

Low-temperature synthesis of SrAl_2O_4 by a modified sol–gel route: XRD and Raman characterization

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Abstract

Among other alkaline-earth aluminates, the monoclinic (M) polymorph of SrAl_2O_4 can be used as host material for Eu^{2+} luminescence based phosphors. With the aim of reducing the synthesis temperature of this polymorph, we have produced and characterized by XRD and Raman scattering solid solutions of the $\text{SrAl}_{2-x}\text{B}_x\text{O}_4$ system ($x \leq 0.3$) obtained by two different methods, a ceramic route and a modified sol–gel synthesis. Though the addition of boron lowers the temperature of obtention of the M polymorph in both type of samples, lower B contents are needed to stabilize the M form as single phase for samples prepared by the sol–gel method than through the ceramic route. In the sol–gel method, the M polymorph can be obtained at temperatures as low as 1200 °C, with a Boron content of just 1%. Rietveld profile analysis allows us to conclude that coexistence of the monoclinic and hexagonal polymorphs of SrAl_2O_4 occurs for samples synthesized below an onset temperature of about 1000–1100 °C, that depends on the sample composition. Above those temperatures, only the monoclinic phase is formed.

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1. Introduction

Eu^{2+} -activated alkaline earth aluminates are known as phosphorescent materials due to their high quantum efficiency in the visible regions, as indicated in investigations on the MAl_2O_4 : Eu^{2+} and $\text{MAl}_{12}\text{O}_{19}$: Eu^{2+} ($M = \text{Ca}, \text{Sr}, \text{Ba}$) phases described by Blasse et al. [1]. Later, the Eu^{2+} and Dy^{3+} co-activated SrAl_2O_4 phase with tridymite-like structure was reported by Murayama et al. [2] to exhibit long persistent and bright bluish-green phosphorescence and greater chemical stability than traditional sulphide-based $\text{ZnS}:\text{Cu}, \text{Co}$ phosphors.

However, the preparation of MAl_2O_4 phases without flux requires high temperatures, as shown in the phase diagram [3] of the $\text{SrO}-\text{Al}_2\text{O}_3$ system (above 1900 °C in

the case of SrAl_2O_4 obtained by solid-state reactions). It is therefore a technological issue to reduce the temperature of synthesis of the optically interesting phases. Pet et al. [4] have proved that the addition of B_2O_3 reduces the processing temperature in the preparation of $\text{SrAl}_{14}\text{O}_{25}:\text{Eu}^{2+}$. I-Cherng and Chen [5] have proposed a sol–gel route for obtaining $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}, \text{Dy}^{3+}$ using alkyl borate as a source of flux as well as metal-alkoxide precursor for the formation of the above compound, but XRD analysis showed that they had failed to obtain SrAl_2O_4 as a single phase.

SrAl_2O_4 has a stuffed tridymite-like structure [6] related to high- SiO_2 , built up of layers of $[\text{SiO}_4]$ tetrahedra sharing corners that give rise to six-corner rings. In SrAl_2O_4 , Sr^{2+} ions are located in the cavities of the framework of $[\text{AlO}_4]^{5-}$ tetrahedra, occupying two different sites with low symmetry and coordinated by nine oxygen atoms. Moreover, SrAl_2O_4 displays two

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polymorphs: below $\approx 650^\circ\text{C}$, it exhibits monoclinic (M) symmetry (space group (SG) $P2_1$) and above that temperature it turns into a hexagonal (H) phase isostructural to that of high-temperature BaAl_2O_4 (SG $P6_322$) [7]. Structural perturbations such as insertion of small amounts of Ca [8], Ba [9,10] or excess Al [11] stabilize the metastable hexagonal form at room temperature (RT). Since only the monoclinic form shows luminescent properties when doped with rare earth ions [12–14], the characterization of the polymorph content in a sample is of great importance. The presence of the hexagonal polymorph is, however, difficult to detect by means of XRD analysis, because the hexagonal pattern overlaps the monoclinic one.

In order to obtain the monoclinic polymorph at lower temperatures than those mentioned above, in a previous work [15] we studied the effect of B addition in the synthesis temperature of monoclinic SrAl_2O_4 prepared by the so-called ceramic method. In this sense, boron was introduced replacing the Al (III) ions with the aim of generating distortions in the Al-framework that could lead to a decrease in the processing temperature of SrAl_2O_4 . XRD analysis showed that $T > 1400^\circ\text{C}$ is required to obtain monoclinic SrAl_2O_4 without the addition of boron. A temperature of 1400°C is required when $x(\text{B}) = 0.1$, while $x(\text{B}) = 0.2$ allows the obtention of the monoclinic polymorph at 1200°C .

In another work [16], we reported the synthesis of luminescent pigments of the type SrAl_2O_4 : Eu^{2+} , Dy^{3+} by a sol-gel methodology based in a Pechini's method modification. In the original Pechini's method [17], polybasic chelates are formed between hydroxycarboxylic acids containing at least one hydroxyl group, for example citric acid, and glycolic acid with metallic ions. The chelate underwent polyesterification on heating with a polyfunctional alcohol, for example ethylene glycol. Further heating produced a viscous resin, then a rigid transparent, glassy gel and finally fine oxide powder. In our modification, ethanol was used instead of ethylene glycol, so the viscous resin, difficult to manipulate, was not formed. This method allowed the obtention of the monoclinic polymorph at 1200°C for the sample with $\text{SrAl}_{1.7}\text{B}_{0.3}\text{O}_4$ stoichiometry. When the host was doped with Eu, Eu–Nd and Eu–Dy, the samples acquired luminescent properties.

