JOURNAL OF MATERIALS SCIENCE 3 (1968) 344–348

The Detection of Rare Earth Impurities in Ionic Materials by X-ray-stimulated Luminescence

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Received 8 February 1968

The application of X-ray-stimulated luminescence to the detection of trivalent rare earth impurities in ionic materials is discussed. Characteristic luminescent wavelengths allow the identification of individual rare earths. The lower limit of impurity detectable in the particular case of the fluorides is found to be about 0.01 ppm if no positive identification of the rare earth ion is required. This is increased to 1 ppm when positive identification of the specific impurity is required. The application of the technique to the assessment of single crystals and the appropriate starting material is discussed.

1. Introduction

It is well known that the passage of X-rays through matter is often accompanied by luminescence. When the material contains rare earth ions the luminescence consists in part of groups of sharp lines characteristic of the rare earth ion in question. In most situations the rare earth ion is in the trivalent state. This paper, therefore, investigates the application of this phenomenon to the detection of trivalent rare earth ions as impurities in ionic materials, since on occasions [1] such impurities have been known to lead to spurious results, particularly in optical investigations.

The main advantage of X-ray excitation over the more normal optical excitation must lie in the absence of any scattered radiation. This immediately eases the problem of the detection of the luminescence and may thus allow lower limits to be reached. This method would be expected to find its application in all materials where rare earth ions show a strong luminescence but inevitably the sensitivity will depend on the efficiency of the luminescence. In general, however, most ionic materials show this properly when doped with rare earth ions, and the variation in luminescent efficiency only extends over a few orders of magnitude.

For the purposes of this investigation, the fluorides have been selected as a typical group of ionic materials. For the case of the fluorides, characteristic luminescent wavelengths have been selected which enable all the rare earth ions in the lanthanide series to be identified. A lower limit to the level of impurity which can be detected by this technique has been set for the two situations (i) where it is necessary to positively identify the particular rare earth ion and (ii) where no such identification is necessary. Finally the application of this technique is considered with particular reference to the assessment of pure and doped single crystals.

2. Apparatus

The experimental set-up is shown diagrammatically in fig. 1. The luminescence is excited by a conventional X-ray apparatus which was typically run at 55 kV, 18 mA. The X-ray radiation falls on the crystal which is positioned for maximum sensitivity. Under certain conditions it might be necessary to cool the sample in which case it would be mounted in a suitable cryostat. The luminescence from the sample passes through a scanning monochromator, a Bausch and Lomb instrument with a dispersion of 16Å/mm or 32Å/mm and *f* 4.4. The output of this is then detected by an EMI 9558QB (S.20) or a cooled RCA 7102 (S.1) photomultiplier. The signal is finally amplified and recorded.

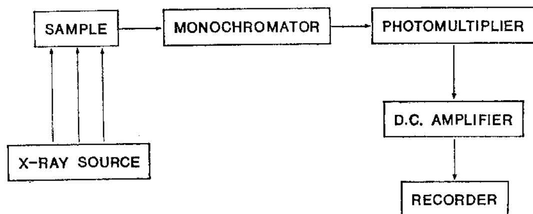

Figure 1 Experimental arrangement.

3. Sample Preparation

All samples were prepared in single-crystal form in a vacuum furnace of the Stockbarger type [2]. The crucibles used were of graphite, as was the heating element. Molybdenum baffles were used to reduce heat losses. To prevent unwanted contamination of the samples with other rare earths, a new crucible was used for each run and the furnace scrupulously cleaned.

Samples containing down to 1 ppm of rare earth were prepared by the progressive dilution of a 0.1% doped sample, the dopant being added as the 99.9% pure fluoride initially. For test purposes two types of samples were prepared: (i) thin cleaved single-crystal slices, and (ii) powders (ground from the single crystal). The powders were subsequently fixed to a test plate with Durofix (Rawplug Co Ltd*), an adhesive whose inherent luminescence, a very weak broad band around 4000Å, in no way hindered the detection process.

