

^{27}Al MAS NMR SPECTROSCOPY STUDY OF Eu^{2+} -DOPED AND Dy^{3+} -CO-DOPED SrAl_4O_7

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The Eu^{2+} -doped strontium aluminate SrAl_4O_7 samples have shown the blue-green persistent luminescence at 490 nm while the co-doping with Dy^{3+} shifts the maximum of emission to 475 nm. Undoped, 3% Eu -doped and 6% Dy -co-doped SrAl_4O_7 samples were prepared by the solid state-reaction method and studied by the solid-state ^{27}Al MAS NMR applying the single pulse-acquire and Hahn-echo pulse sequences. It was shown that the Eu^{2+} with Dy^{3+} ion doping did not affect the bulk structure as well as the local Al environment in SrAl_4O_7 . This means that large shifts of the emission maximum cannot be caused by changes in the local environment upon the co-doping of $\text{SrAl}_4\text{O}_7:\text{Eu}^{2+}$ with Dy^{3+} . However, the spectral features observed in the range between the signals of 4- and 6-coordinated Al (20–40 ppm) indicate that certain phase imperfections are present in all studied samples, and most probably amorphous/glassy domains were formed. Note that such amount of phase impurities was not detected by standard XRD or FTIR methods. This has revealed the ^{27}Al MAS NMR technique to be a very effective tool monitoring the phase perfectness in series of strontium aluminate samples.

Keywords: solid-state NMR, magic-angle spinning, strontium aluminate, europium, dysprosium

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1. Introduction

Strontium aluminates, doped with rare-earth metal ions, have been studied for a long time for their excellent properties, such as a high quantum efficiency and a long persistence of phosphorescence, as well as due to potential industrial applications in fluorescent lamps, plasma displays, light emitting diodes, etc. [1–3]. Beside a very high quantum efficiency and a long persistence luminescence, strontium aluminates doped with Eu^{2+} have a better stability than other alkaline earth aluminates [4]. Several different strontium aluminate phases are well known, e.g. SrAl_2O_4 , $\text{Sr}_4\text{Al}_{14}\text{O}_{25}$, $\text{SrAl}_{12}\text{O}_{19}$ and $\text{Sr}_3\text{Al}_2\text{O}_6$ [5]. However, a particular one – SrAl_4O_7 – was much less in-

vestigated, probably due to the difficulties arising at the preparation of monophasic samples. The amount of phase impurities that can be therein sometimes too small is to be detected by the most widely used methods of characterization (XRD, FTIR, etc.).

Very recently, it has been found that Eu^{2+} -doped strontium aluminate SrAl_4O_7 samples exhibit blue-green persistent luminescence at 490 nm while the co-doping with Dy^{3+} shifts the maximum of emission to 475 nm and, consequently, the colour towards the blue spectral range [6]. It is well known that the emission of Eu^{2+} is very strongly dependent on the host lattice and can occur from the ultraviolet to the red region of the electromagnetic spectrum [4, 7, 8]. The purposes of the present work were to

examine the phase purity and to elucidate the possibility and the extent of structural changes in SrAl_4O_7 environment upon doping and co-doping with Eu^{2+} and Dy^{3+} ions using solid-state nuclear magnetic resonance (NMR), namely ^{27}Al MAS (magic-angle spinning) NMR spectra. These complementary data can be useful in trying to explain the blue shift observed in the $\text{SrAl}_4\text{O}_7:\text{Eu}^{2+}$ emission spectra upon co-doping with Dy^{3+} .

2. Experiment

The undoped, 3% Eu-doped and 6% Dy-co-doped SrAl_4O_7 samples were prepared by the solid state-reaction method. The phase purity of synthesized specimens was examined by powder X-ray diffraction measurements. The details of chemical preparation, synthesis and characterization are presented in Ref. [6].

The solid-state ^{27}Al MAS NMR experiments were performed using a 400 MHz Bruker AVANCE III HD spectrometer with a 4 mm-wide bore double resonance HX CP-MAS probe. The experiments were performed in 9.4 T magnetic field using an Ascend wide bore superconducting magnet. The Larmor frequency for ^{27}Al was 104.3 MHz and chemical shifts were referenced to 1 M $\text{Al}(\text{NO}_3)_3$. The MAS frequency (ν_{MAS}) was 12 kHz. ^{27}Al MAS spectra were measured applying the single pulse-acquire sequence using the short duration (2 μs) excitation pulse, the number of scans was 512 and the recycle delay was 10 s.

