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Preparation and Properties of Some Strontium-Oxometallates

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A number of ternary strontium oxides have been prepared by the flux reaction technique using strontium chloride as a melt medium. The crystal habitus of the small single crystals obtained is invariably related to the structure via the reciprocal lattice. Magnetic measurements, X-ray parameters, analyses, and other pertinent properties are reported for the various compounds.

Introduction

The technique of using a halide flux of one of the cationic constituents of a ternary oxide, part of which interacts with an oxide of the second constituent to form the well-crystallized ternary compound, was first employed for the preparation of $Ba_2Fe_{12}O_{19}$ and $SrFe_{12}O_{19}$ (*1*). Later, the same method was used to prepare a number of other barium and calcium compounds (*2*); in this paper, the preparation of some Sr compounds will be described. The principal reaction is the same as described in (*2*) except that the necessary energy for the conversion of $SrCl_2$ to SrO is only 58 kcal according to Bichowsky (*3*). The possibility of halide incorporation in the reaction product exists where the structure permits it, and indeed, a number of halo-spodiosites and halo-apatites have been obtained. The fact that V_2O_5 yielded platelets of the orthorhombic spodiosite type while P_2O_5 gave needles of the hexagonal apatite type permitted a study of habitus as a function of varying anion concentrations. In both the vanadate and the phosphate systems, two quaternary compositional types, Sr_2MeO_4Cl and $Sr_5(MeO_4)_3Cl$, are known. The formation of only one of the possible phases under the conditions of the reaction indicates the strong thermodynamic preference of one structure versus the other. Stability comparisons are further enlarged by considering the corresponding Ca and Ba examples, and it will be seen that the apatite structure is preferred with an increase in the cation size. The technique also provided an excellent means for incorporating small quantities of transition elements in the tetrahedral phosphorus position. In this way, dilute solutions of the compositions $Sr_5(CrO_4)_3Cl$ (*4*) or $Ba_5(MnO_4)_3Cl$ (*5*) with both Cr and Mn in the pentavalent state could be obtained in the corresponding phosphate hosts.

Experimental

The experimental preparative technique was similar to that previously described (*2*). However, a significant deviation from the basic procedure was made in that all reactions were carried out in recrystallized Al_2O_3 containers of 250-ml capacity. These crucibles are remarkably resistant to molten $SrCl_2$ and can be used repeatedly. The potential contamination with Al was only in the 100 to 1000-ppm range, as determined by repeated semi-quantitative spectrographic analyses. The platinum tube used in the earlier work was replaced in this study by a $\frac{1}{2}$ in. diameter Al_2O_3 tube. In order to increase the water vapor concentration in the gas stream, the wash bottle was held at 80°C.

The oxides used were of the highest commercially available purity, and the strontium chloride was Baker's reagent grade, dehydrated at 150°C. All reaction products were analyzed by wet chemical or X-ray fluorescence techniques and were further characterized by X-ray powder patterns. Refined parameters were obtained from films taken with a Guinier focusing camera; single crystal data were generally based on precession photographs. Magnetic moments for the doped samples were deter-

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mined from the slope of magnetic susceptibility versus reciprocal temperature using data between 78 and 300°K obtained with a Faraday balance.

Results and Discussion

$SrCl_2/Nb_2O_5$. This reaction yielded slightly pale yellow, thin flakes which analyzed: Sr, 38.1%; Nb, 39.6% (calcd for $Sr_2Nb_2O_7$; Sr, 37.04%; Nb, 39.28%). The crystals were indexed as orthorhombic and the parameters were $a = 3.948$ Å, $b = 26.734$ Å, $c = 5.71$ Å. The X-ray density of 5.213 g ml^{-1} corresponded closely to the experimental value of 5.18 g ml^{-1}. Since the space group is *Cmcm* or *Cmc*2_1, this indicates that the product is isostructural with the previously (*2*) described $Ca_2Nb_2O_7$. Again, the large *b* axis corresponds to the thin dimension of the crystal platelet, thus agreeing with the general finding that the habit of most flux grown single crystals corresponds to the reciprocal lattice of its structure.

