run to the next. The remainder of the product consisted of the isomers of III (2–5%) and several unidentified azides. Using an estimated average density for the crude product of 1.6 g/ml and an average molecular weight of 280, the approximate yield of high-boiling products ranged between 30 and 40%. Physical properties other than those presented in Table I are summarized below, the compounds being presented in order of increasing chromatogaphic retention time.

sym-Difluorotetrakis(difluoramino)azomethane, $(NF_2)_2CFN=NCF(NF_2)_2$.—Compound I was a faintly yellow liquid which melted between −75 and −78° and had a boiling point of 81°.[4] Its infrared spectrum exhibited principal absorptions located at 1366 (s), 1148 (m), 1016 (m), 980 (s), 952 (s), and 908 (s) cm^{-1}. The mass spectrum of $(NF_2)_2CFN=NCF(NF_2)_2$ gave the following peaks in order of decreasing relative intensity: 64 (CF_2N^+), 31 (CF^+), 52 (NF_3^+), 83 (CF_2N^+), 45 (CFN^+), 135 ($CF_5N_2^+$), 33 (NF^+), 69 (CF_3^+), 144 ($CF_4N_4^+$), 50 (CF_2^+), 12 (C^+), 97 ($CF_3N_2^+$), 26 (CN^+), 54 (CN_3^+), 76 ($C_2N_3^+$), 125 ($CF_5N_3^+$), 194 ($C_2F_6N_4^+$), and 76 ($C_2N_3^+$). Mol wt of $C_2F_{10}N_6$: calcd, 298; found, 306.

Photolysis of I using a 550-W high-pressure mercury lamp and a blue filter to remove radiation of wavelengths shorter than 330 mμ produced $NF_2CF=NF$, which was identified by its infrared spectrum.[5] Numerous degradation products such as CF_4, NF_3, and $CF_2=NF$ were also formed and the Pyrex reaction bulb was severely etched.

[Bis(difluoramino)fluoromethylazo]trifluoroformamidine, $(NF_2)_2CFN=NC(=NF)NF_2$.—The isomer with the shorter retention time, IIa, was an orange liquid, bp 82°.[4] Its infrared spectrum exhibited bands centered at 1631 (w), 1272 (s), 1214 (m), 1124 (m), 1015 (m), 969 (s), 947 (s), 923 (s), 899 (s), 880 (s), 766 (m) cm^{-1}. The principal ions of its mass cracking pattern presented in order of decreasing relative intensity were: 31 (CF^+), 64 (CF_2N^+), 97 ($CF_3N_2^+$), 52 (NF_2^+), 83 (CF_3N^+), 28 (N_2^+), 135 ($CF_5N_2^+$), 33 (NF^+), 12 (C^+), and 45 (CFN^+). Mol wt of $C_2F_8N_6$: calcd, 260; found, 261.

The second isomer, IIb, was a yellow-orange liquid, bp 83°.[4] Its infrared spectrum, which was similar to that of its isomer, exhibited peaks at 1592 (w), 1272 (s), 1224 (m), 1124 (m), 1016 (s), 974 (s), 948 (s), 898 (s), and 766 (w) cm^{-1}. The mass spectrum showed the following peaks in order of decreasing relative intensity: 31 (CF^+), 64 (CF_2N^+), 52 (NF_2^+), 97 ($CF_3N_2^+$), 28 (N_2^+), 83 (CF_3N^+), 33 (NF^+), 135 ($CF_5N_2^+$), 12 (C^+), and 45 (CFN^+). Mol wt of $C_2F_8N_6$: calcd, 260; found, 258.

