Introduction

Search for Dense, Fast, Radiation Hard Scintillators for High Energy Physics. Inorganic Fluoride Materials

This book summarizes the works on search, preparation and studies of some physical properties of multicomponent optical fluoride materials which are promising for application as scintillators in high energy physics, nuclear physics, nuclear medicine and other adjacent fields.

In these fields the technique of ionizing radiation detection with the aid of scintillator detectors has been widely used as the main tool of research. This has become possible due to a comparatively simple detection of optical radiation, fast scintillation processes, availability of various photo detectors: photo-multipliers, Si-photodiodes, gas-charge proportional chambers filled by gas mixtures with photo-sensitive additives, etc. Many years of research have provided a great deal of inorganic and organic scintillators and optical materials which can be employed for detection of various kinds of ionizing radiation.

Scintillators are widely used in high energy physics for accurate measurements of energies of γ-quanta and electrons (positrons). Homogeneous electromagnetic (EM) calorimeters provide high energy resolution measurements of γ-quanta, as well as reconstruction of parameters of other elementary particles, such as π°, η, η'-mesons, by studying their decay into two γ-quanta. The possibility of accurate measurements of the electromagnetic component of the total energy in jet events is most important, when the density of the particle flux in the jet becomes so high that the generated electromagnetic showers cannot be detected separately.

NaI:Tl was the first scintillator material used in large amounts in EM calorimeters [1]. Later, CsI:Tl crystals were used, and quite recently $Bi_4Ge_3O_{12}$ (BGO) has been employed. CsI and BaF_2 are not so commonly used in high energy physics. The transition from NaI:Tl and BaF_2 scintillators to BGO crystals was mainly caused by the need to employ materials with shorter radiation lengths (see Fig. 1 and section 2.3) and high radiation resistances (10^4 - 10^5 rad).

Development of a new generation of accelerators, such as Superconducting Super Collider (SSC), Large Hadron Collider (LHC), Uskoritelno-Nakopitelny Kompleks (Accelerator-Storage Complex, UNK) will involve a large-scale employment of scintillators and other transparent optical materials, such as Cherenkov radiators. As the main requirements to scintillators are defined by energies of the detected particles (see Chapter 3), the requirements of high energy physics (HEPh) to materials have to be more strict in all respects, except light output.

New requirements to optical materials significantly differ from the previous standards in this field of materials science. That is why a new generation of scintillators is required for a new generation of accelerators.

The special requirements to optically transparent materials for the above goals are, first of all, high radiation hardnesses, which should attain 10^7 rad/year. The required luminescence decay times should be very short - less than 30 nanoseconds, even 3 ns. The required high density of materials, from 5 to 8 - 9 g/cm^3 is accounted for by a necessity of a high radiation absorption, which is responsible for such parameters of the entire detection system as spatial resolution, sizes of optical elements, etc. The unusually large lengths of crystalline elements are required for the total absorption EM-calorimeters, that makes the production of scintillator detectors more expensive. The single crystal industry, however, is not ready to produce such elements in large amounts (dozens of cubic meters) within a short period of time.

In fact, *none of the available scintillators can satisfy all the requirements to materials for high energy physics.* BGO crystals are rather dense (7.13 g/cm^3), but have long luminescence decay time (about 300 ns). Apparently, their production technique will have to be modified so as to make radiation hardness higher by a factor of 10^2 as compared to commercial materials which are currently used. Crystals of NaI:Tl and Cs:Tl have insufficient radiation resistances, densities and too long decay times.

Among crystals of the new generation, fast scintillators based on radiative core-valence (CV) transitions in BaF_2 have the lowest absorption values accepted in high energy physics. Their radiation resistances should also be increased and the intensive slow component should be eliminated or essentially suppressed. Their mechanical properties (perfect cleavage, low hardness) are unsatisfactory, too.

Recently, cerium fluoride scintillator has been chosen as an option. Indeed, this crystal is most good in its parameters among the available single crystals of simple metal fluorides. This choice, however, is not the best one due to the following reasons. Crystals of cerium fluoride are not much "heavier" than barium fluoride (the atomic numbers of Ba and Ce are 56 and 58, respectively), they have luminescence decay times as long as 30-40 ns and a complex spectral composition of the luminescence. Production of large single crystals will be complicated due to a significant anisotropy of coefficients of thermal expansion, typical of compounds with the LaF_3 structural type. This anisotropy concerns other parameters, too, including spectroscopic ones.

