

Solid State Chemistry of Polytungstic (Polymolybdic) Acids and Their Salts. III. Effects of Dopant M' ($M' = \text{Si, Ge, Sn, Pb}$), Hydration, and Reduction on the Photoluminescence of $\text{Na}_5\text{Eu}(\text{MoO}_4)_4$

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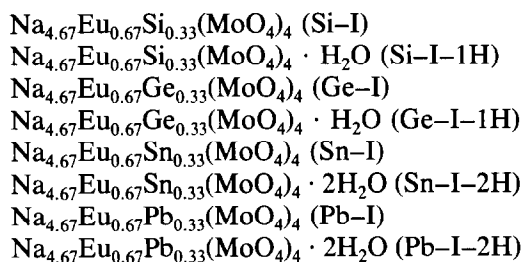
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Doping $\text{Na}_5\text{Eu}(\text{MoO}_4)_4$, which has a scheelite structure, results in an intensity increase of the intrinsic photoluminescence. In the emission spectra an extra emission peak appears in the narrow range of 616.2–616.5 nm throughout the Si–Ge–Sn–Pb dopant series. The increasing intensity of intrinsic photoluminescence seems to be connected to the covalent bonding strength of Si–O, Ge–O, Sn–O, Pb–O. The appearance or disappearance of an extra peak may be explained in terms of a symmetry change of a local site of the Eu(III) ion. The emission intensity of $\text{Na}_{4.67}\text{Eu}_{0.67}M'_{0.33}(\text{MoO}_4)_4 \cdot y\text{H}_2\text{O}$ ($y = 1, 1, 2, 2$ for $M' = \text{Si, Ge, Sn, Pb}$, respectively) is lower than that of their corresponding anhydrous phosphors. This may be explained in terms of the vibrational frequencies and the low valent state of the chemical bonds. © 1990 Academic Press, Inc.

1. Introduction

Huang *et al.* (1, 2) have done considerable research on the luminescence and the calculations of crystal field parameters of undoped $\text{Na}_5\text{Eu}(\text{MO}_4)_4$ ($M = \text{Mo, W}$). Pan *et al.* recently have engaged in the growth of the single crystals of $\text{Na}_5\text{Eu}(\text{WO}_4)_4$ (3, 4). The present author noted the drastic effect of silicon on the luminescence of $\text{Na}_5\text{Eu}(\text{WO}_4)_4$ as we increased the purity of the tungstosilicic acid prepared by us for fluorescent purity (5). It therefore seemed of interest to study the doped systems. In this present paper, the effects of doping, hydration, reduction, and oxidation on the luminescence of the doped- M' ($M' = \text{Si, Ge, Sn, Pb}$) $\text{Na}_5\text{Eu}(\text{MoO}_4)_4$ (I) and their hy-

drates, and an investigation dealing with the appearance of the extra emission peaks in the $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition, are reported. The following compounds were studied:



2. Experimental

2.1 Reagents and Their Purities

The purity of the reagents used in this work are 99.95–100.5% for Na_2CO_3 , 99.99% for Eu_2O_3 , grade 1 for MoO_3 and PbO_2 ,

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99.999% for SiO₂, GeO₂, and SnO₂, and AR for H₂O₂.

2.2 Preparation

The anhydrous phosphors, Na_{5-x}Eu_{1-x}M'_x(MoO₄)₄ (M' = Si, Ge, Ge, Pb) were prepared by thoroughly mixing the reagents in an agate mortar in appropriate stoichiometric ratios and heating them in an alumina crucible in air at 500–600°C. The reaction temperature depended on the *x* value in Na_{5-x}Eu_{1-x}M'_x(MoO₄)₄ and on the choice of dopant. Between successive heatings the products were reground in the mortar. All compounds were routinely checked by X-ray diffraction analysis (Philips powder diffractometer, Cu_α radiation) and appeared to be free of other phases.

2.3 Spectroscopic Measurements

The photoluminescence properties were measured with a Spex spectrometer (Model 1401) under excitation with an argon-ion laser (λ_{ex} = 488 nm) at room temperature (RT). The relative emission intensity (*I*_{rel}) of the parent salt I, prepared at 560°C, is set at 1.00 as the reference for all luminescence measurements in this work.