Hexafluoroazodiformamidine, $NF_2C(=NF)N=NC(=NF)NF_2$. —Compound IIIa was a deep red liquid which was very shock sensitive. The breaking of the liquid surface with an inverted capillary tube in preparation for its boiling point determination caused the sample to explode. Its infrared spectrum, which was almost identical with that of its isomer, IIIb, showed absorptions centered at 1618 (w), 1274 (w), 1220 (w), 1017 (m), 978 (m), 926 (s), 883 (s), and 752 (w), cm^{-1}. The values for IIIb were 1634 (w), 1284 (w), 1229 (w), 1013 (m), 980 (s), 926 (s), and 885 (s) cm^{-1}. The third isomer, IIIc, which was isolated only in trace amounts, had a very simple infrared spectrum with bands being located at 1587 (w), 1239 (w), 977 (s), and 889 (s) cm^{-1}. Mol wt of $C_2F_6N_6$ (IIIa): calcd, 222; found, 218.

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Synthesis of New High-Pressure Pyrochlore Phases

BY R. D. SHANNON AND A. W. SLEIGHT

Compounds with the pyrochlore structure and the formula $A^{III}_2B^{IV}_2O_7$ (where A = rare earth ions and B = Ti, Ru, Ir, Tc, Sn, Hf, Zr, and Pb) have previously been reported by several investigators.[1–12] Hoekstra and Siegel have recently reported the synthesis of $Tl_2Pt_2O_7$.[9] In this paper we describe the synthesis of a new series of pyrochlore compounds with the formula $A_2Ge_2O_7$. These compounds, produced at elevated temperatures and pressures, further illustrate the extension of the stability field of a structure by the use of high pressure.

Experimental Section

The starting materials were high-purity oxides. GeO_2 (Spex Industries) of 99.999% purity was thoroughly mixed with In_2O_3, Tl_2O_3 (Spex Industries, 99.999%), and the rare earth oxides (Lindsay Chemical Division, American Potash and Chemical Corp.) of at least 99.9% purity. These samples were heated at 1100° for 4 hr at a pressure of 65 kbars and rapidly quenched. $In_2Ge_2O_7$ and $Tl_2Ge_2O_7$ were prepared at 1250 and 900°, respectively. The details of the technique have been published previously.[13,14] The products were recovered as highly dense, sintered pellets with a grain size of ∼0.05 mm. An attempt to prepare $Sm_2Ge_2O_7$ resulted in an unidentified product; no trace of a pyrochlore phase could be found in the X-ray pattern.

An X-ray diffraction pattern of $In_2Ge_2O_7$ was taken using a Guinier–de Wolff camera with a KCl internal standard. The films were read on a Mann film reader and d values were calculated using λ(Cu Kα$_1$) = 1.54051 Å and a(KCl) = 6.2931 Å. A cell dimension of 9.711 ± 1 Å for $In_2Ge_2O_7$ was determined by a least-squares refinement of 10 reflections. X-Ray patterns of other germanates were taken using a Debye–Scherrer camera of 114.6-mm diameter and Cu Kα radiation. Cell dimensions of these compounds were obtained by a least-squares refinement using a Nelson–Riley function. Table I presents the powder diffraction data for the new germanates. Observed intensities are given only for $In_2Ge_2O_7$; intensities for the remaining pyrochlores are similar. Although merely indexing powder patterns does not represent proof of structure type, it should be noted

