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Authors

Porter-Chapman, Yetta D.
Bourret-Courchesne, Edith E.
Derenzo, Stephen E.

Publication Date

2007-01-18

Peer reviewed

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Bi³⁺ Luminescence in ABiO₂Cl (A = Sr, Ba) and BaBiO₂Br

Yetta Porter-Chapman^a, Edith Bourret-Courchesne^b, Stephen E. Derenzo^{a,*}

^aDepartment of Functional Imaging, Life Sciences Division

^bMaterials Science Division

Ernest Orlando Lawrence Berkeley National Laboratory,
One Cyclotron Rd, Berkeley CA 94720

*Corresponding author:

(510) 486-4097

Fax: (510) 486-4768

sederenzo@lbl.gov

(Stephen E. Derenzo)

Keyword: scintillator, phosphor, emission, radioluminescence, photoluminescence, bismuth

Abstract

Trivalent bismuth luminescence is reported in three Sillen bismuth oxyhalide phases, SrBiO₂Cl, BaBiO₂Cl, and BaBiO₂Br. These compounds exhibit Bi 6s6p → 6s² emission under UV and X-ray radiation. At room temperature, BaBiO₂Cl shows the most intense light emission, with spectral and decay properties similar to those found in Bi₄Ge₃O₁₂ (BGO). At low temperatures, each phase show an increase in the photoluminescence intensities and a narrowing of the emission peaks. In contrast to the temperature dependence of BGO, X-ray excited luminescence intensities of all three phases remain relatively constant throughout the temperature range 10 – 295 K. This result indicates that the Sillen phases undergo less thermal quenching than BGO. The low temperature and room temperature radio-luminescence decay times were determined from pulsed x-ray measurements. At room temperature, SrBiO₂Cl exhibits faster decays than BGO, while, BaBiO₂Cl and BaBiO₂Br have decay times similar to BGO.

1. Introduction

Trivalent bismuth cations in inorganic compounds or hosts commonly exhibit interesting luminescence properties originating from the excitation and relaxation of its $6s^2$ inert lone pair electrons[1-7]. In this regard, an investigation of compounds containing Bi^{3+} has great potential towards the discovery of new intrinsically luminescent materials. We present three bismuth oxyhalide phases, SrBiO_2Cl , BaBiO_2Cl , and BaBiO_2Br , that exhibit such Bi^{3+} luminescence. In general, the Sillen bismuth oxyhalide phases ($\text{ABi}^{3+}\text{O}_2\text{X}$, where A = divalent cation and X = Cl, Br, I) have garnered significant attention with interests centered around their catalytic properties[8, 9] and interesting crystal structures[10-15]. This work introduces photo- and radio-luminescence properties of these three members of the Sillen bismuth oxyhalide family. Their luminescence properties are compared to $\text{Bi}_4\text{Ge}_3\text{O}_{12}$ (BGO), an important material with electro-optic[16, 17], nonlinear optic[18], and scintillation[2, 7] capabilities. The preparation, photoluminescence, and time resolved x-ray luminescence of these compounds are detailed in this report.

2. Experimental

The oxychlorides, SrBiO_2Cl and BaBiO_2Cl , were synthesized from 1:1 molar ratios of the corresponding alkali earth carbonate, SrCO_3 (99.999 %, Strem) or BaCO_3 (99.8 %, Alfa Aesar) and BiOCl (99.999 %, Alfa Aesar). BaBiO_2Br was synthesized from 3:1:1 molar ratio of BaCO_3 , Bi_2O_3 (99.999 %, Strem), and BiBr_3 (98+ %, Strem). For each sample, the reactant powders were thoroughly ground together into a

homogeneous mixture using a mortar and pestle, transferred to an alumina boat, and subsequently heated in air at 800 °C for 10 hours in a tube furnace. White (SrBiO₂Cl and BaBiO₂Cl) or light yellow (BaBiO₂Br) polycrystalline powders were obtained from these reactions.

