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**PROGRESS AND PROSPECTS IN THE DEVELOPMENT
OF NEW SCINTILLATORS FOR FUTURE HIGH ENERGY
PHYSICS EXPERIMENTS**

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ABSTRACT :

The " Crystal Clear" collaboration has undertaken a systematic research on dense, fast and radiation hard scintillators, as components of high performance electromagnetic calorimeters for the challenging physics at the new generation of accelerators. First results are presented on the most promising candidates, as they are known today, with some consideration on the parameters influencing the cost of a large detector.

* This work has been carried out in the frame of the "CRYSTAL CLEAR" collaboration, CERN R&D project RD-18 [1]

1. Introduction:

The physics at the new pp colliders, at different factories as well as at high intensity fixed target and heavy ion experiments will be dominated by the difficult pattern recognition of the very low cross-section interesting events in the extremely high associated backgrounds. It is generally recognised that the reconstruction of simple and clean leptonic final states with very high resolution gives the best chance to obtain a signal to noise ratio above the detection limit. Moreover, the precise measurement of photon energies and angles in a fast and very high resolution calorimeter at LHC / SSC [2], could lead to the observation of a Higgs boson in the intermediate mass range ($M_Z \leq M_H \leq 2M_Z$).

The "Crystal Clear" collaboration [1] has the task to develop dense, radiation hard and fast scintillating crystals and glasses in view of the construction of electromagnetic calorimeters capable of very high performance in the severe running conditions of the new generation accelerators [3].

This report will summarize the progress already made for the most promising candidates, as well as some prospects for a few other materials.

2- General considerations about scintillators for calorimetry:

Density : The scintillator must have a high stopping power resulting in a small radiation length X_0 . This will allow to build compact calorimeters at a reasonable price. A high density material is therefore needed, but not necessarily with very high Z components as it is often quoted. The density should be preferably based on a high compactness of the crystal lattice (a large number of atoms per unit volume), keeping the atomic number of the components not too large in order to reduce the lateral shower size (Moliere radius: $R_M \approx X_0 \times (Z+1.2) / 37.74$). A small Moliere radius will limit the contamination of the energy measurement by other particles from the same or other events (pile-up) and help for the position reconstruction as well as for the π^0 rejection which will be the dominant background at LHC / SSC.

Scintillation : The material can be intrinsically luminescent if it holds luminescent ions, or doped with a scintillating impurity. Intrinsic scintillators are generally preferred as it is easier to control the light yield uniformity in long crystals. On the other hand, a controlled distribution of the doping could help correcting for the non uniformity caused by the light collection in a pointing geometry.

The excitation generally takes place between the valence and the conduction bands. The excited electron is usually linked to the hole in the valence band, forming an exciton having a band of energy levels just below the conduction band. The excitation can thus migrate through the crystal by thermal transfers between the excitonic and conduction bands. One should avoid situations where the excitation can be thermally transferred to metastable energy levels (like $^3P_1 \rightarrow ^3P_0$), which could give rise to an afterglow or a strong temperature dependence of the light yield. Only optically allowed transitions will give rise to a fast scintillation (like the transition $5d \rightarrow 4f$ for Ce^{3+}). If the recombination also involves a phonon exchange, the luminescence will take

place at a larger wavelength than the absorption (Stokes shift) reducing the risk of self absorption of the emitted light.

For some specific energy band configurations, more energetic excitations from the core states of the cation to the conduction band, give rise to a recombination process from electrons of the anionic valence band. If the recombination energy is smaller than the gap between the valence and the conduction bands, Auger emission is impossible and the recombination is radiative. The induced luminescence (cross-luminescence) is intrinsically fast and temperature independent. This mechanism has been recognized as responsible for the emission of the fast component of BaF_2 [4]. It is likely that this cross-luminescence exists in many compounds and has not been discovered so far because of the high excitation energy required (typically above 15 eV).

