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Detection of Trace Impurities in Stoichiometric Spinel Crystals by Instrumental Neutron Activation Analysis

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High-quality crystals of stoichiometric spinel grown from solution in lead fluoride were subjected to neutron activation analysis to determine rare-earth doping levels. The results have shown that the small rare-earth ion, Er^{3+}, can be incorporated to a small extent, but the larger Nd^{3+} ion is rejected. Contamination of the crystals with iridium was disclosed. This impurity is derived from iridium in the platinum crucibles used to contain the melts at high temperatures. Iridium contamination may well occur in other crystals grown by the fluxed melt technique. No measurable platinum contamination was found.

1. Introduction

Crystals of stoichiometric $MgAl_2O_3$ spinel, grown by the fluxed melt technique, have been shown to be particularly perfect by the use of X-ray diffraction topography, etch pit studies and optical techniques [1]. This perfection, in comparison with the non-stoichiometric material commercially grown by the flame-fusion technique, has given rise to some interesting differences in physical [2] and mechanical [3] properties between the two materials. In particular, when acting as a host lattice for paramagnetic ions, the flux-grown crystals show spectral differences which may be attributed to the higher lattice perfection. These results suggested that the crystals might be of interest as a host for ions other than the first-period transition elements. A survey of known spinel structures had indicated the possibility of incorporating the smaller rare-earth elements, particularly as the flux-growth process provides an advantageous means of doping the crystals, since a reasonably high concentration of dopant can be maintained during growth.

In the present work it was not possible to incorporate sufficient of the rare-earth additive to detect it by conventional means, and an alternative technique was sought. Neutron activation analysis [4, 5] potentially provided an unambiguous, absolute method for the determination of very small concentrations of dopant, and for this particular case provided unexpected additional information on trace impurities of relevance to the physical studies being undertaken on these crystals.

The purpose of this communication is twofold. First, to draw the attention of crystal growers, who are particularly concerned with high purities, to a simple and established analytical technique which has not been applied as often as it might be to single-crystal specimens; secondly, to report the results obtained for this particular and interesting variety of crystal.

2. Crystal Growth

The spinel crystals were grown from solution in lead fluoride by isothermal evaporation in partially sealed platinum crucibles. The method of growth is described more fully by Wood and White [1], but for the present work, evaporation at temperatures between 1200 and 1250° C in 100 cm^3 crucibles were used. Specially prepared high-purity magnesia and alumina were provided by British Drug Houses Limited*, and a high-

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purity grade of lead fluoride obtained from Associated Lead Company Limited† was used as the solvent. This grade of material has been used extensively for crystal growing purposes with very satisfactory results. All of these constituents were low in metallic contaminants (especially transition elements) although precise batch analyses were not available and are not relevant to the results presented below.

Erbium and neodymium oxides of 99.9% purity, supplied by Johnson Matthey Ltd‡ were added in various proportions to the initial mixture, but even at relatively high initial concentrations (approximately 5 mole %) none of the rare-earth additive was detectable by absorption spectroscopy. When grown quickly by using the highest temperature (1250° C), and an open crucible, evidence of colouration of the spinel was observed, but results were ambiguous since the crystals contained obvious inclusions of the solvent (and hence of the dopant). However, at slow growth rates (less than 1 mm/day linear) the $MgAl_2O_4$ spinel crystals were remarkably free from inclusions detectable by light scattering, and such crystals have been shown to have a lead content of less than 10 ppm. For the present investigations therefore, crystals were selected which on careful examination showed no inclusions.

3. Experimental

Crystal specimens of 50 to 100 mg were selected and cleaned by immersion in boiling phosphoric acid for 10 min. These were packed in small, clean polythene containers of 7 mm diameter and 10 mm long. The samples and standards were loaded to the core of the University of London nuclear reactor by means of a pneumatic system and irradiated at full reactor power (thermal neutron flux of 1.5×10^{12} neutron/cm^2 sec) for 2 h.