$SrCl_2/Ta_2O_5$. The habit of the crystals obtained was identical to the previous case, but the compound was pure white, suggesting the possibility of an impurity in the Nb_2O_5 used for the reaction above. Analysis (Sr, 27.5%; Ta, 54.3%; calcd for $Sr_2Ta_2O_7$: Sr, 26.99%; Ta, 55.75%) indicated the formula $Sr_2Ta_2O_7$ and single crystal X-ray study confirmed the isostructural nature with the Nb compound. The orthorhombic parameters were $a = 3.9481 \pm 4$ Å, $b = 27.187 \pm 2$ Å, and $c = 5.6898 \pm$ Å. The X-ray density of 7.05 g ml^{-1} corresponded favorably to the pycnometric value of 6.97 g ml^{-1}.

$SrCl_2/Fe_2O_3$. This reaction gave the previously characterized (*1*) $SrFe_{12}O_{19}$ mostly in the form of transparent hexagonal flakes, with the large c axis (23.00 Å) corresponding to the thin dimension.

$SrCl_2/TiO_2$. Yielded very fine equiaxed transparent crystals of $SrTiO_3$.

$SrCl_2/Yb_2O_3$. Although $SrYb_2O_4$ (*6*) is a well-established composition and could have formed during this reaction, only well-defined almost spherical crystals of Yb_2O_3 were obtained, indicating that the ΔH necessary for the primary hydrolysis of $SrCl_2$ at 1000°C is not supplied by the heat of formation of $SrYb_2O_4$.

$SrCl_2/SnO_2$. Similar to the TiO_2 case, very small transparent crystals of $SrSnO_3$ were obtained.

$SrCl_2/WO_4$. This reaction yielded $SrWO_4$ in the form of transparent flakes and dendritic crystals.

$SrCl_2/V_2O_5$. In view of the fact that the corresponding reaction with $BaCl_2$ yielded the halo-vanadate $Ba_5(VO_4)_3Cl$, and since the structural incorporation of halogen was again possible for a strontium analog, this reaction was of particular interest. The analysis gave Cl, 9.5%; V, 15.2%; Sr, 54.0%, corresponding closely to the 2:1:1 ratio for Sr_2VO_4Cl (calcd: Cl, 10.89%; V, 15.64%; Sr, 53.81%). While a halo-vanadate was formed, it was not of the apatite but rather of the spodiosite type, indicating that spodiosite is thermodynamically favored over also known $Sr_5(VO_4)_3Cl$. Sr_2VO_4Cl has recently been described by Nath and Hummel (*7*) and their cell dimensions of $a = 6.51$ Å, $b = 7.51$ Å, and $c = 11.49$ Å are in good agreement with the parameters that were obtained on the same compound prepared during this study: $a = 7.43$ Å, $b = 11.36$ Å, $c = 6.54$ Å (space group *Pbma*). A more detailed description of this compound and solid solutions with Sr_2VO_4Br will be given in a separate publication. Sr_2VO_4Cl gives a blue emission under 2537 Å uv excitation and a typical fluorescence emission spectrum is shown in Fig. 1. Long uv (3660 Å) X-rays and electrons do not excite Sr_2VO_4Cl. The broad band emission is characteristic of a self-activated phosphor such as $CaWO_4$ or $CaMoO_4$.

$SrCl_2/P_2O_5$. This reaction yielded an exclusively fibrous product with individual needles up to 1-cm long and with aspect ratios between 50 and 100:1. The bulk of the product consisted of 1–5-μ diameter fibers. Chemical analysis (found Sr, 56.7%; P, 12.3%, Cl, 4.3%: calcd. for $Sr_5(PO_4)_3Cl$–Sr, 57.76%; P, 12.25%; Cl, 4.67%) indicated that this reaction product had a composition consistent with that expected for a material with apatite structure. An X-ray pattern was in agreement with that

