BARIUM FLUORIDE AS A GAMMA RAY AND CHARGED PARTICLE DETECTOR

M. R. Farukhi and C. F. Swinehart
Crystal & Electronic Products, Harshaw Chemical Co., Solon, Ohio 44139

I. Summary

"Pure" Barium Fluoride has been found to scintillate to gamma rays and alpha and beta particles. Pulse height of 10% relative to NaI(Tl), emission decay of 0.63 microseconds, fluorescence emission maximum at 3250Å have been measured for currently available crystals of BaF_2. This paper describes the scintillation performance and pertinent physical properties of BaF_2 in relation to some of the commercially available scintillators -- NaI (Tl), CsI(Na), CsI(Tl) and CaF_2 (Eu).

The low solubility,non-hygroscopic nature and a comparable absorption for gamma rays are particular advantages of BaF_2 over the alkali iodide scintillators. Transmission to its fluorescence emission, shorter decay time and a better photelectric absorption cross-section favor BaF_2 over CaF_2 scintillators. However, the scintillation pulse height of BaF_2 is presently lower than the other scintillators, but it is still sufficiently large enough to observe a resolvable Cs^{137} 662 Kev photopeak.

The mechanism responsible for scintillation in BaF_2 is not well understood at present. A preliminary investigation to understand this mechanism was undertaken in the form of adding impurities of various valencies to BaF_2 and also studying the behavior of scintillation with temperature. The data seems to indicate that hole-centers may be playing a primary role in the scintillation emission.

An understanding of the mechanism and the improvement and development of BaF_2 as a scintillator has been an integral part of the High Z Scintillator Research program maintained for some time by Harshaw. Notable developments from this program include the use of CsI(Na)[1] and TlCl (Iodide)[2] for High Z Scintillation detectors and PbF_2[3] as a cerenkov shower detector. As reported here, BaF_2 is usable for many applications which require a High Z non-hygroscopic scintillator.

II. Experimental Procedure

Optical crystals of BaF_2 are grown at Harshaw for clarity and transmittance from the vacuum ultraviolet to the infrared. The transmission requirements dictate the purity of the starting material. Optical absorption bands are a sensitive test for the presence of O^{-2}, Ag^{+1}, rare-earths$^{+2,+3}$, OH^-, CNO^-, BO_2^-, CO_3^{-2}, NO_3^-, SO_4^{-2} and SiO_3^{-2}. Samples free from any absorptions and those having chance impurities were chosen for this study. In addition special research crystals were grown with added deliberate amounts of monovalent, divalent and trivalent cations and the halogen anions. The crystals are grown in modified Stockbarger[4] furnaces in ingots 6, 8, 9, or 14 inches in intial diameter up to 6 inches in length for commercial use and the research crystals with various dopants were grown in diameters of 3/4 inches to 2-1/4 inches.

Fifty-two crystals have been studied in this investigation. Most of the samples were 1" D x 1/4" L and 3/4" D x 1" L in dimensions and these were canned in Harshaw "D" style aluminum cans, packed with MgO reflector, and coupled with DC 200 silicone coupling fluid to quartz windows. Dow Corning 20-057 optical coupling grease was used for coupling irregular shaped samples directly to the photomultiplier (PMT) face and in this case the sample was surrounded by an oversized can with sprayed reflector coating on the interior surfaces of the can.

III. Scintillation Characteristics

The scintillation and physical properties of BaF_2 and the commercially available scintillators - NaI(Tl), CsI(Na),[1] CsI(Tl),[5] CaF_2 (Eu)[6] are summarized in Table 1. BaF_2 will be compared to these scintillators in the following sections.

Physical Properties

The physical properties of BaF_2 are similar to CaF_2 (Eu) and offer several advantages over the alkali iodide scintillators. In particular, there is no limitation in handling BaF_2 in low humidity environment due to its low solubility and non-hygroscopic nature. Also, radioactive samples in solutions can be placed in direct contact with the crystal within the limits of its solubility. Its high resistance to radiation makes it a useful material for space applications[7] and in applications where high intensity fluxes are encountered.