Following this line, the objective of this work is to minimize the boron content and synthesis temperature that allow in obtaining the monoclinic polymorph. For this purpose, a further modification of the Pechini's sol-gel route has been developed, and its results are compared with those of the standard solid-state reaction route.

As one of the crucial points in the characterization of our results is to determine whether the M polymorph of SrAl_2O_4 is formed a single phase or not, and because the H and M diffractograms exhibit overlapped peaks,

XRD patterns are analyzed in detail. The validity for phase-content evaluation of criteria based on relative intensities of particular diffraction peaks is discussed, as compared with full profile fitting. In the same line of determining the coexistence of M and H polymorphs, and complementary to XRD analysis, Raman spectroscopy has been used. This technique is particularly useful for phase identification when, as in SrAl_2O_4 , different phases with very similar diffractograms can be present in the sample. As far as we know, the characterization by Raman spectroscopy of the hexagonal and monoclinic polymorphs has not been reported yet.

2. Experimental

2.1. Sample preparation

Samples with nominal composition $\text{SrAl}_{2-x}\text{B}_x\text{O}_4$ ($x = 0, 0.1, 0.2$ and 0.3) were prepared by the two routes described below:

Ceramic method: Samples were prepared from stoichiometric amounts of SrCO_3 (98%), Al_2O_3 (99.5%) and H_3BO_3 . The mixture was ground in a planetary ball mill for 20 min using acetone as dispersant agent. Finally, the samples were dried at RT.

Sol-gel method: Samples were synthesized by a further modification of the already modified Pechini's method that we have reported above. In that method, only ethanol was used as solvent, so acid water ($\text{pH} = 1$) was added with two purposes: First, to achieve total solution of $\text{Sr}(\text{CH}_3\text{COO})_2$ ($\text{Sr}(\text{Ac})_2$) precursor and, second, to avoid the formation of an aluminium precipitate because Al(III) is highly polarizing and tends to hydrolyze. These two troubles are solved, in this new modification, using acetic acid glacial as solvent for the $\text{Sr}(\text{Ac})_2$ precursor. The new methodology is described in the flow chart showed in Fig. 1.

In order to elucidate the optimal processing temperature, samples obtained through the synthesis methods described above were submitted to different thermal treatments in an electrical furnace model CARBOLITE. As both methods have different reactivity, the temperatures and soaking times applied were slightly different in each case. For the ceramic method, firing temperatures were $1100, 1200, 1300, 1400$ and 1500°C with soaking times of 1 and 10 h at each temperature. Fig. 2 shows the thermal cycle employed.

The sol-gel method, due to its higher reactivity, requires, in general, lower temperatures, so these samples were fired at $700, 900, 1000, 1100, 1200$ and 1400°C with 1 h of soaking time at each temperature. Thermal treatment (Fig. 3) was slightly modified in order to help the combustion and removal of the organic matter.

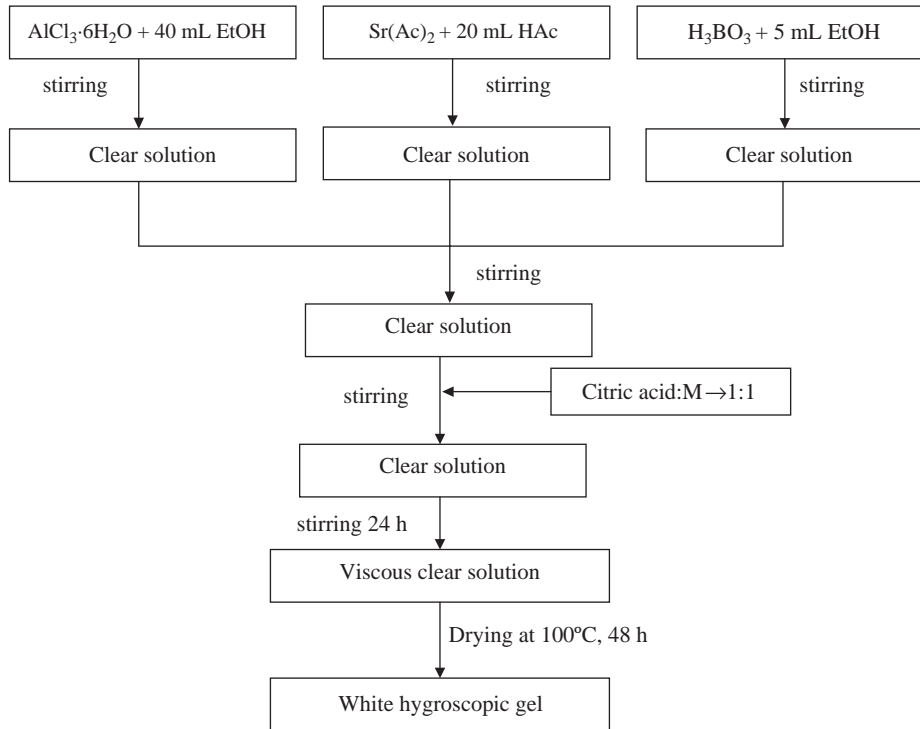


Fig. 1. Flux diagram for sol-gel synthesis method.

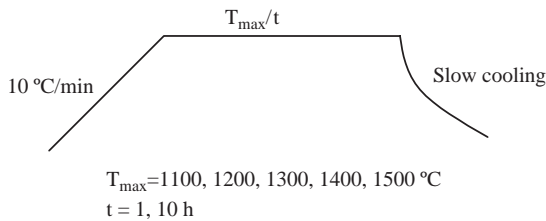


Fig. 2. Thermal treatment employed for the samples synthesized by the ceramic method.

