JOURNAL OF SOLID STATE CHEMISTRY 36, 324–330 (1981)

Synthesis of New Luminescent Materials Activated with Divalent Samarium*

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Received March 14, 1980; in revised form June 2, 1980

A simple technique for the preparation of powder compounds doped with divalent samarium is described. The reaction is carried out in nickel containers sealed in an inert atmosphere. The samarium impurity is introduced as samarium trifluoride SmF_3, and metallic samarium powder acts as the reducing agent to change Sm^{3+} into Sm^{2+}. Using this method, samarium has been stabilized in the divalent state in various fluorides: $KMgF_3$, $BaLiF_3$, BaY_2F_8, and KY_3F_{10}. The resulting compounds show under ultraviolet or visible excitation an intense luminescence in the red region characteristic of Sm^{2+}-doped materials. The emission and excitation spectra of these phosphors are presented and briefly discussed.

I. Introduction

Interest in divalent samarium (Sm^{2+})-doped materials was greatly enhanced after CaF_2:Sm^{2+} was proved to be a suitable system for lasing action (*1*). Single crystals of a large variety of hosts doped with divalent samarium were grown during the years 1960–1970 in view of obtaining either laser materials or samples suitable for fundamental optical studies. The alkaline earth fluorides MeF_2 (Me = Ca, Sr, Ba) first received particular attention, samarium trifluoride SmF_3 being the doping agent in this case. MeF_2:Sm^{2+} single crystals were first grown *in vacuo* according to the Bridgman method in graphite or molybdenum crucibles; graphite powder or metal filings were added to the batch to create reducing conditions needed to change Sm^{3+} into Sm^{2+} (*2, 3*). The Czochralski method and zone melting technique in an ambient inert gas freed of oxygen and water vapor were also used, the starting materials being carefully dried in an atmosphere of dry HF at 800°C before melting the ingot in the graphite crucible or carbon container (*4*). Later on, compounds which did not have the fluorite structure were investigated, such as the alkaline earth halides MeX_2 and halofluorides $MeXF$ (Me = Ca, Sr, Ba; X = Cl, Br) (*5, 6*), the perovskites ABF_3 (A = Na, K, Rb; B = Ca, Mg) (*6*), the alkali halides MeX (Me = Na, K, Rb; X = Cl, Br, I) (*7–10*) and the rare earth anhydrous chlorides (*11*). Single crystals of all these compounds were grown according to methods similar to those used in the case of the MeF_2 hosts; the rare earth impurity was introduced as a samarium salt adapted to the matrix, with purified hydrogen often acting as the reducing agent.

It should be noted now, (i) that the major-

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* This work was partly supported by DGRST Contract 797 0721.

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0022-4596/81/030324-07$02.00/0

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ity of Sm^{2+}-doped compounds known at this date have been prepared using growing techniques and, (ii) that few papers devoted to the synthesis of powder samples can be found. Sm^{2+}-doped materials, however, are generally observed to be efficient phosphors under ultraviolet or visible excitation and one can reasonably expect that their luminescent properties may be of some interest for industrial applications, in fluorescent lamps for example, where single crystals are not needed. In the framework of an exploration research program on Sm^{2+}-doped compounds, we have attempted to work out a simple and reliable method to prepare powder samples containing samarium in the divalent state as impurity. This method has been applied to the perovskite fluorides $KMgF_3$, $BaLiF_3$, BaY_2F_3, and KY_3F_{10}. These hosts have been chosen on account of their stability, their low melting point (our existing equipment being limited to 1200°C), and their capability to be doped by Sm^{2+} ions. Moreover, with the exception of $KMgF_3$, none of the compounds have been doped with divalent samarium up to now.