Crystal phase identifications were performed on a Siemens D500 powder X-ray diffractometer using 1.540510 Å Cu K α radiation, a range of 10 – 50° (2 θ), a scan interval of 0.09° /step, and a step rate of 1° /sec. All luminescence measurements were conducted on samples consisting of 5 – 20 μ m sized particles contained in quartz cuvettes. Low temperature (10 – 250 K) and room temperature (295 K) photo- and radio-luminescence spectra were measured for each Sillen phase, along with a standard Bi₄Ge₃O₁₂ (BGO) sample. Photoluminescence excitation and emission spectra were collected on a Horiba Fluorolog 3 fluorescence spectrometer within the spectral range of 250 nm – 800 nm using excitation and emission slit widths of 3 nm. Each excitation spectrum was taken while observing emission at the predetermined emission wavelength maxima, and likewise, the emission spectra was taken while exciting at the sample's excitation wavelength maxima. Radio-luminescence decay measurements were performed utilizing an in-house pulsed X-ray system that produces 80 ps (fwhm) pulses of X-rays having a mean energy of 18 keV. Fluorescent photons from the sample are detected by a microchannel phototube with 35 ps (fwhm) response [19]. The luminescence decay times were determined by fitting the data to multiexponential decay curves [19]. An Advanced Research Systems, Inc. ARS2-A closed-cycle helium refrigerator was used for the low temperature measurements.

3. Results and Discussion

3.1 Photoluminescence

The energy levels of interest for luminescent ns^2 cations (e.g., Pb^{2+} , Sn^{2+} , and Bi^{3+}) are the ground state, 1S_0 , and the four excited states (in order of increasing energy), 3P_0 , 3P_1 , 3P_2 , and 1P_1 (see Fig. 1). Transitions between 1S_0 and 3P_0 , 3P_1 , or 3P_2 are spin forbidden, however, the 3P_1 level undergoes mixing with 1P_1 by spin-orbit coupling, allowing the $^1S_0 \leftrightarrow ^3P_1$ transitions that are frequently observed in photoluminescence measurements [1, 3, 4, 6, 7, 20]. The $^1S_0 \rightarrow ^1P_1$ transition is also observed in some materials. In the case of Bi^{3+} , broad emission peaks, whose number and positions depend on the crystal field around the cation, and large Stokes shifts are commonly observed [1, 3, 4, 7, 20, 21]. All three Sillen phases are isostructural, crystallizing in the orthorhombic space group $Cmcm$ [13]. Each bismuth cation has C_{4v} site symmetry with coordination to eight substituents ($4O + 4Cl$) in a square antiprismatic arrangement. Excitation and emission spectra of each Sillen phase is presented in Fig. 2. A broad, undefined excitation peak and one emission peak are observed for each Sillen phase and BGO. As reported in Table 1, at 295 K, the excitation peak maxima and emission peak maxima of $SrBiO_2Cl$, $BaBiO_2Cl$, and $BaBiO_2Br$ occur at 280 and 430; 300 and 490; and 305 and 500 nm, respectively. The Stokes shifts of $SrBiO_2Cl$, $BaBiO_2Br$, and $BaBiO_2Cl$ are calculated to be 12,500, 12,800, and 12,900 cm^{-1} , are as expected from the heterotypic bonding of the bismuth cations in these phases. The strontium compound exhibits slightly bluer excitation and emission bands owing to the nephelauxetic effect [1, 22]. In this case, the Sr - O(X) bonds are more ionic than the Ba - O(X) bonds contributing to the shorter excitation wavelength for $SrBiO_2Cl$. Following this trend, the lower

electronegativity of bromine correlates to the smaller Stokes shift found for BaBiO₂Br in comparison to BaBiO₂Cl. For all three Sillen phases, the excitation and emission bands are assigned to transitions between the ¹S₀ ground state and the ³P₁ excited state.

The intensities of the photoemission peaks of the Sillen phases, SrBiO₂Cl, BaBiO₂Cl, and BaBiO₂Br, are shown in Fig. 3 for temperature range 10 K - 295 K. At low temperatures, the emission peaks narrow and the emission intensities increase for Bi₄Ge₃O₁₂ (BGO) [2, 5, 7] and for the three Sillen phases. From 10 – 77 K the emission intensities are relatively constant. As the temperature increases from 77 K to 295 K, the emission intensities decrease by 29 %, 73 %, and 88 % for SrBiO₂Cl, BaBiO₂Br, and BaBiO₂Cl, respectively. In BaBiO₂Cl and BaBiO₂Br, the highest photoluminescence intensities occur at 77 K, while the largest intensity for SrBiO₂Cl occurred at 20 K. At temperatures < 295 K, the emission wavelengths shift to 545 nm for BaBiO₂Cl and 550 nm for BaBiO₂Br, whereas in SrBiO₂Cl, the emission maxima stays the same. This nonshift indicates that the photoemissive states of SrBiO₂Cl are less thermally influenced relative to the other two Sillen phases. This observation was further confirmed by the stability of the emission intensities with variation of temperature for SrBiO₂Cl, (see Fig. 3). Of the Sillen phases investigated, BaBiO₂Cl exhibits the most intense photoluminescence, 1.73 times that of BGO, at room temperature, however, as described below, it does not translate into high radioluminosity (see Table 1).

