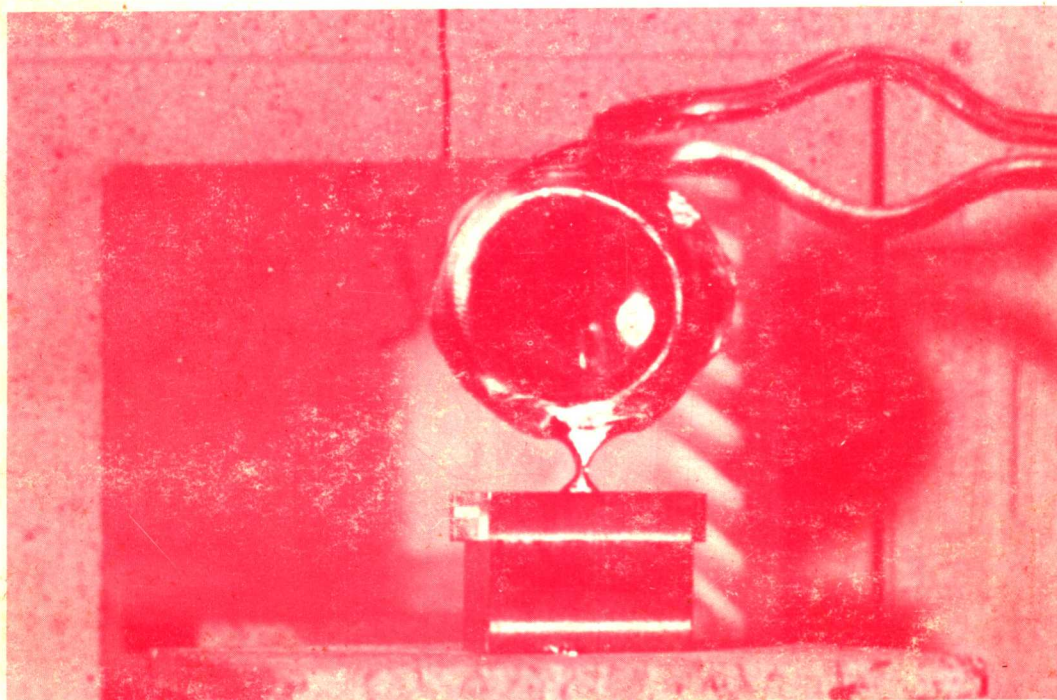


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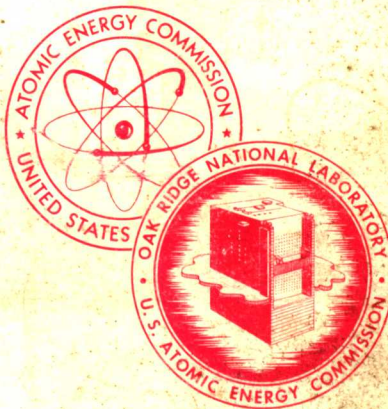
**PROCEEDINGS OF THE
SECOND INTERNATIONAL CONFERENCE
ON LUMINESCENCE DOSIMETRY**



Held at Mountain View Hotel, Gatlinburg, Tennessee

September 23-26, 1968

**Sponsored by
United States Atomic Energy Commission
and
Oak Ridge National Laboratory
Oak Ridge, Tennessee**



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Editors

**J. A. Auxier
K. Becker
E. M. Robinson**

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and
Oak Ridge National Laboratory, Oak Ridge, Tennessee**

FOREWORD

During the three years between the first and second International Conferences on Luminescence Dosimetry, a vast amount of research and development were accomplished in the field. Consequently, the papers selected for presentation at the second conference held in Gatlinburg, Tennessee, September 23 thru 26, 1968, and published in these proceedings, provide a needed reference compilation. The conference was sponsored by Oak Ridge National Laboratory.

