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Suppression of the slow component of BaF_2 crystal by introduction of SrF_2 and MgF_2 crystals

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Abstract

The emission spectrum, the time dependence of the luminescence, the light output, the excitation and the reflectance spectra have been measured for pure BaF_2 crystal, for BaF_2 : Sr crystals with Sr^{2+} concentrations of 2 and 5 mol% and for BaF_2 : MgF_2 crystal with a mole mixing ratio of 1 : 2. The measurements have been made by using synchrotron orbital radiation and high-energy electrons produced by gamma-rays. It is shown that the BaF_2, BaF_2 : Sr and BaF_2 : MgF_2 crystals have a fast component luminescence with decay times around 0.90 ns. The slow and fast components luminescence of the BaF_2 crystal are suppressed by the introduction of Sr^{2+} and Mg^{2+} ions. It is, however, clearly seen that the suppression of the slow component is more effective than that of the fast component, especially in the BaF_2 : MgF_2 crystal. The Sr^{2+} and Mg^{2+} ions act as electron trapping centers, preventing the formation of self-trapped excitons by electron–hole pairs, that is the slow component.

1. Introduction

Pure BaF_2 crystal has been widely applied as a scintillation material because of its high density, high radiation resistance and good time resolution due to the fast component (< 1 ns) appearing in the emission bands around 220 nm and 195 nm [1–6]. This fast components luminescence is called Auger-free luminescence [4] or cross-luminescence [2], and it is attributed to the radioactive recombination of the F^-2p valence band electrons with the outmost-holes of the Ba^{2+} 5p core band.

However, in addition to the fast component, BaF_2 crystal has a slow component at 300 nm with a decay time of about 700 ns, which causes deterioration of the time resolution of the high counting rate [5,6]. This slow component is attributed to the radioactive decay of self-trapped excitons formed by the excitons or the recombination process of the electrons in the conduction band with the holes in the valence band [5,6]. In a pure BaF_2 crystal approximately 80% of the light output occurs in the slow component [8]. The suppression of the slow component is, therefore, a crucial key when applying this crystal to high counting rate experiments in fields such as high energy physics [5] and nuclear medicine [4]. There have been several attempts to reduce the slow component by introduction of a La, Ce component into the BaF_2 crystal [5,6,8,9].

In the present work, the authors have focused the research on a group of BaF_2-based crystals, composed of BaF_2 and MgF_2 with a mole mixing ratio of 1 : 2 and BaF_2 : Sr with Sr^{2+} concentrations of 2 mol% and 5 mol%. Since it is well known that the MgF_2 crystal has no luminescence under ionizing charged particle excitation [10], suppression of the slow component luminescence in the BaF_2 : MgF_2 crystal is, therefore, expected. On the other hand, SrF_2 crystal has a slow component at 4.3 eV with a decay time of 900 ns [12], and the band gap-energy (11.6 eV) of SrF_2 [11] is almost similar to the one of BaF_2 (11.0 eV). Thus one could expect that the number of electron–hole pairs produced by self-trapped excitons in BaF_2 : Sr crystal should not manifest any significant difference from that in pure BaF_2 crystal, unless another effect can interfere in the production of the electron–hole pair.

To ascertain these expectations systematic measurements including the emission spectra, the time dependences of the luminescence, the light outputs and the photoexcitation spectra and reflectance spectra for the above crystals were made. The results show that the slow components are suppressed by introducing MgF_2 and SrF_2. Although a decrease of the fast component is also induced, the suppression of the slow component is more effective than that of the fast component.

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2. Experimental methods

As the detailed experimental procedure has been described in Ref. [6], a brief description is given here. The BaF_2, $BaF_2:Sr$ and $BaF_2:MgF_2$ crystals used in the present work were grown from the melt by the vertical Bridgman method using a graphite crucible. The starting powder for these crystals were of suprapure grade and purchased from E. Merck.

The relative light output of the fast component of the BaF_2-based crystals under irradiation of 662 keV gamma-rays from a ^{137}Cs source were measured with a UV sensitive quartz photomultiplier (Hamamatsu R1668). The output signals from the photomultiplier were shaped with a resistance capacitance (RC) network having an RC clipping time constant of about 5 ns. The output pulses were sent through a fast preamplifier and a main amplifier and were submitted to a multichannel analyzer for pulse height analysis.