Radiation damage : Much progress has been made recently in the understanding of the radiation damage mechanism in inorganic scintillators [5]. The scintillation efficiency remains unchanged, but the optical transmission is reduced, as an effect of the production of colour centres. The colour centres result from the trapping of electric charges by crystal defects and are therefore directly correlated with some impurities of the raw material. A careful analysis of the colour centre properties can be very useful to identify the impurity responsible and to purify the raw material accordingly. In some cases, specific doping of the crystal can create non radiative ways to release the trapped electric charges, and allow a very fast recovery, as it was shown for the BGO:Eu [5,6].

3- Good scintillator candidates :

Very few systematic studies have been made so far for a thorough investigation of scintillators for High Energy Physics [7]. Some crystals are known for having at least one fast scintillating component like BaF_2 or pure CsI . They will not be described here as much information has already been published on them [8]. In addition, their density is probably marginally acceptable for LHC applications. Many crystals are currently studied by the "Crystal Clear" collaboration. We will concentrate here on the most promising candidates.

Cerium fluoride CeF_3 : Recently recognized as a good candidate for calorimetry [9], CeF_3 is a heavy material with a density of Ce^{3+} ions as large as $1.88 \times 10^{22} \text{ cm}^{-3}$ (see table 1 for a comparison of its properties with other scintillators). Ce^{3+} ions are excited from the 4f level (split into 2 by the spin-orbit coupling) to the 5d level (5 times splitted by the crystal field). The structure of the excitation spectrum corresponding to the 5 components of the 5d level is clearly visible on Fig 1. The recombination between the lowest 5d level to the 2 ground state sublevels, produces a fast and temperature independent luminescence. The average of 5000 pulses on a fast digital scope (Fig 2), shows a time constant for the total light emission of $\approx 20 \text{ nsec}$ with no afterglow. Our measurement of the light yield gives 46% of that of BGO (Fig 3). Moreover, the spectrum of the luminescent signal, with 2 components at 300 and 340 nm (Fig 1), probably to be attributed to 2 slightly different Ce^{3+} sites, is compatible with the use of Si photodiodes with a still reasonable quantum efficiency .

Impressive progress has been made recently by the company Optovac in the pre-growth purification techniques, which has led to significant improvement in the optical clarity, band edge transmission and radiation hardness of CeF_3 . A

systematic characterization of the colour centres is under way. When a long crystal is grown with no addition of melt, the impurity concentration progressively increases when the quantity of melt decreases, as a function of the segregation factor of this impurity in the lattice. In the sample of Fig 4, the radiation damage in the crystal is strongly position dependant, reflecting the gradient of impurity concentration. It is encouraging to notice that on one end of the crystal, the absorption induced by a 1000Gy ^{60}Co irradiation is as small as 0.5 m^{-1} , which corresponds to an acceptable value for use at LHC. This means that raw material of the desirable purity is now available.

Cerium doped Yttrium aluminate YAP(Ce) : Developed for laser applications, this crystal has a very strong luminescence in the visible spectrum at 370 nm (Fig 1), matching well the Si photodiodes efficiency. Our measurement of the decay time of the emitted light is of the order of 30 nsec (Fig 2) although other measurements on other samples give 17 nsec [10]. The difference could be attributed to a different Ce concentration for samples of different origins. Quoted to be very radiation hard [11], this crystal has a radiation length of 2.8 cm, due to a rather low density ($\rho = 5.36 \text{ g / cm}^3$) but still a small Moliere radius (2.8 cm). As it looks very attractive in all other aspects, we have a program in the "Crystal Clear" collaboration, involving the company Monokrystal Turnov (Czechoslovakia) to increase its density by replacing yttrium by isoelectronic cations like ytterbium.