In addition, the ^{27}Al MAS spectra were acquired with the rotor synchronized Hahn-echo sequence ($\pi/6 - \tau - \pi/3 - \tau - \text{acq}$) [9], setting $\tau = 10/\nu_{\text{MAS}}$ (Fig. 1).

The NMR spectra were processed using the Topspin 3.2 software. Some additional processing was carried out using the Microcal Origin 9 package.

3. Results and discussion

The structure of SrAl_4O_7 has been studied in several works [10–12]. The structure was deduced to be a monoclinic structure with the space group $C12/c1$ [10, 11]. The SrAl_4O_7 lattice consists of corner sharing AlO_4 tetrahedral layers and strontium ions, which are embedded in between the layers [2, 13]. Layers of highly interlinked AlO_4 tetrahedra extend in the xy plane and give rise to the enhanced growth speed in the x and y direction. In between the layers, one finds the Sr ions as well as the AlO_6 octahedra that act as bridges [13]. Each Sr atom in SrAl_4O_7 is surrounded by ten O atoms with interatomic distances from 2.50 to 2.79 Å [2]. This compound also has a high-pressure form $\beta\text{-SrAl}_4\text{O}_7$. The crystal lattice of this form consists of a 3-dimensional network of $\text{Al}(1)\text{O}_6$ octahedra, and $\text{Al}(2)\text{O}_4$ and $\text{Al}(3)\text{O}_4$ tetrahedra. The Al–O bond lengths were found to be 1.795 to 1.968 Å for the octahedra and 1.449 to 1.537 Å for the tetrahedra [6]. These distances in AlO_4 units are considerably shorter than those in other aluminates.

In literature there are known several synthesis routes used for the preparation of SrAl_4O_7 . They are reviewed in Ref. 6. However, the route of conventional solid-state reactions is seldom reported. Moreover, in some works it was claimed that SrAl_4O_7 cannot be synthesized by the solid-state reaction. In our earlier paper [6], a successful synthesis of SrAl_4O_7 samples doped with Eu^{2+} and co-doped

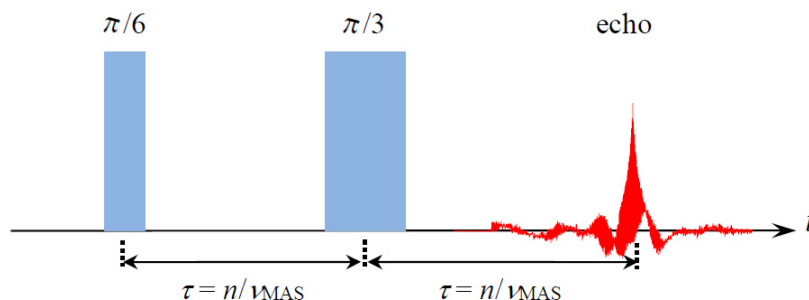


Fig. 1. The rotor synchronized Hahn-echo pulse sequence used in ^{27}Al MAS NMR experiments. The value $n = 10$ was chosen for all experiments in the present work.

with Dy^{3+} by the conventional solid-state reaction method was carried out.

A broad variety of solid-state NMR techniques, such as ^{27}Al MAS, multiple quantum magic-angle spinning (MQ-MAS) and heteronuclear multiple quantum coherence (HMQC) spectroscopy, have been effectively applied elucidating very fine structural details in series of ions-doped aluminates [1, 14–19]. Therefore, in the present work the ^{27}Al MAS NMR was applied in order to complementarily characterize the synthesized SrAl_4O_7 , using the conventional solid-state reaction method as well as 3% Eu-doped and 6% Dy-co-doped SrAl_4O_7 .