The emission spectra and the time characteristics of the luminescence from the crystals were measured by employing time resolved spectroscopy using the single photon counting technique. A BaF_2 scintillator (about $2 \times 2 \times 3$ cm^3) and the sample crystal were simultaneously excited by correlated 511 keV gamma-rays from a ^{22}Na source. A UV sensitive photomultiplier (Hamamatsu Photonics, H2431QX) coupled to the BaF_2 scintillator generates zero-time signals and its outputs were used as start pulses for the time-to-amplitude converter. The delayed luminescence photons from the sample crystal were monochromatized with a monochromator (Shimadzu Bausch & Lomb) detected with a UV sensitive micro-channel-plate photomultiplier (Hamamatsu Photonics, R2809U-01) and its outputs were used as a stop for the time-to-amplitude converter. The pulses of the time-to-amplitude converter were fed into a multichannel analyzer where the decay curve was accumulated at a given wavelength of the emission. The emission spectra of the crystals under investigation were measured by counting the numbers of the stop pulses at various wavelengths of luminescence in a common accumulation time.

Table 1
Decay times for the fast and slow components. The ratios I_1/I_2 of the intensity of the τ_1 decay component and τ_2 decay component are also summarized

Crystal	Decay time (ns)			I_1/I_2
	Fast component at ~ 5.8 eV (~ 210 nm)	Slow component at ~ 4.2 eV (~ 300 nm)		
		τ_1	τ_2	
BaF_2	0.90 ± 0.06	330 ± 30	670 ± 60	0.44 ± 0.10
$BaF_2:Sr(2\%)$	0.89 ± 0.05	300 ± 40	680 ± 70	$0.30 \pm 0\,06$
$BaF_2:Sr(5\%)$	0.87 ± 0.05	150 ± 20	700 ± 70	$0\,15 \pm 0.03$
$BaF_2.MgF_2$	0.89 ± 0.04			

To obtain complementary information, the photoexcitation and reflectance spectrum were measured by using the synchrotron orbital radiation (SOR) at the Institute for Solid State Physics, Tokyo University. A surface of the crystal to be studied was excited to the monochromatized UV photons with a normal angle. The luminescence photons emitted from the crystal were monochromatized and were detected with a quartz window photomultiplier. The photoexcitation spectra were measured as a function of the excitation photon energy. The reflectance spectra were also obtained by measuring the intensity of reflected photon signals detected with a photomultiplier (Hamamatsu Photonics, R105) coated with a thin layer of sodium salicylate.

3. Results and discussion

Table 1 summarizes the values of the fast and slow decay times of the BaF_2, $BaF_2:Sr(2\%)$, $BaF_2:Sr(5\%)$ and $BaF_2:MgF_2$ crystals. No significant difference was observed in the decay time of the fast component among four crystals, i.e. the decay times were found to be about 900 ns. The slow component luminescence appears to contain two different contributions with decay times τ_1 and τ_2. Although no crystals showed any τ_2 difference in relation to BaF_2, the determined value of τ_1 for the $BaF_2:Sr$ (5%) crystal was found to be nearly half of the BaF_2 crystal. The relatives intensities of the two contributions of the slow component are also shown in Table 1. The decay time for the slow component in the $BaF_2:MgF_2$ crystal could not be obtained, since the emission intensity was not as intense as those in the BaF_2 and the $BaF_2:Sr$ crystals.

The relative light output of the fast components was measured to be 1.0, 0.41, 0.27 and 0.22 for the BaF_2, $BaF_2:Sr$ and $BaF_2:MgF_2$ crystals, respectively, under the excitation of high-energy electrons generated by 662 keV gamma-rays. Fig. 1 shows the emission spectra for four crystals under high-energy electron excitation generated by 511 keV gamma-rays. The intensities at the maximum values of the fast component luminescence at around 5.8 eV (214 nm) were scaled by using their relative light output ratios indicated above. It is to be noted here that the spectrum width of the fast component for the $BaF_2:MgF_2$ crystal is 4.2 eV, which is larger than those (2.7 eV) from the BaF_2 and $BaF_2:Sr$ crystals. These results suggest that the valence band width in the $BaF_2:MgF_2$ crystal is about 1.5 eV wider than those in the BaF_2 and $BaF_2:Sr$ crystals [4].

The slow component peaks were located around 4.2 eV (300 nm) for four crystals, while the fast component peaks were located at 5.9 eV (210 nm) for the BaF_2 and $BaF_2:Sr$ crystals and at 5.7 eV (217 nm) for the $BaF_2:MgF_2$ crystal. Table 2 compiles the relative light outputs of the fast and slow components together with the ratios of the fast component intensity to the slow component intensity for four crystals.