3.2 X-ray Luminescence

Pulsed x-ray measurements were performed on polycrystalline samples of the three Sillen phases and BGO. The room temperature x-ray excited luminosities of

SrBiO₂Cl, BaBiO₂Br, and BaBiO₂Cl are found to be 24 %, 27 %, and 81 % of the luminescence found for BGO (Table 1). As shown in Fig. 4, the two barium bismuth oxyhalides exhibit consistent luminosities throughout the temperature range 10 K - 250 K. SrBiO₂Cl behaves in a manner similar to BGO at temperatures >100 K, where nonradiative thermal quenching processes compete with radiative transitions. However, the x-ray excited emissive states of BaBiO₂Cl and BaBiO₂Br are temperature dependent only at temperatures > 250 K, where the luminosities decrease slightly.

The time resolved decay measurements yield multiexponential decays for all three Sillen phases (see Fig. 5). At low temperatures, the majority of the X-ray excited emission have decay times > 1000 ns. As the temperature increases, the decay time components for all three Sillen compounds decrease, as shown for BaBiO₂Cl in Fig. 6. A complete listing of the three largest decay components and their fractions for SrBiO₂Cl, BaBiO₂Cl, BaBiO₂Br, and BGO measured at various temperatures can be found in Appendix A. The strontium compound, SrBiO₂Cl, exhibits relatively fast decay times of 50, 200, and 300 ns at 295 K for its most significant decay components when compared to the other two Sillen compounds and BGO. The shorter decay times observed at higher temperatures are attributed to nonradiative quenching commonly found in Bi³⁺-activated materials. This is usually accompanied by significantly lower luminosities at high temperatures, however, the radio-luminescence observed in BaBiO₂Cl and BaBiO₂Br are not as temperature dependent in comparison to the luminosities found in SrBiO₂Cl and BGO.

5. Conclusion

Three Sillen bismuth oxyhalides, SrBiO₂Cl, BaBiO₂Cl, and BaBiO₂Br were found to exhibit photo- and radio-luminescence. Their luminosities originate from the ³P₁→¹S₀ emission of the Bi³⁺ luminescent ion. At low temperatures, the radio-luminescence decay times increase, the photo-emission wavelengths shift to lower energy (in the case of the barium phases only), and the photo-emission bands narrow. These features are explained by the decrease in thermal population of the excited states at low temperatures. The three Sillen compounds have been characterized for their optical and scintillation properties and compared to Bi₄Ge₃O₁₂ (BGO).

Acknowledgements. The authors would like to thank Marvin Weber for his invaluable advice towards the work presented in this manuscript. This work was supported in part by the Director, Office of Science, Office of Biological and Environmental Research, Medical Science Division of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231 and in part by Public Health Service grant number R01EB00339 awarded by the National Institute of Biomedical Imaging and Bioengineering, Department of Health and Human Services.

Appendix A. Radio-luminescence decay constants and fractional contributions at various temperatures for SrBiO₂Cl, BaBiO₂Cl, BaBiO₂Br, and Bi₄Ge₃O₁₂.

Temperature (K)	SrBiO ₂ Cl		BaBiO ₂ Cl		BaBiO ₂ Br		Bi ₄ Ge ₃ O ₁₂	
	τ	Fraction	τ	Fraction	τ	Fraction	τ	Fraction
10	100	6%	100	4%	100	6%	900	21%
	800	39%	800	28%	800	38%	5950	45%
	3500	50%	4200	59%	3000	51%	6000	33%
25	100	6%	100	4%	150	3%	100	2%
	800	39%	800	27%	700	28%	950	20%
	3800	52%	4200	61%	3750	62%	6150	78%
77	100	6%	150	7%	150	3%	100	2%
	800	39%	900	39%	950	33%	900	18%
	3500	50%	3600	50%	5800	48%	6150	80%
100	100	8%	150	10%	150	9%	900	21%
	750	38%	800	43%	800	40%	5300	57%
	2850	50%	2450	43%	2900	48%	5350	19%
150	150	8%	150	10%	150	9%	100	2%
	700	41%	650	42%	600	40%	850	24%
	2400	45%	1650	42%	1700	46%	3650	71%
200	200	13%	200	18%	150	15%	100	4%
	750	55%	700	62%	650	55%	800	33%
	1900	26%	1600	14%	1400	24%	2400	61%
250	150	15%	150	11%	100	11%	200	8%
	300	20%	300	19%	300	23%	800	70%
	650	48%	700	56%	600	54%	1500	16%
295	50	28%	100	22%	100	21%	100	12%
	200	38%	300	41%	300	54%	300	79%
	300	14%	600	23%	700	12%	1000	4%

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Figure Captions

Fig. 1. Sketch of Bi^{3+} energy levels and possible electronic transitions.

