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(Received August 31, 1936)

As a preliminary to a study of the relation between the fluorescence and the absorption spectra of crystals, we photographed the absorption spectra of single crystals of $Sm_2(WO_4)_3$ and of $Sm_2(MoO_4)_3$ at 78°K, 113°K, 169°K, and 298°K. Evidence was found that an activated state 76 cm^{-1} from the basic state exists in the tungstate. The general patterns of the spectra of the tungstate and of the molyb-date are not the same, indicating that the crystals do not belong to the same space group, an inference likely to be made from crystallographic data. There is also evidence for a dissociation, perhaps an incipient dissociation in the lattice, as if the tungstate and especially the molybdate dissociated into the basic and acidic oxides within the single crystal.

THIS work, somewhat preliminary in its nature, is the first step in our study of the relation between the emission and the absorption spectra of crystals. The emission spectra are to be obtained from a crystal whose absorption spectra are also available and the spectra are to be identified with a single rare earth at a time. Rare earths are known to fluoresce strongly in native calcium tungstate, scheelite, and in calcium molybdate, powellite, giving their characteristically sharp line spectra.[1]

Zambonini[2] has studied the miscibility of the crystals of the rare earth tungstates in the alkaline earth tungstates as well as the miscibility of the corresponding molybdates. The effect on the axial ratios of the pure substances was found to be:

CaWO₄	tetragonal c = 1.530
CaWO₄ with 10.3% Ce₂(WO₄)₃	tetragonal c = 1.532
CaMoO₄	tetragonal c = 1.551
CaMoO₄ with 39% De₂(MoO₄)₃	tetragonal c = 1.542
CaMoO₄ with 21% Ce₂(MoO₄)₃ 24.7%½(MoO₄)₃	tetragonal c = 1.544

A few percent of a rare earth are ample for obtaining absorption spectra from single crystals of such size as may be grown in the laboratory.

A similar example is fluorite, calcium fluoride, from which the very word fluorescence is derived. The emission spectra of fluorite as excited by light or cathode rays are rich in sharp lines which have been identified by Urbain[3] and others as due to the rare earth fluorides in solid solution.

As examples of the mixed crystals of these fluorides in calcium fluoride, the following may be taken :[4]

Yttrofluorite regular crystal contains about 15 percent fluorides of the rare earths.

Yttrocerite, presumably regular, contains about 25 percent rare earth fluorides.

Yttrocalcite hexagonal contains about 50 percent rare earth fluorides.

The hexagonal symmetry is characteristic of yttrium fluoride (tysonite) at room temperature.

We selected samarium as the rare earth in the hope of making contact with the recorded spectra of a number of its hydrated salts and with the energy levels which have been derived from them.

This communication deals with pure samarium tungstate $Sm_2(WO_4)_3$ and with pure samarium molybdate $Sm_2(MoO_4)_3$. Both of these salts were prepared from pure samarium oxide which Professor B. S. Hopkins of the University of Illinois was kind enough to supply us. The oxide was converted into the chloride by adding hydrochloric acid and evaporating to dryness. The chloride was dissolved in water and filtered through a sintered glass disk to remove dust and any other particles which might subsequently reduce the tungstate (or molybdate). The solution was diluted to a large volume and the percipitating agent (sodium tungstate or sodium molybdate) was added drop by drop and with constant stirring to minimize occlusion. The precipitates were white to a very pale yellow and very gelatinous. They were separated from the supernatant liquid by centrifuging and washed with water five to eight times by the

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[1] Ch. de Rohden, Ann. de Chimie IX **3**, 338 (1916).

[2] F. Zambonini, Bull. Soc. Fr. Min. **38**, 206 (1915), cited by A. N. Winchell in *Microscopic Characters of Artificial Minerals* (John Wiley and Sons, New York, 1931).

[3] G. Urbain, Comptes rendus **143**, 825 (1906).

