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Alkaline-Earth Vanadium (IV) Oxides Having the AVO_3 Composition

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The preparation and properties of the perovskite-type metavanadates, $CaVO_3$ and $SrVO_3$ are reported. The calcium phase has orthorhombic symmetry while the strontium phase has the cubic perovskite structure. They are both metallic conductors and exhibit Pauli paramagnetic behavior. The $BaVO_3$ composition was only obtained at high pressure and may be nonstoichiometric. Single crystal data indicate that the predominant phase has a 14-layer hexagonal stacking sequence, previously observed in the $BaCrO_3$ system. Curie–Weiss magnetic behavior was observed on this phase above 77°K.

Introduction

Several investigations of the AVO_3 system, where A is an alkaline earth ion, have been carried out but little has been reported concerning the chemical and physical properties of these materials. In an attempt to contribute to the knowledge of the first-row transition metal ternary oxides having the perovskite structure, several pure AVO_3 compositions were prepared and characterized *via* crystallographic, magnetic, and, where possible, electrical measurements.

Experimental

Reactants

The alkaline-earth oxides were prepared by the thermal decomposition of their respective carbonates at 1000°C in a high vacuum system. These oxides were handled in a dry box to minimize their exposure to air and moisture. Pure vanadium dioxide was prepared by the symproportionation reaction of V_2O_3 and V_2O_5 in an evacuated, fused silica tube at 1000°C for 48 hr. The reactants were all found to be single phase by crystallographic studies. Reactions of the alkaline-earth oxides and vanadium dioxide were carried out in sealed, evacuated fused silica tubes at autogenous pressure or under a flowing noble gas atmosphere in a tube furnace. Several reactions were also carried out at high pressure in a tetrahedral anvil press (*1*) under 60–65 kbar pressure.

Apparatus and Measurements

The X-ray data on the products were obtained at 20°C with a Hägg or deWolff Guinier camera utilizing monochromated CuK_{α_1} radiation and an internal KCl standard. Cell dimensions were refined by a computerized program (*2*) utilizing a least-squares method.

The electrical measurements on $SrVO_3$ were made on a single crystal using a four-probe, van der Pauw method. Superconducting transition in $SrVO_3$ was studied by observing the Meissner effect at temperatures above 1.50°K. The magnetic data were obtained on powders in a Faraday system utilizing a Cahn microbalance in the temperature region of 77–600°K for $CaVO_3$ and $SrVO_3$, and 77–300°K for $BaVO_3$. The low temperature system was standardized with $HgCo(CNS)_4$ as the calibrant and the high temperature assembly was calibrated with Gd_2O_3. Corrections (*3*) for atomic diamagnetism were included in the calculations of magnetic moment.

Results and Discussion

$CaVO_3$

The reactions of CaO and VO_2 at 1000°C and autogenous pressure in a sealed silica tube yielded a slightly heterogeneous product which contained a phase previously characterized by Deduit (*4*) as cubic ($a = 9.30$ Å) $CaVO_3$. On heating this phase at 900°C for ten days in a sealed system, a perovskite-type product was not obtained.

The high-pressure reaction of CaO and VO_2 yields a black crystalline product which was found to have the orthorhombic perovskite-type structure. The indexed powder pattern of $CaVO_3$ is given in Table I and the refined lattice dimensions are: $a = 5.4215 \pm 8$, $b = 5.3353 \pm 9$, and $c = 7.5406 \pm 8$ Å respectively. The magnetic data from 77–600°K suggest Pauli paramagnetic behavior (Fig. 1) with the following molar susceptibilities at various temperatures (°K): 461×10^{-6} (77), 441×10^{-6} (270), 432×10^{-6} (420) and, 443×10^{-6} (620°K). Wollnik (*6*) gives the molar susceptibility (corrected for atomic diamagnetism) of $CaVO_3$ at three temperatures, viz., 301×10^{-6} (295), 300×10^{-6} (195), and 329×10^{-6} (80°K). These values are similar to those obtained in our study. The reported (*5*) electrical resistivity on a powder compact indicates metallic conductivity in the region of 4×10^{-1} Ωcm at room temperature. A much lower value would be expected on a single crystal. The thermoelectric power value of -5 μV/deg for $CaVO_3$ has also been reported (*5*). These data would indicate a metallic conductor having electrons as the major charge carriers.

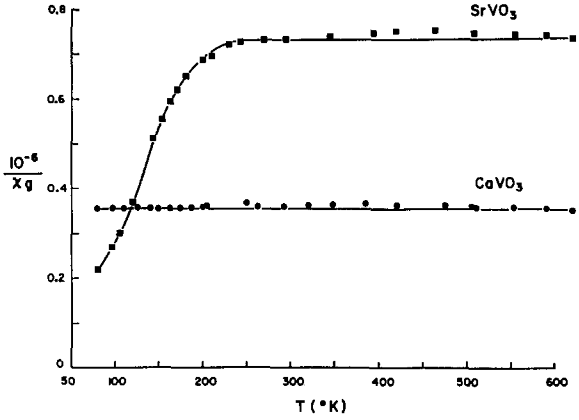

FIG. 1. Reciprocal of gram magnetic susceptibility vs. absolute temperature for $SrVO_3$ and $CaVO_3$.