The linear photoelectric, compton, pair-production and total attenuation coefficients for BaF_2 have been calculated from elemental cross-sections[8] and the values are represented by curves in figure 1. These values may be used for calculating the x-ray and gamma ray absorption efficiencies. The total linear attenuation coefficients of BaF_2, NaI(Tl), CsI(Na), CsI(Tl) and CaF_2 (Eu) are given by respective curves in Figure 2. It is apparent that BaF_2 is quite comparable in "stopping power" to the alkali iodide scintillators. The increase in the total linear absorption for BaF_2 in region 0.3 Mev to 5 Mev is really due to an increased cross-section for Compton interactions rather than photoelectric interactions.

BaF_2 is a relatively hard material and is best cut or shaped by diamond tools. It cleaves in the (111) plane so some additional sawing is needed to make cylinderical or parallelopiped shapes.

Pulse Height

Pulse heights as high as 8% and 10% relative to NaI(Tl) have been measured for BaF_2 scintillators with an RCA 8850 and a RCA 6903 photomultipliers (PMT), respectively. The RCA 8850 PMT is of the bi-alkali variety and has a GaP first dynode for low-light level detection. The RCA 6903 is a standard uv PMT with a S-13 spectral response. A Harshaw NB-11 preamplifier and a NA-16 shaping amplifier with a 512 channel analyzer provided the electronics for signal processing. A single differentiation of 6.4 microseconds was used.

Of the two non-hygroscopic scintillators, BaF_2 and CaF_2 (Eu), the better photoelectric absorption cross-section of the former is evident in the full energy photopeak of Cs^{137} gamma spectrum in Figures 3 (a) and 3 (b). The loss in the full-energy photopeak for CaF_2 (Eu) starts at 200 Kev so that it is of little use in counting applications for energies higher than 200 Kev. The suitability of BaF_2 for this need is evident.

Typical response of BaF_2 to beta and alpha particles is illustrated in Figure 4. The Bi^{207} β-spectrum in Figure 4 (a) clearly shows the presence of the 480 Kev and 970 Kev electron photopeaks. Figure 4 (b) is a spectrum for Cs^{137} betas and Figure 4(c) is the spectrum for $A_m{}^{241}$ alphas. Resolutions of 22% and 13% were found for the Cs^{137} 625 Kev electrons and Am^{241} 5.48 Mev alphas, respectively. The gamma equivalent for the 5.48 Mev alphas is 1.85 Mev, which is higher than 1 Mev for CaF_2 (Eu) but lower than 3.2 Mev for CsI(Na).[6,1] The charged particles were made incident on a cleaved (111) face for the above measurements.

BaF_2 was also examined for linearity of response to gamma ray energies up to 1.33 Mev and the results are summarized in Figure 5. The linearity of response with gamma ray energies appears to acceptable for most practical purposes.

Decay Constant

The decay constant was measured by photographing the oscilloscope patterns of the output of a charge sensitive preamplifier connected to the photomultiplier. The ordinate was taken as $1-v(t)/V_{max}$ and was plotted as a function of time on a semi-log graph paper. A straight line could be drawn through the points indicating that the emission decay is exponential in character. Decay times were determined for several samples and an average value of 0.63 ± 0.08 microseconds was computed.

Emission Spectra

The fluorescence emission spectra of BaF_2 to Cs^{137} gamma excitation has two maximum: a ultraviolet band at 3250Å ± 150Å and a red band at 6250Å ± 150Å. The spectra was recorded using a Bausch and Lomb monochromator, 500 mm focal length, 600 grooves/ mm grating blazed at 5000Å, for a spectrometer. A RCA 8850 PMT with a quartz window was used for a detector. The scintillation light was found to be in the ultraviolet through the use of appropriate Kodak wratten filters.

The transmission cut-off at the short wavelength limit for a 2.3 mm thick sample is at 1345Å.[9] As there is no overlap of the absorption and emission bands, the scintillation pulse height in BaF_2 is not a function of crystal size and thickness and large volume scintillators can be considered. The index of refraction , at the fluorescence emission maximum of 3250Å, is 1.495 matching excellently the index of many available optical coupling materials and PMT end faces, ensuring a maximum collection of light at the PMT cathode.

