[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, POLYTECHNIC INSTITUTE OF BROOKLYN]

The Preparation of Lanthanum Oxysulfide and its Properties as a Base Material for Phosphors Stimulated by Infrared[1]

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Some recent papers by Urbach[3] and Smith[4] have shown that infrared-stimulated phosphors can be produced by the activation of alkaline earth sulfides or selenides with the activator pairs, samarium and cerium or samarium and europium. G. R. Fonda[5] and Pearlman[5a] have shown that zinc sulfide activated with lead and copper also emits visible light when exposed to infrared radiation after previous excitation.

In the effort that was made to secure a greater variety of substances which would give rise to infrared phosphors upon activation, it was natural to turn to lanthanum sulfide.

Experimental

A solution of lanthanum nitrate was treated with hydrogen sulfide to precipitate some of the heavy metal impurities. The oxalate was then precipitated from acid solution, washed, dried and ignited to the oxide. The oxide was dissolved in sulfuric acid. From this solution the sulfate was crystallized or the carbonate was obtained by precipitation with ammonium carbonate which had been prepared by dissolving ammonia and carbon dioxide in distilled water. Lanthanum sulfide was prepared by heating the carbonate in carbon disulfide vapors or by heating the sulfate above 650° in hydrogen sulfide according to well established procedures.[6,7] The product is a yellow powder.

A wide variety of transition metals in the proportions usually employed in the activation of phosphors were added to the carbonate or sulfate prior to their conversion to the sulfide. None of the products was found to be an infrared sensitive phosphor.

When the reduction of an activated lanthanum sulfate sample was carried out with hydrogen, however, a white powder was obtained which could be excited with ultraviolet radiation and was stimulated to visible emission with infrared.

The white product contained 81.18% lanthanum and 9.48% sulfur corresponding closely to La_2O_2S. Several experiments were carried out to establish the mechanism by which this compound is formed.

Anhydrous lanthanum sulfate, according to Wohler and Grunzweig,[8] has an appreciable vapor pressure of sulfur trioxide at temperatures as low as 450°. Other sources[6,7] report the formation of a basic lanthanum sulfate, $La_2O_2SO_4$, when the normal sulfate is heated in air above 700°.

Hydrated lanthanum sulfate, prepared by crystallization from solution, was dried at 200° for twenty-four hours to give the anhydrous sulfate, $La_2(SO_4)_3$. Several samples were heated to constant weight in a tube furnace at 750° in a stream of dry oxygen-free nitrogen. The average weight loss was 29.52% while the theoretical loss in weight for conversion to $La_2O_2SO_4$ is 28.29%. Analysis of the products gave La 66.5%, SO_4 23.4%, which corresponds closely to $La_2O_2SO_4$: La 68.1%, SO_4 24.0%.

The basic sulfate was reduced by heating in a stream of dry hydrogen at 750° until constant weight was reached. The average weight loss of 15.3% is in fair agreement with the theoretical, 15.8%, for the conversion of the basic sulfate to La_2O_2S. By analysis, the products were shown to contain 81.18% lanthanum and 9.48% sulfur as compared to La_2O_2S: La 81.28%, S 9.36%.

When anhydrous lanthanum sulfate was heated above 800° in a stream of dry hydrogen about 39% decrease in weight occurred, as compared to a theoretical weight loss of 39.3% for the formation of La_2O_2S. The product was established as La_2O_2S by analysis.

It appears likely that the reaction proceeds first to give the basic sulfate which is then reduced to lanthanum oxysulfide.

An analogous series of reactions is thought to occur in the reduction of lanthanum selenite. The products, however, are easily oxidized in moist air and are nearly always contaminated with selenium. At 1000° the decomposition proceeds to give lanthanum oxide. A typical product, obtained by heating the selenite in dry nitrogen at 800°, was found to contain 65.3% lanthanum and 15.4% selenium, indicating partial decomposition to the oxide. Reduction of this material with hydrogen at 800° gives yellow-brown products which react with water to give hydrogen selenide. Some of the final products contained as little as 5% selenium.

Debye–Scherrer photographs were obtained for each of the sulfur compounds and for the product which was thought to contain lanthanum oxyselenite. The three principal lines are listed in Table I in order of decreasing intensity.

TABLE I

LATTICE SPACINGS FOR THE THREE MOST INTENSE X-RAY REFLECTIONS FOR SOME LANTHANUM COMPOUNDS

Compound	d., Å.		
$La_2(SO_4)_3$	4.90	2.83	2.88
$La_2O_2(SO_4)$	3.10	1.70	1.81
La_2O_2S	3.10	3.48	2.40
La_2S_3	3.55	2.64	2.56
$La_2O_2(SeO_3)$	3.88	2.90	2.65

Preparation of Lanthanum Oxysulfide Phosphors.—Solutions of those elements which usually behave as activators were added to lanthanum sulfate in such proportions that the lanthanum oxysulfide would contain 200 to 500 parts per million of the activator ions. A wide variety of pairs of activators was introduced in this way. The mixtures were evaporated to dryness and the impregnated sulfate was reduced at 800° to the oxysulfide. The products were tested by exposure, first to ultraviolet radiation from a Contiglo lamp and then to infrared. Many of the products exhibited fluorescence or phosphorescence but only a few were stimulated by infrared.

The pairs of activators found to give infrared-stimulated

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[3] F. Urbach, D. Pearlman and H. Hemmendinger, *J. Optical Soc. Am.*, **36**, 372 (1946).

[4] A. L. Smith, R. D. Rosenstein and R. Ward, THIS JOURNAL, **69**, 1725 (1947).