In addition to the usual topics of radiophotoluminescence and thermoluminescence, one session was devoted to the field of exoelectron emission. The rapid developments in this field during 1968 were of great interest and stimulated many hours of informal discussion. Other topics which received considerable attention included supralinearity, mechanisms of trapping, types of centers involved, and some of the less common luminescence substances such as lithium borate.

This publication presents the papers as given at the conference with minor editing of papers at the request of authors to whom English is not the native tongue. The mode of printing was chosen because it was the fastest available. The papers are grouped by sessions as given, including papers read by title, and all discussion is presented at the end of the grouping; this too follows the format of the conference. There were 144 registered attendees representing 11 countries: Belgium, Canada, Czechoslovakia, Denmark, England, France, Germany, Italy, Japan, Sweden, and U.S.A.

It was apparent to the participants that this was an excellent symposium; the papers were well chosen by the Program Committee, the conferees were most interested as shown by superb attendance at every session, and the environment was pleasant. Many people worked to make the conference so successful, and their contributions can be inferred, in general, from the various committee, session chairmen, and speaker lists. However, a large measure of the arrangements planning was done by Mr. Charles E. Normand of the ORNL Personnel Division and by the secretarial staff of the DOSAR Facility at ORNL. Mrs. Brenda Hickey and Miss Sandra Cash worked during the conference, and they were assisted before and after the conference by Miss Jo Brown in all aspects of preparing these proceedings for publication. For their hundreds of hours of hard work, the Arrangements Committee is most grateful. Also, the committee is both pleased and grateful for the cooperation of the authors in getting their papers to us promptly. The audio-visual group from ORNL did a superb job in both projection and recording.

J. A. Auxier
K. Becker
E. M. Robinson

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Opening of the Conference

J. A. Auxier: It is my pleasure to open the conference by presenting to you the man that is known throughout all of the countries represented here as "Mr. Health Physics," the man who is the founding father and the first president of the Health Physics Society, the founding father and first and present president of the International Radiation Protection Association, and what is more important to me, the Director of the Health Physics Division of the Oak Ridge National Laboratory, Dr. K. Z. Morgan.

K. Z. Morgan: On behalf of the Oak Ridge National Laboratory and the Health Physics Division, I am pleased to have the honor to welcome you to the Second International Conference on Luminescence Dosimetry. I was impressed with the quality of the first conference held at Stanford and have every expectation that this conference will be equally as effective. I am particularly happy that so many of our friends and co-workers from overseas are with us at this conference. I haven't made a final check, but I believe there are ten countries represented here, and I trust you will find this conference very helpful and of great value.

As I have watched the field of radiation dosimetry over the past quarter of a century, I have witnessed phenomenal improvements in the basic concepts, instrumentation, techniques, and, most important of all, an improved understanding of the basic physics involved. When health physics began at the University of Chicago back in 1942, we had to depend primarily on electrometers, Geiger counters, and photographic emulsions. There were times when for a period of several years we witnessed no specific new developments, that is developments of any great importance, but had to be content with the gradual improvement of old systems and techniques. However, I think this conference is being held at a most propitious time in view of the recent marked advances in the field of radiation dosimetry, particularly in the area of solid state dosimetry. I am sure that the reports here of new developments of photoluminescence and thermoluminescence will be quite exciting and that the discussions in the related field of thermally stimulated exoelectrons will be the basis for many hours of informal discussions. One of the advantages of having the conference here, I think, is that you can have these informal discussions in the lobbies, in the bars, and on hikes, and I hope this proves to be a very profitable experience for everyone.

Of course, we at Oak Ridge National Laboratory are equally excited about other areas of dosimetry and research, including such relatively new techniques as the etch-pit method of rendering visible charged particle tracks in insulating materials.

I am sorry that I personally cannot be here for the entire meeting to listen to the papers and participate in the discussions, for I have to leave in the morning for a meeting in Wiesbaden, Germany. However, I hope that all of you are able to stay and participate actively in this conference. I sincerely hope also that you find the time to enjoy the

scenery and the southern hospitality of the Tennessee mountains. I think it is particularly pleasant and beautiful in these mountains at this time of year.