TABLE I

X-RAY DIFFRACTION DATA

$CaVO_3$ Orthorhombic				$SrVO_3$ Cubic				$BaVO_3$ Hexagonal (14-H)			
hkl	*I*	*d*(obsd)	*d*(calcd)	*hkl*	*I*	*d*(obsd)	*d*(calcd)	*hkl*	*I*	*d*(obsd)	*d*(calcd)
110	40	3.7688	3.7677	100	15	3.8399	3.8424	10 2	20	4.7126	4.7155
111	5	3.3723	3.3704	110	100	2.7170	2.7170	0010	10	3.2147	3.2122
020	100	2.6672	2.6677	111	75	2.2188	2.2184	10 8	70	3.1133	3.1141
200	80	2.6612	2.6607	200	90	1.9213	1.9212	10 9	35	2.8937	2.8916
210	2	2.3821	2.3811	210	10	1.7184	1.7184	11 0	100	2.8489	2.8480
103	15	2.2728	2.2728	211	90	1.5687	1.5687	11 4	35	2.6851	2.6842
022	25	2.1799	2.1777	220	75	1.3584	1.3585	1011	10	2.5131	2.5129
202	15	2.1733	2.1739	300	5	1.2808	1.2808	20 2	30	2.4416	2.4379
113	5	2.0912	2.0910					1012	15	2.3526	2.3528
122	5	2.0172	2.0155					11 8	15	2.3167	2.3230
004	90	1.8851	1.8852	310	40	1.2157[a]	1.2151[b]	20 5	30	2.3032	2.3026
023	5	1.8298	1.8294	311	15	1.1590	1.1585	20 6	90	2.2482	2.2402
031	2	1.7311	1.7310	222	20	1.1101	1.1092	20 7	20	2.1736	2.1725
130	15	1.6873	1.6867	320	5	1.0661	1.0657	20 8	5	2.1024	2.1016
131	10	1.6481	1.6461	321	30	1.0267	1.0269	21 0	10	1.8635	1.8645
132	75	1.5412	1.5397	400	10	0.9604	0.9606	21 2	30	1.8511	1.8520
312	70	1.5370	1.5370	330	40	0.9054	0.9057	21 3	5	1.8375	1.8368
040	25	1.3357	1.3338	331	15	0.8813	0.8815	2014	15	1.6841	1.6799
224	60	1.3332	1.3325	420	40	0.8589	0.8592	21 9	10	1.6525	1.6526
400	20	1.3296	1.3304	421	2	0.8384	0.8385	1116	20	1.6408	1.6409
				332	5	0.8190	0.8192	30 4	15	1.6110	1.6109
				442	60	0.7842	0.7843	2016	15	1.5563	1.5570
								22 0	30	1.4243	1.4240

[a] Debye-Scherrer data.

[b] *d*(calcd) using CuK_α (average).

Several investigators have reported the preparation of $CaVO_3$ (*4–6*, *10*, *11*, *13*) but little is known of its physical and chemical properties. Many reports on the $CaVO_3$ phase are in conflict. Deduit (*4*) claims that the autogenous pressure phase is cubic ($a = 9.30$ Å) which converts to a cubic perovskite on heating at 900°C for several days. Some authors (*5*, *11*, *13*) report the direct formation of this cubic perovskite-type product ($a = 3.76$–3.78Å) by different reaction routes. Roth (*10*), however, did obtain an orthorhombic product from CaO and VO_2 at 1300°C in a He atmosphere and reports similar lattice parameters as those obtained in this investigation. Wollnik (*6*) also studied the $CaVO_{3-x}$ system and observed that a cubic phase could no longer be obtained when x had a value greater than 0.15.

The pure $CaVO_3$ product obtained in this study was observed to have orthorhombic symmetry, or the distorted perovskite-type structure. The metallic conductivity reported by Reuter and Wollnik (*5*, *6*) and Pauli paramagnetic behavior are all consistent with a delocalized electron system. These data are also consistent with the model proposed by Goodenough (*12*) for perovskite-type compounds having one electron system such as Ti^{3+} and Re^{6+}.