[5] G. R. Fonda, *J. Optical Soc. Am.*, **36**, 382 (1946).

[5a] D. Pearlman, J. Nail and F. Urbach, paper presented at the Conference on Luminescent Materials at Cornell University, Ithaca, N. Y., in October, 1946.

[6] Mellor, "Treatise on Inorganic and Theoretical Chemistry," Vol. 5, 648–652 (1924).

[7] Roscoe and Schorlemmer, "Treatise on Chemistry," Vol. 2, 788 (1923).

[8] L. Wohler and M. Grunzweig, *Ber.*, **46**, 1726 (1913).

phosphors are listed in approximate order of decreasing sensitivity in Table II.

TABLE II

ACTIVATORS WHICH GIVE INFRARED SENSITIVE PHOSPHORS WITH La_2O_2S

Activators		Color for phosphorescent and stimulated light
Pb	In	Green
Pb	Eu	Orange
Bi	Eu	Orange
Sm	Eu	Orange
Gd	Eu	Orange
In	Eu	Orange
Bi	In	Green

Indium and lead were tested using concentrations varying from 50 to 500 parts per million of lead and 50 to 2000 parts per million of indium. The most sensitive were those containing about 200 parts per million of lead to about 400 parts per million of indium. None of the phosphors was as sensitive as strontium sulfide activated with samarium and europium.

The lanthanum oxysulfide phosphors differ from those of the alkaline earth sulfides and selenides in that they do not appear to be affected adversely by grinding. On the other hand, no suitable flux was found for these phosphors. Several phosphates, fluorides, borates and sulfates were used but only to the detriment of the infrared sensitivity.

Summary

The preparation of a new compound, lanthanum oxysulfide, La_2O_2S, is described. It is apparently formed by the reduction of the oxysulfate, $La_2O_2SO_4$, which is produced by the thermal decomposition of $La_2(SO_4)_3$ above 700°. Lanthanum oxysulfide when activated with several pairs of elements is shown to give a phosphor which can be stimulated with infrared. The most outstanding activators found were lead–indium and lead–europium. The phosphors are excited by ultraviolet radiation.

Somewhat analogous reactions occur with lanthanum selenite but the decomposition tends to proceed to give lanthanum oxide.

Lattice spacings corresponding to the three most intense X-ray reflections are given for $La_2(SO_4)_3$, $La_2O_2SO_4$, La_2O_2S and $La_2O_2SeO_3$.

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A Comparison of the Abundance Ratios of the Isotopes of Terrestrial and of Meteoritic Iron[1]

BY GEORGE E. VALLEY AND HERBERT H. ANDERSON

The identity of elements occurring in meteorites with the same elements from terrestrial sources has been the subject of numerous investigations during the past thirty years.[2] Only with carbon have even slight differences been detected, but in this case the percentage difference between the masses of the isotopes is favorable for isotopic separation by physical means as well as by isotopic exchange. Even if it is assumed that the genesis of the elements in the solar system was the same throughout and if, as is generally supposed, most meteorites are of solar origin, it is an open question whether some may have arrived on the earth's surface from more distant sources, and consequently the component elements may be of different isotopic composition. Such a difference with elements of greater isotopic masses might well be due to differences in the conditions of genesis rather than to isotopic separation after formation.

Because iron occurs abundantly both on the earth and in meteorites, in this investigation we have compared the abundance ratios of the isotopes of iron from various terrestrial and meteoritic sources. Within the limit of accuracy of the method no differences were detected among the various specimens of material.

The known isotopes of iron have the mass numbers 54, 56, 57 and 58. The mass spectroscope used for the determination of abundance ratios was capable of detecting an ion present to the extent of about $^1/_{10000}$; hence it was necessary that the specimens of iron examined should be essentially free from every element which contains isotopes of these mass numbers or any multiple of them. Since nickel accompanies iron in meteorites the most important isotope from this standpoint is Ni^{58} which constitutes about 66.4% of nickel. The isotope Cr^{54} (2.3 per cent.) is obviously to be avoided, while Mn^{55} which falls between the two lower iron isotopes is objectionable.

Doubly charged ions of Cd^{108}, Cd^{112}, Cd^{114} and Cd^{116}, Sn^{114} and Sn^{116} and Pd^{108} all fall in close

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(1) This work was initiated and supervised by the Committee on Meteorites of Harvard University: G. P. Baxter (Chairman), K. T. Bainbridge, H. Berman (deceased), Francis Birch, A. B. Greninger, F. G. Watson. Financial aid was received from the Associates of Physical Science of Harvard University. The following results have already been reported briefly: Valley and Anderson, *Phys. Rev.*, **59**, 113 (1941).

(2) Below are references to the most recent results: Baxter and Hoover, *ibid.*, **34**, 1657 (1912); nickel: Baxter and Ishimaru, *ibid.*, **51**, 1729 (1929); cobalt: Baxter and Dorcas, *ibid.*, **46**, 357 (1924); chlorine: Harkins and Stone, *ibid.*, **48**, 938 (1926); silicon: Jaeger and Dijkstra. *Koninkl. Verslag. Akad. Wetenschappen Amsterdam*, **27**, 393 (1924); oxygen: Manian, Urey and Bleakney, THIS JOURNAL, **56**, 2601 (1934); carbon: Murphey and Nier, *Phys. Rev.*, **59**, 771 (1941); uranium: Schumb, Evans and Hastings, THIS JOURNAL, **61**, 3451 (1939); potassium: Schumb, Evans and Leaders, *ibid.*, **63**, 1203 (1941).