Again on behalf of Oak Ridge National Laboratory and our Director, Dr. Weinberg, and the entire staff, I bid you welcome to this conference and wish you every success during the course of this meeting. Thank you.

J. R. Cameron: I want to thank everybody for coming. If we didn't have something important to discuss, I think we would have tried to arrange this conference just to see our friends. We are especially pleased to see our friends from overseas, such as Herb Attix. I don't know if many of you know that we had to reimport him from England. We are very pleased with the number of foreign participants.

In an affair such as this, there is a certain amount of work that has to be done, but I think you should be aware that the chairman does very little of it. The only person that does less than this is the vice-chairman, who happens to be our very honorable Jim Schulman from the Naval Research Laboratory, but this is fair enough because at the Stanford meeting, I was the vice-chairman and he was the chairman. The real work, I think is done by the Program Committee and by the Local Arrangements, and Herb Attix did an excellent job again as the Program Committee Chairman. I think you will see that as the times goes on, Klaus Becker, Jack Fowler, Vagn Mejdahl, Jim Schulman, and myself are also on the committee. The Local Arrangements Committee, headed by John Auxier and helped also by Klaus Becker and Eddie Robinson, did a lot of work during the last few months trying to arrange all the details, and I think so far we can be very happy with the way things are working out. I should also thank the Oak Ridge National Laboratory and the Atomic Energy Commission for sponsoring this get-together, and I think we should also thank our commercial exhibitors for coming and participating. I am sure they would appreciate having you stop down and visit their booths and discuss their products with them. We appreciate the financial support that they contributed to this meeting. Of course, we also appreciate your financial support. If times were not quite so hard I think the fee might have been a little bit less, but on the other hand, by the time the meeting is over, I think you will feel that you have gotten your money's worth out of it. If I hurry up and terminate this, we may have time to discuss the opening remarks, but rather than do that, maybe we can start a minute early.

The first session, if you may look at it, is completely a foreign session, even the speaker from Wisconsin on the 10:00 o'clock paper is Viennese. It wasn't planned this way, it just happened that way; but we are honored to have as the chairman of the first session Professor Scharmann, University of Giessen, Germany, Department of Physics.

Session A: THERMOLUMINESCENT MATERIALS

Chairman: A. O. Scharmann

CALCIUM SULFATE PHOSPHOR ACTIVATED BY RARE EARTH

T. YAMASHITA, N. NADA, H. ONISHI AND S. KITAMURA
Matsushita Electric Industrial Co., Ltd., Central Research Laboratory,
Kadoma, Osaka, Japan.

ABSTRACTS

CaSO_4 crystals activated by rare earth elements were found to be free from the serious disadvantage of rapid fading in $\text{CaSO}_4:\text{Mn}$ and yet retain the outstanding property of high sensitivity of $\text{CaSO}_4:\text{Mn}$, the most sensitive thermoluminescence dosimeter available at present. Among fourteen kinds of phosphors tested, $\text{CaSO}_4:\text{Dy}$ and $\text{CaSO}_4:\text{Tm}$ showed the highest sensitivity with essentially a single glow peak at about 220°C . Emission spectrum of $\text{CaSO}_4:\text{Tm}$ consists of a main sharp peak at $450\text{ m}\mu$ with minor ones at 360 , 470 and $520\text{ m}\mu$ and $\text{CaSO}_4:\text{Dy}$ has two main peaks at 480 and $570\text{ m}\mu$ without any minor one. The dosimetric characteristics of $\text{CaSO}_4:\text{Dy}$ and $\text{CaSO}_4:\text{Tm}$ are excellent except for their non-tissue equivalence: (1) little fading (1-2 % per month), (2) minimal detectable exposure is lower than $500\text{ }\mu\text{R}$ with standard deviation of $\pm 20\%$, (3) dose response is linear up to $3 \times 10^3\text{ R}$, superlinear from 3×10^3 to 10^4 R , and tends to saturation around 10^5 R , (4) tribothermoluminescence is very low (about 30th of that in LiF), (5) highly resistant against various spurious effects such as sun beam, artificial light, ambient gases, (6) constant thermoluminescence efficiency for more than 100 times of irradiation after repeated heating to erase previous dose.