$SrVO_3$

The reaction of SrO and VO_2 in a sealed system at 1000°C and at ambient or high pressure, yields a black crystalline product having a blue tint. This phase was found to have the cubic perovskite structure. The indexed powder pattern is given in Table I. The unit-cell dimensions for all the pure products obtained in this study fell in the region $a = 3.8424 \pm 2$ Å. These results suggest that the composition remains unchanged and is independent of reaction temperature or pressure. The phase is presumed to be stoichiometric and does possess a much smaller unit cell than that of $SrVO_{2.5}$ which contains the larger trivalent vanadium ion (*14*). The magnetic data on $SrVO_3$ suggest Pauli paramagnetic behavior above room temperature, but below 200°K the reciprocal susceptibility decreased with decreasing temperature (Fig. 1). The corrected molar magnetic susceptibilities above room temperatures are: 315×10^{-6} (294.5), 315×10^{-6} (321), 307×10^{-6} (509), 310×10^{-6} (556), and 312×10^{-6} (619°K). The magnetic data (corrected for atomic diamagnetism) for $SrVO_3$ at three different temperatures are given by Wollnik (*6*) as: 254×10^{-6} (295), 243×10^{-6} (195), and 265×10^{-6} (80°K).

The single crystal electrical resistivity at room temperature was 2.6×10^{-5} Ωcm and decreased to 4.6×10^{-7} Ωcm at liquid helium temperature (Fig. 2). A thermoelectric power of −12 μV/deg was measured on crystals of $SrVO_3$ indicating that the charge carriers are electrons. The product was not superconducting at the lowest temperature studied.

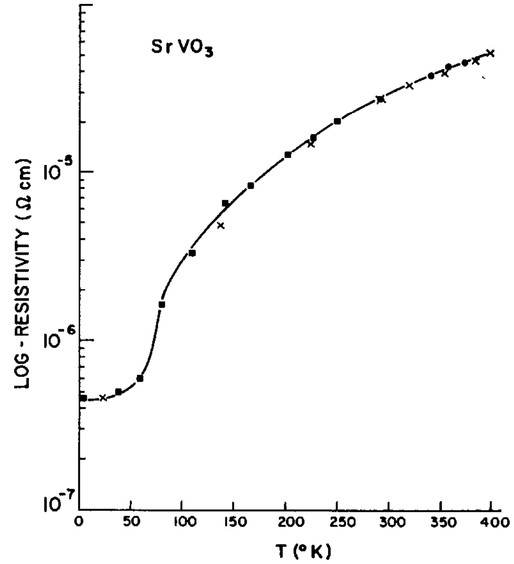

FIG. 2. Log resistivity (in Ωcm) vs. absolute temperature for $SrVO_3$. (Legend: × increase in temperature, ● and ■ decrease in temperature.)

The $SrVO_3$ composition has also been studied by several investigators and some differences in results were noted. Reuter and Wollnik (*5*, *6*) report the isolation of a metallic perovskite-type product while Roth (*10*) reports the isolation of a new phase not related to the perovskite structure. Kestigian et al. (*14*) studied the $SrVO_{2.5+x}$ system and concluded that under the conditions utilized in their study, the limit of cubic phase was not far beyond $SrVO_{2.75}$. Their reduced phase $SrVO_{2.5}$ had a cubic unit-cell dimension of 3.848 ± 5 Å. The similar composition prepared by Rüdorff and Reuter (*15*) was reported as having a supercell with $a = 7.70$ Å.

The results of this investigation show that $SrVO_3$ is indeed a highly conducting perovskite-type product with Pauli paramagnetic behavior above room temperature. There was little magnetic field dependence throughout the temperature region studied.

It is interesting to note the similarity between the resistivity versus temperature plot and the reciprocal susceptibility versus temperature plot. They both follow the same path indicating that the lone electron on V^{4+} is delocalized and exhibits similar conducting and magnetic behavior. (Figs. 1 and 2.) These data suggest that a possible distortion from cubic symmetry might occur in the region 100–150°K which gives rise to higher conductance and increased molar susceptibility. Aside from this anomaly, the physical properties of this system are all consistent with Goodenough's delocalized electron model for a d^1 perovskite-type compound.

$BaVO_3$

Attempts to prepare $BaVO_3$ by the reaction of BaO and VO_2 *in vacuo* or $Ba(NO_3)_2$ and V_2O_3 under H_2 (Ref. 7) always produced $Ba_3(VO_4)_2$ and an impurity phase. The controlled hydrolysis of $BaVS_3$ yielded only $BaSO_4$ and V_2O_5 as primary products. The high-pressure reaction of BaO and VO_2 at 1200°C and 60–65 kbars, and treatment with dilute (2*N*)HCl, yielded small amounts, approximately 25% of the product, of a black crystalline phase in the form of hexagonal plates. Precession data on crystals isolated in the products of two different reactions showed hexagonal symmetry. The *c*-axis unit-cell dimension in both crystals was observed to be approximately 32.1 Å. The possible space groups were: $P6_3/mmc$, $P\bar{6}2c$, or, $P6_3mc$. The Guinier data were suitably refined with the hexagonal cell dimensions: $a = 5.6960 \pm 7$ and $c = 32.122 \pm 9$ Å. (Volume, 902.6 $Å^3$.) These cell dimensions and the space group $P6_3/mmc$ are consistent with a 14-layer hexagonal $BaMO_3$ structure. The powder data for this product are given in Table I. Some lines which were not indexed include: 4.629 (60), 3.703 (20), 2.831 (65), 2.711 (70), 2.094 (25), and 1.415 (30). These extra diffraction lines may originate from some other polytype in the product as often occurs in systems of this type (*8*, *9*). In fact, most of the above additional reflections could be indexed as arising from a 12R polytype. ($a = 5.726 \pm 1$, $c = 27.821 \pm 6$ Å, Vol. = 790.1 $Å^3$.)