Fig. 2. Room temperature excitation and emission spectra of SrBiO_2Cl , BaBiO_2Cl (and BaBiO_2Br , and $\text{Bi}_4\text{Ge}_3\text{O}_{12}$ (BGO)). Intensities normalized to the emission peak maxima of BGO. Note: λ - emission and excitation wavelengths used in measurements.

Fig. 3. Temperature dependence of the photoluminescence of SrBiO_2Cl , BaBiO_2Cl and BaBiO_2Br . (Excitation wavelengths identical to those used in Fig. 2)

Fig. 4. Temperature dependence of radio-luminescence of SrBiO_2Cl , BaBiO_2Cl , BaBiO_2Br , and $\text{Bi}_4\text{Ge}_3\text{O}_{12}$.

Fig. 5. Radio-luminescence decay curves of SrBiO_2Cl , BaBiO_2Cl , BaBiO_2Br , and $\text{Bi}_4\text{Ge}_3\text{O}_{12}$ at room temperature.

Fig. 6. Temperature dependence of the multiexponential decay of BaBiO_2Cl .

Table 1. Densities, relative radioluminescence intensities, and emission wavelengths of ABiO_2Cl ($A = \text{Sr}, \text{Ba}$), BaBiO_2Br , and $\text{Bi}_4\text{Ge}_3\text{O}_{12}$ at room temperature.

Compound	Density	Relative Radio-luminescence	Emission maxima (nm)
SrBiO_2Cl	6.10	0.24	430
BaBiO_2Cl	6.36	0.81	490
BaBiO_2Br	6.71	0.27	500
$\text{Bi}_4\text{Ge}_3\text{O}_{12}$	7.1	1.00	460

