fragment prefers to bind to the more electron-rich site. With **2**, the Cr(0) fragment was found to bind to both rings A and B with a ~2:1 preference for the *latter* ring. Binding to ring A was indicated by the presence of two doublets (6.5 and 5.7 ppm, $J = 6.2$ Hz) and a singlet (6.2 ppm) of equal intensities in the ^{1}H NMR spectrum. Binding to ring B was shown by the presence of a doublet (6.0 ppm, $J = 7.1$ Hz), a doublet of doublet (5.6 ppm, $J = 7.1, 6.1$ Hz), and a triplet (5.4 ppm, $J = 6.1$ Hz) in the intensity ratio of 2:2:1. Replacing **2** with **3a** and **3b**, which have electron-releasing alkyl groups on ring B, resulted in the formation of arene complexes in which the $Cr(CO)_3$ fragment was now bound to rings B and A in a 4:1 ratio. The preference of Cr(0) for ring B in compounds **2** and, especially, **3a,b** correlates well with the observation that the ^{1}H NMR resonances for the hydrogens on ring B occur upfield of ring A in the free ligand, indicating that the electron density in ring B is higher than in ring A. In compound **4**, ring C is the only arene ring lacking electron-withdrawing substituents and would be expected to be the preferred binding site. Indeed, the π-arene complex of ring C was the only Cr(0) complex isolated in the reaction of $Cr(CO)_3(MeCN)_3$ with **4**.

Finally, the amic acid functionality is often present in PI samples because of incomplete ring closure.[10] Thus, it was of interest to verify whether Cr(0) would form arene complexes even in the presence of such a reactive functionality. The product observed in the reaction of *excess* Cr(0) with **5** was a species in which one $Cr(CO)_3$ fragment was π-bound to each of the two rings A and B.

Although the π-arene complex was the only Cr-containing species isolated in the reactions described above, it was possible that other Cr species were also being formed but did not survive the workup and isolation procedures. To test this possibility, we monitored the progress of the reaction of $Cr(CO)_3(MeCN)_3$ with **3a** and **3b** by ^{1}H NMR spectroscopy using THF-d_8 as the solvent. However, except for the π-arene complexes, no other organometallic or organic species was detected.

The results of our study of the interaction of $Cr(CO)_3(MeCN)_3$ with compounds **1**–**5** lead to the following conclusions: (a) Cr(0) prefers to form π-arene complexes (even with electron-deficient arene rings) rather than react with oxygen functionalities, including the reactive carboxylic acid functionality; (b) the tendency to form a π-arene complex increases with increasing electron density on the ring. On the basis of these conclusions, it would appear that the *thermodynamically* preferred binding site for Cr(0) in PI is the ring derived from *p,p*′-oxydianiline rather than the anhydride ring or the oxygen functionalities. Note, however, that our study does not address the question of the relative *kinetic* accessibility of the different binding sites on PI. Thus, upon deposition on PI, the Cr atoms may well bind to the carbonyl groups on PI if these are more accessible from a kinetic standpoint. Our study does, however, indicate that if π-arene complexes are formed, these would be likely to involve the amine fragment rather than the anhydride ring.

Although our conclusions are derived from the study of (arene)$Cr(CO)_3$ complexes, there are no compelling reasons to believe that they would not be valid for other (arene)-Cr(0) species such as those which may form through the interaction of Cr atoms with PI.[11] Unlike Cr(0), Cu(0) does not form stable π-arene complexes,[12] and this may be one reason why the bonding between PI and Cr is significantly stronger than that between PI and Cu.

Acknowledgment. Support of this research by the U.S. Department of Energy, Office of Basic Energy Sciences (DE-FG02-84ER13295), is gratefully acknowledged.

Registry No. 1, 139-59-3; **2**, 85090-26-2; **3a**, 119596-19-9; **3b**, 119596-20-2; **4**, 119596-21-3; **5**, 119596-22-4; $Cr(CO)_3(MeCN)_3$, 16800-46-7; Cr, 7440-47-3; (pyromellitic dianhydride) (*p,p*′-oxydianiline) (copolymer), 25038-81-7; (pyromellitic dianhydride) (*p,p*′-oxydianiline) (SRU), 25036-53-7.