IV Discussion

Historically, we have detected scintillation of low pulse height in BaF_2 and have tried to enhance it by the addition of various dopants. In each case where measurable scintillation pulses were observed, a subsequent analysis of the material and procedure of manufacture indicated that the added dopant had either boiled away during growth or that the dopants made little or no difference to the pulse height. At this stage of the investigation we are inclined to believe that the scintillation phenomena is inherent to the host crystal.

Examination of the emission spectra to gamma excitations has shown the presence of two maxima: a UV band at 3250Å and a red band at 6250Å. The scintillation light was identified with the ultraviolet emission through the use of Kodak wratten filters and by comparing the pulse heights of some typical BaF_2 scintillators to a standard NaI(Tl) crystal. On photomultipliers with S-13 type response, the pulse heights were higher than for S-11 type PMTs indicating that the scintillation light for BaF_2 is in the ultraviolet range.

The mechanism for scintillation in BaF_2 is not well understood at the present time. However, an idea for the scintillation phenomena in BaF_2 may be obtained by comparing it to the mechanism for scintillation luminescence in the unactivated alkali halides. The room temperature emission for NaI is also in the ultraviolet with a maximum at 3100Å .[10] Exciton decay at a I^- ion lattice site is believed to be responsible for the emission. This emission is associated with the tendency of holes to be self-trapped at halogen ion sites. This is the currently accepted model for intrinsic luminescence in the alkali halides.[11] Tzalmona and Pershan have correlated thermoluminescence data with electron paramagnetic resonance measurements to identify two types of holes centers in BaF_2.[12] They also reported a faint thermoluminescence which existed up to 320°K and is not explained in their work. We have found that the scintillation pulses become unmeasurable above 330°K. Thus with the presence of holes-centers in BaF_2 and the scintillation emission being intrinsic to the crystal it is plausible to suggest that the mechanism for scintillation is associated with some modification of hole-centers.

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TABLE I. SCINTILLATION AND PHYSICAL PROPERTIES OF COMMERCIAL SCINTILLATORS

PROPERTIES	BaF_2	NaI(Tl)	CsI(Na)	CsI(Tl)	CaF_2(Eu)
SCINTILLATION LIGHT OUTPUT	10	100	85	40-45	50*
DECAY CONSTANT, MICROSECONDS	0.63	0.25	0.65	1.1	0.9
EMISSION MAXIMUM-ANGSTROMS	3250	4200	4200	5800	4350
INDEX OF REFRACTION	1.495	1.850	1.838	1.799	1.470
ALPHA/BETA RATIO	0.34	0.5	0.58	0.8	0.18
MOLECULAR WEIGHT	175.34	149.89	259.81	259.81	78.08
DENSITY g/cc	4.88	3.67	4.53	4.53	3.18
SOLUBILITY AT 25°C, g/100g H_2O	0.12	185.0	85.5	85.5	0.0017
THERMAL EXPANSION AT °C, /°C x 10^{-6}	18.4	45.6	47.0	47.0	18.0
MELTING POINT °C	1354	651	621	621	1402
HYGROSCOPIC	No	Very	Slightly	Slightly	No

*SAMPLE SIZE 1/2" THICK OR LESS

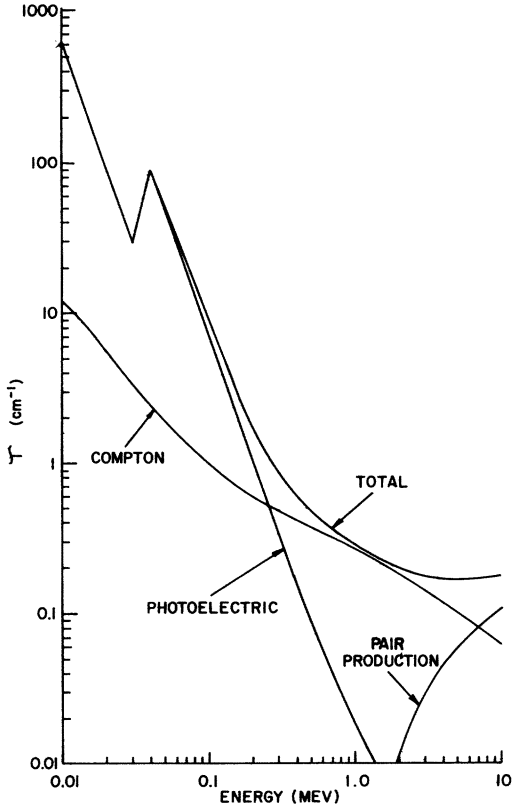

Figure 1. Linear attenuation coefficients of BaF_2.