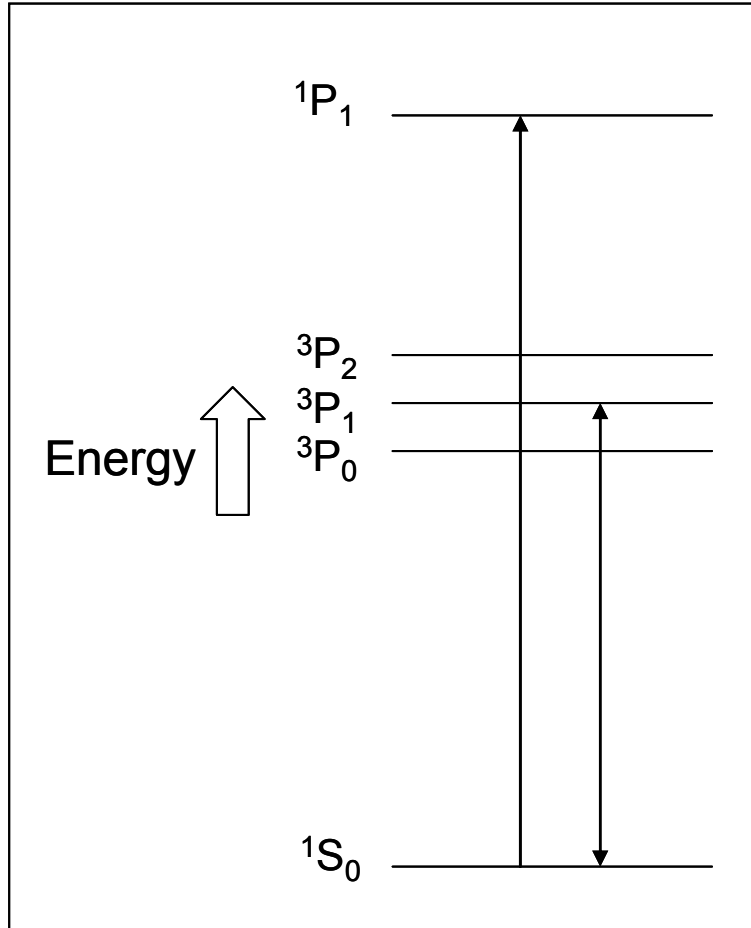


Fig. 1

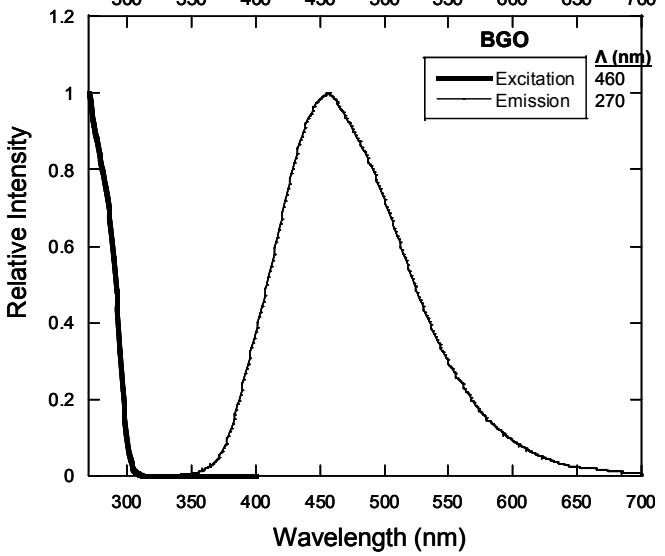
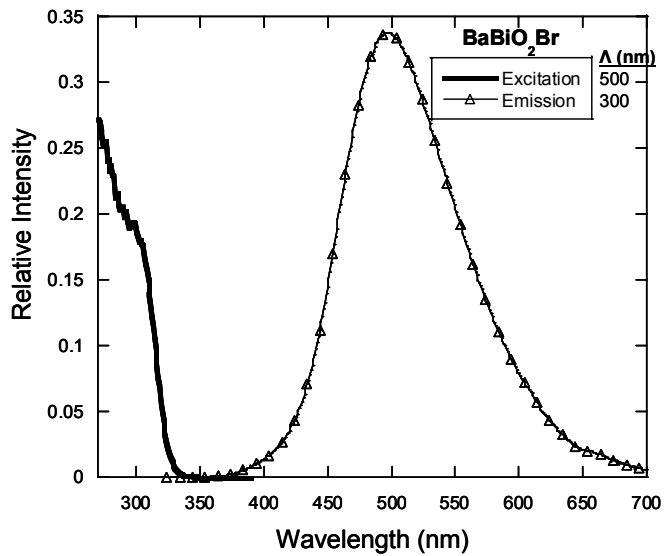
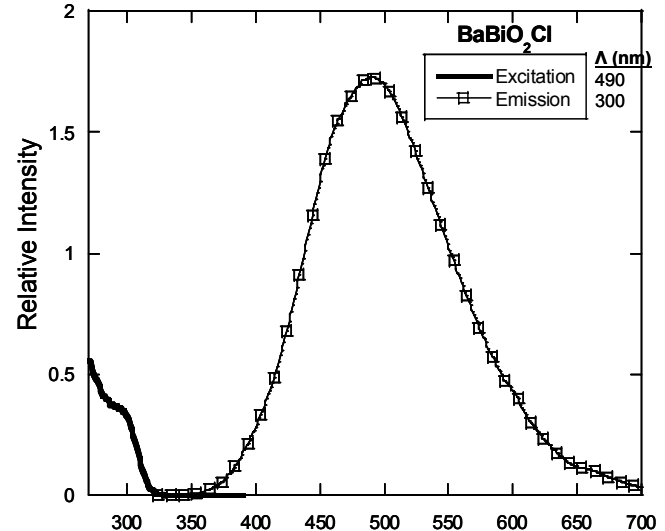
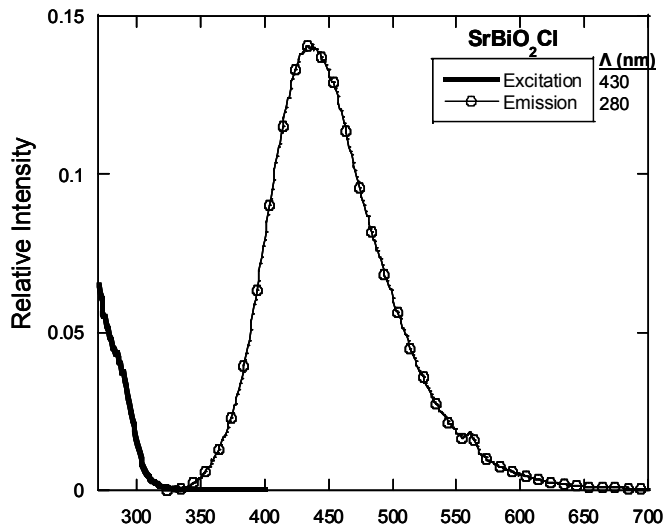


Fig. 2.