3. Results and Discussion

3.1 Principal Differences of Emission Spectra of I from Those of Si-I, Ge-I, Sn-I, and Pb-I

The emission spectra of I and Si-I consists principally of the emission from the ⁵D₀ level. Under excitation with an argon ion laser at 488 nm, it was possible to observe two well-resolved transitions, from ⁵D₁ and ⁵D₂ (Table I), having a reasonable intensity, whereas no emission lines from ⁵D₃ or ⁵D₄ levels were recorded. For the whole dopant series, the following results were obtained from these spectra reproduced in Figs. 1 to 4.

(1) Under favorable conditions of the

TABLE I
PART OF THE LUMINESCENCE SPECTRA (505–657 nm)
OF I AND Si-I AT λ_{ex} = 488 nm AND AT RT

Transition	I			Si-I		
	(Å)	<i>E</i> (cm ⁻¹)	<i>I</i> _{rel}	(Å)	<i>E</i> (cm ⁻¹)	<i>I</i> _{rel}
⁵ D ₂ → ⁷ F ₃	5051	19,798	15	5066	19,739	30
	5083	19,673	20	5075	19,704	45
	5092	18,639	80	5084	19,670	100
	5105	19,589	100	5096	19,623	95
	5123	19,520	10	5119	19,593	10
	5141	19,452	10	5135	19,474	<10
⁵ D ₁ → ⁷ F ₀	5261	19,008	<10			
⁵ D ₁ → ⁷ F ₁	5361	18,653	80	5381	18,584	65
	5379	18,591	100	5404	18,505	100
	5397	18,529	80	5430	18,416	75
⁵ D ₁ → ⁷ F ₂	5487	18,225	20	5508	18,155	15
	5532	18,077	85	5574	17,940	85
	5564	17,973	100	5587	17,899	100
	5591	17,886	80	5613	17,816	85
	5747	17,400	25	5635	17,746	40
	5760	17,358	40	5691	17,572	20
				5709	17,516	15
				5739	17,425	25
				5754	17,319	75
⁵ D ₁ → ⁷ F ₃	5800	17,241	20	5820	17,282	60
	5860	17,065	80	5878	17,013	<5
	5878	17,013	95	5911	16,918	<5
	5887	16,978	100	5922	16,886	100
⁵ D ₀ → ⁷ F ₁	5945	16,821	70	5967	16,759	75
	5962	16,773	100	5983	16,714	100
	5986	16,705	65			
⁵ D ₀ → ⁷ F ₂	6006	16,650	<10	6006	16,650	<10
	608	16,434	<10	6075	16,461	10
	6106	16,377	<10	6098	16,399	<10
	6145	16,273	50	6137	16,295	90
	6187	16,163	100	6163	16,226	100
				6179	16,184	95
⁵ D ₁ → ⁷ F ₄	6253	15,992	<5	6261	15,972	<5
⁵ D ₀ → ⁷ F ₃	6465	15,468	35	6459	15,482	10
	6517	15,345	40	6500	15,385	25
	6542	15,286	100	6536	15,300	30
				6554	15,258	35
				6568	15,225	100

preparation of I doped with SiO₂, GeO₂, SnO₂, or PbO₂, the *I*_{rel} of doped phosphor was higher than that of undoped phosphor. This was particularly true for SiO₂ doping where the intensity was doubled (Fig. 1).

(2) In running through the dopant series from Si to Pb, an extra emission peak (indicated by an arrow in Fig. 2) in the narrow range of 616.2–616.5 nm in the ⁵D₀ → ⁷F₂ transition, was observed. The ⁵D₀ → ⁷F_{0,2,4}

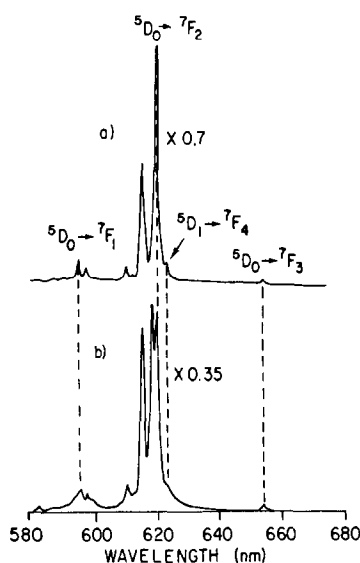


FIG. 1. Part of the emission spectra of I (a) and Si-I (b) at $\lambda_{\text{ex}} = 488 \text{ nm}$ and RT.