4. Experimental Measurements

4.1. Identification of Rare Earth Ions

Before luminescence can be used to establish the presence of a particular rare earth ion it is essential to know the characteristic luminescent wavelengths for that ion. It is well known that the energy levels (within the $4f$ configuration)

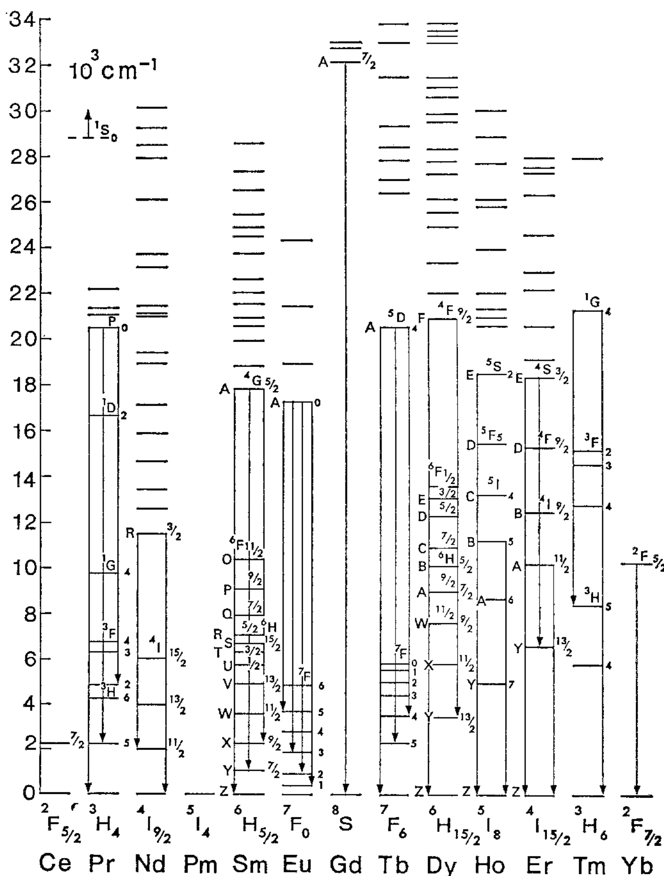

Figure 2 Energy levels of the trivalent rare earths.

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characteristic of rare earth ions are, to a first order, independent of the nature of the local crystal field. That is to say, the electrostatic crystal field splitting, of the order of a few hundred centimetres, can be treated as a perturbation on the "free ion" energy levels. As a result of this the position of the characteristic luminescent bands will be independent of the particular material under test. Fig. 2 shows the position of the relevant energy levels as given by Dieke [3]. Also indicated on this figure are the most suitable transitions with which to characterise the particular rare earth ion. In most cases at least two transitions have been selected in order to minimise the possibility of mistaken identity. The approximate wavelengths of the transitions involved are indicated on fig. 3.

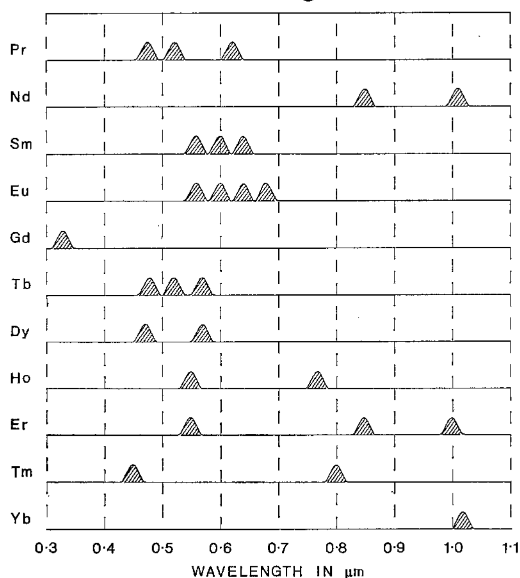

Figure 3 Characteristic luminescent wavelengths for the trivalent rare earths.