II. Preparation

1. Starting Materials

The simple fluorides LiF, KF, MgF_2, BaF_2, and YF_3 are commercial (Alfa Division or Merck) ultrapure fluorides. SmF_3 is a 4*N* fluoride kindly provided by Société Rhône-Poulenc Chimie Fine. The metallic samarium powder is a 40-mesh *m*3*N* Alfa Division product and the nickel containers are purchased at Weber Métaux.

2. Drying of the Reacting Products

As pointed out in Refs. (*4*) and (*6*), the starting materials have to be carefully dried and freed of surface oxide to prevent the formation of oxyfluorides (YOF and SmOF are especially stable) and the contamination with oxidizing reagents during the synthesis. In view of this, two methods are used.

(i) The simple fluorides including SmF_3 are finely powdered and combined with the proper stoichiometries. A few decigrams of the mixture are placed in a tungsten boat of dimensions $1 \times 1.5 \times 3$ cm³, a similar boat is filled with 1 to 5 g of NH_4HF_2 and the boats are both introduced in a nickel cylindrical demountable reactor (internal diameter: 28 mm, full length: 300 mm) equipped with a refrigerated monel valve. The reactor is first evacuated with a primary vacuum by means of a pump equipped with a liquid-nitrogen-cooled copper trap and progressively heated to about 350°C for 3 to 4 hr. The temperature is then slowly lowered to room temperature, the reactor is again evacuated and purged with pure argon, these two last steps being repeated two times. The reactor is then introduced in an argon-filled glovebox equipped with an evacuable air lock. The boat containing the reacting products is then recovered and stored in a dessicator over molecular sieves in the glovebox. This procedure, however, presents some disadvantages mainly due to the attack of the nickel reactor and tungsten boats by the hydrogen fluoride. Moreover, the presence of nickel fluoride and hydrogen fluoride in the dessicated products may be observed. Therefore, a more reliable procedure has been preferred.

(ii) A tungsten boat filled with a few decigrams of the mixture of the simple fluorides including SmF_3 (finely powdered and combined with the proper stoichiometries) is introduced in the nickel reactor which is evacuated with a vacuum in the range of 10^{-6} Torr. The reactor is then progressively heated to about 350°C for 3 to 4 hr (it is to be noted that heating to higher temperatures would favor the formation of oxyfluorides such as SmOF or YOF). The temperature is then slowly lowered to room temperature and the reactor is introduced in the air lock of the glovebox before being demounted in a pure argon atmosphere. The tungsten boat is then stored in the glovebox as in the above procedure.

3. Reduction of Samarium to the Divalent State

A few milligrams of metallic samarium powder is weighed in calibrated argon-filled ampoules and intimately mixed with the dessicated fluorides in the glovebox. A small nickel container (internal diameter: 2.1 mm, external diameter: 5.0 mm, full length: 100 mm) is filled with the mixture in the inert atmosphere of the glovebox. Before filling, this container has to be sealed at one end with an oxyacetylene torch, carefully freed from grease and dried under vacuum. The free end of the nickel tube is then closed and the tube is taken out of the glovebox to be sealed with the oxyacetylene torch without heating the part containing the reacting products. The container is then introduced into a horizontal Adamel T5HT furnace and subjected to the following thermal cycle. The temperature which is measured with a Pt to Pt–10% Rh thermocouple is raised at a rate of about 250°C/hr to a value slightly above that of the host-lattice melting point and stabilized for 5 hr before being lowered at a rate of 50°C/hr. The container is then cut open and the nickel particles possibly present in the powder compound are removed with a permanent magnet.

The undoped matrices are prepared in the same experimental conditions. Their melting point is determined by differential thermal analysis, and both doped and undoped materials are subjected to a radiocrystallographic analysis.

