3) | 1.749(4) | 1.755(3) | 1.750(3) | 1.750(4) | 1.744(5) | 1.743(6) | 1.747(5) |
| Mo(1)–O(3) | 1.761(3) | 1.764(4) | 1.761(3) | 1.763(4) | 1.761(4) | 1.763(5) | 1.764(6) | 1.769(5) |
| Mo(1)–O(4) | 1.814(3) | 1.812(4) | 1.820(3) | 1.814(3) | 1.821(4) | 1.824(5) | 1.819(6) | 1.823(5) |
| Mo(2)–O(5) | 1.731(3) | 1.719(4) | 1.736(3) | 1.738(4) | 1.736(4) | 1.737(6) | 1.749(6) | 1.750(5) |
| Mo(2)–O(6) | 1.733(3) | 1.731(4) | 1.731(3) | 1.727(4) | 1.729(4) | 1.731(5) | 1.729(6) | 1.728(5) |
| Mo(2)–O(7) | 1.742(3) | 1.746(4) | 1.741(3) | 1.737(4) | 1.737(4) | 1.738(5) | 1.733(6) | 1.743(5) |
| Mo(2)–O(8) | 1.815(3) | 1.806(4) | 1.815(3) | 1.813(3) | 1.814(4) | 1.812(5) | 1.817(6) | 1.810(5) |
| A(1)–O(2) × 2 | 2.426(3) | 2.407(4) | 2.357(3) | 2.343(3) | 2.342(4) | 2.319(5) | 2.299(5) | 2.285(5) |
| A(1)–O(4) × 2 | 2.470(2) | 2.451(4) | 2.393(3) | 2.384(3) | 2.366(4) | 2.347(5) | 2.338(5) | 2.322(5) |
| A(1)–O(7) × 2 | 2.523(3) | 2.506(4) | 2.477(3) | 2.465(4) | 2.465(4) | 2.449(5) | 2.438(6) | 2.427(5) |
| A(1)–O(9) × 2 | 2.476(3) | 2.452(3) | 2.394(3) | 2.381(3) | 2.362(4) | 2.338(5) | 2.327(5) | 2.318(5) |
| A(2)–O(1) × 2 | 2.489(3) | 2.474(4) | 2.425(3) | 2.414(4) | 2.401(4) | 2.387(6) | 2.365(6) | 2.363(5) |
| A(2)–O(3) × 2 | 2.451(3) | 2.427(3) | 2.371(3) | 2.360(4) | 2.346(4) | 2.323(5) | 2.312(6) | 2.296(5) |
| A(2)–O(5) × 2 | 2.477(3) | 2.468(4) | 2.399(3) | 2.377(3) | 2.368(4) | 2.340(6) | 2.313(6) | 2.304(5) |
| A(2)–O(6) × 2 | 2.490(3) | 2.475(4) | 2.431(3) | 2.419(4) | 2.412(4) | 2.390(5) | 2.383(6) | 2.382(5) |

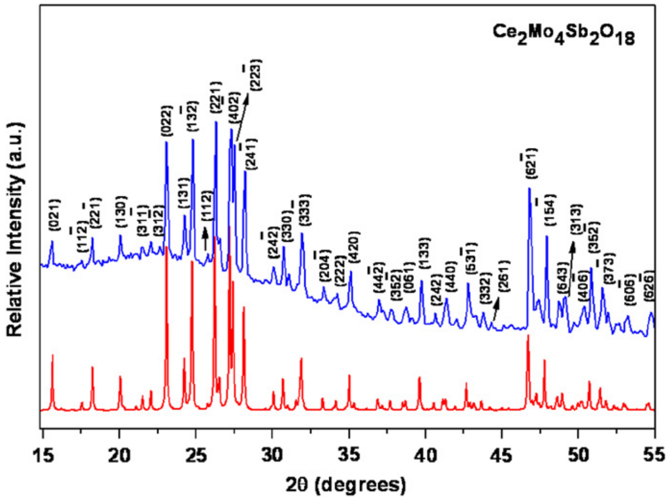

**Fig. 1.** Observed (blue) and simulated (red) powder XRD patterns of $Ce_2Mo_4Sb_2O_{18}$ compound (for interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