INTRODUCTION

General properties required for phosphors to be useful for thermoluminescence dosimetry have been summarized by Schulman¹⁾ in his excellent review article to the following effect: 1) high intrinsic efficiency, 2) long storage of trapped electrons or holes at normal working temperature, 3) simple trap distribution, 4) thermoluminescence spectrum of short wavelength and 5) stability of traps, activators and host lattice.

Lithium fluoride activated by magnesium is now one of the most popular thermoluminescence dosimeters because of its nearly tissue equivalent property. Overall properties^{2, 3)} of this phosphor are, however, far from satisfying Schulman's requirements. This phosphor lacks somewhat the stability against various spurious effects, such as tribothermoluminescence. Fading and complicated response to pre- or post-annealing treatment are often troublesome for practical use of this phosphor. Furthermore, it has minor peaks in addition to a single major peak.

Calcium sulfate activated by manganese^{2~7)} is at present the most sensitive thermoluminescence dosimeter but it has the serious disadvantage to lose

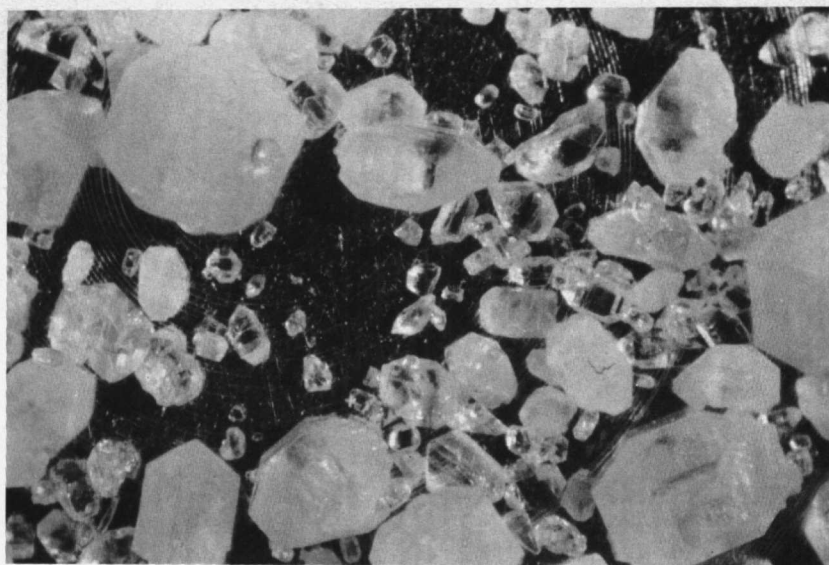


Fig. 1 $\text{CaSO}_4:\text{Dy}$ crystals, magnification: $\times 10$.