4. Initial Intended Stoichiometries

The Sm^{2+}-doped perovskite fluorides $BaLiF_3$, $KMgF_3$, BaY_2F_8, and KY_3F_{10} are prepared according to the stoichiometric equations of Table I. The starting materials are nominally depleted either in BaF_2 or KF with the aim of favoring the substitution at Ba^{2+} or K^+ sites, respectively. This choice appears to be particularly judicious for the BaY_2F_8 and KY_3F_{10} lattices, where the intended substitution may be expected to favor the change of Sm^{3+} to Sm^{2+}. As a matter of fact, it is clear that Sm^{3+} ions will have the tendency to enter these lattices at Y^{3+} sites and one can reasonably assume that the reduction to the divalent state will be less efficient at these sites than at divalent or monovalent sites. On the other hand, one can argue that Eu^{2+} has been observed to enter either the K^+ or Y^{3+} sublattices in KY_3F_{10} (*12*), but the situation is quite different in this case since the europium impurity is directly in-

TABLE I

STOICHIOMETRIC EQUATIONS[a, b]

$$[(1 - 3x)BaF_2 + 2xSmF_3 + LiF] + (x + \epsilon)Sm \rightarrow Ba_{(1-3x)}Sm_{3x}LiF_3$$
$$[(1 - 6x)KF + 2xSmF_3 + MgF_2] + (x + \epsilon)Sm \rightarrow K_{(1-6x)}Sm_{3x}MgF_3$$
$$[(1 - 3x)BaF_2 + 2xSmF_3 + 2YF_3] + (x + \epsilon)Sm \rightarrow Ba_{(1-3x)}Sm_{3x}Y_2F_8$$
$$[(1 - 6x)KF + 2xSmF_3 + 3YF_3] + (x + \epsilon)Sm \rightarrow K_{(1-6x)}Sm_{3x}Y_3F_{10}$$

[a] The quantities within the brackets correspond to the fluoride mixture submitted to the dessication procedure described in Section II.2.

[b] ϵ is the excess of metallic samarium powder introduced to favor the change of Sm^{3+} to Sm^{2+} and to compensate the effects of oxidizing reagents eventually present in the dessicated fluoride mixture.

troduced in the divalent state, as EuF_2. Most probably, Sm^{2+} ions cannot occupy the Li^+ or Mg^{2+} sites in $BaLiF_3$ and $KMgF_3$, respectively, on account of the size of these cations, but should be substituted for the larger Ba^{2+} or K^+ ions in these hosts. As a matter of fact, Eu^{2+}, whose ionic radius is close to that of Sm^{2+}, is observed to enter the monovalent rather than the divalent sublattice in $KMgF_3$ and $NaMgF_3$ (*13, 14*). Besides, it is to be noted that the probability of finding a F^- interstitial defect in a lattice as dense as $KMgF_3$ is low. Therefore, a K^+ vacancy is assumed to be created for compensating the charge defect due to the Sm^{2+} substitution at a monovalent site. The data concerning the compounds prepared according to the technique described in this work are presented in Table II.

III. Fluorescence

The compounds of Table II exhibit at room temperature an intense fluorescent emission in the red region, when irradiated with the beam of the high-pressure mercury lamp equipped with a Wood filter. We report here the results of a preliminary analysis of this emission.

1. Experimental Details

The powder samples are placed in a liquid nitrogen cryostat. The luminescence is analyzed through a Monospek 1000 Hilger and Watts scanning monochromator (linear dispersion in the first order: 0.8 nm/mm) the entrance- and output-slit width being set at 50 μm. A VJ 44 Sovirel filter is placed before the monochromator entrance slit to eliminate the ultraviolet radiations of the exciting lamp. The fluorescence signal is detected by an EMI 9658 R Peltier effect cooled photomultiplier and recorded after amplification. The excitation spectra of the observed emissions are recorded by using an iodine tungsten lamp, whose beam is focused onto the entrance slit of the scanning monochromator. The sample receives the output monochromatic beam and the resulting fluorescence signal is detected by the EMI photomultiplier equipped with a VR 67 Sovirel filter which eliminates the radiations at wavelengths lower than 670 nm.