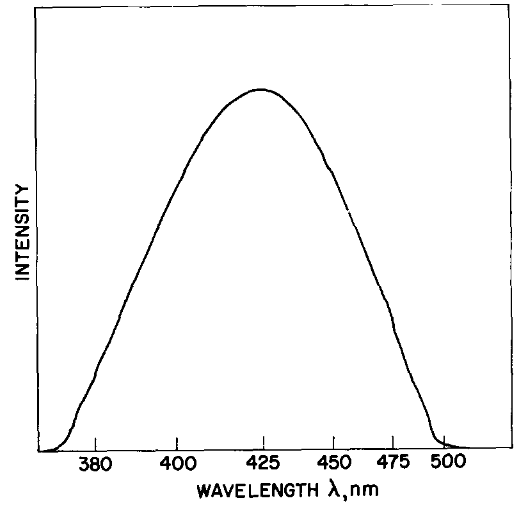

FIG. 1. Fluorescent emission spectrum of Sr_2VO_4Cl.

recorded in ASTM file card 16-666 for $Sr_5(PO_4)_3Cl$. The needle axis corresponds to the shorter c axis (7.174 Å). This finding of two different structures for the vanadate and phosphate case prompted a more general examination of the structures obtained by these flux reactions as a function of the size of the cation. This was done under identical experimental conditions with $CaCl_2$, $SrCl_2$ and $BaCl_2$ and the results are summarized in Table I. It is obvious that the smaller cation seems to prefer the spodiosite structure with the strontium case taking an intermediate position. This is, of course, the most interesting example since the structural transition as well as the associated change in crystal habit can here be studied as a function of the anion concentration in compounds of the type $Sr_2V_{1-x}PO_4Cl$ and $Sr_5(P_{1-x}V_xO_4)_3Cl$. This was done by varying the V_2O_5/P_2O_5 ratio for the original 200-g $SrCl_2$ charge and the results are summarized in Table II.

It is obvious from these data that the presence of P_2O_5 dominated the formation of the preferred apatite structure and only at a molar ratio of 9:1 for V:P was the spodiosite structure attained. Again, all apatite compositions crystallized in the highly acicular habit which is best demonstrated in Fig. 2. With the strong tendency for the $SrCl_2/P_2O_5$ flux to form apatite compositions, it was now of interest to see what the influence of Sr would be when $SrCl_2$ was added to a $CaCl_2$ flux system from which only spodiosite-type compounds had been crystallized previously. This was done in a melt consisting of 100 g each of $SrCl_2$ and $CaCl_2$. The surprising result was a pure apatite, which contained no Sr (analysis—Ca, 38.1%; P, 17.2%; Cl, 6.7%; calcd for $Ca_5(PO_4)_3Cl$—Ca, 38.48%; P, 17.84%; Cl, 6.81%). This can only be explained if one assumes that small quantities of $Sr_5(PO_4)_3Cl$ *nucleated* the growth of the apatite phase upon which $Ca_5(PO_4)_3Cl$

TABLE I

DIFFERENT STRUCTURES OBTAINED BY THE FLUX REACTION TECHNIQUE

		P_2O_5				V_2O_5	
Salt Melt	a, Å	b, Å	c, Å	Size of Cation	a, Å	b, Å	c, Å
		Ca_2PO_4Cl				Ca_2VO_4Cl	
$CaCl_2$	17.00	10.83	6.19	0.99 Å	7.08	10.99	6.27
		$Sr_5(PO_4)_3Cl$				Sr_2VO_4Cl	
$SrCl_2$	9.953	—	7.174	1.12 Å	7.43	11.36	6.54
		$Ba_5(PO_4)_3Cl$				$Ba_5(VO_4)_3Cl$	
$BaCl_2$	10.29	—	7.65	1.34 Å	10.41	—	7.55