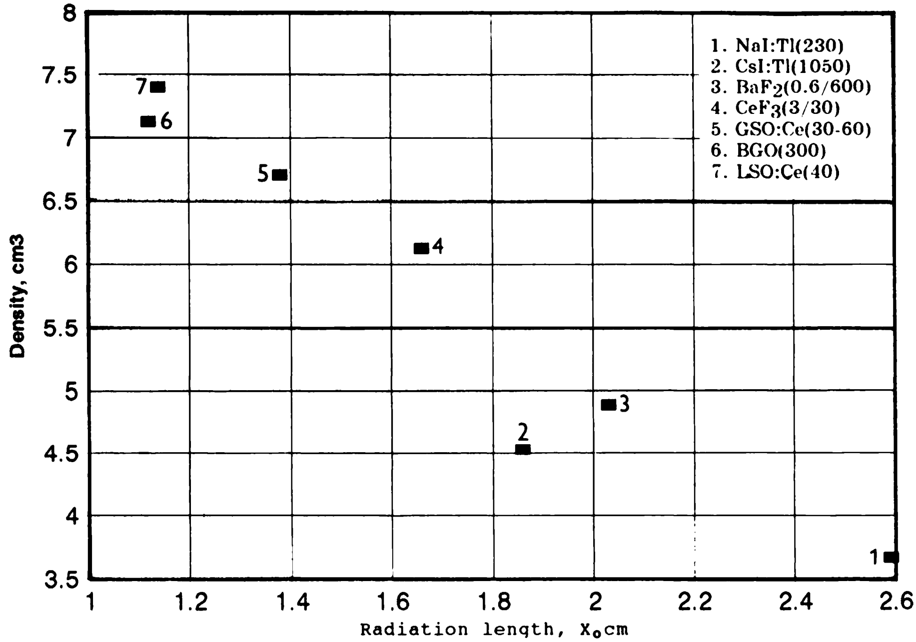

Fig. 1. Densities and radiation lengths for some popular scintillators

In general, we can illustrate how the characteristics of the available dense scintillators conform to wanted parameters by Fig. 1, which presents the correlation between radiation lengths of materials and their densities. In contrast to radiation resistances or luminescence parameters, these characteristics are absolute and they are not affected by controlled or uncontrolled factors. Bold horizontal lines denote the range of minimum densities (5.5 - 6.5 g/cm^3) which are acceptable for high energy physics. Luminescence decay times in nanoseconds (which are slightly affected by various factors) are shown in brackets after the chemical formulas or abbreviations of the materials. All the commonly used scintillator crystals are close to the lower limit of the absorption capacity and their luminescence decay times are rather far from subnanosecond ones.

There are still many unresolved problems which pertain to employment of scintillators in high energy physics (some of them we have mentioned above). First of all, theoretical foundations as well as technologies of production of optical materials with the required high radiation hardnesses have not been developed. To a certain extent, this is due to an insufficient scale of studies of the influence of dopants on the radiation hardness in optically transparent multicomponent materials. *A priori* any impurity was supposed to deteriorate radiation hardness, that is why the main goal was to obtain single-component crystals as pure as possible.

Luminescence decay times of most common inorganic scintillators are, in fact, inadequate for the high counting rates expected at new accelerators. The recently discovered mechanism of core-valence (CV) transitions, which gives rise to fast luminescence in some inorganic scintillators (mostly fluorides), requires intensive studies for a better understanding of their possible applications in high energy physics. That is why special attention has been paid to CV transitions in this book.

New scintillators cannot be obtained on the basis of simple chemical compounds. In particular, among single-component inorganic fluorides, which possess such indispensable parameters as, e.g., a high density, only a few were of interest as possible scintillators for HEPh.

The problem of broadening the range of optical materials in order to obtain crystals with desired properties had been formulated in the mid-seventies owing to the advances in quantum electronics. This problem was solved due to a transition from simple (single component) substances to complex (multicomponent) chemical materials. Search for multicomponent materials, in its turn, required data on the chemistry of the particular class of chemical compounds, without which search for new materials would be a matter of luck. Such data are not available for all the chemical classes of compounds which are considered to be promising because of their properties.

Recent developments in high temperature chemistry of inorganic fluorides have gone beyond practical demands for fluoride materials. This is a rare case in materials science, that has led to search for new multicomponent fluoride materials based on data on the available phase diagrams of appropriate chemical systems.

