

α - and β -AgVO₃ polymorphs as photoluminescent materials: An example of temperature-driven synthesis



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ABSTRACT

Controlling the synthesis of a given polymorph of an inorganic material is a further step in the design of property and function. In this letter, we report for the first time a simple procedure to effectively control the reversible transformation between the crystalline polymorphs α -AgVO₃ and β -AgVO₃. Photoluminescence emission (PL) performance is analyzed; at low temperatures (up to 35 °C) when α -AgVO₃ is formed the PL emission is red, while at temperatures larger than 45 °C when β -AgVO₃ is obtained the color of emission PL emission goes from green to blue. The findings highlight the ability of temperature to dramatically alter the nature of phase transformation at the atomic level. The phase transformation is driven by the short-range structural and electronic changes of [VO₄] and [AgO_x] (x = 5, 6, and 7) clusters (building blocks of both monoclinic structures), and hence is dependent on the temperature employed during synthesis. These outcomes clearly demonstrate that the AgVO₃ crystals exhibited appropriate activity for application in visible lamps, displays, and other optical devices.

1. Introduction

The development of new applications has driven the field of materials design and synthesis to investigate materials that are not thermodynamically stable, i.e., metastable phases of one compound with different crystal structures [1]. These metastable phases are increasingly important because each polymorph can present unexplored physical and chemical properties that are distinct from the properties of their thermodynamically stable counterparts and will be vital in applications [2].

In solid-state chemistry, a major challenge appears in establishing controllable synthesis routes towards metastable polymorphs because there are limited numbers of very deep minima on the potential energy surface corresponding to a given stoichiometry in the phase diagram. Solid-state synthesis methods typically rely on equilibrium routes; non-equilibrium or metastable phases may be attained by quenching an intermediate of the reaction or by particular synthesis procedures such as gas phase, hydrothermal, mechanochemical, or template synthesis [3]. However, these procedures suffer from difficulties in rational

handling for function design. Thus, the formation of such metastable materials requires complete understanding of their chemical and physical properties through state of the art experimental or theoretical investigation. In this respect, unravelling the relationship between the atomic structure and the functional properties can be a crucial step, especially in complex materials where short-range interactions rather than the average structure can define their actual properties and behaviors.

AgVO₃ is the most commonly occurring silver vanadium oxide-based material in the solid state [4] and has attracted interest owing to its technological applications in areas such as lithium ion batteries, antibacterial agents, sensors, and optical materials [5–14]. AgVO₃ has two phases that correspond to the metastable α -AgVO₃ and stable β -AgVO₃ phases with monoclinic space groups *Cm* and *C2/c*, respectively. α -AgVO₃ can be irreversibly transformed to β -AgVO₃ at around 200 °C [13,15]. To date, the procedure regarded as optimal for the preparation of the stable β -phase of AgVO₃ is a co-precipitation process at ambient temperature [13,16]. Syntheses of metastable α -AgVO₃ have either reported poorly crystalline samples and demanding requirements such

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as high temperatures or long reaction times [13,17,18], while Shao *et al.* successfully synthesized pure α -AgVO₃ with high crystallinity through a biomimetic process [19]. Very recently, α -AgVO₃ nanowires decorated with Ag nanoparticles were successfully prepared by hydrothermal treatment of a mixture of ammonium metavanadate and silver nitrate. Heating the as-prepared nanowires to 475 °C in N₂ results in a structural conversion from α -AgVO₃ to β -AgVO₃ for application as cathode material in Li-ion batteries [20]. It has previously been suggested that the electrochemical performance of β -AgVO₃ is superior to that of α -AgVO₃ due to a unique tunnel structure that accommodates cations [5,12].