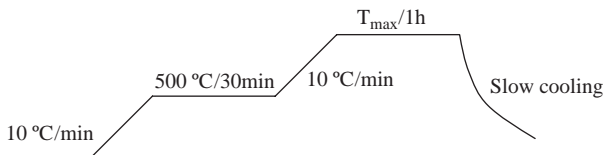


Fig. 3. Thermal treatment employed for the samples synthesized by the sol-gel method.

2.2. Characterization techniques

Fired samples were ground in an agate mortar and meshed up to 50 μm grain size. At this point, it is worth recalling that, especially in ceramic samples, an increase in boron content is accompanied by an increase in the sample hardness, probably due to the low melting point of boric acid that increases the sinterization of the samples. Crystalline phase evolution was carried out

with a Siemens D5000 diffractometer with Bragg-Brentano geometry using $\text{CuK}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$). Data have been collected by step-scanning 2θ from 18° to 40° and 2.5 s counting time at each step at RT. The goniometer was controlled by the “SIEMENS DIF-FRACT plus” software, which makes the integration of the diffraction peaks. The instrument was calibrated using an external SiO_2 standard, which served also as a reference for grain-size determination. Rietveld analysis was performed with help of Fullprof program [18].

Raman measurements were performed at RT in a DILOR XY spectrometer with a diode array multi-channel detector and excitation through microscope, using the 514.5 nm line of an Ar^+ laser (model Coherent INNOVA 305). The Si Raman line at 520 cm^{-1} was used for wavelength calibration of the Raman lines. The spectral linewidth was always better than 3 cm^{-1} .

3. Results and discussion

Since one of the objectives of this work is to compare between ceramic and sol-gel methods, samples with the same composition and synthesis temperature were produced through each of these methods and analyzed by XRD. In a first step, XRD was used to identify the presence of impurity phases of composition different from SrAl_2O_4 . Then, Rietveld analysis was performed in order to determine whether the monoclinic polymorph of SrAl_2O_4 was the only one formed or if phase

coexistence occurs, specifically with the high-temperature hexagonal modification of SrAl_2O_4 .

Fig. 4a shows the diffractograms of SrAl_2O_4 samples (no boron added) produced by the ceramic route as a function of the calcination temperature. These patterns can be compared with those of undoped samples produced by the sol-gel method (Fig. 4b).

By comparing the diffractograms of Fig. 4a with the standard for the monoclinic phase of SrAl_2O_4 (JCPDS card no. 74-794) it becomes evident that the ceramic route favors the appearance of secondary phases of the $\text{SrO-Al}_2\text{O}_3$ phase diagram, such as $\text{Sr}_3\text{Al}_2\text{O}_6$ (very intense) and SrAl_4O_7 (weakly), up to very high temperatures. In fact, $\text{Sr}_3\text{Al}_2\text{O}_6$ was formed for $x = 0$ until $T = 1400^\circ\text{C}/10\text{h}$, for $x = 0.1$ until $T = 1200^\circ\text{C}/10\text{h}$ and for $x = 0.2$ until $T = 1100^\circ\text{C}/10\text{h}$. It was not detected when $x = 0.3$ (patterns not shown). The amount of $\text{Sr}_3\text{Al}_2\text{O}_6$ decreases on increasing the boron

content, processing temperature and/or soaking time, in parallel with the stabilization of the monoclinic polymorph.

Fig. 4b shows that such Sr–Al–O impurities are not formed in the sol-gel synthesis or are very weakly formed and only at low temperatures. Therefore, we decided to discard the ceramic route; only results for sol-gel samples will be presented in the following. Within this method, the effect of boron addition and variation of the synthesis temperature were investigated. Again, by simple comparison of the XRD of boron-doped samples with the monoclinic reference it was seen that some other impurity formed for high boron content, which suggests that its appearance is related to the boron introduction. For a given composition, the impurity tends to disappear with increasing treatment temperature, which indicates that boron enters the matrix more easily at higher temperatures. To avoid these boron-related impurities we decided to discard compositions with boron content higher than $x = 0.1$. Fig. 5a shows the diffractograms of $x = 0.1$ samples, as a function of synthesis temperature. A first glance shows that, for the same temperature, the diffractograms of boron-containing samples present narrower peaks than the undoped ones, which indicates a better crystallization. In order to investigate the phase purity and possible coexistence of the monoclinic and hexagonal polymorphs, we have performed Rietveld analysis of all the diffractograms presented in Figs. 4 and 5a. For comparison, we represent in Figs. 5b and c, the theoretical X-ray diffractograms for the hexagonal and monoclinic SrAl_2O_4 polymorphs. The data have been taken from JCPDS files no. 31-1336 and 74-794, respectively. The data for the hexagonal polymorph included in JCPDS file no. 31-1336, were obtained at 700°C . At RT, the diffractogram is expected to shift toward slightly higher 2θ values due to lattice contraction.