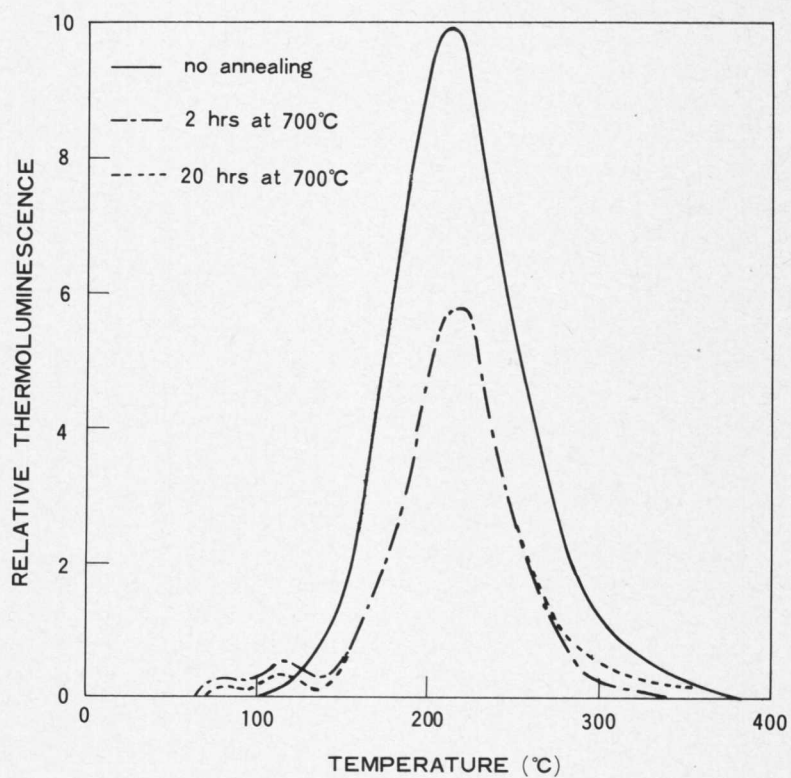


Fig. 2 Effect of pre-irradiation annealing on the glow curve of $\text{CaSO}_4:\text{Dy}$.

its thermoluminescence output very rapidly after irradiation^{2, 3}). Except this defect, however, this phosphor satisfies essentially all other Schulman's requirements. That is, if we can improve the fading character, then calcium sulfate phosphor will become rather close to an ideal thermoluminescence dosimeter except for the tissue equivalence.

Krasnaya et al⁸) found that the fading character of $\text{CaSO}_4:\text{Mn}$ can be eliminated by replacing the activator manganese by samarium. However, this replacement also brought the serious disadvantage that the light emitted from this phosphor is of longer wavelength ($\sim 6000 \text{ \AA}$).⁸)

The phosphors reported in the present paper are calcium sulfate activated by rare earth elements. These newly synthesized phosphors show little fading and yet retain almost all other advantageous properties of $\text{CaSO}_4:\text{Mn}$. Phosphors were prepared by a recrystallization method followed by an annealing treatment. This method may be partly responsible for the high qualities of these newly synthesized phosphors to be reported in this paper.

METHOD OF PHOSPHOR PREPARATION AND QUALITIES OF PREVIOUSLY KNOWN CaSO_4 PHOSPHORS PREPARED

Analytical-reagent-grade $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ and reagent-grade activator material were mixed in a proper ratio and dissolved in sulfuric acid to form saturated solution of CaSO_4 . The mixed solution was kept at about 300°C by heating so that crystalline samples appeared as the acid evaporated. Samples thus prepared usually consisted of single crystals 1-3 mm long as shown in Fig. 1 for $\text{CaSO}_4:\text{Dy}$ samples.

The crystalline phosphors prepared by the above-mentioned method already possessed ability of thermoluminescence without any further post-treatment. Characteristics of these "virgin" crystals, however, varied from batch to batch. In order to reduce the variability in the phosphor characteristics and to increase stability for repeated uses by post-annealing, the virgin crystals were subjected to pre-irradiation annealing treatment. A crystalline powder, mesh size from 100 to 200, was divided into 100 mg portions in quartz pans. The samples were isothermally annealed in air at 700°C for 2 or 20 hrs and then allowed to cool to room temperature. The annealed samples were then exposed to ^{137}Cs γ -rays at 10 R. The glow curves of these irradiated samples were obtained by heating at the rate of about $40^\circ\text{C}/\text{min}$ and the luminescence outputs were detected by a photomultiplier 1P21 of S4 type. Fig. 2 shows the effect of annealing on the glow curve of $\text{CaSO}_4:\text{Dy}$. First, the glow curve of $\text{CaSO}_4:\text{Dy}$ had essentially a single peak. Second, this peak decreased after pre-annealing at 700°C for 2 hrs but the reduced peak height remained constant for further pre-annealing at the same temperature.

Fig. 3 shows the result of more detailed studies on the effect of annealing time; height of the glow peak was plotted against time of the annealing treatment at 700°C . As will be seen from the figure, the glow height decreased very rapidly, about half in the first 10 min but it leveled off beyond 1 hour treatment. Because of this heat stability, a pre-annealing for 2 hrs at 700°C was applied to all the phosphors used in the rest of the present experiments so as to make uniform the characteristics of the phosphor samples.