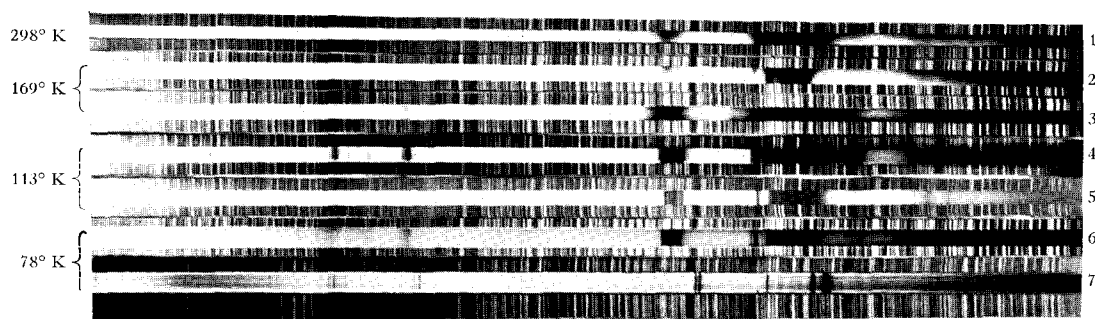[4] Doelter's *Handbuch der Mineralchemie*, Vol. 4.

FIG. 1. Absorption lines and bands of samarium tungstate. 1 to 6 inclusive are spectra of the tungstate at the temperatures marked at the left. 3 and 4 are prints which were overexposed in the blue to bring out the very faint structure in the red region. 7 is the absorption spectrum of hydrated samarium chloride at liquid nitrogen temperature.

FIG. 2. Absorption bands of samarium moybdate. 1, 2, 3 and 4 are the absorption spectra of the salt at the temperatures noted at the left. 5 is the absorption spectrum of hydrated samarium chloride at liquid nitrogen temperatures.

FIG. 3. B. Spectrum of samarium tungstate at the temperature of liquid nitrogen. A. Spectrum of samarium molybdate at the temperature of liquid nitrogen.

same method. The final filtrations were carried out through a sintered glass plate.

An enormous shrinkage in volume occurred when these hydrated solids were heated to dull redness. They were therefore "pre-shrunk" by heating for several hours at 900°C in an atmosphere of oxygen before they were put into the large furnace in which the crystal was to be grown. During this heating the color changed to a deeper yellow.

The furnace consisted of an alundum core wound with molybdenum wire. However, within this core a nonporous mullite cylinder closed at the bottom served to keep the hydrogen gas (which constituted the atmosphere surrounding the molybdenum heating element) from diffusing

into the region where the tungstate (molybdate) was being melted and crystallized. As a further precaution a stream of oxygen was directed just over the tungstate (molybdate) to insure that the salt remain in the oxidized state.

The crystals were grown from the molten state (1200° to 1300°C) by the method described by Kyropolous.[5]

The spectra were complicated by a phenomenon which may perhaps be thought of as a dissociation within the lattice, as a sort of dissociation of the salt into its basic and acidic oxides. This phenomenon showed itself more pronouncedly in the molybdate in that the color of the molybdate, a light yellow, darkened upon

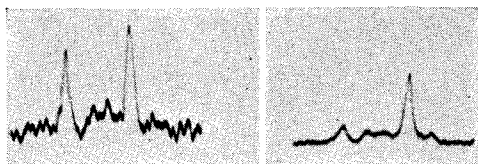[5] S. Kyropolous, Zeits. f. Physik **63**, 849 (1930).

FIG. 4. Microphotometer curves of the 4520A multiplet in $Sm_2(WO_4)_3$. Left, liquid N_2; right, liquid CH_4.

heating into a tan and on cooling the color paled again but not to such a degree as to end in the original yellow. The resulting heterogeneity within the lattice was brought out in the general diffuseness of the spectra of the molybdate as compared with sharper spectra of the tungstate and with the especially sharp spectra of the hydrated chloride. It was to be expected that any departure from regularity within the lattice would impress such a diffuseness on the spectrum of Sm^{+++} ions. The ions would not be in exactly equivalent situations in the lattice, the electrical fields to which an ion would be exposed would differ from ion to ion and correspondingly the energy levels or frequences would also differ slightly and since the spectrum registers the

absorption of all the ions traversed by the beam of light it would show closely neighboring frequencies, i.e., diffuse bands. We have not investigated this "dissociation" further. However, Jander[6] had come to consider the possibility of such a phenomenon in connection with the electrical conductivity of powders consisting of tungstates and also of molybdates of the alkaline earths. The fact that scheelite and powellite are known to contain more than the stoichiometrical amount of molybdic oxide confirms in some measure this point of view.

