DISCLAIMER

Bi^{3+} Luminescence in $ABiO_2Cl$ (A = Sr, Ba) and $BaBiO_2Br$

Yetta Porter-Chapman[a], Edith Bourret-Courchesne[b], Stephen E. Derenzo[a,*]
[a]Department of Functional Imaging, Life Sciences Division
[b]Materials 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, $SrBiO_2Cl$, $BaBiO_2Cl$, and $BaBiO_2Br$. These compounds exhibit Bi $6s6p \rightarrow 6s^2$ emission under UV and X-ray radiation. At room temperature, $BaBiO_2Cl$ shows the most intense light emission, with spectral and decay properties similar to those found in $Bi_4Ge_3O_{12}$ (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, $SrBiO_2Cl$ exhibits faster decays than BGO, while, $BaBiO_2Cl$ and $BaBiO_2Br$ 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 ($ABi^{3+}O_2X$, 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 $Bi_4Ge_3O_{12}$ (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 ($SrBiO_2Cl$ and $BaBiO_2Cl$) or light yellow ($BaBiO_2Br$) 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 Kα radiation, a range of 10 – 50° (2θ), 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 μm 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 $Bi_4Ge_3O_{12}$ (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

Te 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 $BaBiO_2Br$ in comparison to $BaBiO_2Cl$. For all three Sillen phases, the excitation and emission bands are assigned to transitions between the $^1S_0$ ground state and the $^3P_1$ excited state.

The intensities of the photoemission peaks of the Sillen phases, $SrBiO_2Cl$, $BaBiO_2Cl$, and $BaBiO_2Br$, 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 $Bi_4Ge_3O_{12}$ (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 $SrBiO_2Cl$, $BaBiO_2Br$, and $BaBiO_2Cl$, respectively. In $BaBiO_2Cl$ and $BaBiO_2Br$, the highest photoluminescence intensities occur at 77 K, while the largest intensity for $SrBiO_2Cl$ occurred at 20 K. At temperatures < 295 K, the emission wavelengths shift to 545 nm for $BaBiO_2Cl$ and 550 nm for $BaBiO_2Br$, whereas in $SrBiO_2Cl$, the emission maxima stays the same. This nonshift indicates that the photoemissive states of $SrBiO_2Cl$ 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 $SrBiO_2Cl$, (see Fig. 3). Of the Sillen phases investigated, $BaBiO_2Cl$ 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

$SrBiO_2Cl$, $BaBiO_2Br$, and $BaBiO_2Cl$ 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. $SrBiO_2Cl$ 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 $BaBiO_2Cl$ and $BaBiO_2Br$ 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 $BaBiO_2Cl$ in Fig. 6. A complete listing of the three largest decay components and their fractions for $SrBiO_2Cl$, $BaBiO_2Cl$, $BaBiO_2Br$, and BGO measured at various temperatures can be found in Appendix A. The strontium compound, $SrBiO_2Cl$, 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 Bi^{3+}-activated materials. This is usually accompanied by significantly lower luminosities at high temperatures, however, the radio-luminescence observed in $BaBiO_2Cl$ and $BaBiO_2Br$ are not as temperature dependent in comparison to the luminosities found in $SrBiO_2Cl$ and BGO.

5. Conclusion

Three Sillen bismuth oxyhalides, $SrBiO_2Cl$, $BaBiO_2Cl$, and $BaBiO_2Br$ were found to exhibit photo- and radio-luminescence. Their luminosities originate from the $^3P_1 \rightarrow {}^1S_0$ emission of the Bi^{3+} 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 $Bi_4Ge_3O_{12}$ (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 $SrBiO_2Cl$, $BaBiO_2Cl$, $BaBiO_2Br$, and $Bi_4Ge_3O_{12}$.

Temperature (K)	**$SrBiO_2Cl$**		**$BaBiO_2Cl$**		**$BaBiO_2Br$**		**$Bi_4Ge_3O_{12}$**	
	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%

References

[1] G. Blasse, A. Bril, J. Chem. Phys. 48 (1968) 217.