The magnetic data suggest Curie–Weiss behavior from 77°K to 250°K with possible ferromagnetic ordering below this temperature region (Fig. 3). The Curie–Weiss moment is 1.93 μ_B and the extrapolated intercept of the temperature axis is +48°K.

The $BaVO_3$ system was most difficult to study since all low-pressure experiments yielded the highly stable $Ba_3(VO_4)_2$ phase. This same phase predominated all ambient and autogenous pressure reactions. The results of U. Spitsbergen (*16*) also supports these findings and the high stability of the $Ba_3(VO_4)_2$ by-product.

The $BaVO_3$ compound can be prepared at high pressure in small yields but the exact composition of this product is not known. Several crystals were found to have the 14-layer hexagonal structure. This stacking sequence was also observed in the $BaCrO_3$ system (*8*) but the possibility of nonstoichiometry cannot be dismissed. The 14-layer stacking sequence is not an ordinary or standard phase found in other stable systems (*17*) investigated at high pressure. This might further indicate that the 14-layer product is nonstoichiometric.

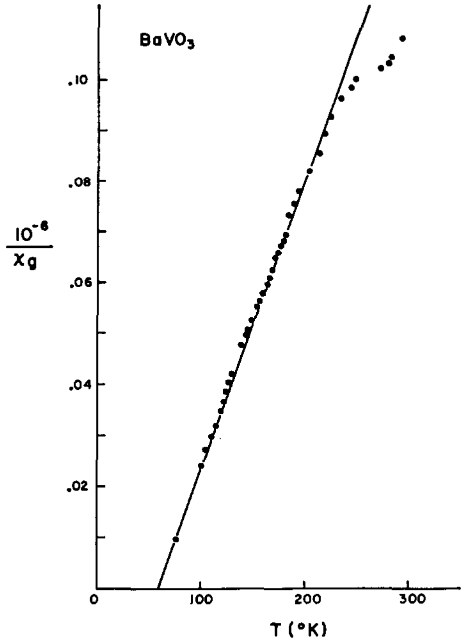

FIG. 3. Reciprocal of gram magnetic susceptibility vs. absolute temperature for $BaVO_3$.

The ease by which V^{4+} tends to disproportionate is a predominant factor which leads to the formation of other more stable phases. This was evidenced in the barium system and also observed in the $NiVO_3$ system (*18*). This same disproportionation phenomena has been detected in the Co/V/O, and the Zn/V/O system (*19*).

The magnetic moment of $BaVO_3$ was calculated to be 1.93 μ_B from the Curie–Weiss equation. Figgis and Lewis (*20*) list the observed magnetic moments for V^{4+} in several coordination compounds to be in the region 1.68–1.78 μ_B. The theoretical free spin value for the d^1 ion is 1.73 μ_B. Recently, however, the magnetic moments observed on solid state oxide systems have been reported. The vanadium "bronze" systems were observed (*21*) to have higher moments ranging between 1.9–2.2 μ_B. Lower moments were observed in the $VOSO_4$ system (*22*). The Curie–Weiss moment for V^{4+} in $CdVO_3$ was observed to be 1.80 μ_B (*19*).

The higher moment than that given by the free spin value might arise from the fact that oxygen deficiency in $BaVO_3$ would create V^{3+} (d^2) ions which could increase the magnetic moment. Other types of nonstoichiometry (*8*) could also be responsible for deviations from the theoretical free spin value of V^{4+}.

Conclusions

Tetravalent vanadium is the last element of the first-row transition elements to be incorporated in the perovskite or related perovskite-type structure having the ternary composition AVO_3. Orthorhombic $CaVO_3$ and cubic $SrVO_3$ were both found to be related to the perovskite structure and both exhibited metallic conducting properties and Pauli paramagnetic behavior consistent with the model proposed by Goodenough for perovskite-type derivatives having a d^1 electron system. $BaVO_3$, having a hexagonal layer type structure, could only be prepared at high pressure. The magnetic properties and structure, however, strongly suggest that this phase might be nonstoichiometric.

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