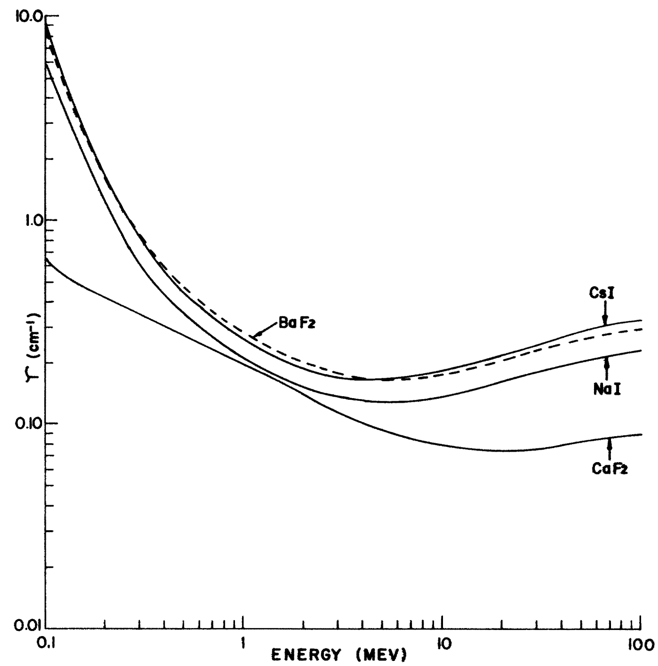

Figure 2. Total linear attenuation coefficients of BaF_2, NaI(Tl), CsI(Na) and CaF_2 (Eu).

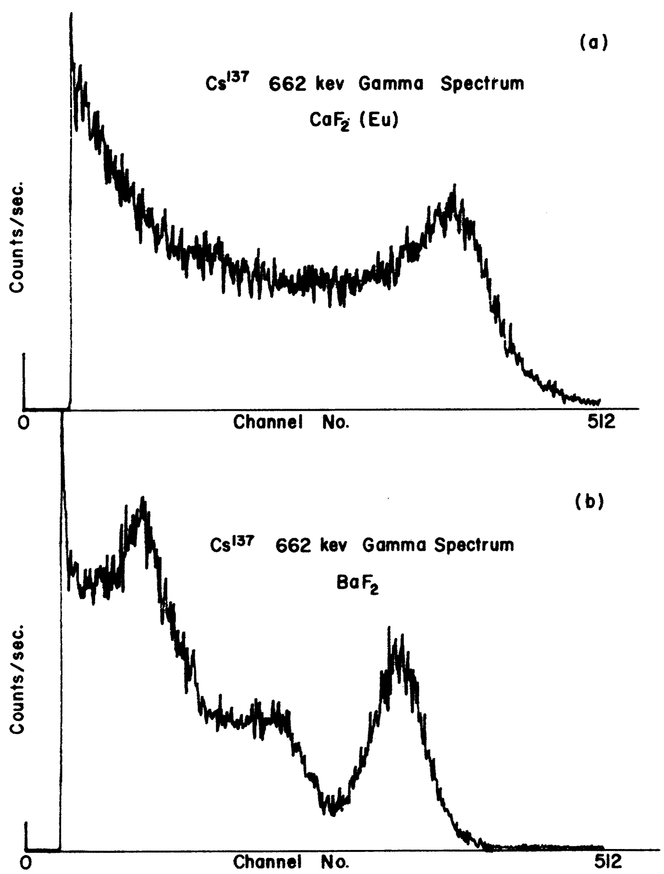

Figure 3. Response of (a) CaF_2 (Eu) and (b) BaF_2 to Cs^{137} gamma rays.