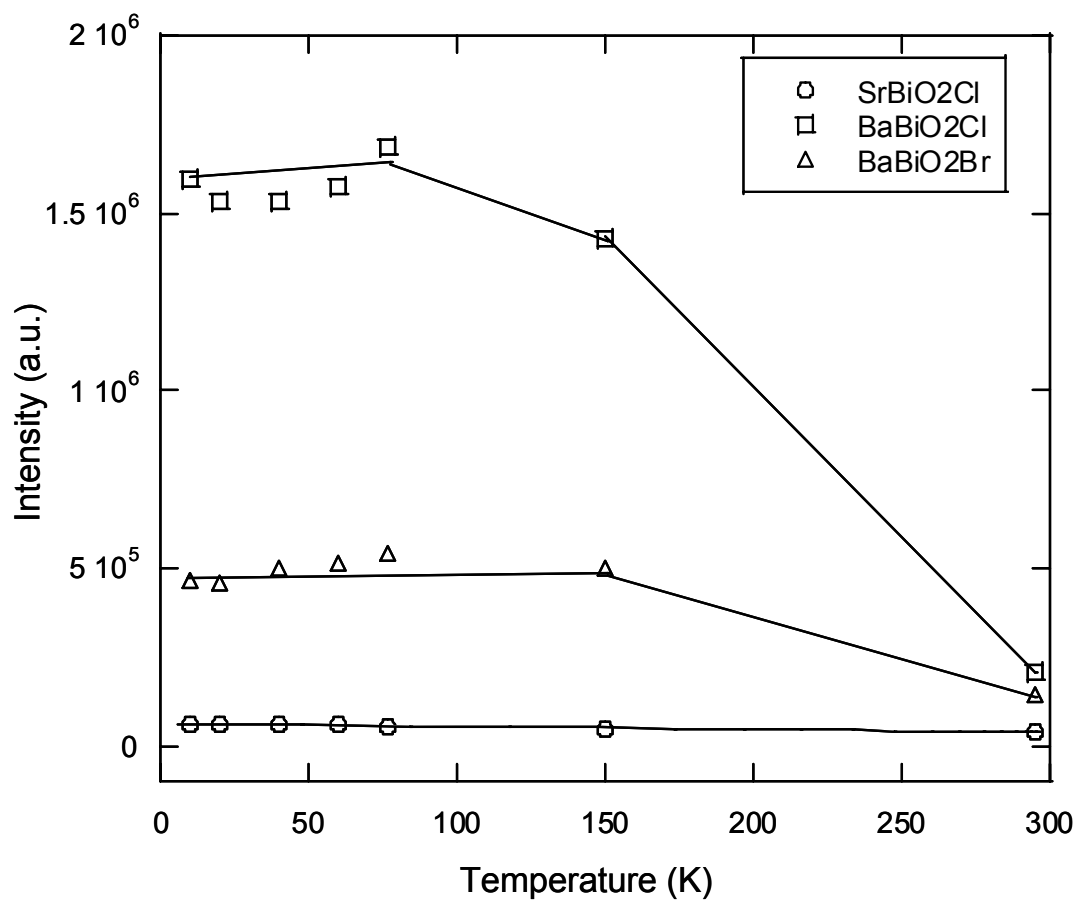


Fig. 3.