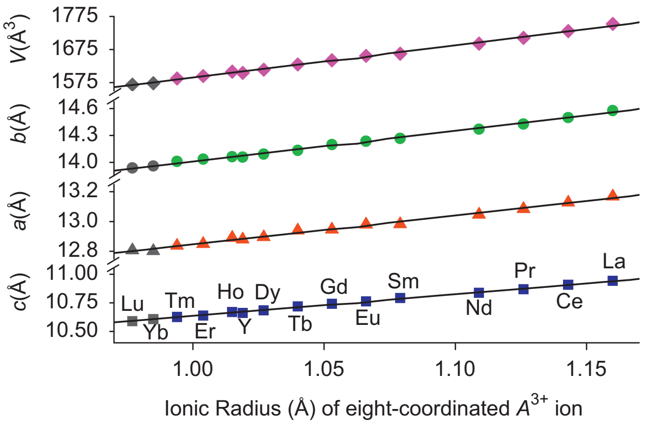

**Fig. 2.** Plots of unit cell parameters ($a$, $b$, $c$) and volumes ($V$) of $A_2Mo_4Sb_2O_{18}$ ($A$=Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu) compounds against the ionic radii of eight-coordinated $A^{3+}$ ions.

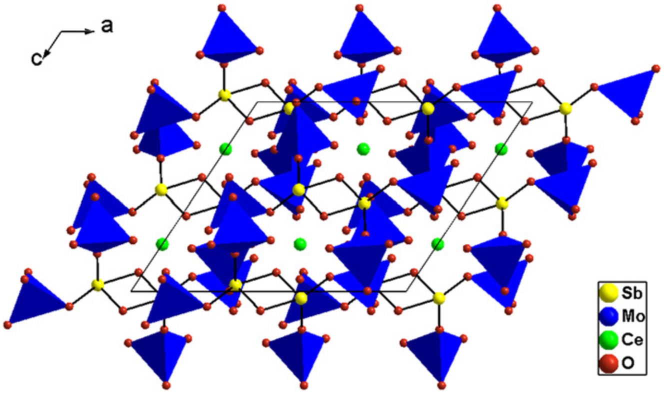

**Fig. 3.** Polyhedral representation of the unit cell of $Ce_2Mo_4Sb_2O_{18}$ viewed along $b$-axis. $MoO_4$ tetrahedra are shaded in blue (for interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

crystallographic data and bond lengths are presented in Tables 1 and 2, respectively. The CIF files for these eight compounds are deposited in the Fachinformationszentrum Kalsruhe, Germany (Fax: +49-7247-808-666; E-mail: crysdata@fiz-karlsruhe.de) and given the deposition numbers, CSD-422101 (Ce), CSD-422102 (Pr), CSD-422103 (Eu), CSD-422104 (Gd), CSD-422105 (Tb), CSD-422106 (Ho), CSD-422107 (Er) and CSD-422108 (Tm). As the crystal growth attempts for ytterbium and lutetium compounds were unsuccessful, their monoclinic unit cell parameters have been obtained from their powder XRD data, by using the programme CELREF [12]. The values of $a$ (Å), $b$ (Å), $c$ (Å), $\beta$ (°) and $V$ (Å$^3$) are 12.801(10), 13.960(5), 10.606(10), 123.88(5) and 1573(2) for ytterbium compound and 12.806(8), 13.936(5), 10.589(6), 123.87(3) and 1569(2) for lutetium compound, respectively. Thus the present and previous [5] reports together represent the synthesis of fifteen isostructural $A_2Mo_4Sb_2O_{18}$ ($A$=Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu) compounds, of which all, but ytterbium and lutetium compounds, are structurally characterized by single crystal X-ray diffraction study.

Powder XRD patterns of all nine new isostructural $A_2Mo_4Sb_2O_{18}$ compounds are similar and, as shown for cerium