emissions are, essentially, purely electric dipole in character, and their intensities are very sensitive to the local site symmetry of the Eu(III) ions (6). These extra peaks usually originate in the $^5D_0 \rightarrow ^7F_2$ transition, because the emission intensity is strongest in $\text{Na}_5\text{Eu}(\text{MO}_4)_4$ ($M = \text{Mo}, \text{W}$) which has the scheelite structure. The above symmetry was probably greatly altered even with a slight change of the dopant species and concentration and with the sample preparation temperature. For example, I_{rel} for the extra peak at the concentration $x_{\text{Si}} = 0.33$ in I was higher than that for $x_{\text{Si}} = 0.2$ and 0.4 (Fig. 3). The Sn-I prepared at 590°C exhibited an obvious extra peak (Fig. 4a). After it was hydrated at 50°C , to become the Sn-I-2H, this material still retained the extra peak (Figs. 4b and 4c), whereas the peak disappeared after it was dehydrated at $460\text{--}470^\circ\text{C}$ (Fig. 4d).

(3) The energy distribution of the spectra in the $^5D_0 \rightarrow ^7F_2$ transition was changed due to the appearance of the extra emission peak. For example, the height of the

shorter wavelength peak is usually about half that of the main peak (at longer wavelength) (Figs. 1a and 4d). Its half-width was increased as the extra peak appeared; thus I_{rel} increased about 20% compared to that of samples where no extra peak appeared.

(4) The individual wavelength magnitude of $^5D_0 \rightarrow ^7F_{1,2,3}$ and $^5D_1 \rightarrow ^7F_{0,1,2,3,4}$ transitions for I was not the same as for Si-I. For example, the emission wavelength of Si-I shifted to a longer wavelength at an average of 20 \AA per emission line in the above-mentioned transitions as compared with I. In addition, the Si-I has more (36) spectral lines than I (32) between 505 and 657 nm (Table I).

The compounds of composition $\text{Na}_5\text{RE}(\text{MO}_4)_4$ (RE = rare earth series including

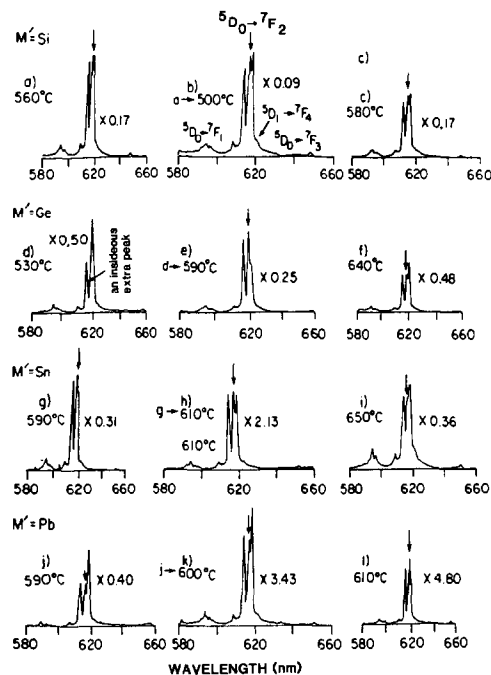


FIG. 2. Dependence on the temperature and dopant species of the extra emission peaks (indicated by an arrow) of Si-I, Ge-I, Sn-I, Pb-I at $\lambda_{\text{ex}} = 488 \text{ nm}$ and RT.

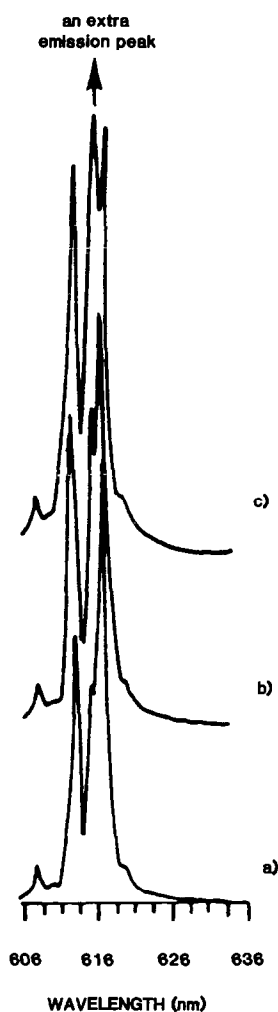
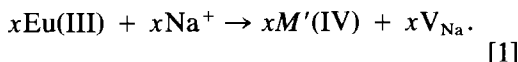


FIG. 3. Part of the emission spectra of $\text{Na}_{5-x}\text{Eu}_{1-x}\text{Srx}(\text{MoO}_4)_4$ for $x = 2$ (a), 0.4 (b), 0.33 (c) at $\lambda_{\text{ex}} = 488 \text{ nm}$ and RT.