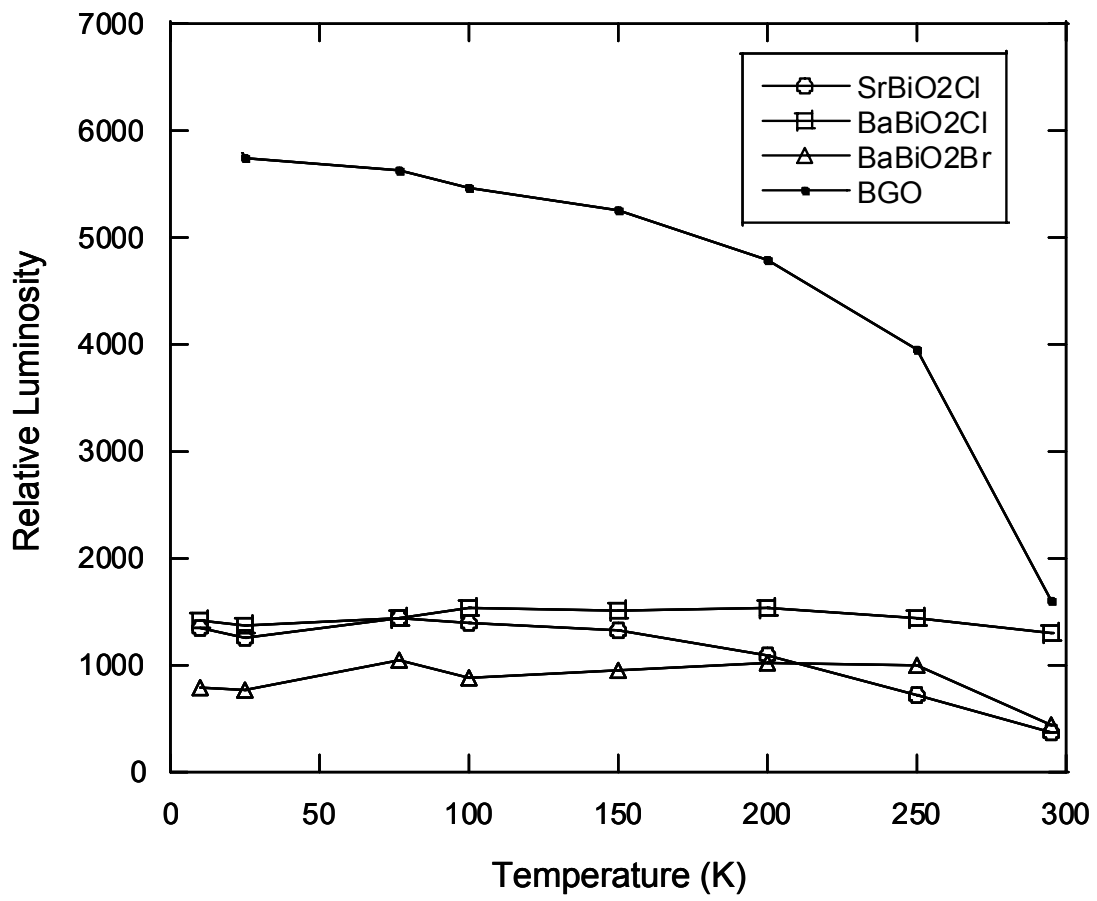


Fig. 4.