[2] E. Dieguez, L. Arizmendi, J. M. Cabrera, J. Phys. C: Solid State Phys. 18 (1985) 4777.

[3] B. Jacquier, G. Boulon, G. Sallavuard, F. Gaume-Mahn, J. Solid State Chem. 4 (1972) 374.

[4] C.-H. Kim, C.-H. Pyun, H. Choi, S.-J. Kim, Bull. Korean Chem. Soc. 20 (1999) 337.

[5] R. Moncorge, B. Jacquier, G. Boulon, J. Luminescence 14 (1976) 337.

[6] S. Shinonoya, W. M. Yen, The Phosphor Handbook, CRC Press, Boca Raton, FL, (2000) 141.

[7] M. J. Weber, R. R. Monchamp, J. Appl. Phys. 44 (1973) 5495.

[8] R. Burch, S. Chalker, R. Loader, J. M. Thomas, W. Ueda, Appl. Catal. 82 (1992) 77.

[9] J. M. Thomas, W. Ueda, J. Williams, K. D. M. Harris, J. Chem. Soc. Faraday Discussions 87 (1989) 33.

[10] D. O. Charkin, P. S. Berdonosov, V. A. Dolgikh, P. Lightfoot, J. Solid State Chem. 175 (2003) 316.

[11] V. A. Dolgikh, L. N. Kholodkovskaya, Russ. J. Inorg. Chem. 37 (1992) 488.

[12] S. M. Fray, C. J. Milne, P. Lightfoot, J. Solid State Chem. 129 (1997) 115.

[13] M. A. Kennard, J. Darriet, J. Grannec, A. Tressaud, J. Solid State Chem. 117 (1995) 201.

[14] L. G. Sillen, Z. Anorg. Allgem. Chem. 242 (1939) 41.

[15] L. G. Sillen, Naturwissenschften 22 (1942) 318.

[16] R. Nitsche, J. Appl. Phys. 36 (1965) 2358.

[17] P. A. Williams, A. H. Rose, K. S. Lee, D. C. Conrad, G. W. Day, P. D. Hale, Appl. Opt. 35 (1996) 3562.

[18] S. K. Kurtz, T. T. Perry, J. Appl. Phys. 39 (1968) 3798.

[19] S. E. Derenzo, M. J. Weber, W. W. Moses, C. Dujardin, IEEE Trans. Nucl. Sci. NS-47 (2000) 860.

[20] P. A. Rodnyi, Physical Processes in Inorganic Scintillators, CRC Press, Boca Raton, FL, (1997) 142.

[21] W. C. De Gruijter, J. Solid State Chem. 6 (1973) 151.

[22] J. A. Duffy, Bonding, energy levels, and bands in inorganic solids, Wiley, Essex, Eng, (1990).

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 $Bi_4Ge_3O_{12}$ (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 $Bi_4Ge_3O_{12}$.

Fig.5. Radio-luminescence decay curves of $SrBiO_2Cl$, $BaBiO_2Cl$, $BaBiO_2Br$, and $Bi_4Ge_3O_{12}$ 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 = Sr, Ba), $BaBiO_2Br$, and $Bi_4Ge_3O_{12}$ 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
$Bi_4Ge_3O_{12}$	7.1	1.00	460