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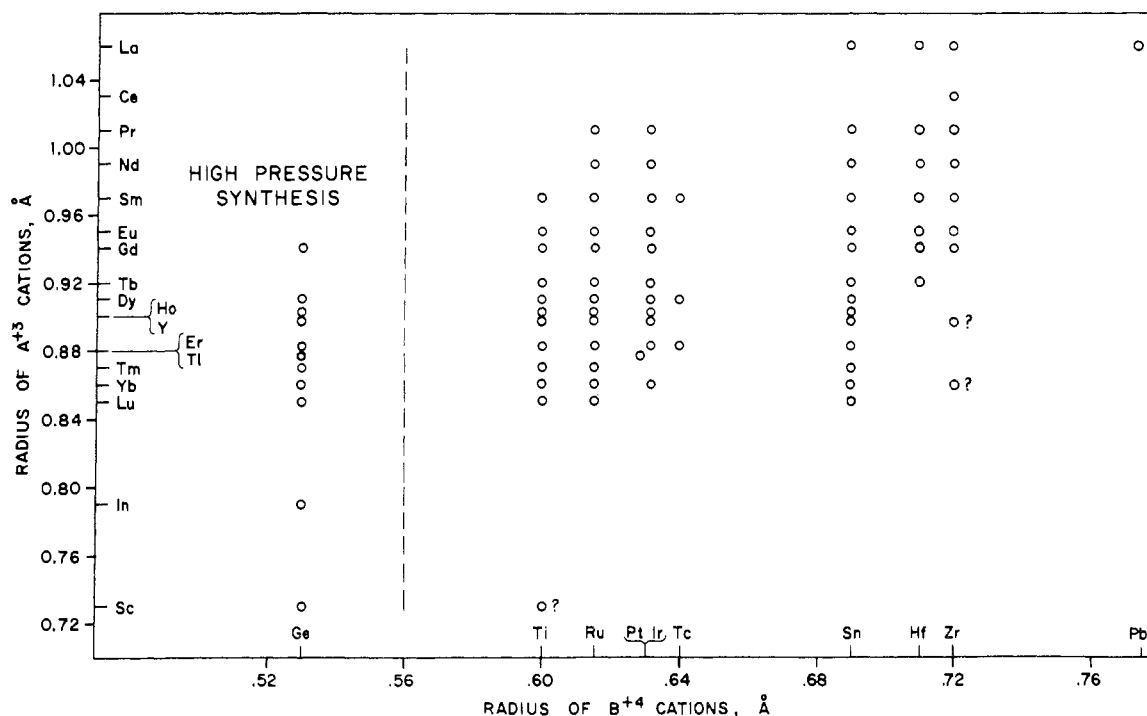(14) T. A. Bither, J. L. Gillson, and H. S. Young, *ibid.*, **5**, 1559 (1966).

Figure 1.—Stability field for $A^{III}_2B^{IV}_2O_7$ pyrochlores.

TABLE I

H K L	In₂Ge₂O₇ d	In₂Ge₂O₇ I	Sc₂Ge₂O₇ d	Y₂Ge₂O₇ d	Lu₂Ge₂O₇ d	Yb₂Ge₂O₇ d	Tm₂Ge₂O₇ d	Er₂Ge₂O₇ d	Tl₂Ge₂O₇ d	Ho₂Ge₂O₇ d	Dy₂Ge₂O₇ d	Gd₂Ge₂O₇ d
1 1 1	5.604	10	5.540	5.695	5.665	5.623	5.684	5.677	5.753	5.717	5.733	5.753
3 1 1	2.927	10	2.890	2.958	2.956	2.950	2.967	2.966	2.979	2.981	2.991	3.004
2 2 2	2.803	100	2.767	2.856	2.831	2.826	2.842	2.844	2.852	2.857	2.865	2.875
4 0 0	2.427	70	2.396	2.472	2.453	2.449	2.461	2.462	2.470	2.475	2.480	2.492
3 3 1			2.199	2.269	2.249	2.247	2.258	2.258	2.266	2.270	2.278	2.289
4 2 2	1.982	5	1.957	2.017	2.000		2.007	2.007	2.200	2.022		2.039
5 1 1 / 3 3 3	1.869	15	1.845		1.887	1.887	1.894	1.896	1.901	1.904	1.909	1.924
4 4 0	1.717	85	1.695	1.749	1.733	1.734	1.740	1.742	1.746	1.750	1.754	1.763
5 3 1	1.642	10	1.620	1.675	1.657	1.658	1.663	1.666	1.669	1.674	1.675	
5 3 3									1.505			
6 2 2	1.464	80	1.446	1.491	1.478	1.479	1.484	1.487	1.487	1.492	1.496	1.504
4 4 4	1.402	25	1.384	1.428	1.415	1.417	1.421	1.423	1.424	1.428	1.432	1.441
7 1 1			1.343		1.374	1.375	1.377	1.381	1.382	1.385	1.389	1.393
7 3 1			1.249	1.288	1.276	1.278	1.282	1.284	1.285	1.289	1.292	1.300
8 0 0			1.199	1.237	1.226	1.228	1.230	1.232	1.234	1.237	1.240	1.249
7 3 3				1.209	1.198	1.200	1.202	1.204	1.206	1.210	1.212	1.220
6 6 0				1.166				1.161		1.166		
7 5 1					1.132		1.136	1.138	1.140			
6 6 2			1.100	1.134	1.125		1.129	1.131	1.132	1.136	1.138	1.145
8 4 0			1.072	1.106	1.096	1.099	1.103	1.103	1.103	1.107	1.109	1.116