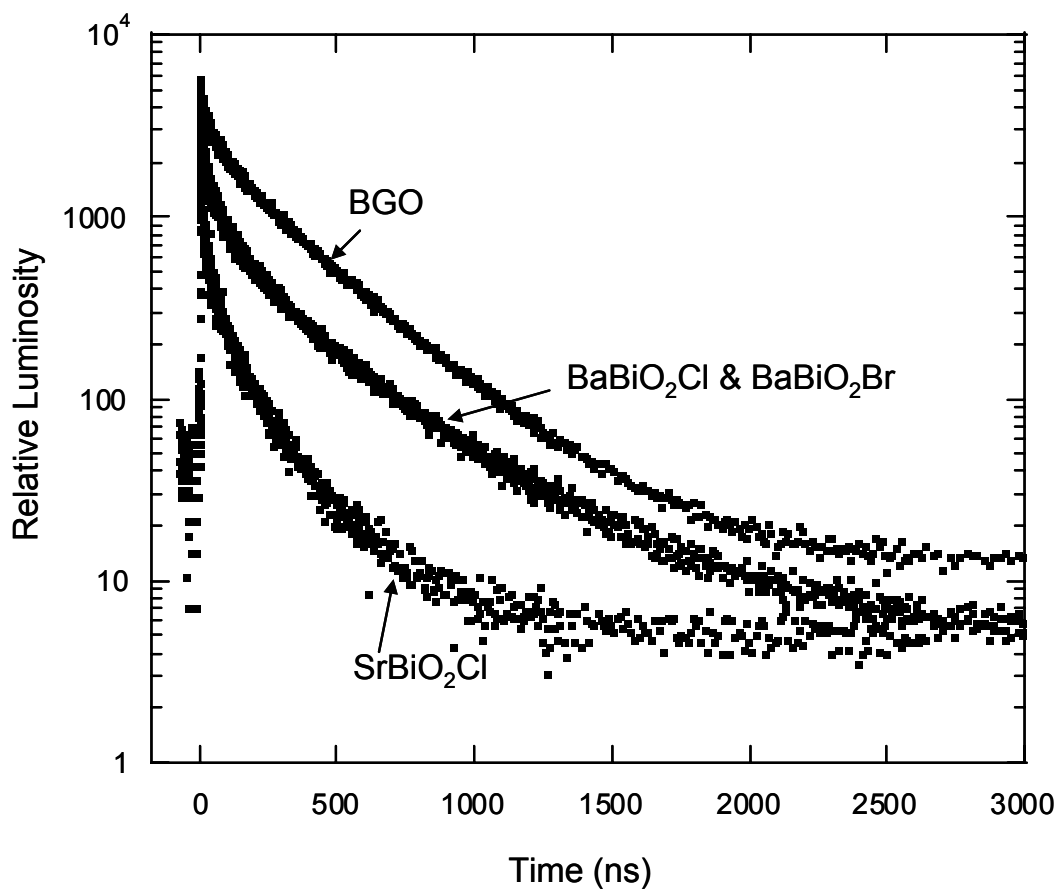


Fig. 5.

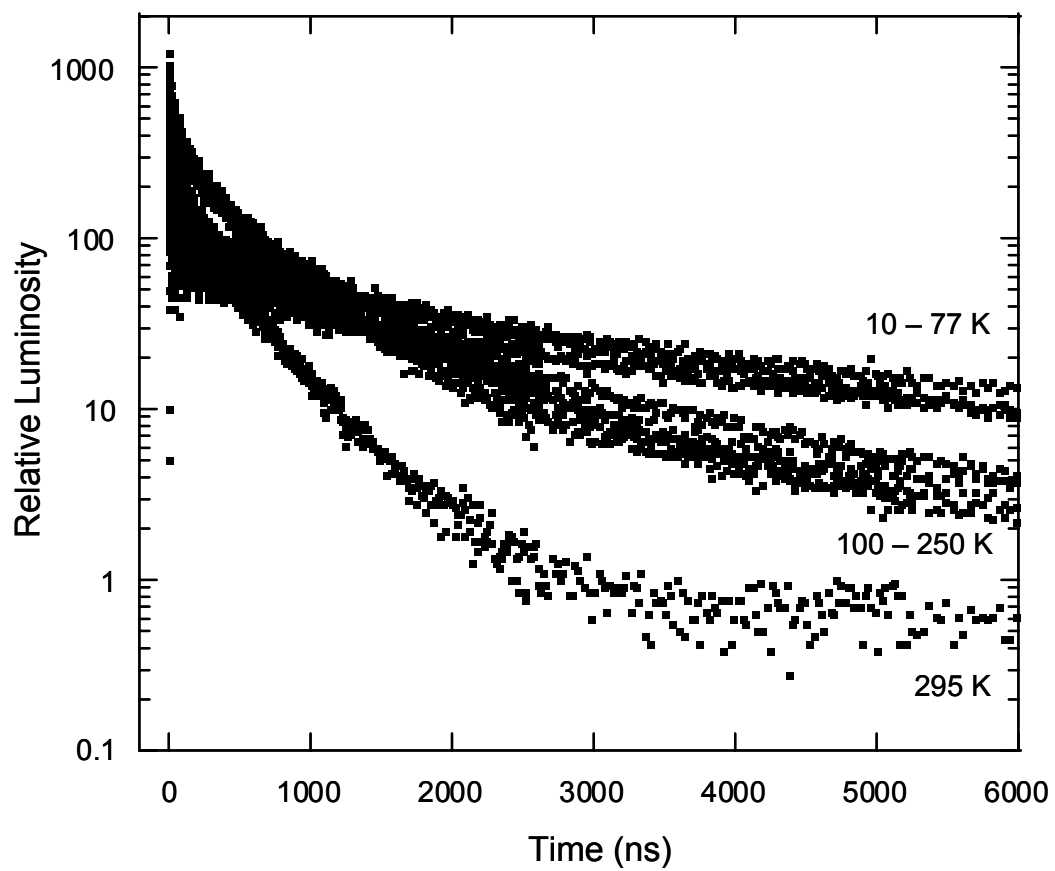


Fig.6.