2. Experimental Results

For the sake of clarity, the point symmetries of the cationic sites in the lattices under investigation are indicated in Table III.

The spectra of the fluorescent emission observed at 77 K in the $BaLiF_3$:0.015 Sm^{2+} and $KMgF_3$:0.03 Sm^{2+} compounds on one hand, and in the BaY_2F_8:0.015 Sm^{2+} and KY_3F_{10}:0.03 Sm^{2+} compounds on the other hand, are presented in Figs. 1 and 2, respectively. They exhibit groups of narrow

TABLE II

CHARACTERISTICS OF THE PREPARED COMPOUNDS

Compound	x	Measured melting point (°C)	Maximum temperature of the thermal cycle (°C)	Natural color of the powder sample
$Ba_{1-3x}Sm_{3x}LiF_3$	0.005	874	950	bluish white
$K_{1-6x}Sm_{3x}MgF_3$	0.010	1095	1100	pale yellow
$Ba_{1-3x}Sm_{3x}Y_2F_8$	0.005	1016	1060	rosy white
$K_{1-6x}Sm_{3x}Y_3F_{10}$	0.010	1000	1050	rosy white

TABLE III

CATIONIC SITE POINT SYMMETRIES

	Li^+	K^+	Mg^{2+}	Ba^{2+}	Y^{3+}
$BaLiF_3$	O_h			O_h	
$KMgF_3$		O_h	O_h		
BaY_2F_8				C_{2h}	C_2
KY_3F_{10}		T_d			C_{4v}

lines and no band is observed, even at room temperature. Generally speaking, three groups centered at about 680, 695, and 720 nm are of prominent intensity. They may be reasonably attributed to the Sm^{2+} $^5D_0 \rightarrow {}^7F_0$, $^5D_0 \rightarrow {}^7F_1$ and $^5D_0 \rightarrow {}^7F_2$ transitions, respectively.

The $^5D_0 \rightarrow {}^7F_1$ group is by far the most intense in $BaLiF_3$ (Fig. 1a) and is composed of a single sharp line at 693.76 nm. This result is in good agreement with the assumption of Sm^{2+} centers at the cubic Ba^{2+} sites in this lattice.

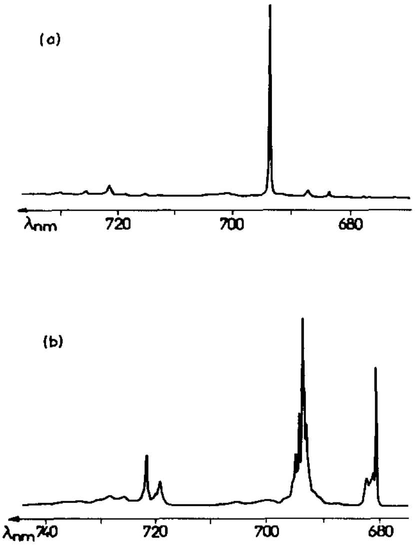

FIG. 1. $BaLiF_3$:0.015 Sm^{2+} (a) and $KMgF_3$:0.03 Sm^{2+} (b) emission spectra under ultraviolet excitation at 77 K (uncorrected for the photomultiplier response).

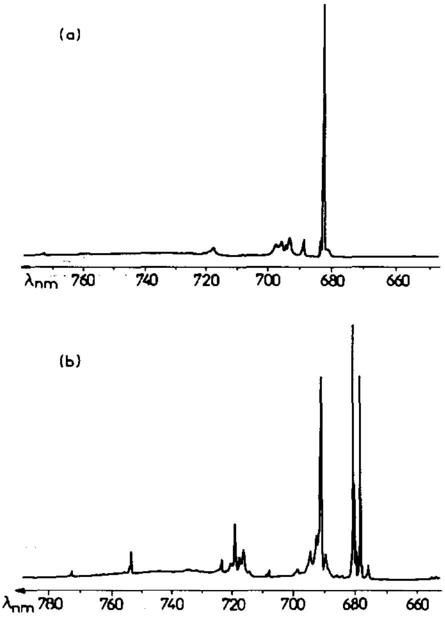

FIG. 2. BaY_2F_8:0.015 Sm^{2+} (a) and KY_3F_{10}:0.03 Sm^{2+} (b) emission spectra under ultraviolet excitation at 77 K (uncorrected for the photomultiplier response).