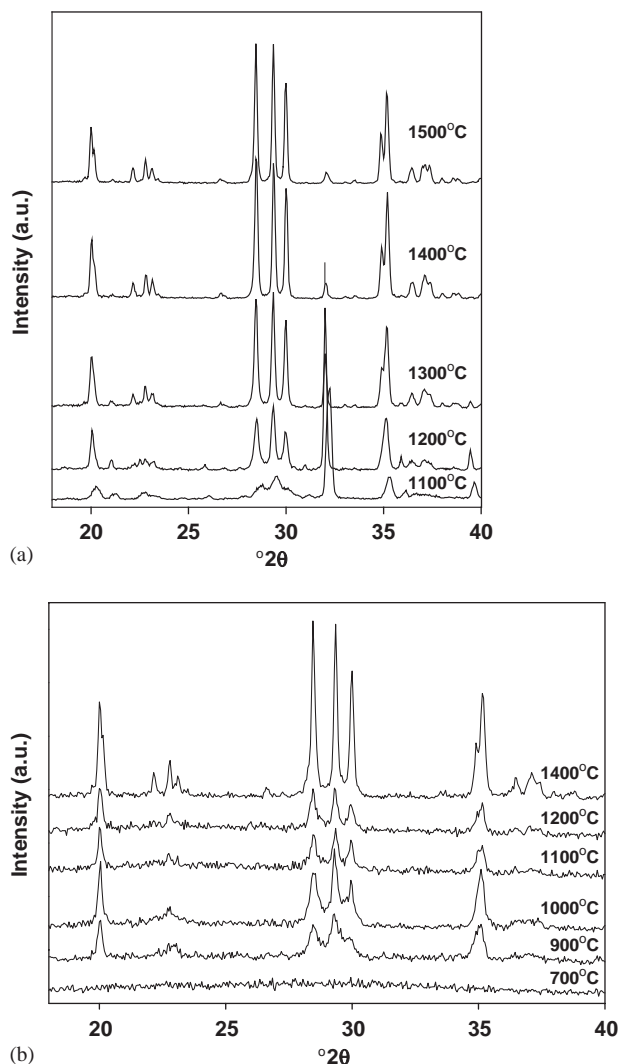


Fig. 4. X-ray diffractograms registered at different temperatures and 1 h of soaking time for the sample $\text{SrAl}_{2-x}\text{B}_x\text{O}_4$ ($x = 0.0$) obtained by (a) the ceramic method and (b) the sol-gel method.

3.1. XRD analysis

The analysis of XRD data of SrAl_2O_4 phases is usually qualitative, just based on relative peak intensities. Thus, the presence of an intense peak at the position of the (220) monoclinic reflection (about 29° in 2θ scan with $\text{CuK}\alpha$), is taken as an indication of the presence of the hexagonal polymorph. In order to quantify the proportion of M and H phases in $\text{SrAl}_2\text{O}_4\text{-BaAl}_2\text{O}_4$ solid solutions, Henderson and Taylor [9] proposed to use the parameter

$$R = \frac{\bar{2}11_{\text{mon}}}{220_{\text{mon}} + 102_{\text{hex}}}$$

In this expression, $\bar{2}11_{\text{mon}}$ and 220_{mon} stand for the intensities of the highest peaks of the monoclinic

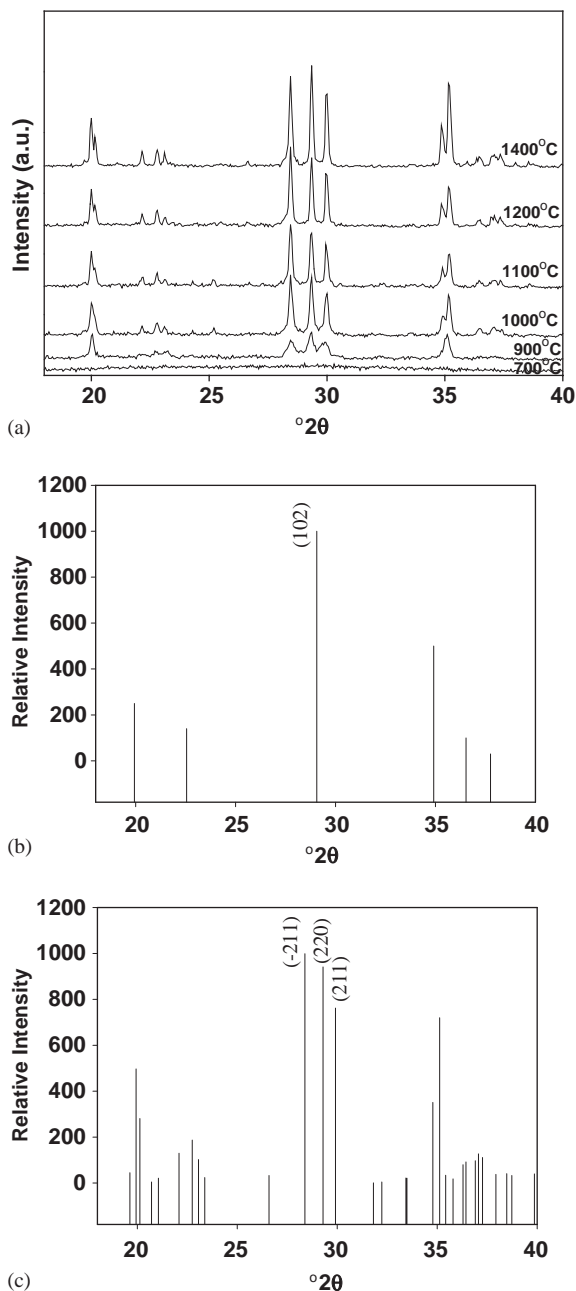


Fig. 5. (a) X-ray diffractograms registered at different temperatures and 1 h of soaking time for the sample $\text{SrAl}_{2-x}\text{B}_x\text{O}_4$ ($x = 0.1$) obtained by the sol-gel method, (b) theoretical X-ray diffractogram for hexagonal SrAl_2O_4 polymorph taken from JCPDS file no. 31-1336 and (c) theoretical X-ray diffractogram for monoclinic SrAl_2O_4 polymorph taken from JCPDS file no. 74-794.

polymorph and 102_{hex} is the intensity of the highest peak of the hexagonal polymorph. According to JCPDS files no. 74-794 and 31-1336 for the monoclinic ($P2_1$) and hexagonal ($P6_322$) polymorphs, respectively, the (102) hexagonal reflection ($2\theta \sim 29.09$ at 700°C) overlaps the monoclinic (220) peak ($2\theta \sim 29.3$), while the monoclinic ($\bar{2}11$) ($2\theta \sim 28.4$) is not superposed to any hexagonal reflection. Therefore, R aims to establish the ratio

between monoclinic and hexagonal polymorphs. If only the monoclinic polymorph is present, the R value should be ~ 1.09 , while $R < 1.09$ would indicate an increase in the hexagonal phase content.