The widely used trial-and-error technique of search for new materials requires a lot of time, but this is not the only disadvantage. The method does not ensure the optimum properties for a particular task. The danger is most great when the search is made within a wide range of materials that should satisfy quite a number of requirements.

Taking into account the overall cost of up-to-date accelerators, it is unwise to save money by not optimizing parameters of their detection systems as most important units. That is why in recent years many research centers are concerned with search for new scintillators which meet to the maximum extent the strict requirements imposed by HEPh. The most well-known are such programs as the Crystal Clear in CERN, Geneva, and the

GEM collaboration, USA. A wide-scale search for new dense scintillators is carried on by a group of the Donner Laboratory, LBL, Berkeley, USA.

The program reported in this book is part of the general research. The program is carried out by scientific groups of the Institute of High Energy Physics (IHEPh, Protvino), the Institute of Crystallography, Russian Academy of Sciences, (Moscow), the St. Petersburg Technical University (St. Petersburg), the Moscow Institute of Engineering Physics (Moscow), the National Laboratory for High Energy Physics (KEK, Tsukuba, Japan).

The main scintillation characteristics of new materials were studied at IHEPh. The authors do not claim that the interpretation of the reported experimental results is comprehensive. An appropriate theoretical analysis is needed. The reason is that this direction is rapidly developing and the formulated problem cannot be resolved at the first stage, namely, a wide-scale search for promising materials based on an artificially limited set of parameters, which has been completed and reported here. Some of the experimental data presented below should be refined, some effects observed should be studied in detail and explained in terms of theory. Studies of all the materials as possible scintillators, even simple, binary (in the basic composition) crystals, despite the restrictions in the parameters, are beyond the possibilities of the co-authors of this book. In view of the above said, *the dense, radiation hard, fast scintillators, obtained and studied by us, cannot be considered as materials with the best attainable parameters for the chosen class of chemical compounds. At the same time, they demonstrate that the suggested systematic approach to search for new materials for HEPh is quite promising [3].*

Studies of optical, luminescence and scintillation properties of various fluorides were performed for many years at the Laboratory of Physics of Ionic Crystals of the St. Petersburg Technical University. The advances in pulse X-ray luminescence spectroscopy led to a discovery of short-wave (220 nm) subnanosecond luminescence in BaF_2 crystals in 1980. This gave a new impetus to wide applications of that material as a fast scintillator. Further research in this direction is stimulated by the need to develop new scintillators for HEPh [5].

High-temperature chemistry of inorganic fluorides has been a major direction of research carried out at the Laboratory of Physico-Chemical Analysis of the Institute of Crystallography since the early seventies. The final stage of studies of phase equilibria in binary system was construction of their condensed state phase diagrams and preparation of appropriate multicomponent materials in various forms, single crystals, in particular. Many physical characteristics of samples of the new materials have been determined in collaboration with several scientific groups [4]. In recent times the attention of scientists has been focused on the class of nonstoichiometric crystals because of their specific (partially disordered) structure. This distinctive feature is responsible for specific physical properties which make nonstoichiometric fluorides quite interesting for applications as optical media with parameters which can be controlled over a wide range. The available experience of preparation of single crystals of fluoride materials for various applications was used for search for fast, dense, radiation hard scintillators.

We have divided the problem of development of new fluoride scintillators into two stages. At the first stage, new crystalline matrices are sought, which in their conservative characteristics (high density, improved mechanical properties, congruent character of melting, optical characteristics in UV and IR ranges, etc.) correspond to the HEPh requirements [3]. At the second stage, the techniques which provide such optical media with the required functional properties and ensure their high stability in environments are studied [7].

Such an approach to the search for new multicomponent optical media sets off the general problem of development of fluoride optical materials with qualitatively different properties from a more particular problem in materials science, namely, the problem of high-density, radiation hard, fast scintillators. *Therefore, the sections of this book which are concerned with the chemistry of fluorides in binary* MF_m - RF_n *systems and technology of production of multicomponent crystals can be regarded as a standard guide in the search for new fluoride materials, irrespective of their applications.* That is why we have included into the book the sections which deal with physicochemical foundations of search for fluoride binary materials, although the scope of these sections is wider than it is required for solving a particular problem of preparation of dense optical media.