TABLE II

STRUCTURES OBTAINED FROM MIXED V_2O_5/P_2O_5 CHARGES TO $SrCl_2$

	Amount of Oxides Used			Analysis, %				
Sample No.	P_2O_5, g	V_2O_5, g	Structure and Parameters of Obtained Product	Sr	V	P	Cl	Closest Corresponding Composition and Calculated Amount
1	1.00	4.00	S* $a = 7.459$ Å $b = 11.436$ Å $c = 6.513$ Å	53.4	12.7	1.0	10.4	$Sr_2V_{0.9}P_{0.1}O_4Cl$ 54.14, 14.17, 0.95, 10.96
2	2.00	3.00	A° $a = 10.02$ Å $c = 7.25$ Å	54.7	9.5	5.9	4.3	$Sr_5(V_{0.5}P_{0.5}O_4)_3Cl$ 55.57, 9.69, 5.89, 4.49
3	3.00	2.00	A° $a = 9.953$ Å $c = 7.207$ Å	55.2	6.5	7.5	4.4	$Sr_5(V_{0.35}P_{0.65}O_4)_3Cl$ 56.21, 6.86, 7.75, 4.55
4	4.00	1.00	A° $a = 9.905$ Å $c = 7.194$ Å	56.2	2.0	10.9	4.5	$Sr_5(V_{0.1}P_{0.9}O_4)_3Cl$ 57.31, 1.99, 10.94, 4.68

S* = Spodiosite-type.
A° = Apatite-type.

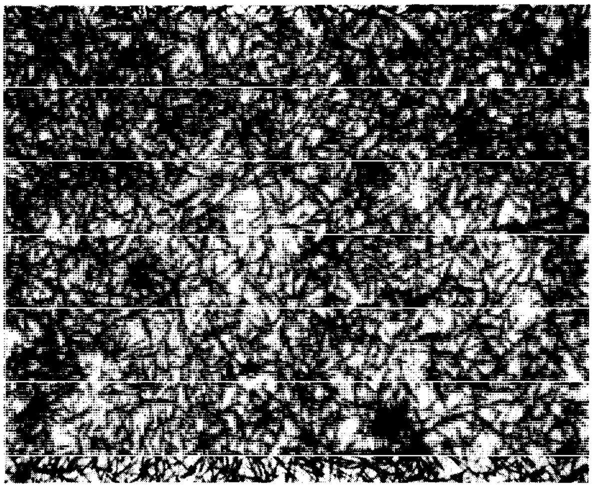

FIG. 2. Typical $Sr_5(PO_4)_3Cl$ needles at 100×.

continued to grow until the P_2O_5 was depleted. A somewhat similar example to this case is found in nature, where the presence of small quantities of Sr nucleate aragonite growth of certain sea shells. $Ca_5(PO_4)_3Cl$ gave a broad band blue emission (peak at 430 nm) upon excitation with 2537 Å uv.

Doping of $Sr_5(PO_4)_3Cl$ with Transition Elements

These experiments were run under identical conditions with a standard charge of 200 g $SrCl_2$, 5.0 g P_2O_5 and 0.5 g oxide of Cr, Mn, Fe, Co, and Ni. Pure apatites with pentavalent Cr and Mn in the tetrahedral P position such as $Sr_5(CrO_4)_3Cl$ and $Ba_5(MnO_4)_3Cl$ had previously been described in the literature and solid solutions could therefore readily be expected. Fe^{5+} and Co^{5+}, established in such compounds as K_3FeO_4 and $KCoO_3$ (*8*), were questionable substituents. Ni^{5+} was, of course, without precedent. Of the five substitutions attempted, only Cr, Mn, and Co were incorporated into the apatite structure. It is assumed that the formation of $SrFe_{12}O_{19}$ as a competing phase precluded the incorporation of Fe. Pertinent characteristics observed for the three substituted apatites obtained are summarized in Table III. All samples were obtained in the form of highly acicular crystals with the larger ones up to 10 mm in length. It is interesting to note that the Cr-doped sample still has the same green color (although much lighter) as the pure $Sr_5(CrO_4)_3Cl$ compound prepared by Banks (*4*), whereas the dilute Mn composition is blue compared to the dark green color of pure $Ba_5(MnO_4)_3Cl$ (*5*). The observed magnetic moments, Table III, for the Cr-doped sample, 1.4 ± 0.2 μB, and the Mn-doped sample, 3.0 ± 0.2 μB, are consistent with the pentavalent state of the dopants for which the spin only magnetic moments are correspondingly 1.73 μB and 2.83 μB. The large uncertainty, 10–15%, in the observed moments is due primarily to the uncertainty in the metal analyses. These results are in agreement with Kingsley et al. (*9*) who have clearly established the pentavalent state of Mn in these compounds by detailed spectroscopic and careful analytical studies. More recently, Nath and Hummel (*7*) came to the same conclusions by making band assignments and determining ligand field parameters for Mn^{5+} in $Sr_2(VO_4)_3Cl$. The transmission spectrum of Example 2 from Table III is shown in Fig. 3 and corresponds to the absorption spectra reported both by Kingsley et al. and by Nath and Hummel.