We shall postpone the detailed discussion of these spectra until we have studied the spectra by emission. For the moment, it may be pointed out again that the spectra of the tungstate, Fig. 1, are much sharper than those of the molybdate, Fig. 2. Fig. 3 permits the comparison of these spectra to be made more easily. Both spectra arising from crystals at 78°K are here reproduced. The tungstate ion and the molybdate ion begin with their own continuous absorption

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[6] W. Jander, Zeits. f. anorg. allgem. Chemie 192, 286, 295 (1930).

TABLE I. *Absorption lines and bands of samarium tungstate at 78°K. Intensity was estimated on a rough scale of 10 with very faint lines considered as 0. S (sharp), d (diffuse), b (broad) and vb (very broad) are used to indicate the character of the lines and edges. Primed values are band edges.*

WAVE-LENGTH	WAVE NUMBER	INTENSITY	WAVE-LENGTH	WAVE NUMBER	INTENSITY	WAVE-LENGTH	WAVE NUMBER	INTENSITY
5645.6	17,708.0	0s	4751.4	21,040.6	1vb*	4096.8	24,402.4	4s
5636.7	17,736.0	1s	4743.5	21,075.6	1vb*	4093.0	24,425.1 }	1sd
5311.6	18,821.5	1s	4736.3	21,107.5' }	2d	4091.4	24,434.6 }	6s
5306.3	18,840.3	2s	4721.2	21,172.2' }	2d	4090.1	24,442.4 }	6s
5020.6	19,912.4	5s	4715.5	21,200	0vb	4088.2	24,353.7 }	2d
5014.9	19,935.0	1sd	4657	21,467'	0d	4083.8	24,480.1	3s
5007.4	19,964.9	1sd	4652	21,490	0vb	4078.6	24,511.3	2vb
4992.3	20,025.3	0d	4639.6	21,547.5	5vb	4075.6	24,529.4' }	4d
4984.9	20,055.0	0d	4630.5	21,590'	1d	4072.5	24,548' }	2d
4920.7	20,316.7	2d	4530.4	22,066.9	5s	4064	24,599' }	2vd
4913.9	20,344.8	3s	4524.9	22,093.8	0s	4027	24,825' }	0vd
4909.8	20,361.8	3s	4520.8	22,113.8	0s	4019	24,875	0d**
4899.3	20,405.4	4sd	4514.8	22,143.2	3s	3998	25,005	0d
4891.7	20,437.1	4sd	4456.1	22,434.9	0b*	3994	25,031	0d
4885	20,465	0b	4417	22,633	vfvd*	3991.5	25,045' }	0d
4876.5	20,502	0b*	4411.5	22,662	vfvd*	3988	25,068' }	0d
4865.3	20,549.0	0vb	4405	22,690	vfvd*	3986	25,081' }	0d
4855.4	20,589.9	0b	4401	22,716	vfvd*	3980	25,118' }	0d
4842.2	20,646.0	0b	4206.5	23,766' }	10sd	3935	25,406	0d
4829	20,702 }	1b	4201.8	23,792.6' }	10sd	3931	25,430	0d
4821.6	20,734.2 }	4b	4200	23,803' }	8sd	3914	25,540	0d
4814.5	20,764.8 }	1b	4197	23,820' }	5sd	3911	25,559	0d
4806	20,801 }	2b	4195.6	23,827.8' }	5sd	3907	25,587	0d
4782	20,906	1vb*	4189.5	23,862.5' }	2d	3905	25,600	1d
4774.5	20,938	1vb*	4186.9	23,877.3	3vd	3897	25,648	0d
4766	20,976	1vb*	4184	23,894' }	2d	3799	26,310	***
4758.5	21,009	1vb*	4180.2	23,917' } }	10sd			

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* May be 2–3A wide.
** Region from this point to the blue is very faint and difficult to discern.
*** Transmission ceases.