After irradiation, the samples and standards were allowed to "cool down" for up to one day to allow the activity of the matrix elements to decay. They were then counted in a gamma spectrometer based on a 3 in.* by 3 in. thallium-doped sodium iodide crystal. The crystal was contained in a cavity surrounded by 4 in. thick lead walls and shielded from beta particles by a 3 mm aluminium sheet. The pulse height analyser used was a 400 channel Intertechnique Model SA 04B.

4. Preparation of Standards

For the determination of rare earths a standard solution containing about 10 μg/ml of the element was prepared by dissolving the oxide (99.9% purity) in 0.1 N nitric acid. From this solution fractions of a millilitre were pipetted into a similar small polythene container and dried with an infrared lamp. The measurement of standards verified the linearity expected, provided that peak areas were used. Heights of peak channels were not linear.

For the determination of iridium, a standard solution of ammonium chloroiridate, $(NH_4)_2IrCl_6$, in 0.1 N hydrochloric acid was prepared, and for sodium a standard solution of sodium hydroxide was used. Both solutions were in the concentration range 20 to 40 μg/cm^3 in the sought element.

A mixture was made up by dry grinding AR grade magnesia and alumina in different proportions with the estimated amount of rare earth, in order to check the impurities introduced during crystal growth. This mixture also showed the amount of Na^{24} produced by reactions with fast neutrons.

5. Results

A result typical of the many analyses made is given in table I.

TABLE I Analysis of erbium-doped crystal.

Element	Concentration (μg/mg)
Rare earth (Er)	0.048
Iridium	0.013
Sodium	(0.17)*

*The validity of this result is questionable, see text.

The error involved in these figures is about 1% in the preparation of standards and less than 2% in counting and evaluation of the results. Other crystals doped with neodymium were analysed, but were found to contain none of this element within the limit of sensitivity (< 0.5 μg).

The presence of iridium in all of the crystals examined was surprising. This was attributed to the dissolution of iridium present as an impurity in the platinum crucibles used into the lead fluoride solvent, with subsequent incorporation in the crystal. The sodium recorded was most probably produced by fast neutron reaction with magnesium of the crystal matrix but could also arise from impurity of the starting materials.

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*1.0 in. = 2.5 cm

However the relative contribution of these two sources was not evaluated.

The spectra were evaluated using the "least squares" [6] method. This is a numerical technique based on finding the best values of factors by which standard spectra must be multiplied so that their combined result approximates to the actual sample spectrum obtained. These factors then give the ratio of the quantity of sought element in the sample to the quantity in the standard. The best values of the factors are defined so that the squares of the channel deviations between the combined standard spectrum and the sample spectrum are minimised. This technique was shown here to be about 2% more accurate than the integration of areas and if computing facilities are available would be the preferred method of evaluating spectra.

In the case of erbium analysis, the crystal was counted after 30 min "cooling" to determine the 7.5 h Er^{171} formed. Standards of erbium, magnesium, and iridium were used as linear components of the crystal spectrum and the technique was applied over a limited number of channels of the analyser to evaluate only the 0.118 MeV peak of Er^{171}, because of a problem of interference presented by the 0.32 MeV peak of the 74 day Ir^{192} on the 0.305 MeV peak of Er^{171}. A comparison of the spectra of a doped crystal, an undoped crystal and erbium standard is shown in fig. 1.

The analysis of neodymium was made on the 0.21 MeV peak of the 1.9 h Nd^{151}, but can also be made on the decay product 28.4 h Pm^{151}.

For the iridium and sodium analysis, the crystal was counted after a "cooling" period of one day, and the 0.32 MeV peak of 74 day Ir^{192} and 1.37 MeV peak of 15 h Na^{24} were measured using compound spectra of erbium, sodium, and iridium in the least squares fit. One of the advantages of this method of resolution of the gamma ray spectra is that the system of counting can be easily automated by using a computer which receives the data of the multichannel analyser directly [7, 8].