Interest from a basic scientific viewpoint is fueled by novel synthesis routes to a stable phase, β -AgVO₃ [16] and a metastable phase, α -AgVO₃ [21]. In particular, we have achieved the synthesis of α -AgVO₃ powders using a co-precipitation method at 10, 20, and 30 °C [16,21]. These polymorphs possess coordination environments for Ag and V cations that are highly sensitive to variations in temperature, pressure, irradiation, doping, and particle size. This characteristic allows evaluation of the structural and electronic disorder behaviors and correlations with bonding and structural characters. Encouraged by the findings from these recent experimental/theoretical works, in this work, we first report the temperature-controllable phase transformation of AgVO₃ in solid-state material that is manipulated so that the system evolves via the lowest barrier path. Though frequent in molecular chemistry, this process is uncommon in solid-state chemistry.

Herein, we prepare AgVO₃ by co-precipitation and polymorphic control of this complex metal oxide is reached by tuning the reaction temperature. As a result, structural transformation between the two different monoclinic and crystalline phases (α -unstable and β -stable) of AgVO₃ was realized. In addition, photoluminescence (PL) emission offers a wide range of colors from red to blue as a function of temperature, suggesting AgVO₃ crystals are a promising candidate for optical material in technological applications. The PL behavior can be correlated to the structural and electronic changes at short range of the [VO₄] and [AgO_x] ($x = 5, 6, \text{ and } 7$) clusters, which are building blocks of the monoclinic structures of both phases.

2. Method

2.1. Synthesis of AgVO₃ crystals

The AgVO₃ crystals were obtained by controlled co-precipitation method at 0, 15, 25, 35, 45, 65, and 75 °C for 10 min. The precursors utilized in this synthesis were silver nitrate, AgNO₃ (99% purity, Synth) and ammonium monovanadate, NH₄VO₃ (99% purity, Aldrich). 1 mmol of NH₄VO₃ was dissolved in 60 mL distilled water at 30 °C, under magnetic stirring for 15 min, and 1 mmol of AgNO₃ was dissolved in 15 mL distilled water, under magnetic stirring for 15 min. Both solutions were placed in an ice bath at 0 °C and quickly mixed promoting the instantaneous formation of AgVO₃ precipitate (for the synthesis at 0 °C). The other synthesis was carried out by varying the temperature using a heating plate. A magnetic stirrer with heating (IKA HS 7) coupled to a thermocouple (ETS-D6), which according to the manufacturer has accuracy of temperature measurement: ± 0.05 + tolerance PT1000 (DIN IEC 751 Class A). The precipitated was washed with distilled water several times, and drying in a conventional furnace at 60 °C for 10 h.

2.2. Characterization

The AgVO₃ crystals were characterized by XRD using CuK α radiation ($\lambda = 1.5406$ Å) (Rigaku diffractometer, Model D/Max-2500PC, Japan) in the 2θ range of 10–80° at a scan speed of rate of 2°/min. The morphology was investigated with a field emission scanning electron microscope (FE-SEM) Supra 35-VP Carl Zeiss (Germany) operating at 15 kV. The PL measurements were performed with a Monospec 27

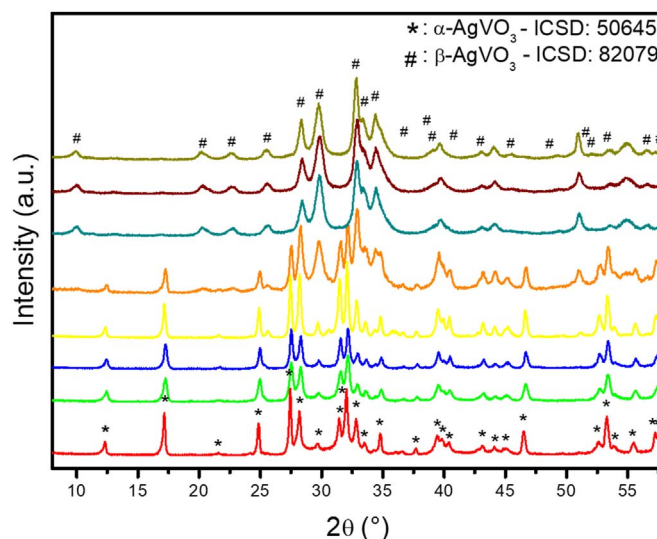


Fig. 1. XRD patterns of the AgVO₃ samples prepared at different synthesis temperatures.

monochromator (Thermal Jarrel Ash) coupled to a R446 photomultiplier (Hamamatsu Photonics). A krypton ion laser (Coherent Innova 90 K) ($\lambda = 350$ nm) was used as excitation source, keeping its maximum output power at 500 mW. All experiments measurements were performed at room temperature.