The situation with the Co-doped sample, however, is not so clear. If the cobalt is substituted directly for phosphorus as pentavalent Co d^4, one would expect a magnetic moment of 4.9 μB for a high spin state or 0.0 μB for the low spin state. The observed moment,

TABLE III

CHARACTERIZATION OF Cr-, Mn-, AND Co-DOPED $Sr_5(P_{1-x}Me_xO_4)_3Cl$

Sample No.	Me	x	Analysis, % Sr	P	Me[a]	Cl	Corresponding Formula and Theoretical Amounts	Color	μB
1	Cr	0.01	57.1	12.4	0.2	4.6	$Sr_5(P_{0.99}Cr_{0.01}O_4)_3Cl$ 57.72, 12.12, 0.20, 4.67	Bright apple green	1.4 ± 0.1
2	Mn	0.01	57.0	12.1	0.23	4.9	$Sr_5(P_{0.99}Mn_{0.01}O_4)_3Cl$ 57.71, 12.11, 0.21, 4.67	Brilliant blue	3.0 ± 0.2
3	Co	0.005	57.3	12.2	0.065 ± 0.035	4.5	$Sr_5(P_{0.995}Co_{0.005}O_4)_3Cl$ 57.74, 12.19, 0.09, 4.67	Purplish pink	2.0 ± 0.7

[a] ± 20–30%.

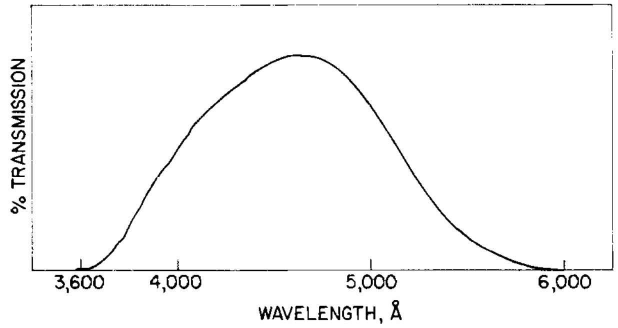

FIG. 3. Transmission spectrum of $Sr_5(PO_4)_3Cl:Mn$.

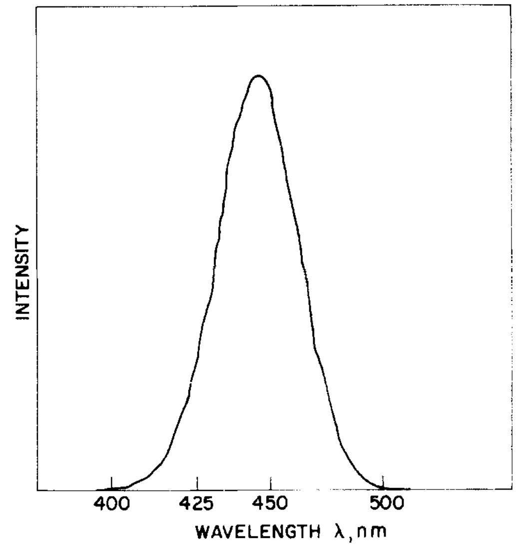

FIG. 4. Fluorescent emission spectrum of $Sr_5(PO_4)_3Cl:Eu$.

2.0 ± 0.7 μB thus excludes Co^{5+} in the *P* site. The other possibilities are listed in Table IV. The only magnetic moment in Table IV close to the observed value is 1.7 μB for low-spin octahedral Co^{2+}. This is highly unlikely, however, since this state is not found in oxides due to the low ligand field arising from oxygen. One is left with some mixture of oxidation states for cobalt, the most likely candidate being low-spin octahedral Co^{3+} (diamagnetic) and high spin octahedral Co^{2+} ($\mu = 3.8$–5.2 μB). Such a mixture would result in an observed moment $\mu = \sqrt{F(\mu_{Co^{+2}})^2}$, where *F* is the fraction of cobalt atoms in the divalent state.