It may be worth while to mention that the annealing treatment affected slightly but significantly the shape of the glow curve; small shoulders at the lower temperature side of the main peak appeared (Fig. 2). Once this pre-annealing treatment was given to $\text{CaSO}_4:\text{Dy}$ or $\text{CaSO}_4:\text{Tm}$ crystals, the samples acquired remarkably constant sensitivity in response to radiation for repeated

uses after post-annealing at 400°C. Similar but more complicated effects of pre-annealing treatment on thermoluminescence characteristics of LiF:Mg were reported by Zimmerman et. al.⁹⁾ This is an important advantage of CaSO₄:Dy over LiF:Mg.

To test the level of our phosphor preparation technique, previously known phosphors^{2, 3)} CaSO₄:Mn and CaSO₄:Sm, were prepared by our method.

Fig. 4 shows electron paramagnetic resonance spectra of a single crystal CaSO₄:Mn prepared by our method. This spectrum reflects the magnetic properties of unpaired 3d electrons of manganese ions in the magnetic field produced by interaction among magnetic moments ($I=5/2$) of Mn²⁺ nuclei, crystal field and the applied external field. The observed spectrum consists of sharp lines widely separated from each other when the crystal axis is parallel to the applied magnetic field (Fig. 4a) but it contains additional satellite shoulders, presumably due to forbidden transitions in Mn²⁺ ions, when it is rotated slightly from the parallel orientation (Fig. 4b). Combined with other experimental data, we may conclude from these spectra that our CaSO₄:Mn samples have regular crystal structure; Mn²⁺ impurity ions substitute for Ca²⁺ ions so that crystal field around each Mn²⁺ impurity ion is almost regular and hence the field symmetry around Mn²⁺ ion is almost identical to orthorhombic symmetry of the crystal (space group V_h¹⁷). This powerful method to analyze the fine structure of doped activator ions inside phosphors is, however, not applicable to the rare-earth-activated phosphors reported in the following sections due to several technical difficulties. The glow curve of our CaSO₄:Mn was similar to that previously reported by Patterson and Friedman⁵⁾; it had essentially a single major peak at about 100°C.

A typical glow curve of our CaSO₄:Sm sample is shown in Fig. 5 together with the curves previously reported by Bjärngård¹⁰⁾ and Witzmann et al.¹¹⁾. Our curve agrees with Witzmann's except for minor peaks but completely disagrees with Bjärngård's curve. Whether this discrepancy is due to difference in phosphor preparation or other factors is not known. Anyway, our samples gave rise to a simple glow curve. This is an important character for applying the phosphors to radiation dosimetry as pointed out by Schulman¹⁾.

THERMOLUMINESCENCE CHARACTERISTICS OF CaSO₄ ACTIVATED BY RARE EARTH ELEMENTS

Calcium sulfate crystals doped with 10⁻³ mol rare earth ions were prepared and their glow curves were compared after an equal exposure of 10 R with ¹³⁷Cs γ -rays. Fig. 6 shows typical glow curves of fourteen kinds of samples thus prepared. Most of the rare-earth-activated phosphors showed similar glow curves with a single peak at 210-230°C except the two phosphors, CaSO₄:Eu and CaSO₄:Ce which showed a main peak at 130°C with additional one or two peaks at different temperatures. This difference in glow peaks may be attributable to different valence values of rare-earth ions substituting for Ca²⁺ ions. As will be seen from the figure, CaSO₄ crystals activated by dysprosium and thulium showed the highest luminescence sensitivity. Therefore, the characteristics of these two phosphors were most thoroughly studied as reported in the following sections.

Thermoluminescence Spectra of CaSO₄:Dy and CaSO₄:Tm

The thermoluminescence spectra were observed photometrically with use of a quartz-prism monochromator after 10⁴ R exposure of samples. The