3. Results and discussions

Fig. 1 shows the X-ray diffraction (XRD) patterns of AgVO₃ powders synthesized at different temperatures. Diffraction peaks for the samples obtained at 0, 15, and 25 °C can be assigned to metastable α -AgVO₃ with monoclinic structure (ICDS No. 50645, space group: C2/c (No. 15)). Peaks of other phases were not detected, indicating the high purity of the product. When the powders were obtained at 35 and 45 °C, all diffraction peaks could be indexed to the metastable α -AgVO₃, but the onset of the formation of β -AgVO₃ was observed via the weak peaks around 25.5°. The slight β -AgVO₃ phases might transform from the metastable α -AgVO₃ phase during reaction progress. However, when the synthesis temperature was increased to 55, 65, and 75 °C, all the XRD diffraction peaks could be indexed to the stable β -AgVO₃ phase with monoclinic structure (ICDS No. 82079, space group: Cm (No. 8)) and without the presence of a secondary phase.

The transformation from α -AgVO₃ to β -AgVO₃ with temperature can be followed by scanning electron microscopy (SEM). Fig. 2 displays a survey of the morphology and structure. As can be seen, α -AgVO₃ nanowires with lengths of several tens of micrometers were obtained during synthesis at 0 °C. At 15 °C, some nanowires and micro-rods with defined faces were obtained. In the sample synthesized at 25 °C, the micro-rods presented defined faces and some urchin-like microspheres were obtained by the self-assembly of micro-rods. At 35 °C, α -AgVO₃ crystals with urchin-like morphologies were mainly obtained, but a phase that corresponds to β -AgVO₃ could be observed. The phase transformation from α -AgVO₃ to β -AgVO₃ was clearly observed at 45 °C, since in addition to the micro-rods, a second morphology that corresponds to nanowires of the β -AgVO₃ phase was observed. According to the literature [19,22], this transformation is explained by the “ripening-splitting model” that takes place when α -AgVO₃ micro-rods are fragmented into β -AgVO₃ nanowires. During the syntheses performed at temperatures above 55 °C only nanowires were obtained, which indicates that the pure β -AgVO₃ phase was obtained. No significant differences were observed in the morphologies among the three samples obtained at 55, 65, and 75 °C.

The crystal structures of both β -AgVO₃ and α -AgVO₃ are known and a graphical representations are given in Fig. 3. AgVO₃ exhibits a rich