TABLE II

CELL DIMENSIONS (± 2 Å) OF GERMANATE PYROCHLORES

Compound	a, Å	Compound	a, Å
Gd₂Ge₂O₇	9.995	Yb₂Ge₂O₇	9.829
Dy₂Ge₂O₇	9.929	Lu₂Ge₂O₇	9.813
Ho₂Ge₂O₇	9.903	Y₂Ge₂O₇	9.897
Tl₂Ge₂O₇	9.872	In₂Ge₂O₇	9.711
Er₂Ge₂O₇	9.864	Sc₂Ge₂O₇	9.600
Tm₂Ge₂O₇	9.845		

that all of the compounds reported here did show lines where $h + k + l = 2n + 1$. Consequently, these compounds are not disordered fluorite types which is apparently the case for $Sc_2Ti_2O_7$[11] and $La_2Ce_2O_7$.[15] Table II gives the refined cell dimensions.

A two-probe resistivity measurement on a sintered piece of $In_2Ge_2O_7$ indicated a room-temperature resistivity greater than 3×10^{10} ohm-cm. Exposure to strong incandescent light reduced the resistivity by a factor of about 100.

Dta experiments performed on the new pyrochlore phases in air showed the transformations to occur irreversibly and endothermically above 1000° for all phases except $Tl_2Ge_2O_7$, $Lu_2Ge_2O_7$, and $Sc_2Ge_2O_7$. $Tl_2Ge_2O_7$ underwent an endothermic change at 525° whereas $Lu_2Ge_2O_7$ and $Sc_2Ge_2O_7$ were not found to transform at temperatures as high as 1200°.

Discussion

The enlargement of structure fields by means of pressure has been demonstrated for rutile-,[16] corundum-,[17] and perovskite-structure[13] types. Synthesis of the pyrochlore germanates provides another example of the extension of the stability field of a structure by the use of pressure. In Figure 1 the stability field of 3–4 pyrochlores is illustrated by plotting the radius of A^{3+} *vs.* the radius of the B^{4+} ions for all reported pyro-

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chlores.[1-12] Sixfold radii of A ions[18] were used because
no set of eightfold radii was available. Previously the
smallest A and B ions to be found in the pyrochlore
structure were Lu^{3+} and Ti^{4+}, respectively. In these
new pyrochlores two new A ions, In^{3+} and Sc^{3+}, and
one new B ion, Ge^{4+}, have been introduced. Although
$Sc_2Ti_2O_7$ was reported to be a pyrochlore, Brisse[11] has
shown that it is actually a disordered fluorite. The
new phases $Sc_2Ge_2O_7$ and $In_2Ge_2O_7$ both have smaller
cell dimensions than the value 9.801 quoted by Hoek-
stra and Siegel[9] as a "virtual lower limit" for the pyro-
chlore structure. Brisse and Knop[19] found that the
stability of the pyrochlore structure depends upon the
ratio of the ionic radii, r_A/r_B, and that the upper limit
of this ratio at normal conditions is 1.55. This study
indicates that pressure extends this ratio to approxi-
mately 1.8 (r_{Gd}/r_{Ge}).

The germanates are believed to be formed by taking
advantage of the difference in compressibility between
the oxygen anions and the A and B cations. Pressure
has been used to force a smaller ion into a structure by
using compressibility differences in SiO_2 (rutile),[20]
Lu_2O_3 (B rare earth oxide),[21] $MgGeO_3$ (ilmenite),[22]
and $InCrO_3$ (perovskite).[13] It might also be noted that
$In_2Ge_2O_7$, $InCrO_3$,[13] and $InRhO_3$[13] are the first examples
of compounds containing In^{3+} in greater than sixfold
coordination.