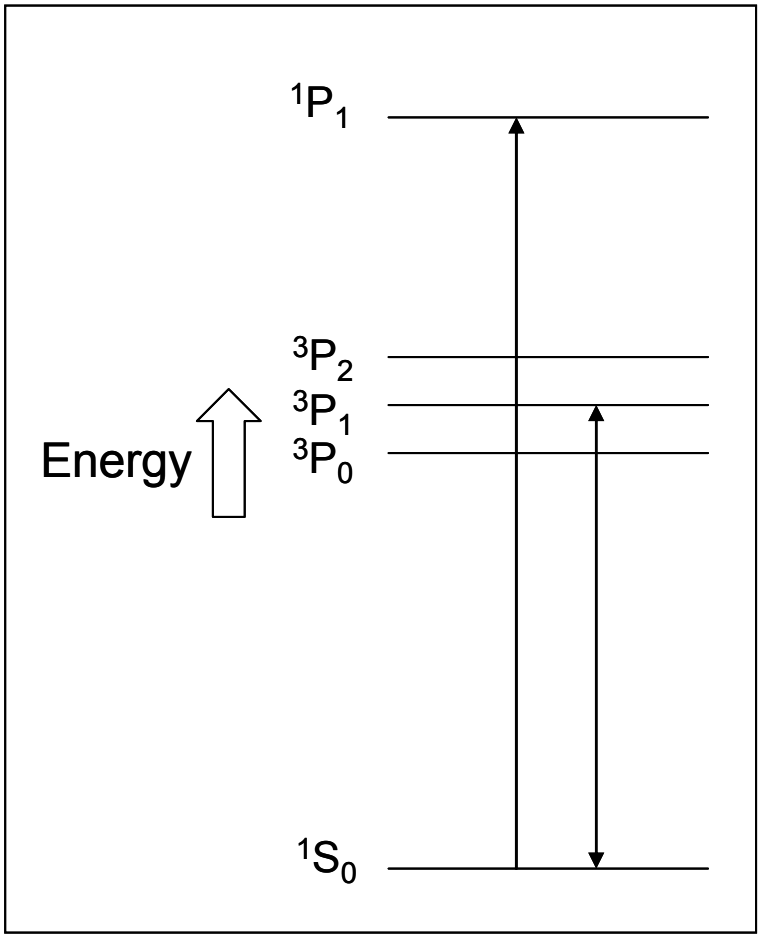

Fig. 1

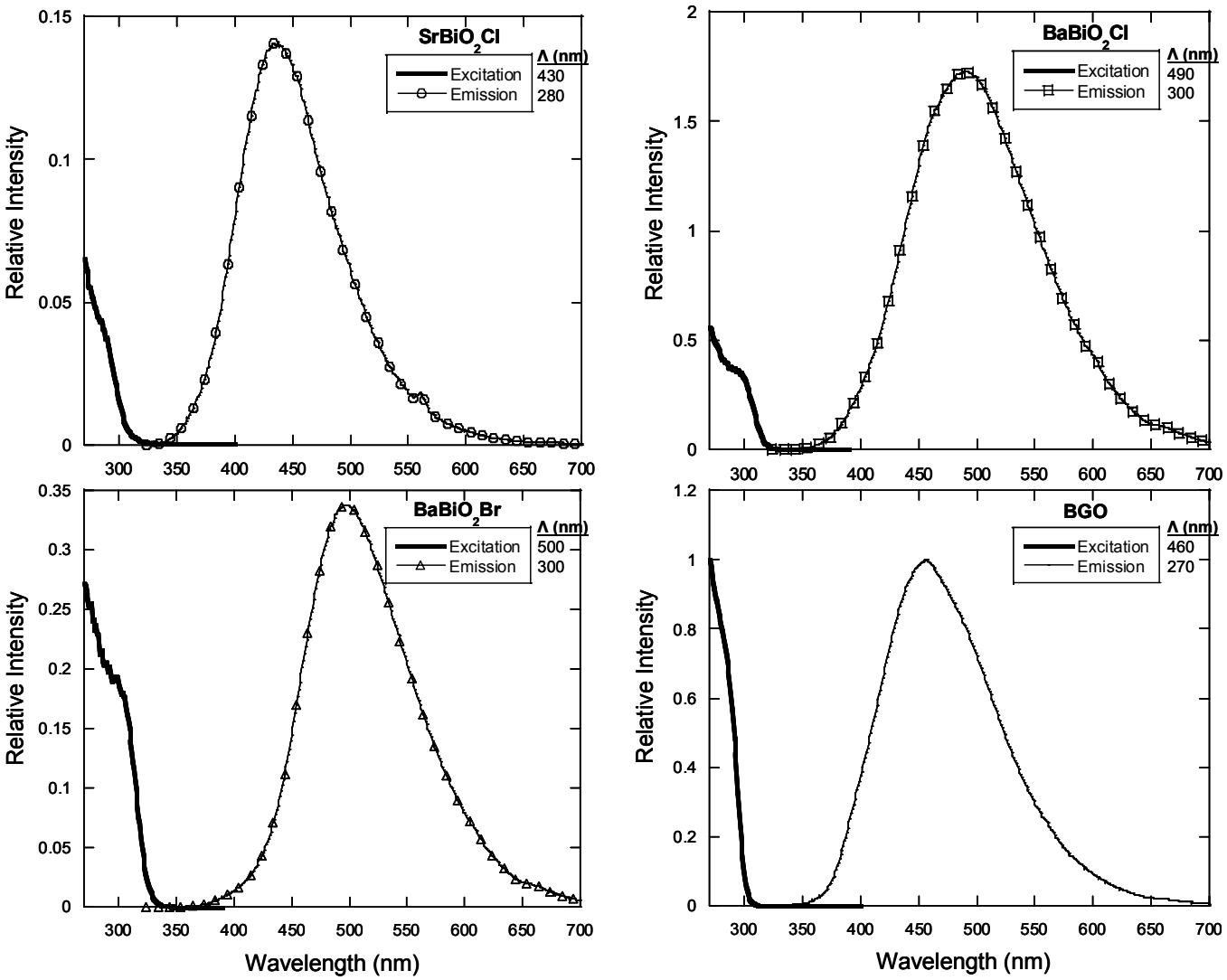
SrBiO2Cl
Excitation
Emission
λ (nm)
430
280
BaBiO2Cl
Excitation
Emission
λ (nm)
490
300
BaBiO2Br
Excitation
Emission
λ (nm)
500
300
BGO
Excitation
