in the region of a 50‰ mixture of ZnS and ZnO. Outside the region of a 50:50 mixture the films are amorphous, but they become more crystalline as the stoichiometry approaches either of the pure compounds. The films do not exhibit very bright cathodoluminescence but are of interest as phosphor host materials. As the amount of sulfur increases in the films, the intensity of the red peak decreases and then increases again, following the crystallinity of the film. Resistivity measurements confirm anomalous behavior in the mixed films, possibly associated with amorphous/crystalline phase change.

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Registry No. ZnO, 1314-13-2; Si, 7440-21-3; $ZnO_{0.05-0.99}S_{0.01-0.95}$, 142395-69-5.

Synthesis and Luminescence Properties of $BaNbOF_5$ with Isolated $[NbOF_5]^{2-}$ Octahedra

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$BaNbOF_5$ has been prepared and characterized by X-ray powder diffraction. It crystallizes in the low-temperature cubic $KSbF_6$ structure with lattice constant $a = 9.893$ Å. Weak reflections in the powder diffraction pattern indicate a deviation from the space group $Ia\bar{3}$, assigned to $KSbF_6$. We comment on the structure of $BaNbOF_5$ and propose $Pa\bar{3}$ as the alternative space group. Efficient blue luminescence is observed for $BaNbOF_5$ and is attributed to the high-energy position of the lowest absorption band. Comparison of luminescence properties is made with those reported for other isolated niobate octahedra.

Introduction

Examples of efficient luminescence from structurally isolated niobate octahedral groups in the literature is rare. Recently, Blasse and Dirksen[1] studied the luminescence of $MgNb_2(P_2O_7)_3$, a compound with no correlation between the niobate octahedra. Their results indicated a low quantum efficiency of luminescence even at 4.2 K. The absence of luminescence from ordered perovskites containing isolated niobium octahedra such as La_2LiNbO_6, $SrLaMgNbO_6$, and Ba_2YNbO_6 was also noted in ref 1. Furthermore, the reasons for efficient luminescence from condensed niobate octahedra and its absence in isolated niobate octahedron has been discussed by Blasse.[2,3] In contrast to these works, we have recently described the efficient room-temperature luminescence of Cs_2NbOF_5, which does contain discrete $[NbOF_5]^{-2}$ octahedral groups.[4] We accounted for its behavior using the single configuration coordinate model for luminescence. There it was shown that small Stokes shifts should not be the only indicator of efficient luminescence for a structurally isolated system, but the excitation energy of the lowest electronic absorption band needs to be considered as well. When a high-energy excitation is present, it is possible to have a large Stokes shift in conjunction with efficient room-temperature luminescence. These conditions could be met in other compounds having isolated oxofluoroniobate octahedra. This possibility initiated our search for structures which could contain such species to determine whether their luminescent properties would be similar to those of Cs_2NbOF_5.

The low-temperature structure of the fluoride $KSbF_6$ has been described in the literature.[5] It also contains isolated MX_6 octahedra with the K^+ ion also in an octahedral 6-coordination. The compound $BaNbOF_5$ could be derived from $KSbF_6$ by making the following substitution:

$$K^+ + Sb^{5+} + F^- \rightarrow Ba^{2+} + Nb^{5+} + O^{2-}$$

Thus, the MX_6 octahedra would then be of the stoichiometry $NbOF_5^{2-}$, identical to that in Cs_2NbOF_5, so that $BaNbOF_5$ would be an excellent candidate for our luminescence search.

Experimental Section

$BaNbOF_5$ was prepared via the dispersion of 0.01 mol of BaF_2 and 0.005 mol of Nb_2O_5 in 500 mL of 25% HF–75% H_2O at 95 °C in a PTFE beaker. The solution was allowed to evaporate to dryness after which an additional 500 mL of acid solution was added and reevaporated. The acid additions were continued until the X-ray diffraction pattern indicated a single phase. The production of a single phase was also indicated by a uniform blue luminescence from the dry product when irradiated with short-wavelength UV light.

A second method of preparation began with the preparation of a mixed phase oxide precursor followed by treating with the HF/H_2O solution. In this method 0.01 mol of $BaCO_3$ was mixed with 0.005 mol of Nb_2O_5 and placed in an alumina crucible. The mixture was then heated to 1100 °C for 12 h and then air quenched. The resulting solid mass ground and refired to 1100 °C for 4 h. After requenching and regrinding, the colorless oxide powder was dispersed in 500 mL of 25% HF–75% H_2O and processed as before. No differences in either the structure or luminescence were seen between samples prepared by these two methods. All materials used are of the highest purity available, ≥99.99%.

