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High-Pressure Synthesis of $YScO_3$, $HoScO_3$, $ErScO_3$, and $TmScO_3$, and a Reevaluation of the Lattice Constants of the Rare Earth Scandates

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The rare earth scandates $AScO_3$ where A = Y, La, Nd, Sm, Gd, Dy, Ho, Er, and Tm have been prepared and their unit-cell constants determined. The single-phase compounds $YScO_3$, $HoScO_3$, $ErScO_3$, and $TmScO_3$ have been prepared for the first time using high pressures.

Introduction

A large amount of work has been done on the synthesis and crystallographic properties of rare earth scandates, vanadites, galliates, orthochromites, aluminates, and especially orthoferrites (*1*). Most of the perovskite-like compounds in this series are isostructural with $GdFeO_3$ (*2*), which consists of four $GdFeO_3$ distorted perovskite units in an orthorhombic unit cell with space group D_{2h}^{16}–*Pbnm*. The structure consists of corner-shared octahedra where the cooperative buckling of these octahedra leads to the orthorhombic distortion. The interest shown in these compounds has been due to their interesting physical properties, in particular magnetic properties.

Earlier reports on compounds in the systems Ln_2O_3–Sc_2O_3 (Ln = Y, La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu) are those of Keith and Roy (*3*), who produced partial formation of $LaScO_3$ and $NdScO_3$; Geller (*4*), who presented crystallographic data on $LaScO_3$, $PrScO_3$, $NdScO_3$, $GdScO_3$ and $YScO_3$; Schneider *et al.* (*5*) who presented synthesis and crystallographic information on the pure perovskites $SmScO_3$, $EuScO_3$, $GdScO_3$, and $DyScO_3$ and information on the partial formation of the perovskites $HoScO_3$ and $YScO_3$ at reaction temperatures as high as 1900°C. They also reported that no perovskite formation took place for Ln = Er, Yb, Lu. Instead, cubic solid solutions were formed. More recently Badie and co-workers (*6–8*) have reported high-temperature studies on $LaScO_3$, $NdScO_3$ and the compounds Dy_3ScO_6, Ho_3ScO_6, and Y_3ScO_6. Comprehensive powder data have recently been presented for $EuScO_3$ (*9*).

The method most used for predicting the possible stability of perovskites has been the Goldschmidt (*10*) tolerance factor

$$t = \frac{r_A + r_X}{2^{1/2}(r_B + r_X)}$$

where r_A, r_B, and r_X are the empirical ionic radii of the respective ions in the compound ABX_3. The perovskite structure occurs within the range $0.75 < t < 1.00$. For $t = 1$ the ideal cubic perovskite structure occurs, and as t decreases the unit cell shows a fourfold increase in volume as it enlarges to accommodate the distortion caused by the buckling

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TABLE I

Compound	Goldschmidt tolerance factor	Ionic radius[a] RE^{3+}_{IX}
$LaScO_3$	0.863	1.216
$PrScO_3$	0.850	1.179
$NdScO_3$	0.845	1.163
$SmScO_3$	0.835	1.132
$EuScO_3$	0.831	1.120
$GdScO_3$	0.827	1.107
$TbScO_3$	0.823	1.095
$DyScO_3$	0.819	1.083
$YScO_3$	0.816	1.075
$HoScO_3$	0.815	1.072
$ErScO_3$	0.812	1.062
$TmScO_3$	0.808	1.052
$YbScO_3$	0.805	1.042
$LuScO_3$	0.802	1.032

[a] Radii were taken from Shannon (*11*). Ideally the A atoms in the $ASCO_3$ compounds are 12-fold coordinated. No data are available for RE^{3+}_{XII} so we have used the *largest* observed values for the A cations, i.e., 9-fold coordinated. Values of Sc^{3+}_{VI} = 0.745 Å and O^{2-} = 1.40 Å are used (*11*).

of the corner-shared octahedra. Table I shows the calculated tolerance factors for the present series of compounds. According to the above criterion all these compounds should yield perovskites, but from Schneider *et al.* (*5*) it is apparent that certain compounds prefer *C*-type solid solutions where the preference for both *A* and *B* atoms to be in octahedral sites becomes predominant. The *C*-type M_2O_3 structure consists of two types of corner-shared six-coordinated sites.