In the following we discuss the validity of such a procedure by comparing its results with those of the full profile fitting. From Figs. 4 and 5 we see that, if the criterion based on the R parameter were correct, we would have M + H coexistence in two situations: First, for samples produced at low temperatures (typically below 1100°C), that present a broad diffractogram, but also, and unexpectedly, for some samples synthesized at high temperatures that present very narrow diffraction peaks. This separation between low and high-temperature samples is relevant for the discussion, as we shall see.

Since the M + H coexistence was expected for low T samples but is somewhat surprising for the high- T ones, we decided to perform a Rietveld profile analysis of all diffractograms. The Fullprof program was used [18], with pseudo-voigt peak profile, using as fitting parameters the unit cell dimensions, the atomic coordinates, the linewidth and the isotropic thermal parameters, besides the background polynomial coefficients. Inclusion of anisotropic thermal parameters did not improve the fitting meaningfully. Preferential orientation and grain-size distribution were not necessary either and were not included.

Fig. 6 shows the profile fitting of some representative samples. The results of this study can be summarized as follows:

For each series of samples of a given composition, as a function of synthesis temperature, there is a cross-over temperature T^* above which diffractograms can be very well fitted with only M phase, irrespective of the R value. This tolerance is mainly due to the high number of free parameters (atomic coordinates) of the $P2_1$ structure, which affect the relative intensities and allow a wide range of R ratios. On the contrary, below T^* the fitting with only M phase is unsatisfactory and the introduction of the hexagonal polymorph is necessary. This is illustrated in Figs. 6b and c, which show the diffractogram of the sol-gel sample with 0.1B produced at 900°C and its fitting with only M (b) and with M + H phases (c). The lattice parameters of the hexagonal phase were $a = 5.12\text{--}5.13 \text{ \AA}$ and $c = 8.36\text{--}8.41 \text{ \AA}$, very close to those proposed in Ref. [7] by extrapolation at RT of the high temperature data.

From this analysis, a sort of phase diagram can be established (see Fig. 7). Of course, this diagram is only qualitative since, for instance, an increase of the retention times at a fixed temperature stabilizes the M phase at the expenses of the H one, lowering the cross-over temperature.

The coexistence of M and H phases for samples produced at low temperatures is attributed both to