Room-temperature X-ray powder diffraction patterns were obtained with a Philips D500 diffractometer calibrated before and after each measurement with pure Silicon. Nominal scan rate of $^1/_4$° 2θ/min were employed. Refined cell dimensions were obtained by least-squares procedures using a local computer program.

Luminescence excitation and emission spectra were measured at room temperature with a Spex Fluorolog II System, yielding automatically corrected spectra, i.e., the excitation spectra have

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(1) Blasse, G.; Dirksen, G. J. *Inorg. Chim. Acta* **1989**, *157*, 141.
(2) Blasse, G. *J. Chem. Phys.* **1968**, *48*, 3108.
(3) Blasse, G.; Bril, A. *J. Phys. Chem.* (*Munich*) **1968**, *57*, 187.
(4) Srivastava, A. M.; Ackerman, J. F. *Mater. Res. Bull.* **1991**, *26*, 443.
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Table I. X-ray Diffraction Pattern of $BaNbOF_5$

d	*I*	*hkl*	*d*	*I*	*hkl*
4.9143	1.3	200	1.7217	1.8	441
4.4031	5.6	210	1.6938	1.4	530
4.0282	0.7	211	1.6478	2.3	600
3.4838	100	220	1.6259	1.4	610
3.2876	5.4	300	1.5632	13.7	620
2.9662	1.0	311	1.5451	5.9	540
2.7360	1.2	320	1.5451	2.4	541
2.6356	1.4	321	1.5267	2.7	630
2.4693	17.9	400	1.4743	2.2	700
2.2523	5.2	331	1.4143	0.6	550
2.2096	14.6	420	1.3975	0.5	711
2.1566	9.5	421	1.3874	2.5	640
2.0171	52.8	422	1.3715	18.7	642
1.9758	3.6	500	1.2675	1.1	650
1.9396	2.4	510	1.2368	1.6	800
1.8362	6.3	520	1.2280	1.7	810
1.8057	1.2	521	1.2193	0.8	811
1.7477	11.7	440	1.1665	5.5	660

been corrected for the variation in Xe lamp intensity and the emission spectra were corrected for the response of the photomultiplier tube. Instrumental limitations would not permit accurate excitation below 250 nm. The relative energy emitted per unit energy, ϕ, is obtained from the relative energy emitted per unit wavelength according to the procedure described by Curie and Prener.[6]

The density of $BaNbOF_5$ was measured using a Quantachrome stereopycnometer. Samples were degassed to 10^{-4} atm prior to exposure to the displacement gas. In all cases, pure helium was used as the displacement medium.

Results and Discussion

Structural Considerations. Powder X-ray diffraction patterns of $BaNbOF_5$ could be indexed on a cubic cell with lattice constant $a = 9.893 \pm 0.003$ Å (Table I). The absence of any other phase ensures that in this cubic material, the barium to niobium ratio, [Ba]/[Nb], is 1. The synthetic conditions are such that only a fluoride or oxofluoride phase may account for this compound. The possible stoichiometries are $BaNbF_7$, $BaNbOF_5$, $BaNbO_2F_3$, and $BaNbO_3F$. The calculated densities for these stoichiometries with the observed cell dimensions are 4.98, 4.68, 4.37, and 4.08 g/cm^3, respectively. The observed density of 4.71 g/cm^3 indicates that the $BaNbOF_5$ stoichiometry is correct.

There are several known cubic phases with the ABX_6 composition, viz., $NaSbF_6$, low-temperature $KSbF_6$, and undistorted $NaSb(OH)_6$. The similarity of B metal/A metal radius ratios and the near equivalence of the lattice dimensions suggests that the structure of $BaNbOF_5$ is related to that of $KSbF_6$, which is shown in Figure 1. This structure is derived from [CsCl] by placing $[SbF_6]^-$ octahedra on the Cl^- sites and K^+ in the Cs^+ sites. The $[SbF_6]^-$ octahedra are then rotated such that a 6-fold coordination of the potassium occurs. Thus, the resulting structure contains isolated $[SbF_6]^-$ octahedra interspaced by potassium ions. As previously indicated, for $BaNbOF_5$ the $[NbOF_5]^{2-}$ is substituted for $[SbF_6]^-$ and barium is substituted for potassium. However, during this substitution, there is a change in the space group. Many very weak systematic reflections for $BaNbOF_5$ are inconsistent for the body centered cell, $Ia\bar{3}$, of $KSbF_6$ which suggests that the true space group is $Pa\bar{3}$. This space group would result if there were small orientation differences along the $\bar{3}$ axis of $[NbOF_5]^{2-}$ octahedra at 0,0,0 and those at $^1/_2,^1/_2,^1/_2$, as indicated by the arrows in Figure 1. Unfortunately, an accurate structure investigation is precluded by the inability to grow large crystals. Attempts to produce this material by high-temperature techniques led to the growth of crystals of a hexagonal form of $BaNbOF_5$, which is presently under investigation.

