The Oxides $M_3Sb_5O_{12}$ (M = Y, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu)

C. M. MARCANO* and I. RASINES**

Instituto de Química Inorgánica 'Elhúyar', Serrano 113, Madrid-6, Spain

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It is known [1] that Nd_2O_3 can react with Sb_2O_3 (Nd:Sb = 1:1, 73) at 873–973 K in vacuum, to produce a cubic oxide, a = 11.000 Å[†]. More recently it has been shown [2] that cubic crystals of $M_3Sb_5O_{12}$ (M = La, Pr, Tb, Yb), a from 11.027 to 10.721 ± 0.003 Å, S.G. $I\bar{4}3m$, can be obtained from mixtures of Sb_2O_3 and M_2O_3 by the hydrothermal method, at 720–820 K and (1.2–1.5) 10^8 Pa. In this communication we wish to report the existence of the new oxides $M_3Sb_5O_{12}$ (M = Y, Nd, Sm, Eu, Gd, Dy, Ho, Er, Tm, Lu), polycrystalline samples of which were prepared from the corresponding sesquioxides by solid-state reactions performed in vacuum at 963 K. These samples, along with those of the compounds of Nd, Tb and Yb, were studied by X-ray diffraction and spectroscopic techniques.

Experimental

$M_3Sb_5O_{12}$ (M = Y, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu) were prepared from mixtures of analytical grade M_2O_3 and Sb_2O_3 (M:Sb = 3:5) heated in vacuum ($\simeq 10^{-3}$ mm Hg) at 963 K for 7 days in quartz ampoules, and quenched in liquid N_2. Experimental details about the furnace and diffractometer employed can be found elsewhere [3]. The unit-cell parameters were refined from the 2θ values of the last seven reflections. Infrared spectra were recorded using a Perkin-Elmer 325 spectrophotometer and KBr disks.

Results and Discussion

TABLE I. Color and X-Ray Diffraction Data for the Oxides $M_3Sb_5O_{12}$ with Standard Deviations in Parentheses.

M	Color	a_o (Å)	V (A^3)	D_c (Mgm^{-3})
Y	white	10.7546(1)	1243.89(3)	5.69
Pr	green	11.0364(3)	1344.2(1)	6.03
Nd	pale purple	10.9917(3)	1327.9(1)	6.16
Sm	pale yellow	10.9202(5)	1302.2(2)	6.38
Eu	white	10.8860(6)	1290.0(2)	6.46
Gd	white	10.8557(4)	1279.3(1)	6.60
Tb	gy y brown	10.8222(5)	1267.5(2)	6.69
Dy	white	10.7872(4)	1255.2(1)	6.81
Ho	pale yellow	10.7558(3)	1244.3(1)	6.91
Er	pale pink	10.7291(4)	1235.0(1)	7.00
Tm	gray	10.7003(4)	1225.1(1)	7.08
Yb	gy y brown	10.6746(4)	1216.3(1)	7.16
Lu	gy y brown	10.6557(3)	1209.9(1)	7.27

TABLE II. IR Absorption Bands Frequencies (cm^{-1}) for the Oxides $M_3Sb_5O_{12}$.

Y[a]	690	600	560	460	380	325	305
Pr[b,c]	685	585	540	425	–	290	–
Nd[b]	685	585	540	425	365	305	275
Sm	685	590	545	450	370	310	275
Eu	685	590	545	450	370	315	280
Gd	685	595	550	450	375	320	290
Tb	690	600	550	455	375	320	295
Dy	690	600	555	455	380	325	295
Ho	690	600	565	455	380	325	295
Er	695	600	565	465	380	325	295
Tm	695	600	565	465	380	325	295
Yb	695	600	565	475	385	335	300
Lu	695	600	565	475	385	335	305

[a]One more absorption band at 270 cm^{-1}. [b]Further bands at 1005, 975, 955, 900, 885, 855 and 835 cm^{-1}. [c]Two additional absorption bands at 925 and 490 cm^{-1}.

$M_3Sb_5O_{12}$ oxides were obtained as polycrystalline powders colored as indicated in Table I. X-ray diffraction data and IR absorption band frequencies are included in Tables I and II respectively. The densities were calculated assuming Z = 4. Interplanar d-spacings and observed intensities can be found in Table III*.

The 82 observed reflections are allowed in the S.G. $I\bar{4}3m$ (No. 127). The a values obtained for the compounds of Nd, Tb and Dy are comparable to those previously reported [1, 2], especially in the first two cases. As Fig. 1 shows, the observed a values correlate well (r = 0.9998) to the Shannon effective ionic radii [4] for eight-coordination.

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*Permanent address: Departamento de Química, Universidad de Oriente, Cumaná, Venezuela.

**Author to whom correspondence should be addressed.

[†] *Cf.* JCPDS card No 26-111.

*Table III is available from the Editor-in-Chief in Padua.

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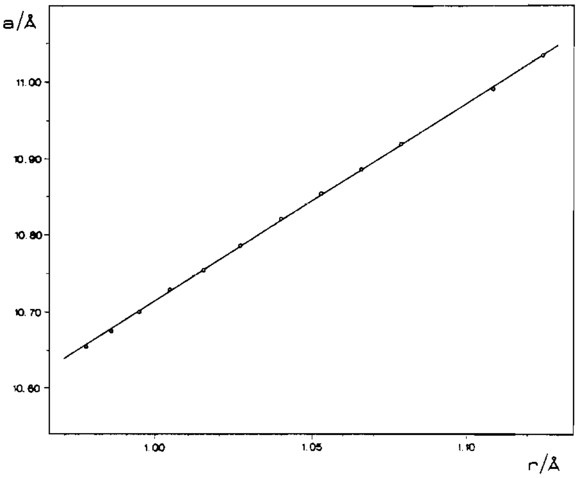

Fig. 1. Cell parameters (Å) *vs.* Shannon ionic radii (Å) for eight-coordination.

As for the IR absorption frequencies included in Table II, the first band in the spectrum occurs at 685 cm^{-1} for Pr and is a strong band which shifts to higher frequencies (up to 695 cm^{-1}, for the compound of Lu) as the formula weight increases. Thus, it is apparent that this strong band does not correlate with mass and has to be considered as an effect of lattice vibration. The six subsequent bands, which occur in the region 600–275 cm^{-1}, also behave in the same manner. Overall, the spectra of the oxides $M_3Sb_5O_{12}$ appear rather similar to those of the cubic M_2O_3 compounds [5].

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