Emission
λ (nm)
460
270
Relative Intensity
Wavelength (nm)

Fig. 2.

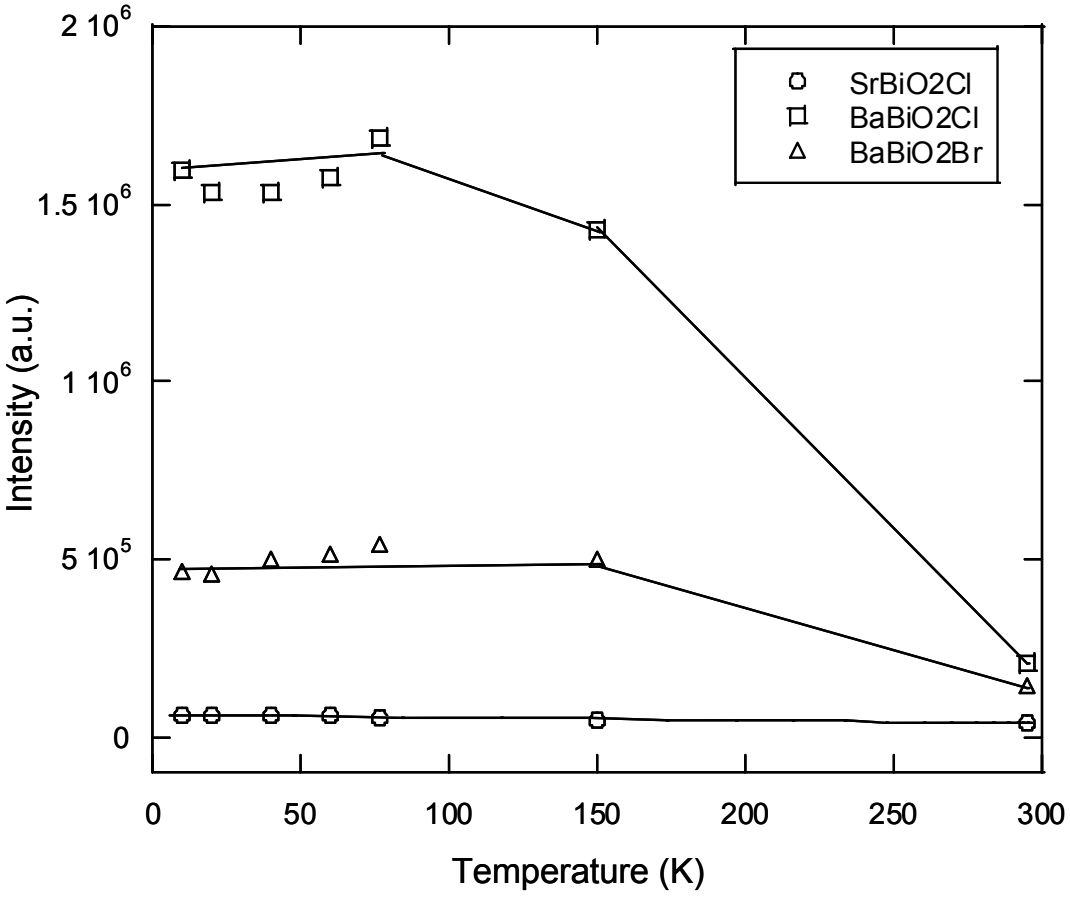
2 10^6
1.5 10^6
1 10^6
5 10^5
0
Intensity (a.u.)
0
50
100
150
200
250
300
Temperature (K)
SrBiO2Cl
BaBiO2Cl
BaBiO2Br