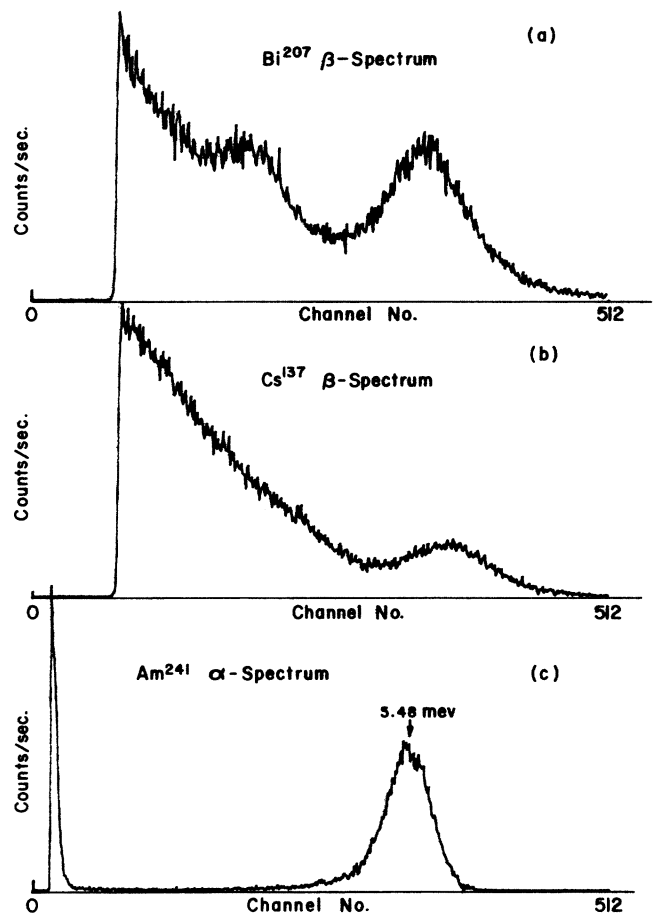

Figure 4. Response of BaF_2 to (a) Bi^{207} betas (b) Cs^{137} betas and (c) A^{241} alphas.

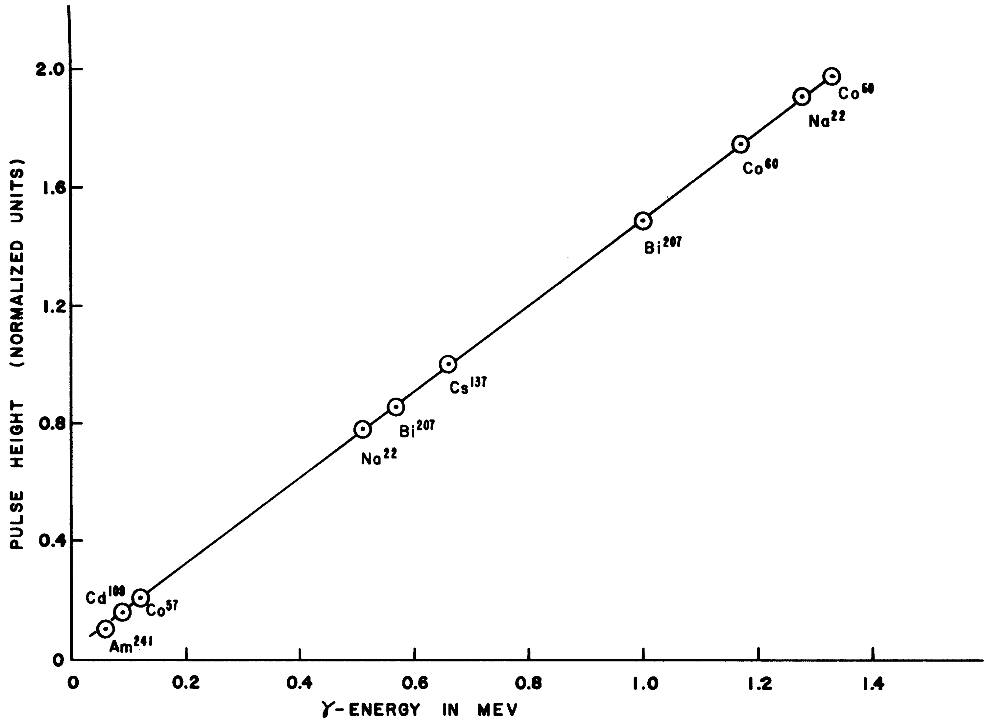

Figure 5. Response of BaF_2 to x-rays and gamma rays.