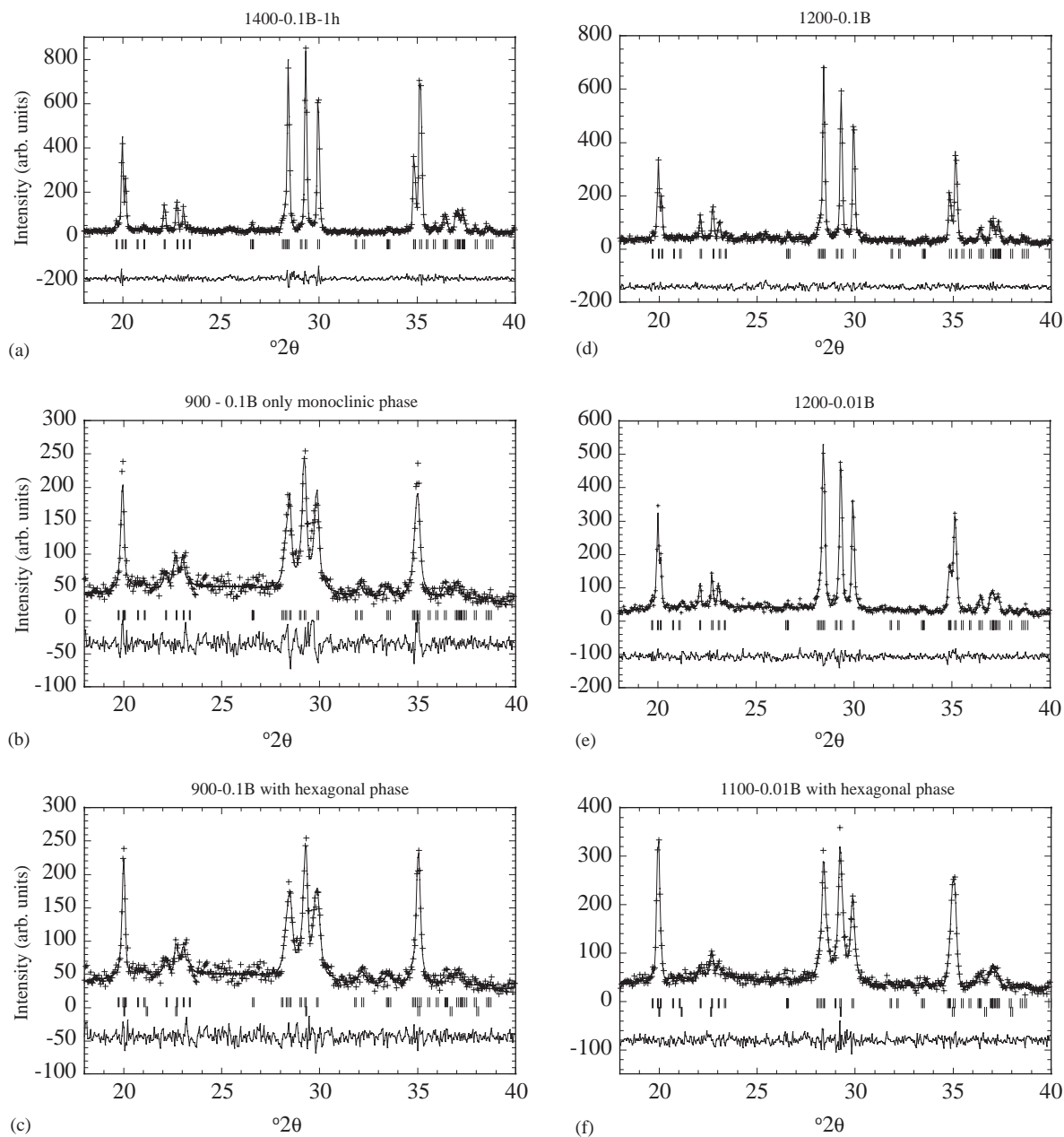


Fig. 6. Rietveld profile fitting of selected diffractograms of sol-gel produced samples with 1 h of soaking time. The synthesis temperature and boron content are indicated in each graph. (a) illustrates that the diffractogram of a high-temperature sample with $R < 1.09$ can be fitted with only monoclinic phase. (b) and (c) show the diffractogram of a low- T sample fitted with only M (b) or M + H (c) phases, to illustrate how the inclusion of the hexagonal phase improves the fitting. (d) corresponds to a situation with nominal $R > 1.09$, that can be very well fitted with only M phase. (e) and (f) pertain to samples with only 0.01 boron content, to show that the M phase is achieved at 1200 °C as pure phase with just 1% boron doping.

compositional disorder and to the small crystallite size, as indicated by the large peak broadening. We have already mentioned that the metastable hexagonal form of SrAl_2O_4 can be stabilized at RT by introduction of dopants or excess Al. In fact, in all cases in which the H phase was introduced, the occupancy of Al in that phase refined to an excess value, as compared to Sr, when occupancy factors were allowed to vary. Typical values of the Al/Sr ratios for the hexagonal phase were between

2.5 and 2.8, much higher than the nominal value of 2. In contrast, the Al/Sr ratio for the monoclinic phase resulted to be very close to the nominal value in all cases. As regards the grain-size effect, we note that prolonging the retention time to 10 h leads on the one hand to narrower peaks (better crystallization) and, on the other hand, to M phase stabilization. Grain sizes were determined by means of the Scherrer's law, using the SiO_2 peak at 26° as a reference for instrumental

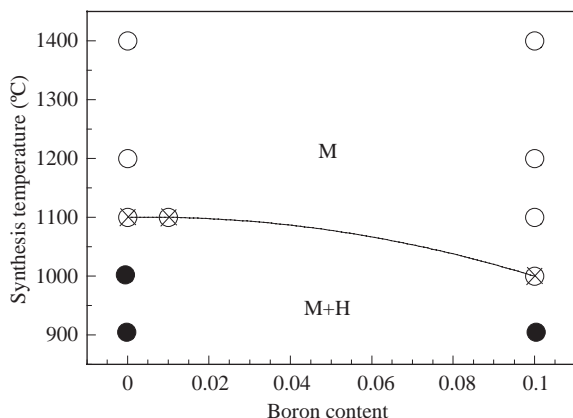


Fig. 7. Phase diagram for $\text{SrAl}_{2-x}\text{B}_x\text{O}_4$ compositions with $x \leq 0.1$ obtained by the sol-gel route with 1 h of soaking time. The assignment M or M+H indicates that the XRD profile could be fitted with only monoclinic phase (M region) or required the hexagonal polymorph as second phase (M+H). Crossed symbols indicate the cross-over from one situation to the other at each composition.

linewidth. The range of sizes varied from 30 nm or less for samples produced at 900 °C with $x = 0$ (1 h) to about 200 nm for those produced above 1400 °C, also with 1 h of retention time. It must be noted that these values are only approximate, since the scan step was too large and the accumulation times too short for an accurate determination.

Once we have seen that monoclinic SrAl_2O_4 can be obtained as single phase through the sol-gel route with a boron content of 0.1 at 1100 °C/1 h, we have investigated which is the minimum boron content that stabilizes the M phase. A new sample with $x = 0.01$ was synthesized by this method and fired at 1100 °C/1 h and 1200 °C/1 h. The analysis by XRD shown in Fig. 6 indicate the formation of the M polymorph single phase after firing at 1200 °C/1 h.

In summary, both in the ceramic and sol-gel methods the addition of boron helps to decrease the processing temperature required to obtain monoclinic SrAl_2O_4 as single phase. However, the sol-gel route has two advantages: First, lower temperature is required to obtain the monoclinic polymorph as a pure phase and, second, impurities are not formed or are less probably formed. A boron content of just 1% is enough to facilitate the reaction of the constituents and yield the monoclinic form without the formation of secondary phases.

3.2. Raman scattering

In order to complement XRD data, particularly as it concerns the coexistence of M and H polymorphs, we have characterized by Raman scattering some representative samples. The idea of using this technique in

combination with XRD is the following: First, by measuring a high-temperature sample whose diffractogram is unambiguously assigned to the monoclinic phase, we identify the Raman spectrum of such a phase, even if we cannot give a detailed interpretation of the spectrum. Once the spectrum of the M phase is known, it should be easy to detect this phase in other samples, as well as its coexistence with other phases, through the finding of different spectra superposed to that of the M phase.