Fig. 3.

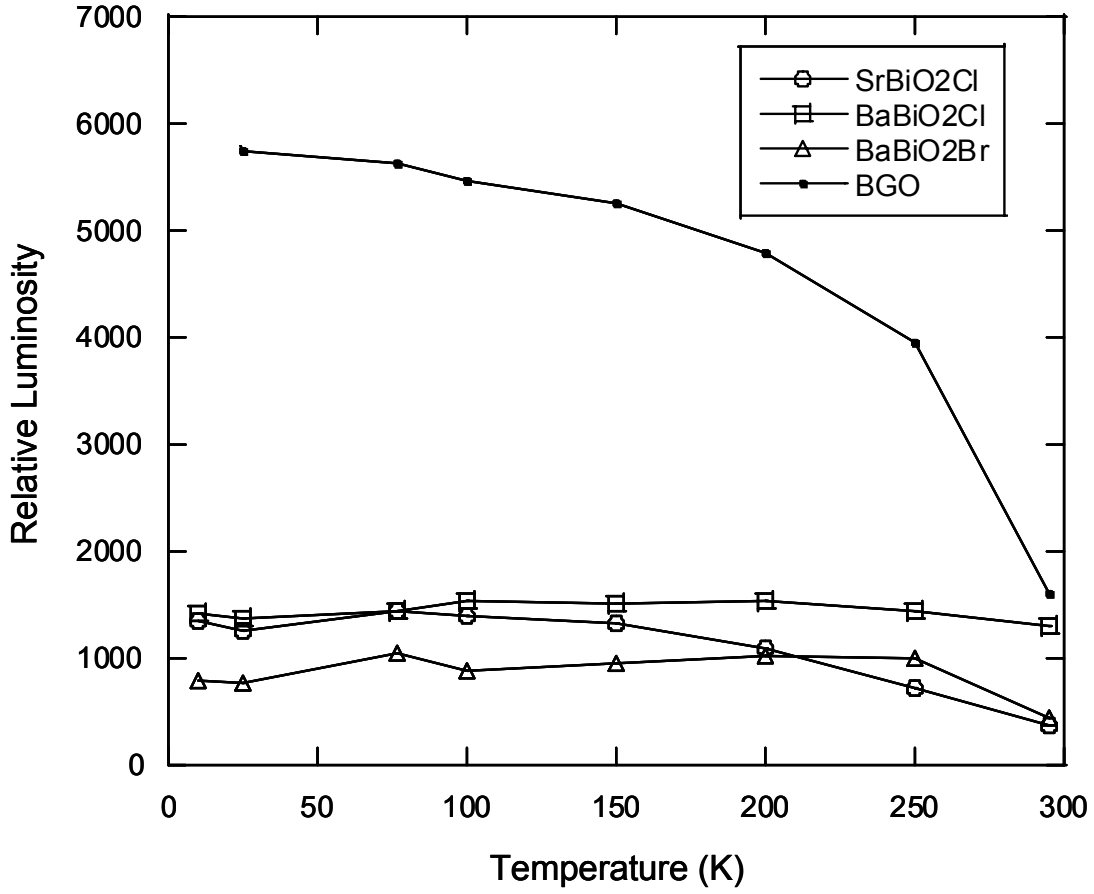
7000
6000
5000
4000
3000
2000
1000
0
Relative Luminosity
0
50
100
150
200
250
300
Temperature (K)
SrBiO2Cl
BaBiO2Cl
BaBiO2Br
BGO