Y; $M = \text{Mo}, \text{W}$) have the scheelite structure (7). Our experiments showed that the doped- $M'\text{O}_2$ ($M' = \text{Si}, \text{Ge}, \text{Sn}, \text{Pb}$) I also belonged to the above structure. The coordination of oxygen atoms in $\text{Na}_5\text{RE}(\text{MoO}_4)_4$ is given in Fig. 5 (7).

A trivalent RE ion was replaced by a $M'(\text{IV})$ ion (8) when $M'\text{O}_2$ was introduced in $\text{Na}_5\text{Eu}(\text{MoO}_4)_4$ with simultaneous formation of a sodium vacancy (9):



One site of NaI type (Fig. 5) is not occupied by a sodium ion but may become part of a larger unit cell. However, the tetravalent ion $M'(\text{IV})$ exhibited the tendency to form a smaller unit cell and to strengthen the covalent bonding in passing from Pb–O to Si–O (see below). Thus the net result produced a contraction in the dimension of the unit cell (9). This may decrease the distance between the Eu(III) ion and MoO_4^{2-} group and thus promote the transfer of energy to the luminescence center, i.e., to the Eu(III) ions. The effect of varying the vacancy concentration in the oxygen sublattice of compounds which have a scheelite structure was recently studied by Grasser *et al.* (10).

In addition, the formation of the $M' \text{--} \text{O}$ covalent bond in $\text{Na}_{5-x}\text{Eu}_{1-x}M'_x(\text{MoO}_4)_4$ led to a redistribution of the electronic cloud of

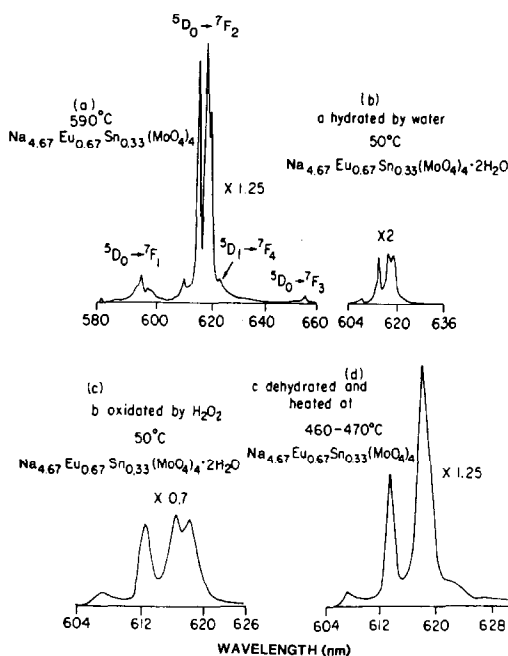


FIG. 4. Part of the emission spectra of Sn-I (a, d) and Sn-I-2H (b, c) prepared under different conditions, at $\lambda_{\text{ex}} = 488 \text{ nm}$ and RT.

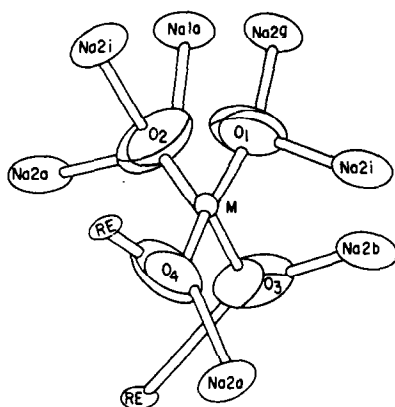


FIG. 5. Coordination of oxygen atoms in the $\text{Na}_5\text{RE}(\text{MoO}_4)_4$ (RE = rare earth elements and yttrium, M = Mo, W) structure (after Ref. (7)).

the luminescence center associated with the Eu(III) ion. Also, the point symmetry of the Eu(III) ion changed at the local site from that present at a normal lattice site. This tendency of increasing lattice symmetry decreased with increasing of atomic number Z of Si, Ge, Sn, Pb. It also correlates with the tendency for a decrease of covalent bonding strength from Si–O to Pb–O (11). It is interesting to note that the bonding strength of B–O ($193.5 \pm 2.6 \text{ D}_{298}^0/\text{kcal mol}^{-1}$) is slightly larger than that of Si–O ($192.7 \pm 1.2 \text{ D}_{298}^0/\text{kcal mol}^{-1}$), the I_{rel} of $\text{Na}_5\text{Eu}_{0.67}\text{B}_{0.33}(\text{MoO}_4)_4$ also was slightly higher than for Si–I.