The $KMgF_3$:0.03 Sm^{2+} spectrum is quite similar to the Sm^{2+} fluorescence spectrum observed in $NaMgF_3$ and $RbMgF_3$ (*6*), which allows the three prominent groups shown in Fig. 1b to be attributed to transitions between the $^5D_0$ and $^7F_{0,1,2}$ multiplets of the Sm^{2+} $4f^6$ ground configuration. The $^5D_0 \rightarrow {}^7F_0$ transition appears to be of noticeable intensity and exhibits at least three components, a fact which reflects the presence of Sm^{2+} ions at inequivalent noncubic sites. This may be explained if the substitution is accompanied by the creation of charge-compensating defects which alter the initial cubic symmetry of the cationic sites in $KMgF_3$. Such defects occur only if Sm^{2+} substitutes for K^+. In fact, on the basis of our data, the possibility of a substitution at Mg^{2+} cubic sites cannot be excluded, but one can reasonably assume that this substitution is improbable on account of the size of the Mg^{2+} cation. It is to be pointed out that our data concerning the $KMgF_3$:Sm^{2+} system differ essentially from those recently published by Valyashko *et al.* (*15*). These authors observe at both room and liquid nitrogen temperatures a broad and intense band in the spectral range 620–760 nm, with a line structure superimposed on it. Recent experiments carried out in our laboratory on a $KMgF_3$:Sm^{2+} single crystal have corroborated our results with regard to the powder sample.

The $^5D_0 \rightarrow {}^7F_0$ group dominates in the BaY_2F_8:0.015 Sm^{2+} spectrum (Fig. 2a). This reflects the presence of Sm^{2+} ions at noncentrosymmetric centers in this compound. Thus, the possibility for the Sm^{2+} centers to occupy Y^{3+} sites may not be excluded.

The KY_3F_{10}:0.03 Sm^{2+} spectrum (Fig. 2b) is very similar to that of the $KMgF_3$:0.03 Sm^{2+} compound. However, it appears to be more intricate. Most probably, this complexity is connected with the possibility for Sm^{2+} to replace either K^+ or Y^{3+} ions, the substitution being accompanied in both cases by the creation of charge compensating defects.

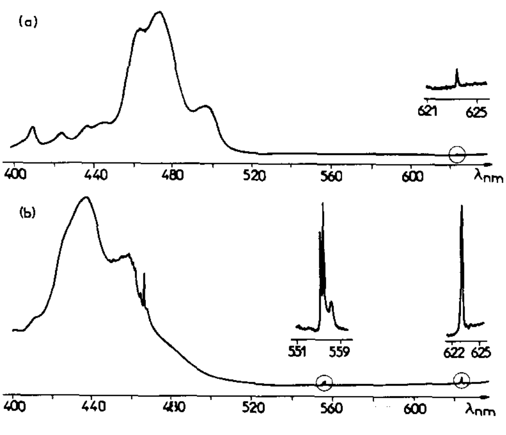

FIG. 3. Excitation spectra of the Sm^{2+} red fluorescent emission in $BaLiF_3$ (a) and $KMgF_3$ (b) at 77 K (uncorrected for the spectral distribution of the exciting source). The open circles and enlargements are related to $^7F_0 \rightarrow {}^5D_{1,2}$ lines.