Fig. 4.

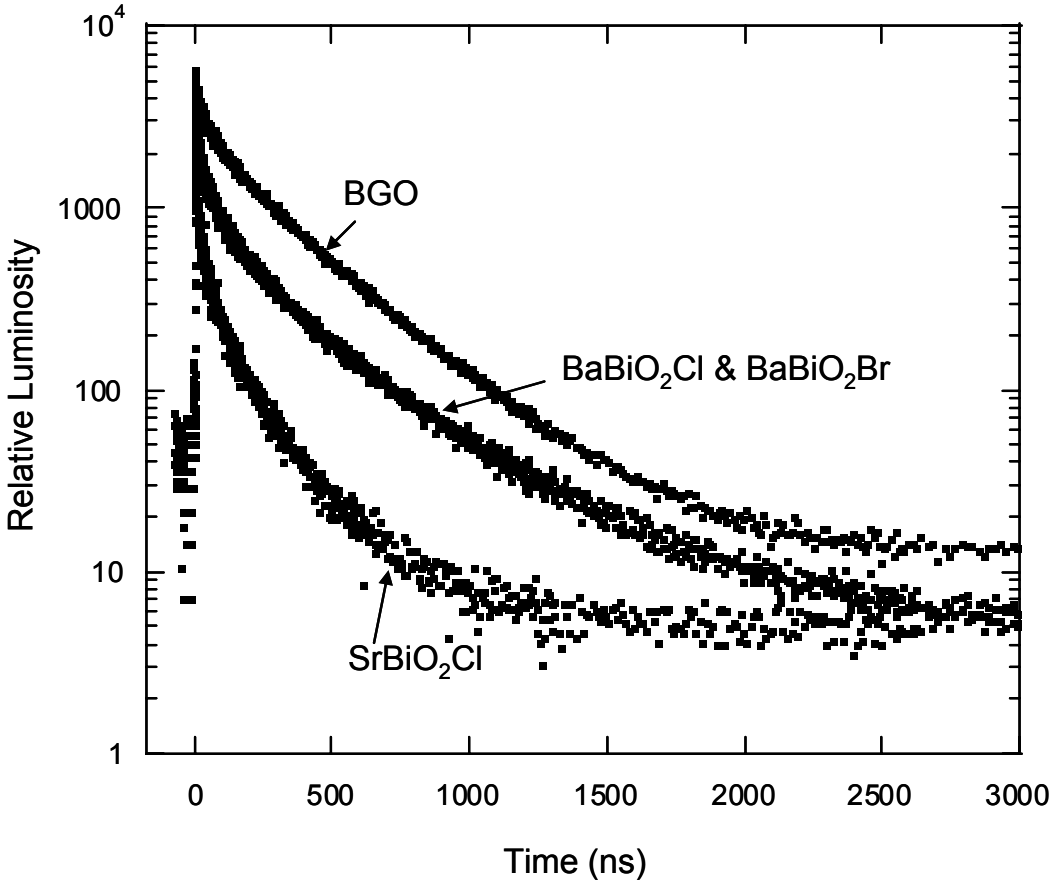
Relative Luminosity
10^4
1000
100
10
1
0
500
1000
1500
2000
2500
3000
Time (ns)
BGO
$BaBiO_2Cl$ & $BaBiO_2Br$
$SrBiO_2Cl$