Pressure is known to favor higher-coordinated sites, and for this reason it was expected that high-pressure synthesis conditions could force compounds with lower tolerance factors to adopt the perovskite structure. In particular, equimolar mixtures of the constituent oxides having the expected general formulas $YScO_3$, $DyScO_3$, $HoScO_3$, $ErScO_3$, $TmScO_3$, $YbScO_3$, and $LuScO_3$ were studied at high pressures.

Experimental

All oxides used in the present study were obtained from Koch–Light and had stated purities of 99.9% with the exception of Sc_2O_3, which had a stated purity of 99.6%. Equimolar mixtures of Sc_2O_3 and the rare earth oxide concerned were thoroughly ground and pellets were pressed at ~5 kbar in a pill press. The pellets were placed in a furnace and heated in air at 1600°C in a Pt 10% Rh crucible for 12 hr.

The compounds that did not yield pure perovskites after this treatment at atmospheric pressure were then treated at high pressures as follows. Samples were sealed in platinum tubes which were then subjected to quasi-hydrostatic pressures in a piston–cylinder device (*12*). The tubes were fitted into holes drilled in boron nitride cylinders, which were then placed in a conventional talc or pyrophyllite oven assembly. Pressures quoted were only approximately corrected for the various effects present in such systems (*13*) and are thought to be correct to within ±2 kbar. Temperatures were determined from previously determined calibration curves of wattage versus temperature and are correct to within ±20°C. In all cases pressure was applied to within ~2 kbar of the quoted values before temperature was raised. Once the desired reaction temperature was reached, pressure was raised to the final value. The reaction conditions were maintained for 1 hr and then temperature was dropped by switching off the heating current and finally pressure was released when the temperature was ~30°C.

X-Ray powder diffraction patterns were recorded on a Huber Guinier camera using monochromatized Cu$K\alpha_1$ radiation (λ = 1.54051 Å). Si was used as an internal calibrant and both film and counter techniques were employed. The angular zone for $2\theta < 90°$ was recorded using the asymmetric transmission mode while the zone $2\theta \geq 90°$ was recorded using the asymmetric back reflection mode.

TABLE II

Composition of final product	Product after heating equimolar mixtures in air at 1600°C for 60 hr	Product after 1 hr at 20 kbar 1000°C	Product after 1 hr at 30 kbar 1000°C
$LaScO_3$	Perovskite	—	—
$NdScO_3$	Perovskite	—	—
$SmScO_3$	Perovskite	—	—
$GdScO_3$	Perovskite	—	—
$YScO_3$	*C*-type solid solution plus trace of perovskite	Perovskite	—
$DyScO_3$	*C*-type solid solution plus perovskite	Perovskite	—
$HoScO_3$	*C*-type solid solution plus perovskite	Perovskite	—
$ErScO_3$	*C*-type solid solution	Perovskite	—
$TmScO_3$	*C*-type solid solution	Perovskite	—
$YbScO_3$	*C*-type solid solution	*C*-type solid solution	*C*-type solid solution
$LuScO_3$	*C*-type solid solution	*C*-type solid solution	*C*-type solid solution

Results

The results obtained are shown in Table II. The results after firing in air at atmospheric pressure are in good agreement with Schneider *et al.* (*5*). Of the remaining equimolar mixtures that did not yield single-phase perovskites, viz, $YScO_3$, $DyScO_3$, $HoScO_3$, $ErScO_3$, $TmScO_3$, $YbScO_3$, and $LuScO_3$, treatment at 20 kbar 1000°C for 1 hr was sufficient to yield pure perovskites for $YScO_3$, $DyScO_3$, $HoScO_3$, $ErScO_3$, and $TmScO_3$. The resulting solid solutions of the Yb and Lu compounds were further treated at 30 kbar, 1000°C for 1 hr, but they remained cubic solid solutions with slight evidence of a possible further phase in both cases. The new phase, although very difficult to detect, did not appear to be the expected perovskite.

