TABLE II

Freq., cm.$^{-1}$	700	755	850	1090	1145	1155	1260	1320	1430	2050	2180	2250	2600	3000	3520
Intensity	s	s	s	s	s	s	vs	vs	m	w	vs	w	w	s	m

The compound was identified by means of its analysis. *Anal.* Calcd. for $(CH_3)_3SiN_3$: Si, 24.4; C, 31.3; H, 7.9; N, 36.5. Found: Si, 24.4; C, 32.0; H, 8.1; N, 37.5. Apparent molecular weight in the vapor phase: Calcd. for $(CH_3)_3SiN_3$: 115. Found: 115.

The melting point of trimethyl silyl azide was observed to be $-95 \pm 1°$ under autogenous pressure. It exhibits the vapor pressure values reported in Table I.

The calculated values in the above table were obtained from the equation: $\log p_{\text{mm}} = (-1915/T) + 8.102$. The value of the normal boiling point extrapolated from these data is 87°.

Trimethyl silyl azide exhibits the infrared absorptions reported in Table II.

The absorption at 1320 cm.$^{-1}$ is characteristic of the symmetrical azide stretching frequency.

Like West and Thayer we were impressed by the stability of this covalent azide. The methyl derivative requires temperatures as high as 500° to induce thermal decomposition. A sample of this substance heated at 200° for 8 hr. was recovered essentially unchanged.

The photolysis of this azide produces nitrogen and a trace of hydrogen, along with a non-volatile oil which we are attempting to characterize further. Pyrolysis or similar decomposition induced by a mercury arc results in a mixture of volatile products consisting of hydrogen, nitrogen, methane, ethane, ethylene, acetylene, hydrogen cyanide, hydrazoic acid, and ammonium azide along with a non-volatile polymer. The nature of these products would raise some question as to the correctness of West and Thayer's statement that the thermal decomposition of this azide is similar to that of organic azides.

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A New Family of Rare Earth Compounds[1]

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Received February 28, 1962

During a study of the phase equilibrium relationships in rare earth sesquioxide–alumina systems,[2] a new type of rare earth compound, having an oxide ratio of 2:1 and the general formula $A_4B_2O_9$, was discovered. The only previously known rare earth aluminates have oxide ratios of 1:12, 3:5, and 1:1.

Experimental

In all instances the starting materials used in making these compounds were coprecipitated hydroxides which were dried below 400°. The initial rare earth solutions were prepared from oxides or hydroxides which were at least 99.8% pure, with most of them being 99.9% pure. X-Ray diffraction examination of the coprecipitated hydroxides indicated that nearly all of them were noncrystalline.

The compounds were formed by heating the starting materials in air for several weeks at 1400°. The products which resulted were generally too finely divided for study with the petrographic microscope and the presence of the new compound was established by powder X-ray diffractometer techniques. In a number of instances, the compound was formed from the molten state with an iridium strip-furnace; these crystals were suitable for study with the petrographic microscope.

Results

This compound, with the general formula $A_4B_2O_9$, is another double oxide of the rare earths (A) and smaller trivalent cations (B). When aluminum is the B ion, the 2:1 compound can be formed with the intermediate and small rare earths from europium through ytterbium. When gallium is the B ion, the compound can be formed with the largest of the rare earths, those of lanthanum through erbium having been synthesized. The molar composition has not been established beyond doubt because it has not been possible to make enough pure material for a chemical analysis or single crystals suitable for a structural analysis. The 2:1 composition is most likely since, under equilibrium conditions, it yields a single phase, while two phases often are detected with neighboring compositions.

X-Ray powder data for $Y_4Al_2O_9$, a typical member of this series, are given in Table I. Its optical properties are: biaxial negative, $n_\alpha \sim 1.82_6$, $n_\beta = 1.83_0$, $n_\gamma \sim 1.83_2$ (precision in $n = 0.003$), $2V > 50°$. The 2:1 rare earth aluminates

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(1) Contribution No. 61–65, College of Mineral Industries, The Pennsylvania State University.

(2) I. Warshaw and R. Roy, *Am. Ceram. Soc. Bull.*, **38**, 169 (1959).

TABLE I

POWDER DIFFRACTION DATA FOR $Y_4Al_2O_9$

d (Å.)	I/I_0
7.46	10
5.28	3
4.71	22
3.71	7
3.33	33
3.01	100
2.91	94
2.62	17
2.56	10
2.53	10
2.46	9
2.29	7
2.27	7
2.07	22
2.06	12
1.843	18
1.828	20
1.816	19
1.793	7
1.732	10
1.722	13
1.716	13
1.711	8
1.575	9
1.561	12
1.551	7
1.484	4
1.436	4

melt congruently at high temperatures, with yttrium aluminate melting at 2030 ± 25°. Its average coefficient of linear thermal expansion is about 80×10^{-7}.

Discussion

This family of compounds is of interest because it forms an extensive series with several types of substitution, similar to that found in the rare earth garnets and perovskite-type compounds. In addition to the substitution of various trivalent ions for each other, calcium and silicon can be substituted for the rare earth ion and aluminum, respectively, to yield the compound $Y_2Ca_2Si_2O_9$. Germanium can replace silicon to form $Y_2Ca_2Ge_2O_9$. Neither trivalent iron nor chromium could be substituted for aluminum in an amount readily detectable by X-ray diffraction techniques.

The optical properties of $Y_4Al_2O_9$, together with the fact that it is possible to index nearly all the X-ray diffraction peaks on the basis of a primitive cubic lattice, lead one to believe that its symmetry probably is orthorhombic with strong pseudo-cubicity.

The probable coördination of the cations in this structure can be obtained indirectly. Since aluminum can be completely replaced by silicon and not at all by chromium, which has never been found in fourfold coördination, the aluminum ions must be in fourfold coördination. The substitution of calcium for the rare earths in this new family of compounds suggests that these ions may be in either eight- or twelvefold coördination. The latter is not likely because only the largest rare earths can be accommodated in the twelvefold positions in the 1:1 perovskite-type compounds without appreciable distortion. Moreover, practically the same group of rare earth ions forms the rare earth aluminum garnets, in which these ions are surrounded by eight oxygens. Thus it is probable that the rare earth ions are in eightfold coördination in the 2:1 compounds.

As was mentioned previously, the 2:1 aluminate compounds can be formed with the smaller rare earths while the galliate compounds are formed with the larger rare earths. Thus, it is apparent that the formation and stability of this new family of compounds are dependent not only on the radius ratio of the cation to oxygen but also on the radius ratio of A to B. The importance of the A/B ratio in the formation of the other rare earth garnets and perovskites has been discussed by Bertaut and Forrat.[3]

Acknowledgments.—This work formed part of the research under Contract No. DA-36-039-SC-85311, U. S. Army Signal Corps.

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[3] F. Bertaut and F. Forrat, *Compt. rend.*, **243**, 1219 (1956).