It seems logical to assume that by the application of
sufficient pressure one could make pyrochlores of the
type $A_2Si_2O_7$. However, reaction of Sc_2O_3 and SiO_2 at
1500° and 65 kbars resulted only in the well-known
$Sc_2Si_2O_7$ thortveitite phase. Apparently, higher pres-
sures are necessary to force Si^{4+} from fourfold to sixfold
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Metal Complexes of Pyrazole

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Although the behavior of imidazole as a ligand is
well documented in the literature, few references are
found regarding metal complexes of pyrazole, the isomer

of imidazole. Pflaum[1] has described the preparation
and properties of a cobalt(II) complex of 3,5-dimethyl-
pyrazole. Crow[2] has investigated the pyrazole com-
plexes of cadmium(II) by polarographic techniques.
The crystal structure of the complex formed between
nickel chloride and pyrazole has recently been reported.[3]

The coordination chemistry of pyrazole should be of
interest for comparison with the coordination chemistry
of imidazole. Since pyrazole is a relatively weak base
and is isoelectronic with cyclopentadiene, the possi-
bility exists of forming π-bonded complexes analogous
to ferrocene. This paper reports the preparation and
properties of some transition metal complexes of
pyrazole.

Experimental Section

Materials.—Pyrazole was purchased from the Aldrich Chemical
Co. and was recrystallized from cyclohexane prior to use. The
recrystallized material melted at 69.5–70.0°. The metal chlorides
and nitrates used were Baker Analyzed chemicals. Metal
tetrafluoroborates, prepared by the reaction of tetrafluoroboric
acid with the appropriate metal carbonate, were recrystallized
from water prior to use. Nickel perchlorate was obtained from
the G. F. Smith Chemical Co. Anhydrous methanol was pre-
pared by refluxing methanol over magnesium turnings followed
by distillation. The acetonitrile used for solution spectra was
Baker Analyzed material which contained 0.12% water.

Preparation of Metal Complexes.—The usual method con-
sisted of mixing 2 ml of a 1 M solution of the metal salt with 3 or
4 ml of a 4 M pyrazole solution. Intense color changes accom-
panied mixing. The reaction mixtures were allowed to stand in
stoppered flasks until crystallization of the complex occurred.
The time required for the complex to crystallize from the solution
depended on the metal salt and solvent used. Ethanol or
methanol was used when crystallization from water occurred
slowly. The complexes were recrystallized from the preparation
solvent, collected by filtration, and washed with a small amount
of ice-cold ether.

Analyses.—Copper was determined spectrophotometrically in
a 2 M ammonia–ammonium chloride buffer. It was necessary
to decompose the copper complexes by boiling with concentrated
nitric acid prior to analysis. Nickel was determined either by
the dimethylglyoxime method or volumetrically by the cyanide
method.[4] Cobalt was determined by the cyanide method. Iron
was determined by reduction to iron(II) with zinc amalgam fol-
lowed by reaction with excess cerium(IV). The excess cerium(IV)
was back-titrated with ferrous sulfate to the ferroin end point.
Chloride was determined gravimetrically. Carbon, hydrogen,
and nitrogen microanalyses were performed by Galbraith Labora-
tory, Knoxville, Tenn.

Spectra.—Solution spectra in the 380–1200-mμ region were
recorded using a Cary Model 14 spectrophotometer. Reflectance
spectra were obtained using a Perkin-Elmer–Hitachi spectro-
photometer, Model 139, equipped with a diffuse reflectance
attachment.

X-Ray Powder Patterns.—Powder patterns were obtained using
a General Electric Model-BR Type 1 instrument employing
nickel-filtered copper Kα radiation.

Results

The data in Table I clearly indicate that pyrazole
(Pz) forms well-defined complexes with a number of
transition metal ions. The complexes contained four

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