Since apatites such as $Ca_5(PO_4)_3F$ (*10*) and $Ca_5(VO_4)_3F$ (*11*) have recently gained some importance as hosts for rare-earth ions, it was of interest to see if Eu^{3+} could be incorporated into the cation site. This was done under the normal reaction conditions, charging 1.0 g Eu_2O_3 and a stoichiometric amount of Na_2CO_3 for valence compensation in addition to the 5.0 g P_2O_5. The resulting fibrous reaction product exhibited a rather intense blue emission, readily excitable with short uv, long uv, electrons, or X-rays. A typical fluorescent emission spectrum is shown in Fig. 4. This emission is characteristic of Eu^{2+} as it has been observed in several other hosts (*12*). In view of the oxidizing reaction conditions (air + H_2O at 1200°C), this is a most surprising finding and can only be explained by the fact that the ionic radii of Sr^{2+} and Eu^{2+} are essentially identical. Eu^{2+} is, therefore, stabilized in a Sr environment. A similar observation of Eu^{2+} stabilization in an Sr^{2+} environment was made in $SrMoO_4$ (*13*) where it was impossible to oxidize a certain Eu^{2+} concentration to the trivalent state and the crystal always remained deep red. The intensity of fluorescent emission as a function of the Eu^{2+} concentration is given in Fig. 5. Figure 6 shows a comparison of the fluorescence obtained by identical 80 kV_P X-ray excitation for $CaWO_4$ (broad band) and $Sr_5(PO_4)_3Cl:Eu$ (narrow band).

Finally, it was of interest to see if some of the bromoapatites and bromospodiosites described in

TABLE IV

TYPICAL MAGNETIC MOMENTS FOR COBALT

Configuration		Expected Moment High Spin	Low Spin
Co^{3+} d^6	Tetrahedral	4.9 μB	2.8 μB
	Octahedral	4.9–5.8	0
Co^{2+} d^7	Tetrahedral	4.4–4.9	3.8
	Octahedral	3.8–5.2	1.7

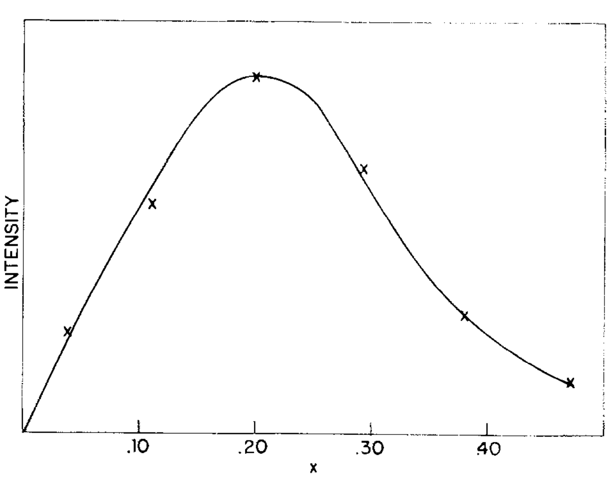

FIG. 5. Intensity versus composition for the $Sr_{5-x}Eu_x(PO_4)_3Cl$ system.

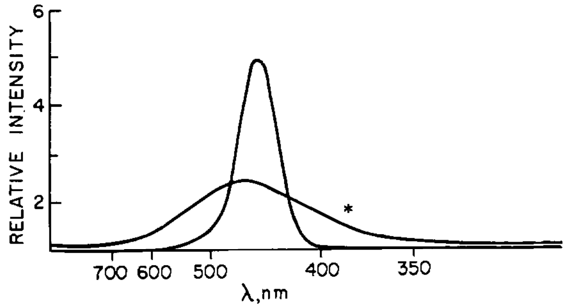

FIG. 6. X-Ray excitation spectra for $Sr_5(PO_4)_3Cl$:Eu and $CaWO_4$ (*).

the literature previously (*14*), could be prepared by this technique. Although the bromides are thermally and hydrolytically far less stable than the corresponding chlorides, the attempted preparations were in principle successful. These compounds will be reported in a separate paper.

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