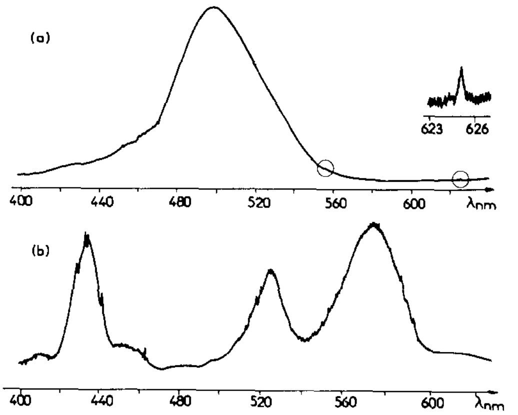

FIG. 4. Excitation spectra of the Sm^{2+} red fluorescent emission in BaY_2F_8 (a) and KY_3F_{10} (b) at 77 K (uncorrected for the spectral distribution of the exciting source). The open circles and enlargements are related to $^7F_0 \rightarrow {}^5D_{1,2}$ lines.

The excitation spectra of the fluorescent emissions observed at 77 K in the compounds under investigation are presented in Figs. 3 and 4. They exhibit intense broadbands which are characteristic of Sm^{2+} $^7F_0 \rightarrow 4f^5\text{–}5d$ electric-dipole-parity allowed transitions. Moreover, weak narrow lines occurring in the spectral ranges 620–630 and 550–560 nm undoubtedly originate from Sm^{2+} $^7F_0 \rightarrow {}^5D_1$ and $^7F_0 \rightarrow {}^5D_2$ transitions, respectively. The $^7F_0 \rightarrow {}^5D_2$ group does not appear in the $BaLiF_3$:0.015 Sm^{2+} spectrum (Fig. 3a), as expected for cubic Sm^{2+} centers. On the other hand, both $^7F_0 \rightarrow {}^5D_{1_{2+}}$ and $^7F_0 \rightarrow {}^5D_2$ groups are of noticeable intensity in the $KMgF_3$:0.03 Sm^{2+} spectrum (Fig. 3b), in agreement with the assumption of Sm^{2+} noncubic centers in this compound. These groups are also visible for the BaY_2F_8:0.015 Sm^{2+} compound (Fig. 4a) but quite missing in the KY_3F_{10}:0.03 Sm^{2+} spectrum (Fig. 4b). This last spectrum mainly exhibits three broadbands, the lower energy bands being shifted towards the red region, relative to the other spectra. To clarify this situation would require additional experiments which depart from the subject of the present paper.

In order to test the quality of the compounds prepared according to the technique described in this work, single crystals of $KMgF_3$:Sm^{2+} and KY_3F_{10}:Sm^{2+} have recently been grown by one of us at the laboratory of Professor Bill at Geneva. The preliminary studies carried out on these samples show that their luminescent properties are quite similar to those of the corresponding powder materials.

IV. Conclusion

We describe in the present paper a simple and reliable method for the preparation of powder fluoride materials doped with divalent samarium. This technique, which does not require any sophisticated equipment, has been applied with success to four perovskite fluorides, $BaLiF_3$, $KMgF_3$, BaY_2F_8, and KY_3F_{10}, three of them having never been activated with Sm^{2+} ions up to now. The evidence for the stabilization of samarium in the divalent state in these compounds is based on a brief analysis of their fluorescence properties. It is observed that the fluorescence originates mainly from the Sm^{2+} $^5D_0$ level even at low temperatures in all the compounds under investigation. The complexity of the $KMgF_3$:Sm^{2+}, BaY_2F_8:Sm^{2+}, and KY_3F_{10}:Sm^{2+} fluorescence spectra is assumed to be due to the multiple-center origin of the luminescence. More detailed investigations on the spectroscopic properties of the Sm^{2+} centers in these hosts are underway and will be presented later.

Acknowledgments

The authors would like to express their thanks to Professors J. Lucas and A. Védrine, and Dr. P. N. Yocom, for helpful discussions and suggestions. They are also greatly indebted to Professor H. Bill for his continued interest in this work.

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