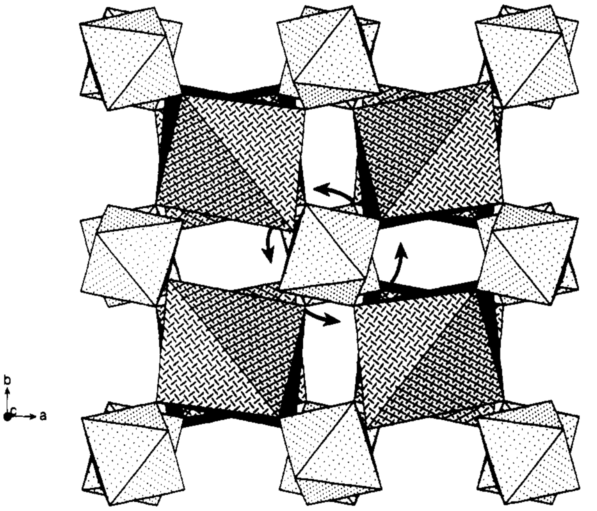

Figure 1. Proposed structure of $BaNbOF_5$; dotted octahedra contain the niobium; cross-hatched octahedra contain the barium ions. Arrows show the rotations needed to change the I-centered lattice of $KSbF_6$ to the primitive lattice of $BaNbOF_5$.

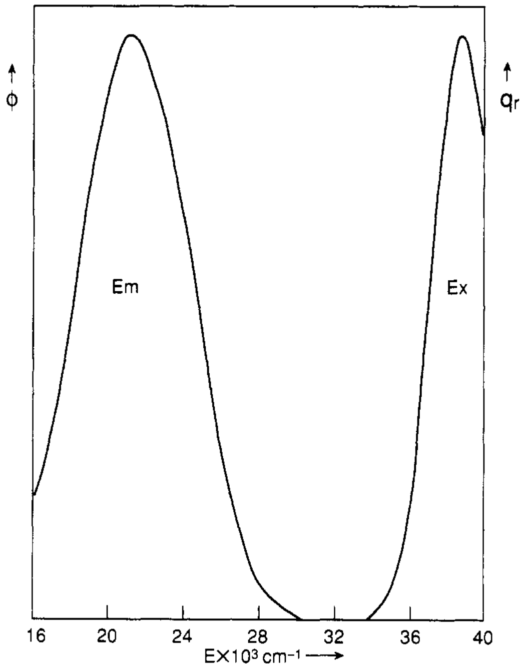

Figure 2. Excitation (Ex, right side) and emission (Em, left side) of $BaNbOF_5$ at room temperature.

Luminescence of $BaNbOF_5$. The compound $BaNbOF_5$ exhibits a blue luminescence when excited by short-wavelength UV radiation. Room-temperature excitation and emission spectra are exhibited in Figure 2. The emission consists of a broad band with maximum at 2.65 eV (21 400 cm^{-1}); the corresponding excitation maximum is situated at roughly 4.82 eV (38 800 cm^{-1}). The Stokes shift of emission is large, 2.17 eV ($\sim$17 400 cm^{-1}), and is comparable to the value of 2.1 eV for Cs_2NbOF_5, 2.2 eV for α-$NbPO_5$,[5] and 2.27 eV for $CsNbOP_2O_5$.[6] The large Stokes shift for the emission indicates the absence of energy transfer between the niobate octahedra, i.e., the spectral overlap between the excitation and emission bands is negligible. Because of the structural isolation of $[NbOF_5]^{2-}$, there will be an absence of appreciable cat-

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[6] Curie, D.; Prener, J. S. *Physics and Chemistry of II-VI Compounds*; Aven, M., Prener, J. S., Eds.; North Holland: Amsterdam, 1967.