However, as Huang *et al.* (2) already showed, it is difficult to determine completely the origin of the extra lines. Some of them are vibronic in nature and others are electronic in origin. The Eu(III) ion site symmetry change even occurred during variations incurred by modifying the temperature, dopant concentration, hydration, reduction, or oxidation, which were sufficient to cause the lines to appear or disappear.

3.2 Optimum Concentration of Dopant

As already stated, doped- SiO_2 , GeO_2 , SnO_2 , or PbO_2 I exhibited a higher I_{rel} than

I. However, every dopant has to have an optimum concentration for I. For example, the I_{rel} of sample with $x_{\text{Si}} = 0.33$, e.g., Si–I, was higher than that of the $x_{\text{Si}} = 0.0, 0.2, 0.4, 0.6$, and 0.8 (Fig. 6). Thus, the choice of $x_{\text{Si}} = 0.33$ represents an optimum concentration. This situation arises because the density of luminescence centers, the Eu(III) ions, is relatively small for $x_{\text{Si}} > 0.33$, while the influence of doped SiO_2 on I was very weak for $x_{\text{Si}} < 0.33$.

3.3 Photoluminescence of S–I–1H, Ge–I–1H, Sn–I–2H, and Pb–I–2H

The I_{rel} of all hydrates *b*, *c* (Table II, *b* and *c*) was lower than that of their corresponding original anhydrides *a* (see Footnote [1] in Table II). The I_{rel} of *a* is not given in Table II). The I_{rel} of treated anhydrate *d* from which anhydrides were obtained after the hydration and dehydration (see Footnote [1] in Table II) was also lower than that of original anhydrate *a*. In addition, the distribution of the spectral energy changed greatly due to the existence of the water of crystallization (Fig. 4). It seems that coordination by one (Si–I–1H, Ge–I–1H) or two

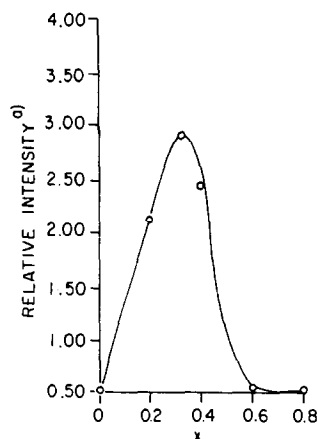


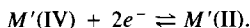
FIG. 6. The effect of x value in $\text{Na}_{5-x}\text{Eu}_{1-x}\text{Si}_x(\text{MoO}_4)_4$ (Si–I) on the I_{rel} of the emission peak at wavelength range of 614–619 nm under $\lambda_{\text{ex}} = 488 \text{ nm}$ and RT.

TABLE II

THE I_{rel} OF THE MAIN PEAK OF Si-I, Ge-I, Sn-I, Pb-I, AND THEIR HYDRATES DEPENDS ON THE MOLES OF WATER (y ; IN PARENTHESES) AND THE STANDARD REDUCTION POTENTIAL (V)

Phosphor	I_{rel}			V e
	b [1]	c	d	
Si-I	0.76 (1)	0.77 (1)	0.85 (0)	-0.86 [2]
Ge-I	0.48 (1)	0.56 (1)	0.59 (0)	-0.00
Sn-I	0.22 (2)	0.42 (2)	0.48 (0)	0.145
Pb-I	0.05 (2)	0.54 (2)	0.58 (0)	0.28

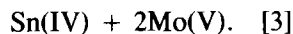
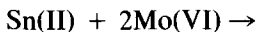
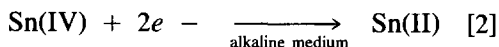
After John A. Dean, *Handbook of Chemistry*, Tables 6-11, 1979. The reaction:



[1] $a \rightarrow b \rightarrow c \rightarrow d$, e.g., an anhydrous phosphor a prepared at 590°C $\xrightarrow[50^\circ\text{C}]{\text{hydration}}$ hydrous phosphor b $\xrightarrow[460-470^\circ\text{C}]{\text{dehydration and heating}}$ anhydrous phosphor d .

[2] The -0.86 V is for the reaction $\text{SiO}_2 + 4\text{H}^+ \rightleftharpoons \text{Si} + 2\text{H}_2\text{O}$.