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The New Borate $Sr_3Sc(BO_3)_3$

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Received February 2, 1989

Energy efficiency has long been an important and critical issue in the development of the science and technology of solid-state lasers, particularly in high-power systems. Additional interest in efficiency and efficient crystalline laser materials has recently developed from the potential to realize new and improved laser characteristics in laser-pumped laser geometries. For example, new compounds doped with the ion Cr^{3+} are of particular interest as potentially efficient lasers for high-intensity pumping and ground-state depletion of Nd^{3+} and other laser crystals.[1]

We are involved in the systematic synthesis and study of new solid-state materials that will serve as hosts for the realization of small excited-state absorption cross sections when doped with the ion Cr^{3+}. Excited-state absorption has been reported to be the primary effect limiting the overall energy efficiency of several solid-state lasers operating from a d^3 transition-metal cation.[2,3] In this communication, we briefly describe our approach to synthesizing one class of these materials, complex scandium borates, presenting as an example the new compound $Sr_3Sc(BO_3)_3$.

The reported slope efficiency, 29%, of the laser material Cr^{3+}:$ScBO_3$[4] ranks fifth among all Cr^{3+} lasers, providing a performance that is better than would be predicted from consideration of the position (810 nm) of its maximum fluorescence intensity in the context of simple models of excited-state absorption for a d^3 cation.[1,2,5] Given the high efficiency of this material with what appear to be less than optimal optical features, it is likely that an even higher efficiency could be achieved if the characteristics of the

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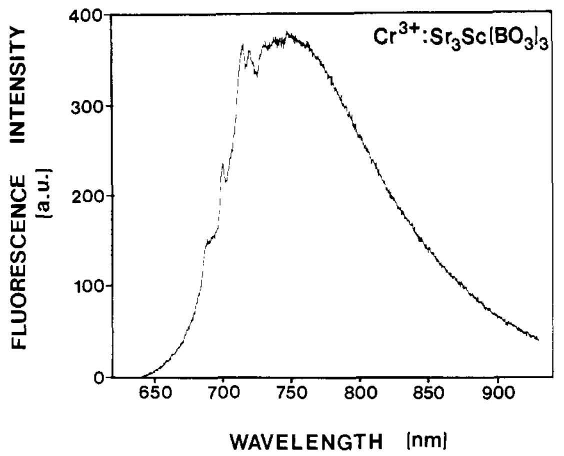

Figure 1. Luminescence spectrum of Cr^{3+}-doped $Sr_3Sc(BO_3)_3$ with excitation at 514.5 nm from an Ar laser. The fluorescence intensity is given in arbitrary units.

Table I. Positional Parameters and Equivalent Isotropic Thermal Coefficients for $Sr_3Sc(BO_3)_3$

atom	x	y	z	$B_{eq}{}^a$
Sr	0.04000 (2)	0.46988 (2)	0.30855 (2)	0.604 (7)
Sc(1)	0	0	1/2	0.42 (2)
Sc(2)	0	0	0	0.43 (2)
B	−0.1404 (2)	0.4702 (2)	0.0994 (3)	0.61 (7)
O(1)	0.0522 (2)	0.1644 (2)	0.3809 (2)	0.76 (5)
O(2)	−0.1779 (2)	0.3683 (2)	0.1934 (2)	0.71 (5)
O(3)	0.0046 (2)	0.2637 (2)	0.1865 (2)	0.78 (5)

$^a B_{eq} = (8\pi^2/3)\sum_i\sum_j U_{ij} a^*_i a^*_j \mathbf{a}_i\cdot\mathbf{a}_j$.

scandium borate host were improved. One such characteristic would be an increase in the crystal field at the Sc site to blue shift the luminescence band relative to that of the excited-state absorption band, thereby reducing their overlap.