Table II. Luminescence Properties of Isolated Niobate Octahedral Complexes

compound	excitation maxima (eV)	emission maxima (eV)	stokes shift (eV)	efficiency	ref
Cs_2NbOF_5[a]	4.7	2.6	2.1	high	1
$BaNbOF_5$[a]	4.82	2.65	2.17	high	this work
α-$NbPO_5$[b]	4.7	2.5	2.2	high at low temp	5
$CsNbOP_2O_5$[b]	4.96	2.69	2.27	high	6
$MgNb_2(P_2O_7)_3$[b]	4.1	2.6	1.5	low	7

[a] Room-temperature data. [b] Liquid helium data.

ion–anion wave function overlap which leads to a broad anionic valence band and broad cationic conduction band extending throughout the crystals. Therefore, luminescence, quenched by electronic delocalization via band formation, as in the cases of β-$NbPO_5$[7] β-$LaNb_3O_9$,[8] and Ba_2WO_5,[9] is clearly impossible. Thus, absorption and emission thus occur on one and only one $[NbOF_5]^{2-}$ complex. The charge transfer transitions within the $[NbOF_5]$ complexes are the lowest energy electronic absorptions and are therefore responsible for its luminescent properties. In view of the high electronegativity of the fluoride ligands (and subsequent deep UV charge-transfer absorption) the observed charge transfer transitions must be localized within the Nb–O bonds. This is similar to the observations in Cs_2NbOF_5, $Cs_2WO_2F_4$,[10] and $K_2NaTiOF_5$;[11] the latter two containing discrete $[WO_2F_4]^{2-}$ and $[TiOF_5]^{3-}$ groups, respectively.

In Table II, we have gathered data regarding the luminescence properties of structurally isolated niobate octahedral group where a strong similarity between the luminescence properties of the oxofluoroniobates and those of α-$NbPO_5$[7] and $CsNbOP_2O_5$[12] is indicated. We have argued that the observed luminescence of Cs_2NbOF_5 and $BaNbOF_5$ are due to charge-transfer transitions within the NbO groups of the $[NbOF_5]^{2-}$ complexes. The crystal structures of $CsNbOP_2O_7$ and α-$NbPO_5$ indicate octahedral oxygen coordination of the Nb^{5+} ions with one exceptionally short Nb–O bond. For $CsNbOP_2O_7$, this particular oxygen belongs only to the NbO_6 octahedron and is not part of a PO_4 tetrahedron. The resulting NbO group is referred to as a niobyl group. Therefore, since the other five oxygen–metal bonds are further stabilized by sharing oxygen electron density with phosphorus, the niobyl groups will be the least stable of the niobium–oxygen bonds. It is therefore expected that the lowest energy excitations will be localized within the short Nb–O bonds. A similar situation exists in α-$NbPO_5$. Hence, the lowest energetic electronic transitions of Cs_2NbOF_5, $BaNbOF_5$, and $CsNbOP_2O_5$ and α-$NbPO_5$ are expected to be localized within the NbO groups, with a similarity in their optical data which is observed experimentally.

Finally, note in Table II that the Stokes shift of niobium pyrophosphate ($MgNb_2(P_2O_7)_3$) is smaller than that of the oxofluorides. This, in terms of configuration coordinate model, should usually lead to higher quenching temperature which is certainly not the case. The position of the lowest absorption band for the phosphate is, however, at lower energies when compared with the oxofluoroniobates. The benefit of a higher energy position for the absorption then clearly outweighs the benefits of a smaller Stokes shift of emission, since the former condition should also yield high quenching temperatures of luminescence in terms of the single configuration coordinate model. Thus, in $BaNbOF_5$, an excitation energy of 4.82 eV is sufficiently high that a large Stokes shift and efficient luminescence can be simultaneously generated.

Conclusions

We have synthesized and studied the luminescence properties of a new oxofluoroniobate $BaNbOF_5$. Efficient luminescence in spite of the large Stokes shift of emission (2.17 eV) is attributed to the high-energy position of the absorption band. It is further shown that electronic delocalization of excitation energy via band formation is clearly impossible in this material. The presence of highly electronegative F^- ions restrict the charge-transfer transitions to Nb–O bonds within the $[NbOF_5]^{2-}$ complexes. Thus, the luminescence of $BaNbOF_5$ is very similar to that observed for Cs_2NbOF_5, $CsNbOP_2O_7$, and α-$NbPO_5$.

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