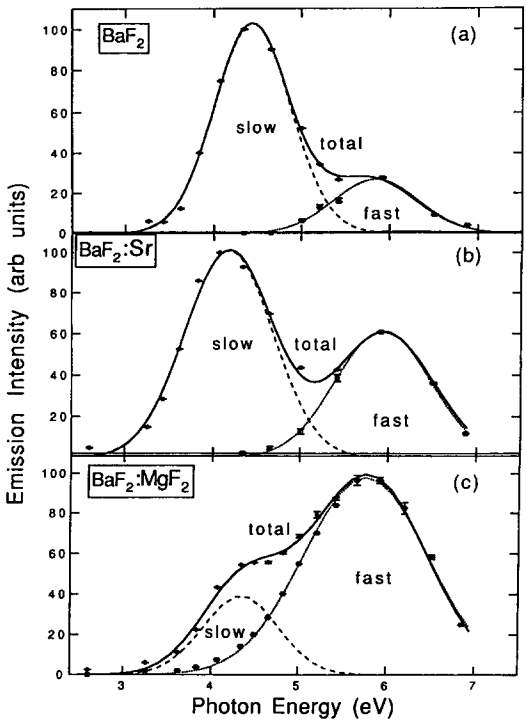

Fig. 1. Emission spectra of the BaF_2, BaF_2:Sr (5%) and BaF_2 : MgF_2 crystals under high-energy electrons excitation. Solid curve: total emission spectra. Dotted curve: fast emission spectra. Dashed curve: slow emission spectra.

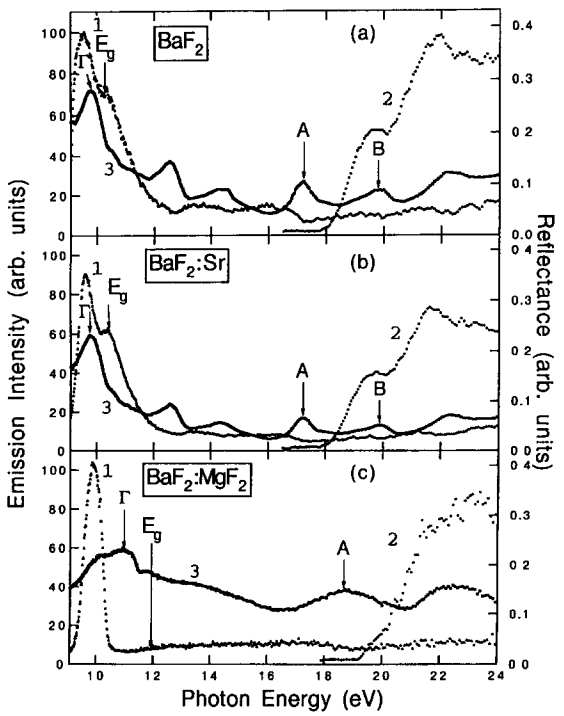

Fig. 2. Excitation spectra for fast component (dotted lines labeled 2) and slow component (lines labeled 1) from BaF_2, BaF_2:Sr(5%) and BaF_2 : MgF_2. Reflectance spectra are shown by lines labeled 3. The peak positions of the excitons are indicated by Γ and those for the core excitons by A and B. The band gap positions are also indicated by E_g.

The experimental results of Fig. 1 shows that the fast and slow components decrease in the BaF_2 : MgF_2 crystal. It is important to pay attention to the fact that the slow component is more effectively suppressed than that of the fast component.

Figs. 2a, 2b and 2c show the photoexcitation spectra for the fast and slow components luminescence and reflectance spectra of the BaF_2, BaF_2 : Sr(5%) and BaF_2 : MgF_2 crystals, respectively. The threshold energies of the fast component luminescence are located at 18.0 ± 0.2 eV, 18.0 ± 0.2 eV and 19.3 ± 0.2 eV for BaF_2, BaF_2 : Sr(5%) and BaF_2 : MgF_2 crystals, respectively.

Table 2
Relative light outputs of the fast and slow components of crystals. The ratio F/S of the fast component intensity to the slow component intensity are also indicated. Experimental uncertainties are 15%

Crystal	Relative light output (%)		F/S
	Fast component at ~ 5.8 eV (~ 210 nm)	Slow component at ~ 4.2 eV (~ 300 nm)	
BaF_2	100	357	0.28
BaF_2 : Sr(2%)	41	85	0.48
BaF_2 : Sr(5%)	27	45	0.60
BaF_2 : MgF_2	22	8	2.70

As it can be seen from the slow component photoexcitation spectrum for the BaF_2 : MgF_2 crystal, this luminescence was efficiently excited at the excitation photon energy of around 10.0 eV, but no significant luminescence was observed at an excitation photoenergy higher than 11.0 eV. This feature apparently contrasts to those of the excitation spectra for BaF_2 and BaF_2 : Sr crystals in which significant luminescence is excited around the excitation photon energy of both the exciton and the valence-band excitations.