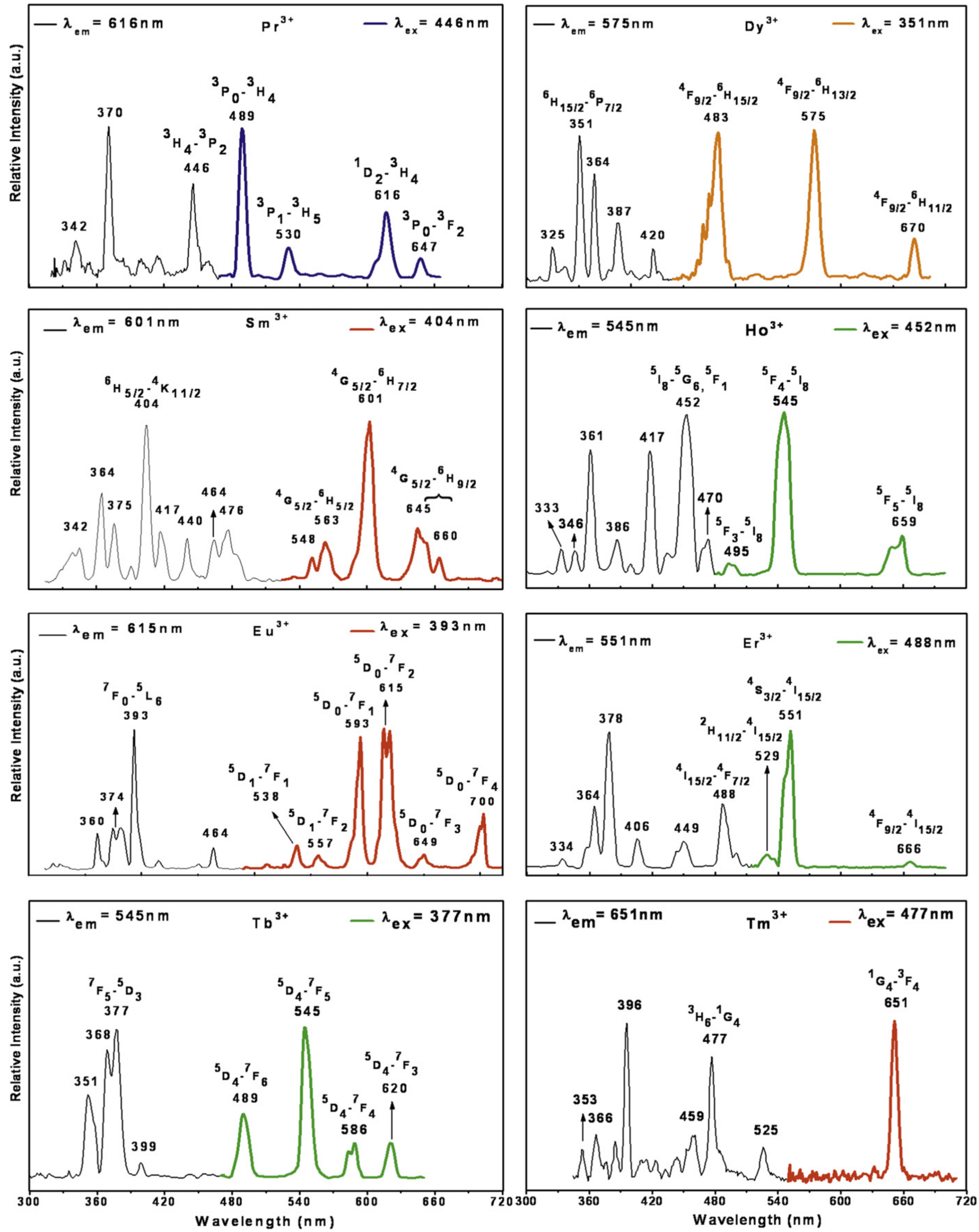

**Fig. 4.** Photoluminescence excitation (black) and emission (blue/red/orange/green) spectra of $A_2Mo_4Sb_2O_{18}$ ($A$=Pr, Sm, Eu, Tb, Dy, Ho, Er, Tm) compounds (for interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

compound (Fig. 1), agree with the simulated ones. As shown in Fig. 2, the values of unit cell parameters *a*, *b*, *c* and volume *V* of the fifteen isostructural $A_2Mo_4Sb_2O_{18}$ compounds vary linearly with the ionic radii of eight-coordinated $A^{3+}$ ions [13], in accordance with Vegard's law. These compounds have ''zero-dimensional'' structures [5] containing $A^{3+}$ cations and discrete, centrosymmetric tetramolybdodiantimonite anionic aggregates $(Mo_4Sb_2O_{18})^{6-}$ (Fig. 3). The $A^{3+}$ ions reside on *4e* Wyckoff sites with two-fold axis of symmetry and have dodecahedral coordination. The molybdenum, antimony and oxygen atoms occupy general *8f* Wyckoff positions. The coordinations of $Mo^{6+}$ and $Sb^{3+}$ ions are tetrahedral and disphenoidal, respectively. The values of bond lengths (Table 2) compare well with those reported in the literature [5]. The values of bond valence sums [14] are found to be in the ranges of 5.85–6.13, 3.08–3.15 and 3.22–3.39 for $Mo^{6+}$, $Sb^{3+}$ and $A^{3+}$ ions, respectively.

