The hard X-ray response of Ce doped lanthanum halide scintillators

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Abstract

We summarize the results of a number of hard X-ray measurements on cerium doped LaCl_3 and LaBr_3 scintillators. The experiment was carried out at the HASYLAB synchrotron radiation facility using highly monochromatic pencil beams across the energy range 10.5 keV to 100 keV. Additional full-area measurements were carried out using radioactive sources. All measurements were carried out at room temperature. The measured FWHM energy resolutions ($\Delta E/E$) under pencil beam illumination were 29% (LaBr_3) and 32.4% (LaCl_3) at 10.5 keV falling to 7.8% (LaBr_3) and 9.2% (LaCl_3) at 100 keV. At 662 keV, the energy resolutions were 3.9% and 3.0% FWHM. The proportionality of the energy responses shows marked deviations from linearity above and below the La edge at 39.8 keV. At the edge the energy response changes by 2%. Fine structure across the edge was also investigated using single photon count rate measurements taken in 1 eV steps across the edge. The data show considerable near-edge structure when compared to curves generated from standard atomic data tables. However, very little evidence was found for extended X-ray fine structure suggesting that the bulk of the structure arises from the local coordination environment.

PACS: 07.57.Kp; 07.85.Nc; 29.40.Mc

Keywords: Lanthanum-halide, scintillator detectors, Hard X-ray spectroscopy

1. Introduction

The recently discovered Ce doped lanthanum halide scintillators ($\text{LaCl}_3\text{:Ce}$ and $\text{LaBr}_3\text{:Ce}$) [1] could potentially revolutionize spectroscopic systems because of their excellent energy resolutions and proportionality of response when compared with traditional scintillating materials. These scintillators have a very fast light output decay (~ 20 ns) and an emission spectrum peaking in the blue end of the spectrum near 370 nm. The light yields are typically 60,000 photons per MeV or 160% relative to NaI(Tl) for LaBr_3 and 50,000 photons per MeV or 130% relative to NaI(Tl) for LaCl_3 . The material density of the tri-chloride is similar to NaI at 3.8 gcm^{-3} , while the tri-bromide has a

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density similar to Ge (5.1 g cm^{-3}). At gamma-ray energies, FWHM energy resolutions of 2.9% (LaBr_3) and 3.3% (LaCl_3) at 662 keV have been reported for very small crystals [1,2]. What is of interest is the response at hard X-ray wavelengths – an energy range not usually exploited by scintillators, because of inherent non-linearities in their energy response, but potentially very interesting for synchrotron and differential X-ray absorptiometry applications.

2. Experimental

Cerium doped LaCl_3 and LaBr_3 crystals were grown from melt by Saint Gobain Crystals and Detectors [3]. The cerium fraction was 10% for the chloride and 5% for the bromide. The ingots were processed into one inch high, one inch diameter, right circular cylinders and packaged in hermetic Al housings to prevent hydration. To detect as much scintillation light as possible the crystals are covered on all sides, except the read-out side, with a reflective material. The read-out side is viewed through a quartz window coupled to a Photonis, XP2060B 10-stage photomultiplier tube (PMT). The PMT bases also contain a unity gain preamplifier whose signal output is shaped and amplified by an external Ortec 671 spectroscopy amplifier. The output of the amplifier, in turn, is digitized by an Amptek 8000A multichannel analyzer (MCA). Detector bias is provided by a Canberra 3106D high voltage supply unit. A PMT bias of 700V and an amplifier shaping time of 1 μs were chosen so as to give an optimum spectral resolution at 662 keV of 3.0% FWHM for the tri-bromide and 4.1% for the tri-chloride, respectively. The relative light yield ($\text{LaBr}_3/\text{LaCl}_3$) between the two crystals was determined at 22.1 keV, 32.2 keV and 60 keV using calibration sources to be 1.75 ± 0.3 . This was achieved by coupling both crystals sequentially to same PMT under identical bias and operating conditions.