We have realized the blue shift in new complex scandium borates containing basic cations. These cations increase the charge on the borate groups relative to those in the compound $ScBO_3$, affording a larger crystal field (more bonding electron density) at the Sc^{3+} (Cr^{3+}) center and the desired shift of the luminescence band.[6] The peak in the luminescence spectrum of the compound $Sr_3Sc(BO_3)_3$ doped to 2 mol % with the ion Cr^{3+} occurs at 750 nm (Figure 1), a blue shift of approximately 60 nm relative to that of $Cr^{3+}:ScBO_3$. This peak compares with the maxima, 775 and 875 nm, that we observe in the borates Cr^{3+}:$Sr_2ScLi(B_2O_5)_2$[7] and $Cr^{3+}:LaSc_3(BO_3)_4$,[8] respectively, and with the maxima near 750 nm reported for the efficient laser crystals $Cr^{3+}:LiCaAlF_6$[9] and $Cr^{3+}:Be_3Al_2(SiO_3)_6$.[10] We note the blue shift observed in the borates as the average electronegativity of the matrix decreases.

The title compound was identified from our analysis of phase equilibria in the system $SrO–Sc_2O_3–B_2O_3$. The single crystal used for the determination of the structure was grown from a melt of composition 40 mol % SrO, 10 mol % Sc_2O_3, 40 mol % B_2O_3, and 10 mol % Li_2O that was cooled from 1313 to 773 K at 6 K/h. Additional small single crystals grown by slowly cooling a stoichiometric melt from 1573 to 1273 K at 5 K/h exhibit identical lattice parameters. The powder sample used for the fluorescence measurement was prepared by heating a stoichiometric mixture of the reagents $Sr(NO_3)_2$ (99.99%, Aesar), $Sc_2(C_2O_4)_3\cdot 4H_2O$ (99.9%, Alfa), $Cr(NO_3)_3\cdot 8H_2O$ (99.99%, Aesar), and B_2O_3 (99.99%, Alfa) at 1223 K for 48 h to afford a nominal 2% doping level of the Cr^{3+} ion.

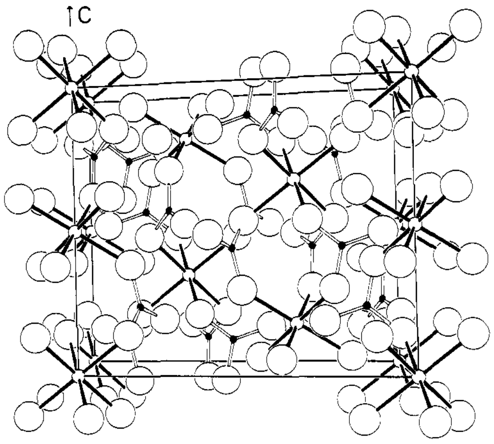

Figure 2. Drawing of the scandium borate framework of the compound $Sr_3Sc(BO_3)_3$. The small filled circles represent B atoms, and the large open circles represent O atoms. Sc–O interactions are indicated by shaded bonds. The Sr atoms have been removed for clarity.

The new compound crystallizes as a unique structure in a high-symmetry, trigonal space group.[11] Atomic parameters are listed in Table I, and the scandium borate framework is sketched in Figure 2. The structure is comprised of triangular BO_3 groups, two crystallographically independent Sc atoms occupying distorted octahedra, and a Sr atom residing in an irregular nine-coordinate site. Unlike the structures of a large number of simple orthoborates that adopt structures similar to calcite and dolomite with discrete layers of BO_3 groups interleaved by cations, the present material exhibits a greater isotropic arrangement of the atoms. In particular, it may be noted that the principal atomic planes of the BO_3 groups are aligned approximately parallel to the 3-fold, c axis. The interatomic distances Sc(1)–O(1), 2.077 (2) Å, and Sc(2)–O(2), 2.142 (2) Å, compare to the value, 2.1200 (4) Å, observed in the compound $ScBO_3$.[12] The small trigonal distortions of the octahedra are demonstrated by the angles O(1)–Sc(1)–O(1), 94.83 (6)°, and O(2)–Sc(2)–O(2), 92.29 (7)°. The distances Sr–O range from 2.500 (2) to 2.857 (2) Å.