No Raman study of tridymite-like AB_2O_4 compounds has been reported to date, neither for the monoclinic nor for the hexagonal forms. The greater number of modes expected from the large size of the unit cell makes the interpretation of the spectrum very complicated. Therefore, we will give only general ideas about the origin of the modes and will use this technique mainly for phase identification. Fig. 8 shows three spectra measured under the same experimental conditions on three different samples. Graph labelled M has been taken on an $x = 0$ sample obtained through the ceramic route at 1400 °C/10 h. Graph labelled X has been recorded on a sample synthesized by the sol-gel method with $x = 0.1$ at 1200 °C/1 h. Finally, spectrum M' was taken on a sample synthesized by the sol-gel method with $x = 0.01$ at 1100 °C/1 h.

Since spectrum M was recorded on a sample presenting a single-phase diffractogram identified as that of the monoclinic $P2_1$ phase, we ascribe that spectrum to the monoclinic phase of SrAl_2O_4 . Spectrum M was the only one found in samples fired at $T \geq 1300$ °C, in agreement with the good fitting achieved for the diffractograms of these samples to the monoclinic polymorph as single phase.

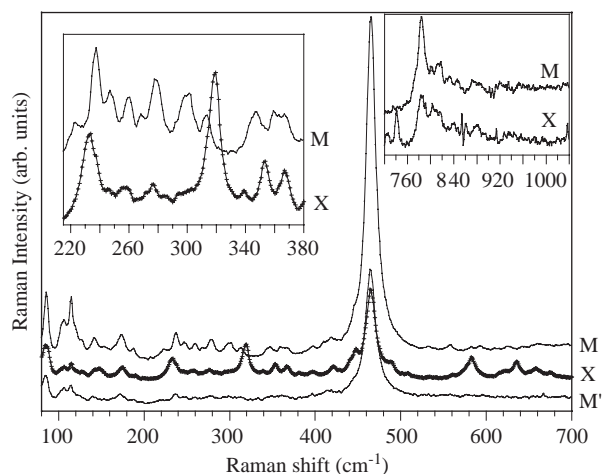


Fig. 8. Graph labelled M shows the Raman spectrum of an $x = 0$ sample obtained through the ceramic route at 1400 °C/10 h. Graph labelled X has been recorded on a sample synthesized by the sol-gel method with $x = 0.1$ at 1200 °C/1 h. Graph labelled M' was recorded in a sol-gel sample with $x = 0.01$ at $T = 1100$ °C/1 h.

At the other end of temperatures, for samples annealed at 1100 °C or below, the spectrum (M') is not well defined, though some weak peaks belonging to the monoclinic phase can be identified, together with the always intense peak at 465 cm^{-1} . Spectrum M' is not interpreted as arising from a different phase; we rather assume that in these samples a crystalline structure is not yet fully achieved and thus the spectrum reflects only partial crystallization. This result is in consonance with the peak broadening found in the diffractograms of low-temperature samples. As regards the $M + H$ coexistence, a spectrum that might be associated to the (probably defective) hexagonal phase in these samples could not be identified due to the disordered character of the spectrum.

At the intermediate temperature of 1200 °C and for a boron content of 0.1, the monoclinic spectrum is found to coexist with another one that shows well-defined peaks, but is different from that of the M phase. The intensity of the extra peaks relative to those belonging to spectrum M varies when measuring different points of the same sample, as shown in Fig. 9. Then, we conclude that those spectra are a superposition of two different ones: the monoclinic spectrum M and another one, labelled X that is tentatively assigned to a different phase of SrAl_2O_4 . Some peaks have been selected as a hint to identify M and/or X phases. In one of the points, spectrum X could be measured independently, and is included in Fig. 8 for comparison. In spectrum X , the intensity of the main peak at 465 cm^{-1} , relative to the rest of peaks, is much lower than in M . Spectrum X is also characterized by a lower number of peaks, denoting higher symmetry than in the M phase. In spite of these differences, the similarities between spectra M and X

suggest that both phases are closely related. We note that spectrum X is found both in ceramic and in sol–gel samples produced at the same temperature and with the same boron content, which supports its origin to be intrinsic, not related to an impurity.

In order to elucidate the nature of phase X , its stability was checked under variation of temperature and soaking time. For this purpose, we measured the Raman spectrum of sol–gel samples with $x = 0.1$ treated at different temperatures. While the monoclinic and hexagonal spectra appeared superposed for $T = 1200$ °C, a purely monoclinic spectrum was found for $T = 1300$ and 1400 °C. The effect of increasing the grain size by prolonged annealing time was also verified for this same composition. It is found that the monoclinic phase is stabilized after long-time annealing, at the expenses of the X phase. While M and X phases coexist in the sample annealed for 1 h, only the monoclinic spectrum appeared in the sample treated for 10 h, in agreement with the better crystallization found by XRD.