Fig. 5.

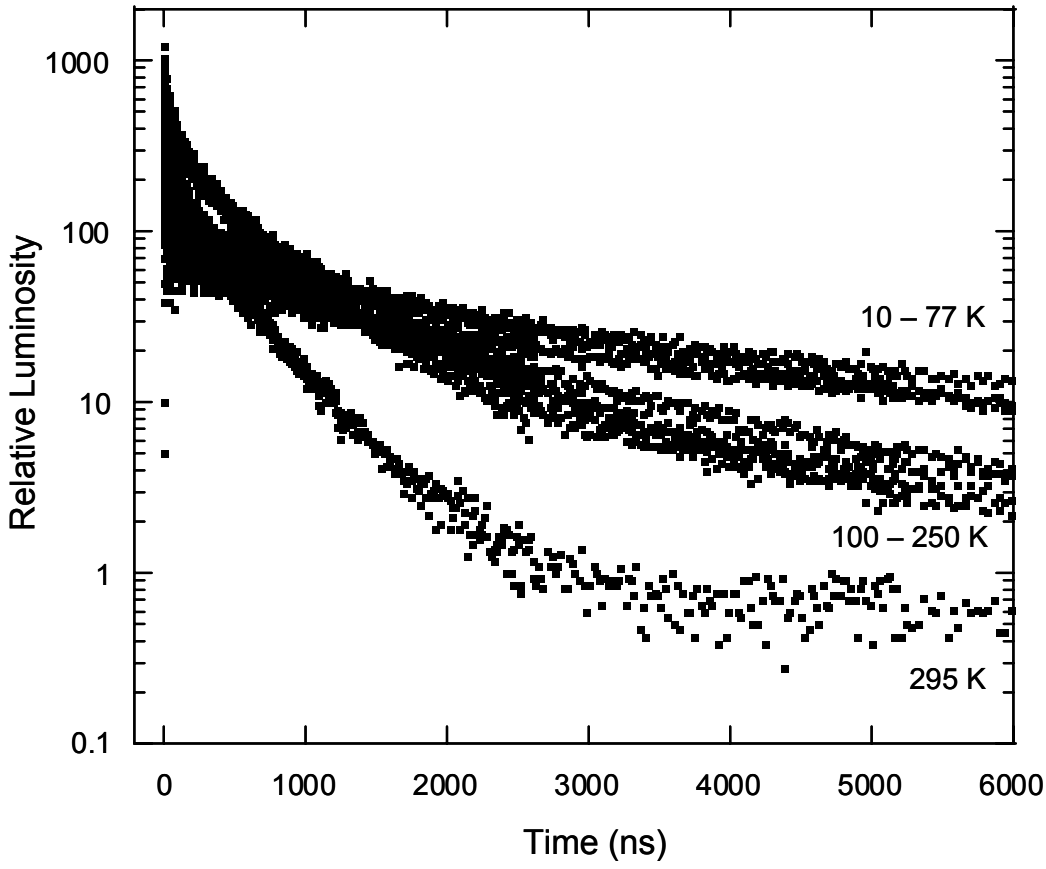
1000
100
10
1
0.1
Relative Luminosity
0
1000
2000
3000
4000
5000
6000
Time (ns)
10 – 77 K
100 – 250 K
295 K

Fig.6.