Search for new dense, fast and radiation hard scintillating crystals has also been carried out for a long time at KEK mainly in the following ways:

(1) preparation of new crystal samples grown in other institutes of crystal study as well as in crystal growing companies;

(2) measurement of the optical and scintillating characteristics;

(3) tests of the crystals by using test beams (electrons) at the 12 GeV proton synchroton;

(4) study of radiation damage and its recovery by using the γ-rays and/or thermal neutrons at the JAERI (Japan Atomic Energy Research Institute) or proton beams at KEK. The results were feed back to the crystal growing. Main scintillating crystals studied and/or employed in physics experiments at KEK include BGO, GSO:Ce, CsI, CeF_3, $PbWO_4$, etc.

A systematic search for new optical media in a large family of inorganic fluorides is suggested and employed in this study. These compounds play a special role in development of dense, fast, radiation hard scintillators.

Fluorides are more preferable, sometimes even unique, among other classes of chemical compounds due to the following features:
- the high-temperature chemistry of most inorganic fluorides in binary systems has been studied extensively and this is the scientific foundation of search for new two-component materials;
-minimum self-absorption of quanta of short-wave (fast) luminescence, typical of fluorides;
- a possibility of the CV transition mechanism of fast luminescence in fluorides, which requires participation of fluorine, as well as mechanisms of interconfiguration electronic transitions which require isomorphic doping with certain activator ions;
- a possibility to obtain a large number of optical materials with high absorption of ionizing radiation in the chemical class of fluorides;
- relatively low cost of raw materials and easy manufacture of the crystals, provided that the substances are chosen under specific conditions;
- crystallization processes have been studied for multicomponent fluoride melts, etc.

A detailed analysis of positive and negative factors which influence the choice of fluoride materials will be made in appropriate sections of the book.

In the **Introduction** the present state of the art in the search for scintillators for a new generation of elementary particle accelerators is outlined. The main parameters of scintillators which are indispensable for their effective applications are considered. Among the available materials there are none, at the moment, which fully satisfy the requirements imposed by HEPh. Some specific features of inorganic fluoride crystals that make them promising objects of studies are discussed. The main principles which have been used as the basis of search for new scintillators are briefly outlined and the potentialities of multicomponent fluoride crystalline materials formed in binary MF_m - RF_n type systems for the solution of this problem are discussed. A digest of the book is presented.

Chapter 1 is devoted to the physical processes of transformation of high energy excitation to scintillation, that occur in the crystalline matrix itself, i.e., they are not related to impurity ions. The two main types of intrinsic luminescence, excitonic and core-valence, can make a substantial contribution to fast scintillation. Features of behavior of self-trapped excitons in fluorides are described. The crystals in which excitonic luminescence retains a high light output in the range of room temperatures, are defined. The mechanism of core-valence luminescence with short decay times, high thermal stability and relatively high light output is described. The directions and prospects for obtaining new materials which possess CV transitions are specified.

Chapter 2 is devoted to impurity luminescence of fluorides with regard to search for fast scintillators. The conventional type of luminescence, in which radiative transitions occur between the excited and ground states of the activator, as well as the mechanism of impurity core-valence luminescence due to transitions between the impurity and the valence bands are discussed. Three kinds of luminescence quenching are considered: temperature, impurity and concentration, as well as relevant physical processes, that influence the light output and decay time. The main concepts of physics of luminofors are given and some typical parameters which are widely used to characterise scintillators, are described. The data on interaction of quanta and particles with the scintillator substance are classified. The problem of radiation hardness of scintillators as well as the recovery of radiation damage is considered briefly.

Chapter 3 deals with the general requirements to inorganic scintillators in various energy ranges of the detected electrons and γ-quanta, illustrated by an example of their application in HEPh and nuclear physics. Some specific applications of scintillator materials, such as experiments on search for neutrinoless double beta-decay, solar neutrino, "dark matter" in the Universe, for gamma and positron-emission time-of-flight tomography, etc., are considered. Luminescence characteristics of some scintillators based on metal fluorides are reported, their possible applications in the above fields are discussed. Applications of heavy Cherenkov radiators in HEPh are assessed. Examples of EM total absorption calorimeters for the new generation of elementary particle accelerators are also described.