It is of interest to note that the colour of the crystal changed during irradiation from colourless to dark brown. This colour diminished on exposure to sunlight and disappeared rapidly on heating to about 600° C.

Other elements, for example platinum, chromium, manganese, and antimony which have suitable nuclear characteristics are detectable but these were not present in significant amounts in the crystals. For elements such as fluorine or silicon it would be necessary to use a neutron generator which can produce a constant flux of 14 MeV neutrons [9].

6. Discussion

Flux-grown spinel crystals doped with erbium to a concentration of approximately 48 ppm have been prepared from melts containing up to

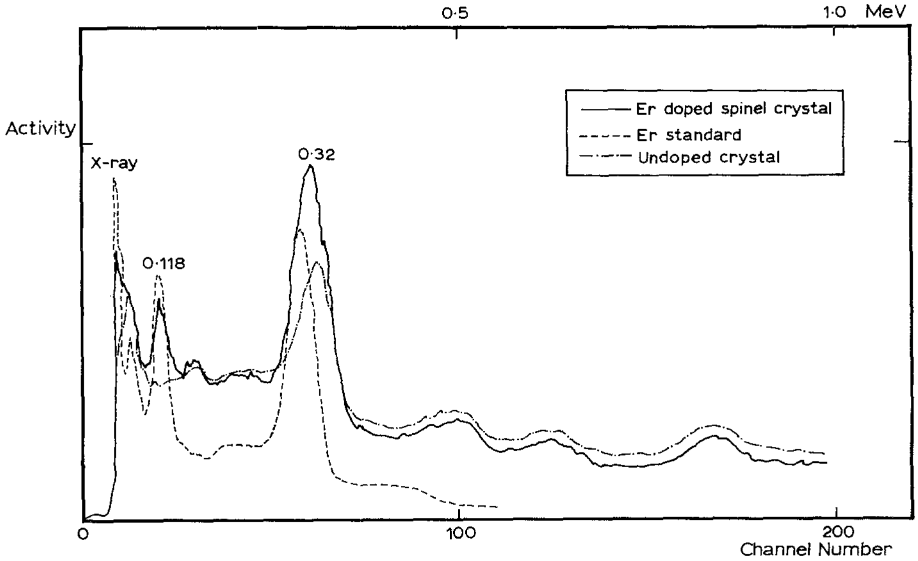

Figure 1 Comparative spectra of Er standard, Er-doped crystal, and undoped crystal.

5 mole % Er_2O_3. This concentration appears to be independent of the concentration of erbium added to the melt initially, but it is uncertain whether this is a limit imposed by the solubility of erbium oxide in the lead fluoride solvent, or by solid solubility in the lattice. The inability to detect Nd suggests that the larger ionic radius of this element precludes its incorporation in $MgAl_2O_4$ spinel.

The demonstration of the presence of significant amounts of Ir in the crystals will be of interest to other users of the fluxed melt process, since platinum crucibles are used almost exclusively for this process. Earlier experiments in which platinum/iridium alloy components were used for the growth of barium titanate crystals confirm that serious contamination by iridium can occur. It is encouraging that no comparable contamination with platinum beyond the practical limit of 0.5 μg has been disclosed. These results suggest that the use of high-purity platinum vessels will have an advantage for the growth of crystals from solution. As an alternative, several preliminary fusions of lead fluoride in ordinary crucibles should reduce the level of iridium contamination.

The absence of discrete inclusions, detectable by light scattering in the crystals studied, indicates that the impurities detected occupy lattice sites substantially. It is perhaps unfortunate that this analytical method is not appropriate for the detection of lead, which is the other major potential contaminant. However, the results show that, in general, this technique is applicable for both routine qualitative and quantitative analysis of doped and undoped crystals, and can be of great help in the interpretation of physical measurements and to the control of crystal growing.

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