Table III lists the lattice parameters of all perovskites formed in the present study. The data for $TmScO_3$ is presented in Table IV. The powder data for the series of compounds was generally similar and in most cases some 100 reflections were reliably indexed. Notable exceptions were $GdScO_3$ and $SmScO_3$ where fluorescence effects raised the background radiation obscuring weak reflections. In these cases the high-angle peaks ($2\theta > 90°$) were weak and difficult to measure and consequently only ~50 peaks were used in the refinement of their unit-cell constants.

TABLE III

Compound	Orthorhombic lattice parameters		
	a (Å)	*b* (Å)	*c* (Å)
$LaScO_3$	5.6748	5.7911	8.0923
$NdScO_3$	5.5772	5.7754	8.0037
$SmScO_3$	5.5294	5.7599	7.9611
$GdScO_3$	5.4908	5.7559	7.9382
$DyScO_3$	5.4490	5.7273	7.9116
$YScO_3$	5.4230	5.7091	7.8907
$HoScO_3$	5.4226	5.7117	7.8904
$ErScO_3$	5.4071	5.6985	7.8852
$TmScO_3$	5.3913	5.6808	7.8860

Discussion

Figure 1 shows the lattice cell constants as a function of the ionic radius of the rare earth ion. Two distinct features are evident. For $TmScO_3$, $ErScO_3$, and $HoScO_3$ the *c* lattice constants are practically equal. To check this feature, tentative values for *c* were obtained by a smooth extrapolation of the data in Fig. 1. When these lattice constants were used to generate a set of *d* values no reliable indexing was obtained. Furthermore, if the data were then refined in four least-squares cycles, the original lattice constants were immediately regained and the data reliably indexed.

The second feature of the data is the overall tendency for *a* to increase sharply from Tm to