A comparison of figs. 2 and 3 shows that with certain combinations of impurities, overlap of the luminescent spectra takes place. Such overlap of the luminescent transitions may lead in certain circumstances to considerable difficulty in identification. At comparatively high concentrations this may, to some extent, be resolved by increasing the resolution of the detecting system so that the detailed structure of the luminescent bands may be studied. This structure will show a change from the single impurity case on the occasions when two rare earth impurities luminesce in the same wavelength region. However, in the case of very low concentrations where it becomes necessary to use very low resolution in the detecting system, confusion may arise in specific cases. For example a material containing at very low concentrations both Nd^{3+} and Yb^{3+} presents the difficulty that while the Nd^{3+} would be immediately detectable by luminescence at both 8800 Å and 1.0 μm the Yb^{3+} which only luminesces at 1.0 μm might be missed. Some indication of the presence of Yb^{3+} might be gained, however, by careful comparison of the intensity of luminescence at 8800 Å and 1.0 μm.

Thus, within these limitations, the transitions indicated in fig. 2 serve as a means of identifying the various rare earth ions between Pr^{3+} and Yb^{3+}. Ce^{3+} must be omitted since it does not have a suitable luminescence within the $4f$ configuration.

4.2. Concentration Determination

The concentration of a particular impurity can be determined provided the variation of luminescent intensity with concentration is known for a fixed excitation level. Since it is reasonable to expect that the variation with concentration will be similar for all rare earth ions at low concentrations, detailed measurements have been restricted to the Er^{3+} ion in the three lattices CaF_2, LaF_3, and $LiYF_4$. Fig. 4 shows the variation of luminescent intensity for concentrations between 1 ppm and 1000 ppm, the transition $^4I_{11/2}$ to $^4I_{15/2}$ (0.98 μm) being used as monitor. The lower limit of 1 ppm is set by the difficulty in controlling the concentration at lower levels. The problems which arise in the control of rare earth concentration are (i) the segregation of dopant during crystal growth, and (ii) trace contamination from the furnace. The segregation was checked by comparing samples cut from the top and bottom of the boule with the result that there was agreement to within + 10%. Distillation effects could result in the complete loss of dopant but experience at higher concentrations, where determinations are more readily made, has shown that provided overall evaporation is kept to less than 5%, the loss of dopant does not give a measureable effect. It has, therefore, been assumed that the same facts will be true at lower concentrations, which means that the lower limit must be set by contamination. A typical level of contamination has been found to be 0.01 ppm so it seems reasonable to set 1 ppm as the lower limit for standard samples.

The choice of the 0.98 μm transition was

mainly dictated by convenience, since the CaF_2 samples tended to have a broad band luminescence in the shorter wavelength regions. It can be seen from fig. 4 that the variation of intensity with concentration is linear within experimental error, which considerably simplifies the determination of concentration since only two standard samples would be necessary as reference points. It should perhaps be noted that this linear relationship will break down if any one rare earth ion increases to a sufficiently high concentration for appreciable energy transfer to take place [4]. This problem will arise in, for example, the determination of the Ho^{3+} impurity in ErF_3. In such cases the variation of intensity with concentration follows a complicated curve, rendering concentration measurements more difficult.

4.3. Detection Limits

The lower limit of rare earth impurity detectable by this method depends on a number of factors, including (i) the intensity of X-rays used for excitation, (ii) the luminescent efficiency of the rare earth ion, and (iii) the sensitivity of the detecting system. However, over and above these considerations the necessity of identifying the particular rare earth ion must set a lower limit to the level of impurity detectable. Therefore, by removing this requirement of identification the lower limit will be considerably reduced, particularly where mixed impurities exist.