As the major factor that controls the ^{27}Al chemical shifts $\delta(^{27}\text{Al})$ is the atomic structural environments of aluminum atoms, i.e. the nearest-neighbour coordination geometry, the ^{27}Al MAS NMR spectra provide useful, sometimes even unique information on Al sites and coordination numbers. However, not always all of the ^{27}Al resonances corresponding to different Al sites are well resolved in the spectra. Going through literature data [4, 18, 19 and Refs. cited therein], it can be stated that in most Al–O environments, the ^{27}Al NMR peaks of 6-coordinated Al (AlO_6) appear in the range covering -20 to $+15$ ppm and are well separated from the signals from the 4-coordinated Al (AlO_4) that appear at 50 to 145 ppm. It looks that the interchange of ions $\text{Sm} \leftrightarrow \text{Cs} \leftrightarrow \text{Sr}$ in various aluminates does not have too much influence on this sequence and the range of variation of ^{27}Al chemical shifts.

The ^{27}Al MAS NMR spectra of pristine as well as 3% Eu-doped and 6% Dy-co-doped SrAl_4O_7 samples studied in the present work are shown in Fig. 2. The Hahn-echo pulse sequence is typically used for solid-state NMR measurements when the single-pulse spectrum experiences a strong background signal due to, e.g. long probe dead time or ringing effects. By changing echo time it could also be used as a relaxation filter, in other words, fast relaxing spectral components could be filtered out if two or more coexisting species, which relax at different rates, are present in the sample. Note that a higher resolution and reduction of spinning sideband intensities were achieved applying the Hahn-echo pulse sequence in the present case (Fig. 2(a)). The peaks of 4- and 6-coordinated Al are well resolved and easily recognized in the spectra. No significant changes in the ^{27}Al chemical shifts upon Eu^{2+} and Dy^{3+} dop-

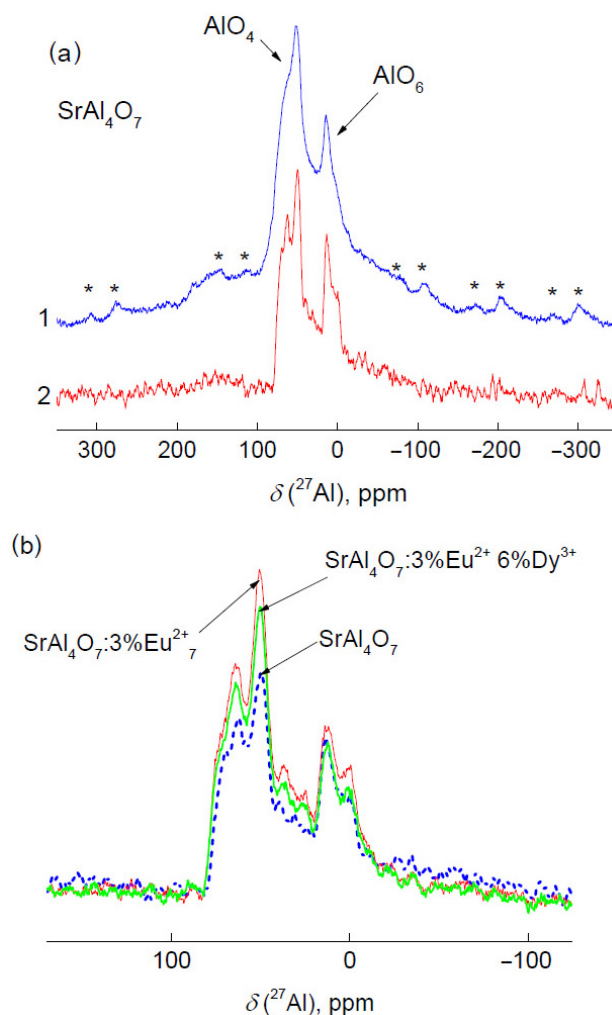


Fig. 2. ^{27}Al MAS NMR spectra of pristine SrAl_4O_7 ((a): 1 for single-pulse, 2 for Hahn-echo experiment, respectively), and 3% Eu-doped and 6% Dy-co-doped SrAl_4O_7 ((b): all Hahn-echo). Asterisks denote spinning sidebands.

ing are seen. Only the relative intensities can be noted, and they are more pronounced for 4-coordinated Al (Fig. 2(b)). A very asymmetric shape of AlO_4 signals with the tails to lower values of ^{27}Al chemical shifts point towards the presence of a local disorder and thus a broad distribution of quadrupolar coupling constants and chemical shifts.