2.1. X-ray measurements

X-ray experiments were carried out at the X-1 beamline at the Hamburger Synchrotronstrahlungslabor (HASYLAB) radiation facility in Hamburg, Germany [1]. This beamline is illustrated in fig. 1 and utilizes a double Si crystal monochromator to produce highly monochromatic X-ray beams across the energy range 10.5 keV to 100 keV. To achieve such a large energy range, a [511] reflection was used, yielding an intrinsic energy resolution of $\sim 1 \text{ eV}$ at 10 keV rising to 20 eV at 100 keV. The beam spot size was set by a pair of precision stepper-driven slits, positioned immediately in front of the detector (see fig. 1). For X-ray Absorption Fine Structure (XAFS) measurements, an ion chamber was inserted between the monochromator and the exit slits. This is used as the controlling element of a servo loop to ensure constant beam intensity at the detector. The detector was mounted on an X-Y table capable of positioning the array to a precision of $<1 \mu\text{m}$ in each axis. For the measurements described here the beam was normally incident at the center of the forward face of the detector. For the majority of the

measurements, a slit size of $50 \times 50 \mu\text{m}^2$ was used. For completeness, additional full-area illumination measurements were carried out using radioactive sources.

Fig. 1. Experimental set-up at the HASYLAB X-1 beamline.

3. Results

The hard X-ray response of the detectors was determined using a number of monoenergetic energies between 10.5 keV and 100 keV. Fig. 2 shows a composite of energy spectra measured for both the LaBr_3 and LaCl_3 detectors. The measurements were carried out at room temperature. The noise threshold (defined to be the lowest energy for which the low energy noise attains an amplitude of 0.5 of the photopeak) is 3 keV for both detectors.

Fig. 2. Composite of pulse height spectra measured for the one inch LaCl_3 (left) and LaBr_3 (right) detectors at HASYLAB measured at a detector bias of 700V. The beam size was $50 \times 50 \mu\text{m}^2$, incident at the center of the detector. The measurements were carried out at room temperature. The FWHM energy resolutions range from ~ 3 keV at 10.5 keV to ~ 30 keV at 100 keV.

3.1. Proportionality of response

In fig. 3 in which we show the proportionality of response or, alternately, the linearity curve for both the LaCl_3 and LaBr_3 crystals. The apparent larger output of the tri-chloride is due to a change in amplifier gain. The data are plotted in the form of centroid ADC channel divided by energy versus energy to accentuate deviations from linearity. For a perfectly linear system, this ratio should be constant with energy. As can be seen from fig. 3, below the La K-shell energy the non-linearity increases rapidly with a clear discontinuity at the edge. At the edge the energy response changes by 2%. For the tri-bromide there is also a discontinuity at the Br K-shell energy at 13.5 keV.

Fig. 3. The detector proportionality of response or linearity curve for both the 1 inch LaBr_3 and LaCl_3 crystals. The data are plotted in the form of centroid ADC channel divided by energy to accentuate structure. Note: the apparent larger output of the tri-chloride is due to a change in amplifier gain. The lower panel shows the corresponding residuals for LaCl_3 , *i.e.*, the percentage deviation from a best fit (measured peak channel - calculated peak channel / calculated peak channel $\times$ 100). Two fits were considered a second order polynomial and a fifth order polynomial. The curve for LaCl_3 is similar and not shown for clarity.

The lower panel in fig. 3, shows the residuals of a best fit calibration curve for the LaCl_3 data - that is, the percentage deviation from the curve (measured peak channel - calculated peak channel / calculated peak channel $\times 100$). The curve for LaBr_3 is similar and not shown for clarity. Two calibration functions were considered - a simple 2nd order polynomial fit and a 5th order polynomial fit. We see that for the 2nd order polynomial fit, the residuals are quite deviant at energies below 15 keV - or $\sim 15\%$ of the dynamic range. Increasing the order of the fit improves the situation - from a maximum deviation of 2.5% for the 2nd order fit down to 1.5% for the 5th order fit. The corresponding rms deviations were 1.5% and 0.8%, respectively. However, overall, the deviations are dominated by the edge and reflect the simplistic nature of the fitting functions.

Fig. 4. Top graph - Measured energy resolution for both crystals. For comparison we also show the energy resolution for a 1 inch NaI(Tl) crystal. Bottom graph - the ratio of the measured energy resolutions of LaBr_3 and LaCl_3 . The ratio continues to fall at higher energies. At 662 keV it is 0.77. The La K-edge is indicated by the dashed line.