Cerium doped Gadolinium silicate GSO(Ce) : This dense crystal (table 1) is a very attractive candidate for calorimetry [12,13]. It produces a large amount of light at 440 nm (Fig 1 and 3). The decay time depends on the cerium concentration, ranging from 55 nsec for 0.5% Ce to 31 nsec for 2.5% Ce (Fig 2). The radiation hardness has been quoted to be probably the best ever seen for a crystal, up to at least 10 MGy [13]. Large crystals have already been grown by Hitachi Chemical Co. Ltd. in Japan, but the temperature conditions must be carefully controlled to avoid cracks during the cool down.

Other scintillating crystals : In addition to the above mentioned crystals, the "Crystal Clear" collaboration is also investigating the very attractive family of tetrafluorides $(\text{Zn}, \text{Zr}, \text{Hf}, \text{Th})\text{F}_4$. ThF_4 for instance is a fast scintillator (less than 25 nsec), has a high density ($\rho = 6.32 \text{ g / cm}^3$) and looks radiation hard, with a small damage up to high doses and a very fast recovery (less than 1 day).

Fig 1 shows the very large and intense emission band of BaLiF_3 centred at 440 nm. The relatively low density of this material ($\rho = 5.24 \text{ g / cm}^3$) can probably be compensated by the fact that PbLiF_3 can enter in solid solution in BaLiF_3 in a proportion of up to 20%.

Starting from the well known laser matrix LiYF_4 , we have also tried to increase the density by replacing yttrium by ytterbium. The resulting LiYbF_4 has a density of $\rho = 6.09 \text{ g / cm}^3$. This crystal has a fast emission band between 400 and 500 nm. A strong irradiation of 1000 Gy improves the optical transmittance which then stays unchanged with time and after different temperature cycles, resulting in identical transmission curves (Fig 5). The reason for this unusual effect is probably a radiation induced bleaching of a crystal for which the post-growth thermal bleaching has not been appropriate.

For all these new crystals, there is a development contract between "Crystal Clear" and the French group including Crismatec, the "Commissariat à l'Energie Atomique" CEA Cadarache, and the University du Maine, Rennes.

4- Not yet scintillating crystals :

Lead fluoride PbF_2 : Lead fluoride is known as a Cerenkov radiator having a radiation length of less than 1 cm [14]. Optovac is now able to grow very high quality lead fluoride crystals of 20 cm length or more. Unfortunately no luminescence has been detected so far, although the Pb^{2+} ion is a scintillator, and many other lead compounds like $PbCO_3$ [15], $PbSO_4$, $PbCl_2$, $PbBr_2$ and $PbFCl$ are known as fast scintillators. However all these other crystals are difficult to grow synthetically. We have some reasons to believe that the luminescence of PbF_2 is hidden as a consequence of the too high local symmetry of the Pb^{2+} ion in the fluorite lattice. We have therefore proposed to Optovac to try to break this local symmetry by replacing 1/12 of the Pb^{2+} ions with some other cations. We are also investigating anionic doping and more complex structures like $CsPbF_3$ and $Pb_2(Zn,Th)F_6$. Results of these studies will be published soon.

Other crystals : Other matrices are under consideration because of their very high density. Most of them have been studied for laser research and their crystallographic properties are already known. Even if they are not intrinsic scintillators, they can be used as host for scintillating ions like Ce^{3+} . Among the most promising one, CdF_2 ($\rho = 6.33 \text{ g / cm}^3$), $BaYb_2F_8$ ($\rho = 6.99 \text{ g / cm}^3$) and YbF_3 ($\rho = 8.17 \text{ g / cm}^3$) are interesting candidates being looked at by the French group under Crismatec.

5- Heavy fluoride glasses : Fluoride glasses have been developed a few years ago for optical communications, because of their good optical properties in the infrared [16]. It was found incidentally that their radiation resistance could be much higher than for other glasses, for reasons which are probably the same as in the corresponding crystals. The development of heavy scintillating glasses with clear advantages, such as ease and speed of manufacturing and probably low prices, would be a major breakthrough for many applications, in particular for high energy calorimeters.