It is known that the 5-coordinated Al (AlO_5) yields $\delta(^{27}\text{Al})$ in the range $+15$ to $+35$ ppm. This was observed in the ^{27}Al NMR spectrum of glassy YAG-4Si, however not seen in the pure crystalline YAG and in the spectra of annealed YAG-4Si [18]. It means that this spectral feature can be used evaluating the structural disorder and phase purity in the sample. However, note that

a certain polemic around the existence and detection of the ^{27}Al NMR signals from AlO_5 sites run in the literature [16, 17, 19]. The AlO_5 signal, if it is at all present in the aluminate under investigation, is often obscured by the overlap with strong AlO_6 signals. The most powerful technique to reveal the presence of AlO_5 is MQ-MAS. The study applying this technique on the synthesized materials is in progress.

4. Concluding remarks

1. The ^{27}Al MAS NMR experiments have shown that the Eu^{2+} with Dy^{3+} ion doping carried out using the solid state-reaction method did not affect the bulk structure and the local Al environment in SrAl_4O_7 .

2. The spectral features observed in the range between 4- and 6-coordinated Al peaks (viz. 20–40 ppm) demand one to recognize that certain phase imperfections are present, most probably the amorphous/glassy domains appear. Also note that the chosen solid state-reaction regime does not alter it, i.e. the spectral features that supposedly may reflect the phase purity were the same in all studied samples.

3. The ^{27}Al MAS NMR technique appeared to be a very effective tool for the analysis of phase perfectness. Such amount of phase impurities was too small to be detected by widely used XRD or FTIR methods [6].

4. Large shifts of the emission maximum (from 490 to 475 nm) by co-doping of $\text{SrAl}_4\text{O}_7:\text{Eu}^{2+}$ with Dy^{3+} cannot be caused by the local environment changes upon the doping. Since the main factor governing the emission of Eu^{2+} is the crystal field surrounding the ion, one possible explanation might be that the charge disbalance induced by 3^+ ions influences the strength of the crystal field around Eu^{2+} (without noticeably affecting the structure).

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Eu²⁺ LEGIRUOTŲ IR Dy³⁺ KOLEGIRUOTŲ SrAl₄O₇ TYRIMAI ²⁷Al MAS BMR SPEKTROMETRIJOS METODU

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Santrauka

Eu^{2+} legiruoti stroncio aluminatai SrAl_4O_7 pasižymi mėlynai žalia išliekančiąja liuminescencija ties 490 nm, o juos kolegiravus Dy^{3+} jonais emisijos maksimumas pasislenka link 475 nm. Kietafazių reakcijų metodu buvo paruošti nelegiruoti, 3 % Eu legiruoti ir 6 % Dy kolegiruoti SrAl_4O_7 mėginiai, kurie ištirti taikant kietojo kūno ^{27}Al MAS („magiško kampo sukimo“) BMR spektrometrijos metodą. Naudotos pavienio impulso ir Hahno sukinių aido impulsų sekos. Nustatyta, kad SrAl_4O_7 legiravimas Eu^{2+} ir Dy^{3+} jonais neturi įtakos kristalinei struktūrai visame bandinio tūryje bei lokaliai Al atomų aplinkai. Tai reiškia, kad toks pastebimas emisijos maksimumo poslinkis SrAl_4O_7 : Eu^{2+} kolegiru-

jant Dy^{3+} nėra nulemtas lokalaus kristalinės struktūros pokyčių. Kita vertus, BMR spektro dalis, stebima tarp keturių ir šešių koordinuotų Al signalų (20–40 m.d.), parodo, kad šiuose bandiniuose yra kitų fazių priemaišų, ir, labiausiai tikėtina, amorfinių / stikliškų domėnų. Pažymėtina, kad tokie maži fazių priemaišų kiekiai nebuvo aptikti įprastais ir bene dažniausiai šiam tikslui pasiekti taikomais rentgeno difrakcijos (XRD) bei Furjė vaizdavimo infraraudonosios spektrometrijos (FTIR) metodais. Tai rodo, kad ^{27}Al MAS BMR metodas gali būti labai efektyvus įrankis kontroliuojant stroncio aluminatų serijos junginių fazinį grynumą.