The identification of phase X is problematic. The most obvious assignment is that it corresponds to the high-temperature hexagonal phase of SrAl_2O_4 (SG $P6_322$ with $Z = 2$), whose coexistence with the monoclinic polymorph has been proposed to explain the XRD diffractograms of samples produced at low temperatures. However, there is an argument against this attribution: Group theory predicts only 15 Raman active modes for it, and it is clear that spectrum X contains many more than 15 modes. (In contrast, 81 Raman active modes are expected for the $P2_1$ monoclinic phase). We may then search for other candidates: In their work on solid solutions of the BaAl_2O_4 – SrAl_2O_4 system, Henderson and Taylor [9] found a compositional phase transition at RT from monoclinic to hexagonal symmetry as Ba was introduced in SrAl_2O_4 , and they assumed that the hexagonal phase was that of high- T SrAl_2O_4 . However, in a later work [10] they suggested that two different hexagonal phases are formed in the Sr–Ba system at RT, both with the same space group ($P6_3$) but with different cell parameters and Z numbers. Distinction between these two candidates is difficult on the basis of mode number: 82 Raman active modes are expected for the RT hexagonal phase of BaAl_2O_4 ($P6_3$, $Z = 8$) while 61 Raman modes would be expected for the $P6_3$ ($Z = 6$) structure proposed in Ref. [10]. Furthermore, the XRD of all these hexagonal phases are almost identical except for small intensity differences and very weak superlattice reflections [19]. In the case of SrAl_2O_4 the stable phase at RT is monoclinic, but this phase is probably very close energetically to the $P6_3$ hexagonal phase. Therefore, it is plausible that spectrum X belongs to a hexagonal phase different from the high- T polymorph and similar to that of BaAl_2O_4 . For the moment, this question remains open.

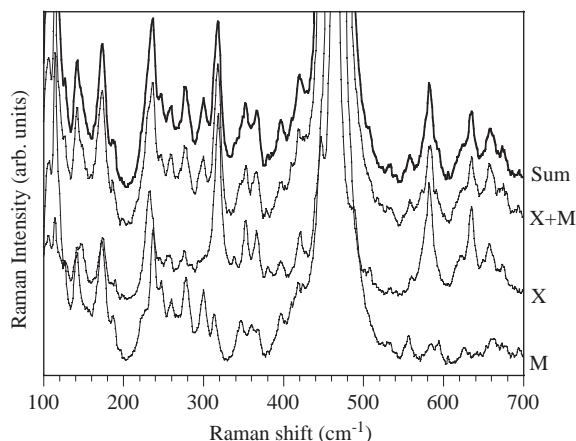


Fig. 9. Three different spectra taken in different points of the sol–gel sample with $T = 1200/1$ h and $x(B) = 0.1$, showing that in this sample monoclinic and X phases coexist, yielding points with purely M or X spectrum, or a superposition of both ($M + X$). Spectrum “sum” was calculated by addition with appropriate weights of spectra M and X , and must be compared with spectrum labelled $M + X$.

As regards the interpretation of the Raman spectrum, the lack of polarization measurements and the expected mixing of atomic shifts prevent mode assignment. In the case of framework structures built up of linked tetrahedral units, it is usual to discuss the Raman spectrum in terms of internal vibrations of the MO_4 units, plus librational modes of those units and translation modes of the cations located in the interpolyhedral cavities. To a first approximation, we attribute modes at frequency higher than 600 cm^{-1} to Al–O bond-stretching vibrations and the narrow, low-frequency peaks below 150 cm^{-1} to tetrahedral librations or tilts. In the intermediate region the assignment is impossible; by analogy with other compounds, we assign the most intense band at 465 cm^{-1} to the bending vibration of the O–Al–O angle. A remarkable fact is that the 465 cm^{-1} mode is the only one that remains with high intensity in highly disordered or non-crystallized compositions, such as those annealed at low temperatures, which suggest that the $[\text{AlO}_4]$ unit is stabilized first as a rigid unit, and that disorder arises solely from the orientation of such units and/or slight oxygen displacements.

4. Conclusions

In summary, we have developed a modified sol–gel route that allows the obtention of the monoclinic polymorph of SrAl_2O_4 as a pure phase at much lower temperatures and boron content than through the standard ceramic route. With this method, a pure M phase has been obtained at $T = 1200\text{ }^\circ\text{C}$ with only $x = 0.01$ of boron content. As regards the analysis of XRD, we conclude that a full Rietveld profile fitting is necessary in order to ascertain the coexistence of the M and H polymorphs of SrAl_2O_4 . Criteria based exclusively on relative peak intensities yield erroneous results for samples synthesized at high temperatures ($\geq 1200\text{ }^\circ\text{C}$), for which the profile can be very well fitted with only M phase. On the contrary, below a synthesis temperature of about $1100\text{ }^\circ\text{C}$, profile fitting requires the introduction of the high-temperature hexagonal form as a secondary phase. In such samples, the diffractogram is notably broadened, with grain sizes of the order of $30\text{--}40\text{ nm}$, while the grain size of the samples produced at the highest temperatures reached in this work is well above 100 nm . Therefore, the coexistence of M and H polymorphs is attributed to incomplete reaction and partial crystallization. In agreement with this explanation, the Raman spectra of samples produced below $1200\text{ }^\circ\text{C}$ do not show well-defined peaks, in contrast with the results for samples synthesized at $1200\text{ }^\circ\text{C}$ or above. The common spectrum of high-temperature samples is attributed for the first time to the monoclinic polymorph.

The bad quality of the spectra pertaining to low-temperature samples prevents us to identify the spectrum belonging to the hexagonal phase. On the other hand, besides the spectrum associated to the monoclinic phase, another spectrum has been found for samples synthesized at $1200\text{ }^\circ\text{C}$ with 0.1 boron content, both through the sol–gel and ceramic methods. The nature of that phase will be elucidated in the future. We tentatively attribute it to another polymorph of SrAl_2O_4 , that forms only in an interval of temperature, composition and grain size. The dependence of the spectra on temperature and soaking time suggest that the formation of phase X may be a grain-size-dependent phenomenon, the monoclinic phase being more stable for increasing grain size. As the firing temperature or retention time is increased, the monoclinic domains grow at the expenses of the hexagonal ones. According to this interpretation, the proportion of X to monoclinic content would depend on the ratio of domain (or grain) surface vs. volume, so that long annealing times, yielding larger domains or grains, would favor the formation of phase M.

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