Chapter 4 dwells on physico-chemical principles of search for new multicomponent fluoride materials. The potentialities of development of scintillators for HEPh have been practically exhausted among single-component fluorides. As a way out, we suggest the transition to multicomponent (without account of activator) materials. The two-component phases that crystallize in $M\mathrm{F}_m$ - $R\mathrm{F}_n$ systems are the simplest multicomponent ones. They are isovalent or heterovalent solid solutions and binary chemical compounds with homogeneity regions or without them. Phase diagrams of two-component $M\mathrm{F}_m$ - $R\mathrm{F}_n$ systems are the basis of search for the new phases. The choice of components of such systems with regard to development of new multicomponent scintillators of HEPh is explained. The amount of the known phase diagrams of two-component systems (561 in total), formed by fluorides of 34 elements: Li, Na K, Rb, Cs; Mg, Ca, Sr, Ba, Cd, Pb, Zn; Sc, Y, La and 13 lanthanides, In, Bi; Zr, Hf, Th, U is assessed. About 300 experimentally studied phase diagrams are divided into 10 types according to combinations of cationic valences (*m*, *n*). 18 schemes of typical phase diagrams are presented and features of melting and thermal stability of phases which are responsible for their possible applications and the choice of optimum techniques of preparation of the single crystals are considered. The analysis of specific weights of the formed solid solutions and binary compounds is made in order to assess possibilities of preparation of high-density optical materials in each group of phases. Prospects for development of more complex multicomponent fluoride materials are discussed. General principles of obtaining fast luminescence in fluorides are considered. A number of two-component compositions are selected for synthesis and studies of their physical characteristics.

Chapter 5 is devoted to preparation of homogeneous multicomponent single crystals by unidirected crystallization from melt. The constraints imposed on the choice of compositions of two-component solid solutions which can be obtained in the form of homogeneous single crystals are discussed. These constraints are due to irregular distribution of the second component during the unidirectional solidification of melts with an incongruent behavior. The techniques which can smooth the incongruent (in the general case) behavior of two-component melts are considered. Crystallization parameters (temperature gradient and growth rate) which are required for preparation of homogeneous crystals of dense nonstoichiometric fluorite type phases have been assessed. Peculiar cases of congruent melting of some phases with variable compositions are considered, such as extrema in the melting curves (maxima for heterovalent and minima for isovalent solid solutions) which yield optical grade single crystals. Specific chemical reactions of pyrohydrolysis, typical of inorganic fluorides at high temperatures are discussed. If such reactions are not controlled in the course of production of single crystals, sample quality is not high.

Chapter 6 deals with techniques of studies of physical properties of multicomponent fluoride materials, used in this work (radiation hardness in fluxes of γ-quanta and hadrons, measurements of luminescence decay times, upon excitation by γ-quanta, determination of light output, recovery time). Data on 70 crystals are presented, dozens of which have the characteristics that satisfy to, or are higher than those required by HEPh for the main service parameters of scintillators.

Chapter 7 dwells on techniques and results of studies of behavior of some typical scintillators at the moment of pulse γ-neutron irradiation or immediately afterwards. The actual response of optical material to irradiation sometimes disagrees with the data on studies of post-irradiation defects in it. The information on fast processes might be lost within a very short time after irradiation. Despite the fact that studies of the formation and kinetics of the behaviour of various types of radiation-induced optical defects in materials are quite tedious, such techniques should be included into the final stage of choice of scintillators for HEPh.

Chapter 8 is concerned with selection of the best materials according to the results of search for fast, radiation hard, dense scintillators for HEPh. 31 materials which most fully satisfy the requirements of density (> 6 g/cm^3), radiation resistance ($> 10^6$ rad), nanosecond luminescence decay times have been chosen. Most of these materials, in their chemical composition, belong to the same type of ternary systems, namely, CdF_2 -PbF_2 - RF_3, where R stands for rare earth elements. The above parameters of the materials can be controlled by a direct variation of the chemical composition of the crystals. Compositions of materials with the best characteristics (among those studied) are reported. The phases which are of primary interest as possible scintillators for HEPh are listed. The prospects for employment of the known mechanisms of fast luminescence and specific features of their application for the search for and development of dense multicomponent fluoride materials are discussed. Besides single crystalline form, other forms of multicomponent materials (glasses, optical ceramics, composite multiphase materials, etc.) are considered. Technical conditions for preparation of each form of the materials, with regard to most typical (in the mode of melting and thermal behaviour upon cooling) fluoride phases of two-component compositions in the MF_m - RF_n systems, are considered.

As the search for scintillators is still in progress, the authors hope that this book,which has been written just in the course of intensive research, will be helpful to investigators who are or will be engaged in such studies. Development of new optical fluoride materials has been a key issue in materials science in recent decades. We hope that our experience in the search for multicomponent fluoride optical media for HEPh will contribute to further advances in this and other fields of inorganic materials science. Then, we shall be convinced that our efforts have not been wasted.

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