Apart from the previously reported [5] structural comparisons of these compounds, $BaMo_2TeO_9$ and other molybdoantimonites, an interesting structural similarity could be envisaged with $Bi_2Mo_2O_9$, which has asymmetric unit content of $Bi_4Mo_4O_{18}$ with four crystallographically distinct atoms of molybdenum and bismuth each [15]. It could be conceived to contain $(Mo_4Bi_2O_{18})^{6-}$ anionic aggregates, similarly built from disphenoidal $BiO_4$ and tetrahedral $MoO_4$ moieties. They are, in contrast, connected to one another through Bi–O bonds, which give rise to three-dimensional network of $(Mo_4Bi_2O_{18})^{6-}$ and those bismuth atoms thus become asymmetrically five-coordinated. The other two bismuth atoms have dodecahedral and disphenoidal coordination geometries. The coordinations of bismuth atoms are based on the cut-off value of 2.65 Å for Bi–O bond length.

$TlPrMo_2O_8$, $TlSmMo_2O_8$, $TlEuMo_2O_8$, $Tl_5A(MoO_4)_4$, $Bi_{2-x}A_xMoO_6$, $Bi_{2-x}Ce_xMo_3O_{12}$, $A_{2/3}[Bi_{12}O_{14}](MoO_4)_5$, $Nd_2MoTe_3O_{12}$, $La_2MoTe_3O_{12}$, $Pr_2MoTe_4O_{14}$, $Nd_2MoTe_4O_{14}$ and $[A(H_2O)_x]_2[TeMo_6O_{24}]\cdot yH_2O$ ($x=6/7$; $y=6/7/8/10$) compounds of *A*–Mo–*M*–O (*A*=rare earth metal; *M*=heavy main group element) system were reported [16–19] to have zero, layered and three-dimensional structures. Almost all of these compositionally diverse phases have, as found in title compounds, tetrahedrally coordinated molybdenum. The exceptions are those (*A*=Gd–Lu, Y) members of $Bi_{2-x}A_xMoO_6$ series with the so-called fluorite-related superstructure of $\alpha$-$R_2MoO_6$, wherein molybdenum is five-coordinated and $[A(H_2O)_x]_2[TeMo_6O_{24}]\cdot yH_2O$ that contain Anderson-type anion with octahedrally coordinated molybdenum. Characteristic rare earth metal photoluminescence was reported [18] for neat $Nd_2MoTe_3O_{12}$, $Pr_2MoTe_4O_{14}$ and $Nd_2MoTe_4O_{14}$ compounds only.

### 3.2. Photoluminescence

Eleven of these fifteen isostructural $A_2Mo_4Sb_2O_{18}$ compounds are potential candidates for a study of rare earth metal photoluminescence, the other four being lanthanum, gadolinium, lutetium and yttrium compounds. However, photoluminescence of only eight $A_2MO_4Sb_2O_{18}$ (*A*=Pr, Sm, Eu, Tb, Dy, Ho, Er, Tm) compounds has been investigated. Cerium compound and, as expected, neodymium and ytterbium compounds are found to exhibit no photoluminescence in the 200–800 nm range studied.

The absorption spectra of $A_2Mo_4Sb_2O_{18}$ (*A*=Sm, Tb, Dy, Tm) compounds are featureless, whereas those of $A_2Mo_4Sb_2O_{18}$ (*A*=Pr, Eu, Ho, Er) compounds consist of bands that are observed in the excitation spectra [20–23]. The room-temperature excitation and emission spectra, in the range 300–720 nm, of eight $A_2MO_4Sb_2O_{18}$ (*A*=Pr, Sm, Eu, Tb, Dy, Ho, Er, Tm) compounds are presented in Fig. 4. All the spectral features agree with those reported in the literature [23–27]. These compounds show characteristic excitation and emission peaks of trivalent lanthanide ion and the electronic transitions for all of the observed emission peaks, except the one at 548 nm of samarium compound, are assigned according to the literature values [23–27]. Each emission spectrum is given in a colour that closely corresponds to the wavelength of intense emission peak. The electronic transition for the excitation peak with the wavelength of $\lambda_{ex}$ is also assigned.