The French company "Le Verre Fluore" has succeeded in growing for us dense and stable compounds of different heavy fluoride materials, doped with Ce^{3+} ions. Two samples with a density of $\rho = 5.75 \text{ g / cm}^3$ and $\rho = 5.95 \text{ g / cm}^3$ (HFG320 and AFG450) have a strong luminescent signal (Fig 1) when excited near the band edge (respectively 320 nm, $\tau = 16 \text{ nsec}$, and 330 nm, $\tau = 28 \text{ nsec}$). The radiation properties of these glasses are much better than for other glasses, although not yet satisfactory for LHC applications. A program of research is under way with this company, to increase the density and improve the radiation hardness.

6- Cost considerations :

A lot of effort is spent in our collaboration to identify low cost materials and to develop cheap production techniques. From this point of view, our work on scintillating glasses is considered with a high priority. As far as crystals are

concerned, the factors influencing the cost are identified and carefully analysed. The availability of the raw materials, and their required purity to reach the wanted performances has oriented our choices to simple materials like PbF_2 or CeF_3 (although cerium is a "rare" earth, its natural abundance of 46.1 g / ton is comparable to that of nitrogen and tin : 46.3 and 40 g / ton respectively). The growing technique and the crucible material are dominant parameters for the cost; most of the crystals listed in this paper can be grown using the relatively cheap Bridgeman method in graphite crucibles. The cost of the energy plays also an important role, as a combination of the melting temperature and the pulling rate. From this point of view, the high melting point of GSO (1900 °C) and the high segregation factor of cerium in this matrix implying a low pulling rate (1 to 2mm / hour) may put some limits to the minimum obtainable price for such a crystal. On the other hand, the low melting point of PbF_2 (822°C) and the abundance of the raw material make it a potentially low cost material. A high crystal density, directly limiting the total volume for a calorimeter, but also the crystal dimensions and consequently the furnace and crucible sizes will be a major parameter of the total cost of a crystal based detector. Finally, the very good mechanical properties of PbF_2 or CeF_3 for instance, allows a high production yield of the mechanical processing, which will also reduce the final cost.

7- Conclusions :

The "Crystal Clear" collaboration has undertaken a systematic investigation of dense, fast and radiation hard scintillating materials for possible use in high performance electromagnetic calorimeters at LHC. Other fields of application are also considered like nuclear or astrophysics experiments, as well as time of flight Positron Emission Tomographs (PET) for medicine, and several industrial applications. Some candidates like CeF_3 seem to reach the required specifications, and many others offer very attractive perspectives but require more work before being seriously considered.

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Table 1: Crystals characteristics

Crystal	Density	Radiation length cm	Moliere radius cm	Decay time nsec	Peak emission nm
BGO	7.13	1.11	2.33	300	480
BaF2	4.89	2.06	3.39	0.6 620	210 310
CeF3	6.16	1.68	2.63	5 20	300 340
YAP:Ce	5.35	2.83	2.82	35	390
GSO:0.5%Ce	6.71	1.39	2.42	55	435
GSO:2.5%Ce	6.71	1.39	2.42	31	450
ThF4	6.32	1.18	2.71	≤ 25	315,330,450
BaLiF3	5.24	2.13	3.13	≤ 25	435
LiYbF4	6.09	1.56	2.70	≤ 25	≈ 450
PbF2	7.66	.94	2.24	-	-

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Fig 1: Excitation, fluorescence and transmission spectra for 5 crystals and 2 scintillating glasses

T/div 20 ns

Fig 2 : Average of 5000 ⁶⁰Co pulses seen by a Lecroy 9450 digital scope for CeF₃, YAP:Ce, GSO:2.5%Ce and GSO:0.5%Ce

Fig 3: Comparison of light yields for different crystals

Fig 4: Radiation damage of CeF3 for 2 positions along an 8 cm long crystal after a 1000 Gy Co-60 irradiation

Fig 5: Transmission of LiYbF4 before and after 1000 Gy Co-60