TABLE II. *Absorption lines and bands of samarium tungstate at 113°K. Intensity was estimated on a rough scale of 10 with very faint lines considered as 0. (Some rather doubtful lines indicated by 00.) S (sharp), d (diffuse), b (broad), vb (very broad) are used to indicate the character of the lines and edges. Primed values are band edges.*

WAVE-LENGTH	WAVE NUMBER	INTENSITY	WAVE-LENGTH	WAVE NUMBER	INTENSITY	WAVE-LENGTH	WAVE NUMBER	INTENSITY
5646.3	17,705.8	00s	4805.1	20,805.4	2d	4199.9	23,803.4'	8s
5637.3	17,734.1	00s	4783.4	20,899.8'	2s	4197.6	23,816.5'	5s
5312.8	18,817.2	00s	4779.2	20,918.2'	2s	4196.0	23,825'	2s
5308.1	18,833.9	00s	4767	20,973	vbvf	4190.2	23,858.5'	2d
5020.6	19,912.4	1d	4751	21,042	vbvf	4187.3	23,875.0	0vd
4992.8	20,022.9	00d	4743	21,077	vbvf	4184.3	23,892.1'	2d
4984.1	20,058.2	00d	4736.0	21,109.0'	1d	4181.0	23,911.0'	7s
4921.1	20,315.0	00d	4720.3	21,179.2'	1d	4097.3	24,399.4'	5d
4914.0	20,344.4	3d	4715.5	21,201	0vd	4095.0	24,413.2'	5d
4910.2	20,360.1	2d	4657.2	21,466.1'	2d	4092.9	24,425.7'	8s
4899.5	20,404.6	1d	4649.2	21,503.1'	2d	4091.2	24,435.8'	3d
4892.0	20,435.8	1d	4645.1	21,522.1	2d	4090.8	24,438.2'	2d
4876	20,503	vbvf	4641.5	21,538.7'	3d	4089.6	24,445.4'	2d
4866	20,545	vbvf	4636.4	21,562.4'	5d	4089	24,450'	0d
4857	20,593	vbvf	4530.5	22,065.9	5s	4087.3	24,459.1'	8s
4843	20,643	vbvf	4524.9	22,093.7	0sd	4084.7	24,475.2'	5d
4831	20,690'	2d	4520.7	22,114.3	0sd	4082.2	24,489.7'	2d
4827	20,711'	2d	4514.9	22,142.7	1s	4079.8	24,504.1'	1d
4823.2	20,726.5'	2d	4419	22,623'	0d	4077.5	24,518'	0d
4820.4	20,739.4'	2d	4400	22,720'	0d	4076.8	24,522'	0d
4816.7	20,755.3'	2d	4207.2	23,762.1'	10s	4023.5	24,847'	0d
4811.1	20,779.0'	2d	4201.7	23,793.2'	8s	3998	25,007	vfvd

TABLE III. *Absorption bands of samarium molybdate at 78°K. Intensity was estimated on a rough scale of 10 with very faint lines considered as 0. S (sharp) and d (diffuse) are used to indicate the character of the edges.*

WAVE-LENGTH	WAVE NUMBER	INTENSITY	WAVE-LENGTH	WAVE NUMBER	INTENSITY	WAVE-LENGTH	WAVE NUMBER	INTENSITY
5635.8	17,739	2d	4913.3	20,347	8s	4656.6	21,460	0d
5624.9	17,773	2d	4904.8	20,382	8s	4645.9	21,518	0d
5304.4	18,847	3d	4822.0	20,733	0d	4634.2	21,573	1d
5292.5	18,889	3d	4792.7	20,859	0d	4622.6	21,627	1d
5019.7	19,916	1d	4773.1	20,945	1d	4523.1	22,103	*
5013.6	19,940	1d	4765.4	20,979	1d	4219.5	23,693	0d
5005.5	19,972	0d	4753.7	21,030	0d	4161.5	24,023	0d
5000.0	19,994	0d	4726.9	21,150	0d	4093.1	24,424	**

* The region around this value is very diffuse.
** Transmission ceases.

at about 3800A and 4100A, respectively. The two salts do not exhibit spectra of the same pattern although the supposed isomorphism of their crystals would lead to a close parallelism in their spectra. The spectra indicate then definitely that the molybdate and tungstate do not belong to the same crystallographic space group.

The tungstate gives evidence that a thermally excited state exists 76 cm⁻¹ removed from the basic state. Fig. 4 shows the relative intensities of two lines associated with this interval. The component of this pair toward smaller wavelengths becomes more intense as the temperature is lowered, a behavior in keeping with the presence of activated ions. To establish these activations beyond question, we plan on measuring the absorption spectrum at the temperature of liquid hydrogen. The long wave component should practically disappear since the number present in such an activated state at this temperature would be negligibly small.