(Si-I-2H, Pb-I-2H) water molecules in b and c is not sufficient to quench the $^5\text{D}_0$ transition and to change the distribution of the spectral energy. However, (i) the water molecule with high vibrational frequencies in comparison to the Si-O, Ge-O, Sn-O, Pb-O, Eu-O, or even Mo-O were related directly to the Eu(III) ion or MoO_4^{2-} group. Haas and Stein (12) already pointed out the very low efficiency for the Eu(III) emission in aqueous solution, which they attributed to high-energy OH vibrations of water, which is one prominent example of many rapid radiationless deactivations. (ii) The low valence states were formed by the process of the hydration of some doped- $M'\text{O}_2$. I. The reduction mechanisms of the Sn(Pb) (IV)-Mo(VI) system was probably as follows:



The luminescence of the quenching by the low valence Mo(V) can probably be explained by assuming a charge-transfer state Sn(Pb)(II)-Mo(VI) with a large offset in the configuration coordinate model.

We speculated why the I_{rel} values (Table II, b) of these hydrates decreased drastically with the increasing atomic number Z of the Si-Ge-Sn-Pb series. This can be correlated with the observation of the molybdenum blue color (increasing the deep of blue color from doped- SiO_2 to PbO_2) and the fact that the I_{rel} values (Table II, c) obviously increased for $M' = \text{Sn}$ and Pb after oxidation with hydrogen peroxide. This change also is consistent with the standard reduction potential (Table II, e).

It should be pointed out that, after these hydrous phosphors c (Table II, c) were dehydrated and heated at $460-470^\circ\text{C}$ to form the anhydrous phosphors d (Table II, d), their I_{rel} values slightly increased by comparison with phosphors c . But the I_{rel} of d do not completely recover the original magnitudes of a . This suggests that the hydration and reduction are unfavorable processes with respect to the application doped- $M'\text{I}$ ($M' = \text{Si, Ge, Sn, Pb}$) as luminescent materials.

By contrast, Clery *et al.* (13) showed that when the pyridine containing a small amount of water is intercalated into $\text{Cd}_2\text{P}_2\text{S}_6$, the photoluminescence intensity increased approximately tenfold. The water in $\text{Cd}_2\text{P}_2\text{S}_6$ (layered structure) exhibits weak van der Waals-type bonding, whereas the water in b and c (scheelite structure) forms a strong covalent bond.

References

1. J. HUANG, J. LORIER, P. PORCHER, G. T. DE SAGEY, P. CARO, AND C. LEVY CLEMENT, *J. Less-Common Met.* **94**, 251 (1983).

2. J. HUANG, J. LORIER, P. PORCHER, G. T. DE SAGEY, P. CARO, AND C. LEVY CLEMENT, *J. Chem. Phys.* **80**, 6024 (1984).
3. J. PAN, L.-Z. YAO, L.-G. CHEN, G.-I. ZHOU, AND G. I. ZHAU, *J. Synth. Cryst.* **16**, 15 (1987).
4. J. PAN, L.-Z. YAU, L.-G. CHEN, G.-I. ZHAU, AND C. X. GUO, *J. Lumin.* **40/41**, 856 (1988).
5. L.-G. CHEN, Y.-I. LIU, AND Y.-Z. CHEN, *J. Solid State Chem.* **68**, 128 (1987).
6. A. F. KIRBY, D. FOSTER, AND F. S. RICHARDSON, *Chem. Phys. Lett.* **95**, 507 (1983).
7. V. A. EFREMOV, V. K. TRUNOV, AND T. A. BEREZINA, *Sov. Phys. Crystallogr.* **27**, 77 (1982).
8. L.-G. CHEN, G.-I. ZHOU, AND H. WANG, unpublished results.
9. V. K. TRUNOV, T. A. BEREZINA, A. A. EVDOKIMOV, V. K. ISHUNNINE, AND V. G. KRONGAUZ, *Zh. Neorg. Khim.* **23**, 2645 (1978).
10. R. GRASSER, A. SCHARMANN, AND J. STÖDE, *J. Cryst. Latt. Def. Amorph.* **17**, 105 (1987).
11. F. A. COTTON AND G. WILKINSON, "Advanced Inorganic Chemistry," 4th ed., p. 374, Wiley, New York (1980).
12. Y. HAAS AND G. STEIN, *Chem. Phys. Lett.* **75**, 366 (1971).
13. D. A. CLERY, A. H. FRANCIS, AND E. LIFSHITZ, *J. Lumin.* **35**, 163 (1986).