TABLE IV
CRYSTALLOGRAPHIC DATA FOR $TmScO_3$

$h\,k\,l$	d_{obs} (Å)	d_{calc} (Å)	I_{obs}	$h\,k\,l$	d_{obs} (Å)	d_{calc} (Å)	I_{obs}
1 0 1	4.445	4.451	3	3 1 4	1.2930	1.2933	2
0 0 2	3.940	3.943	18	3 3 1	1.2860	1.2861	4
1 1 0	3.905	3.911	31	4 0 2	1.2752	1.2754	1
1 1 1	3.500	3.503	22	2 4 0	1.2564	1.2565	0.5
0 2 0	2.836	2.840	23	0 4 3	1.2499	1.2495	2
1 1 2	2.777	2.777	100	1 1 6	1.2462	1.2459	5
2 0 0	2.6930	2.6957	22	2 4 1	1.2411	1.2408	6
0 2 1	2.6704	2.6723	13	3 3 2	1.2380	1.2377	2
2 1 0	2.4326	2.4354	1	2 2 5	1.2279	1.2276	3
1 0 3	2.3617	2.3628	1	4 2 0	1.2179	1.2177	2
2 1 1	2.3264	2.3270	6	4 2 1	1.2037	1.2034	3
0 2 2	2.3041	2.3047	9	2 4 2	1.1976	1.1972	1
2 0 2	2.2244	2.2253	12	1 3 5	1.1823	1.1824	4
1 1 3	2.1811	2.1816	9	4 1 3	1.1737	1.1735	1
1 2 2	2.1190	2.1192	2	3 3 3	1.1680	1.1678	4
2 1 2	2.0709	2.0720	1	4 2 2	1.1636	1.1635	1
0 0 4	1.9709	1.9715	12	3 1 5	1.1605	1.1604	0.5
2 2 0	1.9541	1.9553	20	2 4 3	1.1337	1.1336	5
0 2 3	1.9286	1.9293	8	4 0 4	1.1124	1.1127	2
2 2 1	1.8975	1.8978	15	4 2 3	1.1046	1.1049	2
1 2 3	1.8165	1.8165	1	1 5 1	1.1009	1.1009	5
2 1 3	1.7865	1.7865	1	2 2 6	1.0908	1.0908	1
1 1 4	1.7606	1.7605	5	1 1 7	1.0822	1.0826	1
3 0 1	1.7521	1.7522	3	3 4 2	1.0722	1.0723	1
1 3 1	1.7421	1.7424	21	5 0 1	1.0683	1.0683	1
3 1 0	1.7137	1.7134	3	1 3 6	1.0585	1.0587	2
3 1 1	1.6752	1.6744	3	0 4 5	1.0553	1.0554	2
1 3 2	1.6279	1.6273	8	2 5 0	1.0471	1.0470	1
0 2 4	1.6203	1.6196	7	3 1 6	1.0428	1.0429	3
2 0 4	1.5915	1.5913	8	4 2 4	1.0362	1.0360	2
3 1 2	1.5715	1.5715	23	1 5 3	1.0240	1.0239	2
2 2 3	1.5691	1.5689	5	4 1 5	1.0083	1.0084	0.5
1 2 4	1.5504	1.5511	0.5	3 3 5	1.0048	1.0048	1
3 2 0	1.5185	1.5187	1	5 2 1	0.9998	0.9999	0.5
3 2 1	1.4912	1.4913	1	5 0 3	0.9974	0.9976	0.5
3 0 3	1.4831	1.4836	0.5	0 0 8	0.9856	0.9858	1
1 3 3	1.4773	1.4776	8	5 1 3	0.9827	0.9826	1
1 1 5	1.4623	1.4627	1	2 2 7	0.9763	0.9762	0.5
3 1 3	1.4349	1.4354	0.5	4 4 1	0.9702	0.9702	2
0 4 0	1.4200	1.4202	0.2	1 5 4	0.9683	0.9684	1
3 2 2	1.4165	1.4172	0.5	4 2 5	0.9638	0.9639	0.5
0 4 1	1.3972	1.3977	6	3 5 0	0.9602	0.9603	0.5
2 2 4	1.3879	1.3883	8	1 1 8	0.9557	0.9559	0.5
0 2 5	1.3783	1.3789	2	1 3 7	0.9529	0.9529	2
1 4 0	1.3727	1.3734	1	4 0 6	0.9411	0.9410	0.5
4 0 0	1.3474	1.3478	3	0 2 8	0.9312	0.9313	2
2 3 3	1.3351	1.3349	0.5	3 3 6	0.9255	0.9255	2
2 1 5	1.3233	1.3238	1	0 6 2	0.9205	0.9206	0.5
0 0 6	1.3142	1.3144	1	4 4 3	0.9161	0.9163	1
4 1 0	1.3112	1.3114	0.5	5 3 2	0.9114	0.9116	0.5

TABLE IV (*continued*)

h k l	d_{obs} (Å)	d_{calc} (Å)	I_{obs}	*h k l*	d_{obs} (Å)	d_{calc} (Å)	I_{obs}
1 5 5	0.9086	0.9087	1	4 4 5	0.8310	0.8310	1
3 5 3	0.9019	0.9020	1	3 2 8	0.8269	0.8269	0.2
6 0 0	0.8984	0.8986	0.5	5 1 6	0.8248	0.8248	1
6 1 0	0.8875	0.8875	1	3 5 5	0.8203	0.8203	0.2
0 4 7	0.8824	0.8826	1	6 0 4	0.8177	0.8176	0.5
2 2 8	0.8800	0.8802	1	6 2 3	0.8146	0.8145	0.5
1 4 7	0.8710	0.8710	0.5	5 3 5	0.8058	0.8056	0.5
1 3 8	0.8631	0.8631	0.5	1 7 0	0.8025	0.8025	1
4 1 7	0.8545	0.8546	0.5	1 5 7	0.7914	0.7913	0.5
3 3 7	0.8522	0.8524	0.5	1 3 9	0.7868	0.7867	0.5
2 4 7	0.8388	0.8388	1	6 2 4	0.7857	0.7857	0.2

Gd after which the rate of increase decreases substantially. This behavior is similar to that found for the rare earth orthorhodites by Shannon (*14*). It was explained in terms of a regular increase in the average *A*–O distance of the eight first nearest neighbors and a decrease in the average *A*–O distance of the four second-nearest neighbors as *A* increases from Lu to La, by Marezio *et al.* (*15*).