As representative examples, the photoluminescence of europium and dysprosium compounds is discussed here. The excitation spectra ($\lambda_{em}=615$ nm) of europium compound shows four peaks at 360, 374, 393 and 464 nm, due to *f*–*f* electronic transition of trivalent europium and the intense peak at 393 nm is attributed to $^7F_0$–$^5L_6$ transition. In the emission spectrum ($\lambda_{exc}=393$ nm) shown in red colour, there are six emission peaks at 538, 557, 593, 615, 649 and 700 nm, corresponding to $^5D_1\rightarrow{}^7F_1$, $^5D_1\rightarrow{}^7F_2$, $^5D_0\rightarrow{}^7F_1$, $^5D_0\rightarrow{}^7F_2$, $^5D_0\rightarrow{}^7F_3$ and $^5D_0\rightarrow{}^7F_4$ transitions of $Eu^{3+}$, respectively. As reported [28] for compounds in which europium does not reside on crystallographic inversion centre, electric dipole allowed $^5D_0\rightarrow{}^7F_2$ emission is more intense than magnetic dipole allowed $^5D_0\rightarrow{}^7F_1$ emission. The possible weak $^5D_0\rightarrow{}^7F_0$ emission at 580 nm is not observed.

The emission spectrum ($\lambda_{ex}=351$ nm) of dysprosium compound has three $^4F_{9/2}\rightarrow{}^6H_{j'}$ ($j'=15/2$, 13/2 and 11/2) transitions at 483, 575 and 670 nm, respectively, and the hypersensitive $^4F_{9/2}\rightarrow{}^6H_{13/2}$ transition is allowed [29] because dysprosium atom occupies a symmetry site with no inversion centre. In the lifetime measurement of this compound, the intensity of $^4F_{9/2}\rightarrow{}^6H_{13/2}$ emission ($\lambda_{ex}=355$ nm) is found to decrease exponentially with time (Fig. 5) and lifetime is calculated to be 0.69 μs [25].

The present study is one of a few reports [18,30–36] of rare earth metal photoluminescence in neat ternary and quaternary oxides of lanthanides. The observed distances of ~6.03 Å between the nearest lanthanide *A* atoms in the title compounds are apparently not short enough for quenching of neat lanthanide photoluminescence. Only a systematic photoluminescence study of doped inter-lanthanide $A_2Mo_4Sb_2O_{18}$ compounds could reveal whether or not partial quenching exists in neat compounds. The isostructural nature of these fifteen title compounds is expected to be conducive for the synthesis of a variety of solid solutions amongst them. Therefore, it should be possible to systematically vary the nature and concentration of rare earth metals, as dopants and co-dopants, to obtain inter-lanthanide $A_2Mo_4Sb_2O_{18}$ compounds and, thereby, to tune the energies and intensities of rare earth metal photoluminescence. A preliminary study in this direction is in progress in our laboratory.

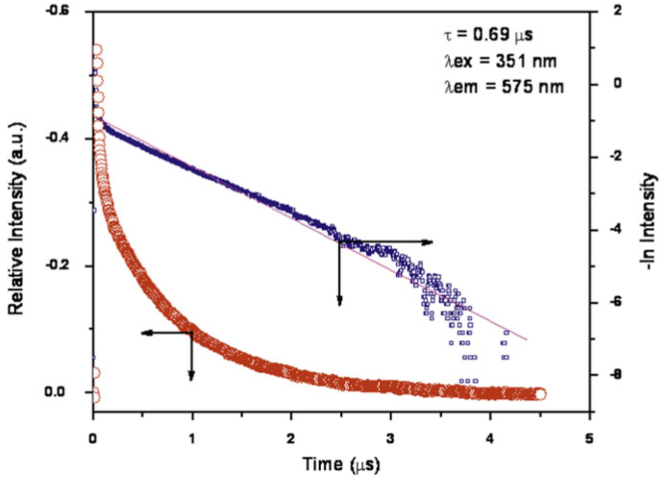

**Fig. 5.** Room-temperature photoluminescence decay curve of $Dy_2Mo_4Sb_2O_{18}$.

## 4. Conclusion

Synthesis of nine new isostructural $A_2Mo_4Sb_2O_{18}$ ($A$=Ce, Pr, Eu, Tb, Ho, Er, Tm, Yb, Lu) compounds has been accomplished. These compounds and the previously reported ones together represent the entire isostructural series of fifteen $A_2Mo_4Sb_2O_{18}$ compounds and their unit cell parameters obey Vegard's law. X-ray single crystal structures of $A_2Mo_4Sb_2O_{18}$ ($A$=Ce, Pr, Eu, Gd, Tb, Ho, Er, Tm) compounds have been determined. Rare earth metal photoluminescence is observed in neat $A_2Mo_4Sb_2O_{18}$ ($A$=Pr, Sm, Eu, Tb, Dy, Ho, Er, Tm) compounds.

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