3.2. Energy resolution

The energy resolutions determined from fig. 2, range from 3 keV FWHM at 10.5 keV to ~ 30 keV FWHM at 100 keV and are plotted in Fig. 4. From the figure, there is a clear discontinuity around the La edge at 38.9 keV for both LaCl_3 and LaBr_3 and a less pronounced Br K-edge at 13.5 keV for LaBr_3 . Both above and below the edge (but above the Br edge for LaBr_3), the resolution data are well fit by power law distributions.

Also shown in fig. 4, is the energy resolution for a 1 inch NaI(Tl) crystal. The data were accumulated using the same PMT, although with a higher bias (750 V). As expected the resolution is better than the halides below 100 keV and worse above [*e.g.*, see ref. 5]. In fact at 662 keV, the FWHM energy resolution of the NaI(Tl) crystal is 6.0% - a factor of 1.5 and 2.0 times broader than measured by the LaCl_3 or LaBr_3 detectors, respectively. In the lower graph of Fig. 4, we show the ratio of the measured energy resolutions of LaBr_3 and LaCl_3 . The ratio continues to fall slowly at higher energies. For example at 662 keV it is 0.77. Both curves below and above the La K-edge are reasonably well fit by power laws. In fact, the best fit for the curve above the edge includes the data point at 662 keV.

Fig. 5. The X-ray Absorption Fine Structure signal extracted from the count rate data of the LaBr_3 detector. The XAFS signal $\mu(E)_d$ contains information on the local atomic structure around absorbing atom, including both pair and many-atom correlation functions (see text). For comparison, we also show the expected signal based on unperturbed isolated atomic cross sections [8].

3.3. X-ray Absorption Fine Structure measurements

Structure around the La edge was investigated on the LaBr_3 crystal by carrying out a standard EXAFS scan while operating the detector as a single photon counter. For the La edge, the monochromator was scanned from 38774 eV to 38892 eV in step sizes of 5 eV; from 38893 eV to 38961 eV in 1 eV steps and from 38962 eV to 39494 eV in equal k-space steps of $0.04 \text{ \AA}^{-1}$. The edge was located at 38919 eV, which is consistent within error with the accepted value of 38925 eV. Note, the absorption energy will be slightly different from the elemental value tabulated in Bearden and Burr [6], since in a compound, the edge energies are dependent on its chemical state, namely the electronic energy difference between the 1-s state and the continuum.

Fig. 6. The structure of lanthanum halides [9].

The X-ray absorption signal was extracted from the detector count rate data using the ATHENA XAFS data processing software [7]. The X-ray absorption signal is shown plotted in fig. 5 from which we see that there is considerable near-edge structure when compared to curves generated from standard unperturbed atomic data tables [8]. However, very little evidence was found for extended fine structure suggesting that the bulk of the structure arises from the local coordination environment. Lanthanum halides crystallize with hexagonal symmetry around a UCl_3 type lattice with $P6_3/m$ spacegroup (see fig. 6). It is assumed that when doped, the Ce atoms uniformly replace the La atoms -

and this could be a source of disorder leading to a suppressed EXAFS signal. If this is indeed the case, then the EXAF signal in LaCl_3 should be smaller than in LaBr_3 due to its increased Ce fraction (10% as opposed to 5%). Unfortunately, structural information extracted from count rate data is too noisy to answer this question and so we have recently carried out a series of transmission EXAFS measurements using $\text{LaCl}_3\text{:Ce}$, $\text{LaBr}_3\text{:Ce}$ and pure LaBr_3 pellets. This data are currently being analyzed but preliminary results show that the EXAFS signal in the tri-chloride is indeed reduced compared to the tri-bromide. These data will be presented elsewhere.

4. Discussion and conclusions

Compared to the other new scintillating materials, such as lutetium based scintillators, the lanthanum halides continue to show great promise and look set to take over as the workhorses of gamma-ray spectroscopy. At hard X-ray energies < 100 keV, the energy resolution of NaI(Tl) is slightly better than LaBr_3 . However, the halides can excel applications where high speed or the very high light output can be exploited – such as synchrotron, differential X-ray absorptiometry or low level single photon counting applications.

This work was supported by the IHP-Contract II-04-016 EC of the European Commission.

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