From the present work it appears that as one progresses through the series $AScO_3$, where *A* = Y, La, ..., Lu, it becomes increasingly difficult to synthesize the perovskite. This factor is also reflected in the decreasing Goldschmidt tolerance factor (Table I). The hypothetical compounds $YbScO_3$ and $LuScO_3$ could not be prepared even after treatment at pressures as high as 30 kbar and temperatures of 1000°C. The question arises as to whether $YbScO_3$ and $LuScO_3$ will in fact become stable at even higher pressures, or whether the *C*-type solid solution will be preferred.

Let us consider the hypothetical perovskite

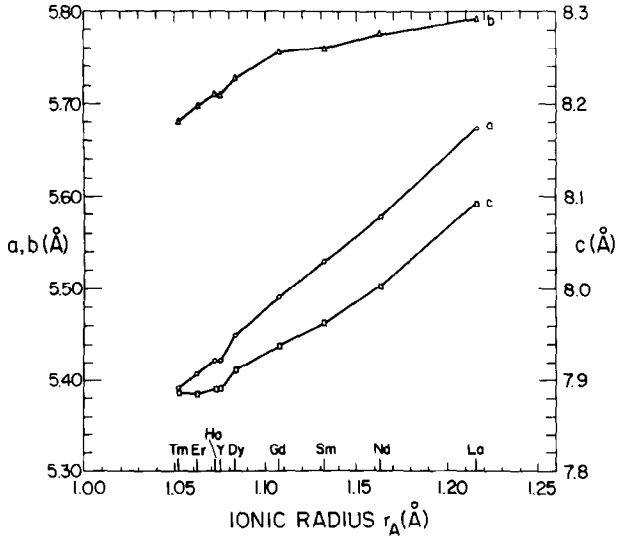

FIGURE 1

$LuScO_3$. Extrapolating the present data for the series we can postulate an expected unit-cell volume of 237.4 Å^3 for $LuScO_3$. This represents a density of 7.5 g cm^{-3}. Using the present data it is possible to estimate that the *C*-type solid solution formed for Lu_2O_3–Sc_2O_3 has a unit-cell constant of ~10.1 Å which implies a unit-cell volume of 1030 Å^3. From this we estimate a density of 6.9 g cm^{-3}. The perovskite unit cell therefore represents an attractive increase in density and must be preferred at higher pressure. Both Lu_2O_3 and Sc_2O_3, however, adopt the monoclinic *B*-type rare earth oxide structure at higher pressures, and this factor could well complicate the picture considerably. Lu_2O_3 adopts the *B*-type structure at ~40 kbar and 1000°C (*16*). Sc_2O_3 does the same at 130 kbar, 1000°C (*17*). Sc_2O_3 remains *C*-type up to ~110 kbar where the *B*-type phase starts forming (*17*). There are therefore two distinct zones. Above 40 kbar Lu_2O_3 will occur in the *B*-type structure while Sc_2O_3 remains *C*-type. If we assume a mixture of these two phases, one can estimate the average density of the mixture as ~7.0 g cm^{-3} which is less than the density offered by the possible perovskite. Above ~110 kbar, when Sc_2O_3 also starts transforming to the *B*-type structure, one can roughly estimate a density of ~7.2 g cm^{-3} for the mixture. This is still marginally lower than the calculated perovskite phase's density. From the above it would therefore be tentatively assumed that perovskite formation will occur for both the Lu_2O_3–Sc_2O_3 and Yb_2O_3–Sc_2O_3 systems at some higher pressure.

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