Intensive peaks of reflectance spectra for the BaF_2 and BaF_2 : Sr crystals at 9.8 eV are assigned to the exciton energy (Γ). For the BaF_2 : MgF_2 crystal, two peaks at 10.0 eV and 11.0 eV are observed in the exciton region. The peak appearing at 11.0 eV is attributed to the exciton creation which is 1.0 eV higher than that of the pure BaF_2 crystal, by considering the increase of band-gap energy E_g (11.9 eV) for the BaF_2 : MgF_2 crystal compared to that (11.1 eV) for the BaF_2 crystal [4]. The first peak at 10.0 eV, which is almost equal to the 9.8 eV in the BaF_2 crystal, is most likely due to the exciton creation originated

by the BaF_2 crystal, which consists in the impurity formed in the crystal.

Therefore, these results suggest that the slow luminescence observed in the $BaF_2:MgF_2$ crystal is attributed to the radioactive decay of the self-trapped exciton formed uniquely from the exciton originating from the impurity of the BaF_2 crystal present in the $BaF_2:MgF_2$ crystal. It is expected, therefore, that the slow component is totally suppressed in a perfect $BaF_2:MgF_2$ crystal.

Figs. 2a and 2b show the photoexcitation spectra and reflectance spectra for the BaF_2 and $BaF_2:Sr$ crystals. Since there are similarities between the spectra from the BaF_2 and those from the $BaF_2:Sr$ crystal, it is concluded that the Sr^{2+} ions introduction has little effect on the resultant band structure for the $BaF_2:Sr$ crystal. However, experimental results showed a considerable decrease in the intensity of the slow component luminescence as it can be seen in Fig. 1 and Table 2. Since the decay times of the slow component of the $BaF_2:Sr$ crystal are almost similar to those from the BaF_2 crystal, it can be concluded that the introduction of Sr^{2+} ions does not affect the decay rate of the self-trapped excitons. The probable explanation of the intensity decrease is, therefore, that the Sr^{2+} ions are acting as electron trapping centers preventing the electrons to recombine with the holes, resulting in the reduction of the number of self-trapped excitons. Schotanus et al. have reported a similar decrease in the intensity of the slow component in a La^{3+} doped BaF_2 crystal, and have interpreted it by the same mechanism [5].

4. Summary

A difficulty was found in synthesizing crystals where the slow component was highly suppressed without a significant decrease in the fast component intensity, which was one of the goals of the present work. However, it can be said that the newly synthesized $BaF_2:MgF_2$ crystal manifested the promising enhancement of the fast component at the expense of partially quenching the original luminescence intensity. On the other hand, for applications in high energy physics, a fast response is more important than high light output.

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References

[1] Yu.M. Aleksandrov, V.N Makhov, P.A. Rodny, T.I. Syreishchikova and M.N. Yakimenko, Sov. Phys. Solid State 26 (1984) 1734.
[2] J.L. Jansons, V.L. Krumins, Z.A. Rachiko and J.A. Valbis, Phys. Status Solidi 144 (1987) 835.
[3] M. Itoh, S. Hashimoto, S. Sakuragui and S. Kubota, Solid State Commun. 65 (1988) 523.
[4] S. Kubota, M. Itoh, J Ruan, S. Sakuragui and S. Hashimoto, Phys. Rev. Lett. 60 (1988) 2319.
[5] P. Schotanus, P. Dorenbos, C.W.E. Van Eijik and R.W. Hollander, IEEE Trans. Nucl. Sci. NS-36 (1989) 162.
[6] M.M. Hamada, Nucl. Instr. and Meth. A 340 (1994) 524.
[7] M.N. Kabler, R.T. Willians, Phys. Rev. B 18 (1976) 725.
[8] C.L. Woody and D.F. Anderson, Nucl. Instr. and Meth. A 265 (1988) 291.
[9] P. Dorenbos, R. Visser, C.W.E. van Eijik, J Valbis and N.M. Khaidukov, IEEE Trans. Nucl. Sci. NS-39 (1992) 506.
[10] R.T. Willians, C.L Marquardt, J.W. Willians and M.N. Kabler, Phys. Rev. B 15 (1977) 5003.
[11] R.T. Poole, J. Szajman, R.C.G. Leckey, J.G. Jenkin and J. Liesegang, Phys. Rev. B 12 (1975) 5872.
[12] Kubota, J. Ruan, M. Itoh, S. Hashimoto and S. Sakuragui, Nucl. Instr and Meth. A 289 (1990) 253.