Since the material is composed of basic oxides (SrO, Sc_2O_3) and a weakly acidic oxide (B_2O_3), the melt of the material is anticipated to be reasonably stable; differential thermal analysis data indicate that the compound melts at 1262 (7) °C. Additional syntheses have revealed that a variety of elements may be stoichiometrically substituted in place of the Sr and Sc atoms. Discussions of structures and results of experiments on the crystal growth and optical characterization of members of this new family of oxides will appear in future articles.

Acknowledgment. This research was supported by the

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US Department of Energy and Lawrence Livermore Laboratory under Contract No. 2143103. The X-ray diffractometer was purchased with funds provided by the US National Science Foundation and by donors of the Foursight! program administered by the Oregon State University Foundation.

Reviews

New Luminescent Materials

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Received March 8, 1989

Recent developments in the field of luminescent materials are reviewed. The role of luminescent rare-earth-metal ions has become predominant. Nevertheless certain classic topics, like Cr^{3+} luminescence and CdS luminescence, reappear, although in a different form. Attention is paid to luminescent materials for lighting, X-ray (storage) phosphors, scintillator crystals, Cr^{3+}-containing crystals and glasses, cryptates for medical diagnostics, and small semiconductor particles.

Introduction

Luminescent materials have a long history, in which chemistry plays an important role. Frequently new materials turn up that sometimes lead to important breakthroughs. Of current interest are the following groups of luminescent materials: phosphors for luminescent lighting,[1] where the classic halophosphate is replaced by mixtures of rare-earth-metal activated phosphors; X-ray phosphors for X-ray intensifying screens;[2] X-ray storage phosphors for digital radiography;[3] broad-band emitting crystals for use in tunable lasers; luminescent glasses and glass ceramics for lasers, fiber optics, solar concentrators, and lighting;[4,5] electroluminescent thin films;[6] cathode-ray phosphors that can withstand high excitation density (projection television);[7] scintillator materials;[7] the use of luminescent lanthanide ions as a probe for the structure of biological macromolecules.[8]

Research of luminescent materials has several aspects. There is, for example, the influence of sample preparation on the luminescence properties. Some materials are required in the form of large crystals of high quality, others in the form of powders with specific requirements on particle size distribution and morphology. Additionally, insight into the physics of the luminescence properties is required to obtain optimum properties in a controllable way. A special aspect is the way in which the luminescence properties depend on the chemical composition of the material.[7,9]

In this review we consider important developments in the field of luminescent materials during the past decade and wish to demonstrate that the study of luminescent materials is still challenging in spite of its long history. Some of these developments were possible because of a sufficient knowledge of the physics of the luminescent processes involved, while some appeared as surprises. In all cases the influence of chemical composition appeared to be of large importance.

Luminescent Materials for Lighting

Phosphors applied in luminescent lighting are excited by the short-wavelength ultraviolet radiation of a low-pressure mercury discharge (mainly 254 nm), which they convert into white light. Until 1975 the phosphor $Ca_5(PO_4)_3(F,Cl):Sb^{3+},Mn^{2+}$ (calcium halophosphate) was used. The UV radiation is absorbed by the Sb^{3+} ion and is reemitted as blue radiation. Those Sb^{3+} ions that are near to a Mn^{2+} ion transfer the excitation energy to Mn^{2+}, which emits yellow radiation. The color of the luminescence can be varied by varying the Mn^{2+} concentration. Roughly speaking, the more blue-emitting lamps give a higher light output, but the more yellow-emitting ones a better color rendering.[10]

In passing we note a recent study on the Sb^{3+} ion in halophosphate that shows that its luminescence is governed by the Jahn–Teller effect.[11]

In the early 1970s it was shown that the combination of three phosphors with narrow emission lines centered around 450, 550, and 610 nm, results in luminescent lamps that combine a high light output with a good color rendering.[12] Such luminescent materials can be realized by

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