With this point in mind, measurements were made to determine the lowest level of impurity detectable when that rare earth ion was the only one present, that is, effectively removing the requirement of identification. The limit was determined by measuring the intensity of luminescence in three samples doped at 100, 10, and 1 ppm, using the strongest transition available, and then extrapolating back to the limit of the detector. The results are shown in table I where the values given represent an average over the four materials CaF_2, LaF_3, $LiYF_4$, and PbF_2, although the efficiencies of all four are very similar. Also shown in table I is the estimated limit of impurity detectable when identification of the particular rare earth is necessary. All these results assume that no one rare earth ion exists at concentrations in excess of around 1 %, where energy transfer effects will cause complications. The values given above apply equally well to powdered samples and single-crystal samples.

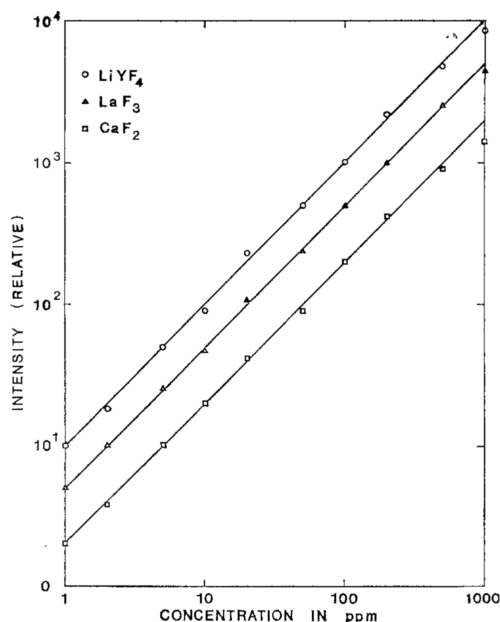

Figure 4 Variation of luminescent intensity against concentration for the 0.98 μm luminescence of Er^{3+}.

TABLE I

Element	Detection limit without identification (ppm)	Detection limit with identification (ppm)
Pr	0.01	1.0
Nd	0.01	1.0
Sm	0.01	5.0
Eu	0.001	5.0
Gd	0.01	0.1
Tb	0.001	0.1
Dy	0.001	1.0
Ho	0.001	0.1
Er	0.0001	0.1
Tm	0.01	1.0
Yb	0.01	10–100*

*The value for Yb^3 depends strongly on which other impurities are present.

5. Discussion

The results of the above investigation indicate quite conclusively that the use of X-ray-stimulated luminescence in the detection of rare earth ion impurities in fluoride lattices has considerable potential. The level of impurity detectable is comparable to, and under ideal conditions somewhat better than, spectrochemical and mass spectrometer techniques. The technique also has the added advantage that the analysis is quickly and easily carried out.

Because of the similarity of the luminescent properties of all rare earth ions in ionic materials, it is almost certain that it can be simply carried over to other ionic materials. Selected measurements have indicated that similar results are obtained for the chlorides ($LaCl_3$) and the oxides ($CaWO_4$ and La_2O_3) which all have high luminescent efficiencies.

The assessment of the suitability of particular chemicals for single-crystal growth presents a typical situation where this technique can be used to advantage. For example, this technique has been used to quickly show that all LaF_3 powders contain Pr^{3+} and Nd^{3+} at concentrations between 50 ppm and 200 ppm, depending on source. It has also been used to show that natural fluorite contains a variety of rare earth ions, in particular Er up to 10 ppm, Nd up to 1 ppm, and Sm up to 1 ppm, rendering such a material of little or no use in the growth of pure CaF_2 crystals for luminescent studies.

The technique can also be used to give a quick and reliable method of testing for rare earth contamination during crystal growth. For example, it has shown that a furnace used to grow rare-earth-doped crystals cannot be immediately transferred to the growth of pure materials, since for a considerable time after the change-over all crystals contain rare earth contamination up to 1 part in 10^8. Also the inadvisability of the simultaneous growth of differently doped crystals in a single furnace can be readily demonstrated, showing the cross contamination of up to 10 ppm.

The few examples discussed give some idea of the cases where the technique of X-ray stimulation can be used, and there are many others. However, the main value of this technique must be in the ease and speed with which it can supply an assessment of the rare earth impurity in the material under test.

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