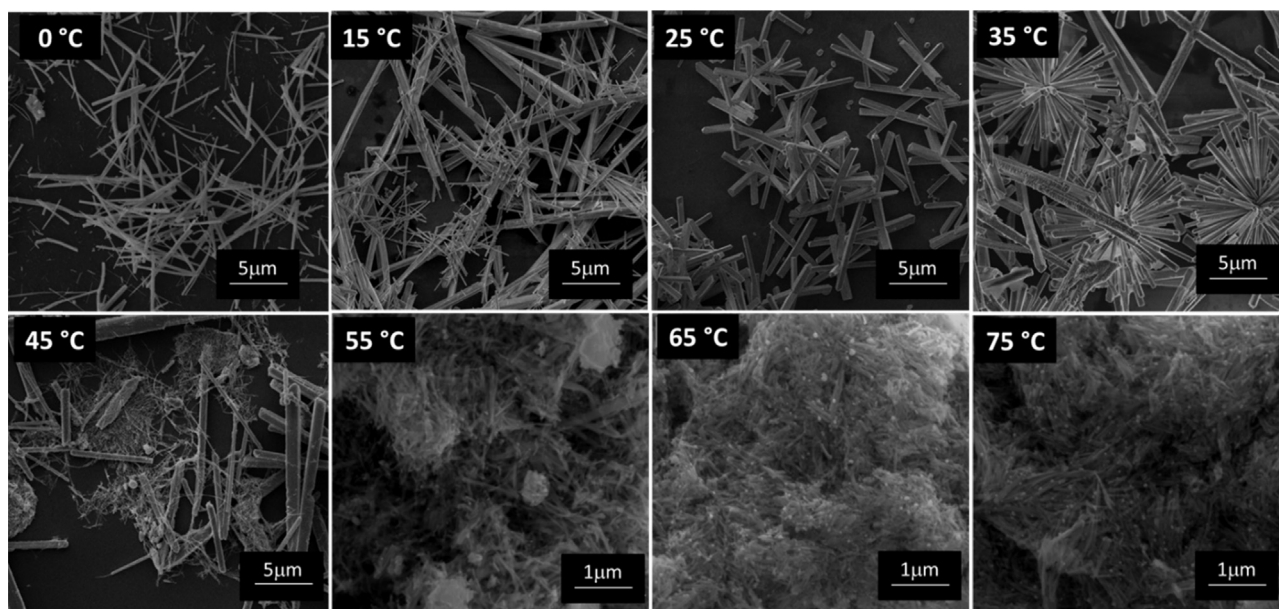


Fig. 2. Micrographs of the AgVO_3 samples obtained at different synthesis temperatures.

diversity of geometric and electronic structures of the $[\text{AgO}_x]$ and $[\text{VO}_4]$ cluster building blocks of these phases, as can be clearly seen in both α and β structures. The geometries of these clusters are reported in the [Supplementary information](#). The number of oxygen atoms coordinating to each V cation in both $\beta\text{-AgVO}_3$ and $\alpha\text{-AgVO}_3$ is four, forming $[\text{VO}_4]$ tetrahedral clusters. Moreover, only one type of V site is present in $\alpha\text{-AgVO}_3$, forming almost regular tetrahedra with O atoms. This is in contrast to the four types of distorted tetrahedra found in $\beta\text{-AgVO}_3$ (see Fig. 3). The $[\text{VO}_4]$ clusters are distorted with four different V–O bond lengths. There are three types of Ag in $\beta\text{-AgVO}_3$ forming square pyramidal, octahedral, and triangular prism tetrahedral $[\text{AgO}_5]$, $[\text{AgO}_6]$, and $[\text{AgO}_7]$ clusters, respectively [4]; the Ag are coordinated with six oxygen atoms to form two types of octahedral $[\text{AgO}_6]$ clusters in $\alpha\text{-AgVO}_3$, resulting in two types of O–Ag–O bond angles. Therefore, $\beta\text{-AgVO}_3$ and $\alpha\text{-AgVO}_3$ can be composed of $[\text{VO}_4]$ and $[\text{AgO}_6]$, and $[\text{VO}_4]$ and $[\text{AgO}_x]$ ($x = 5, 6, \text{ and } 7$) clusters, respectively.

To support the crystal structure from XRD data, first principles calculations and Raman spectroscopy were used in our previous studies. XRD can detect cation order–disorder effects as well as lattice distortion, but it is useless when investigating oxygen distortions at short range. Raman techniques are informative techniques in short-range crystal structure analysis, and are widely used in combination with first principle calculations to examine the vibration modes in the structure, phase transitions, and structural distortions. [16,21]. The distinctive properties of both phases could be ascribed to the flexibilities of the geometries in which V and Ag cations could adopt different local coordination environments. These structural features indicate that both short- and long-range ordering occur. Distortions in these clusters might induce different kinds of deformations in Ag–O and/or V–O bonds as well as O–Ag–O and/or O–V–O bond angles. Hence, the positions of O, V, and Ag atoms can vary and there is structural and electronic disorder at short range. This fact is not an accidental characteristic of a crystal,

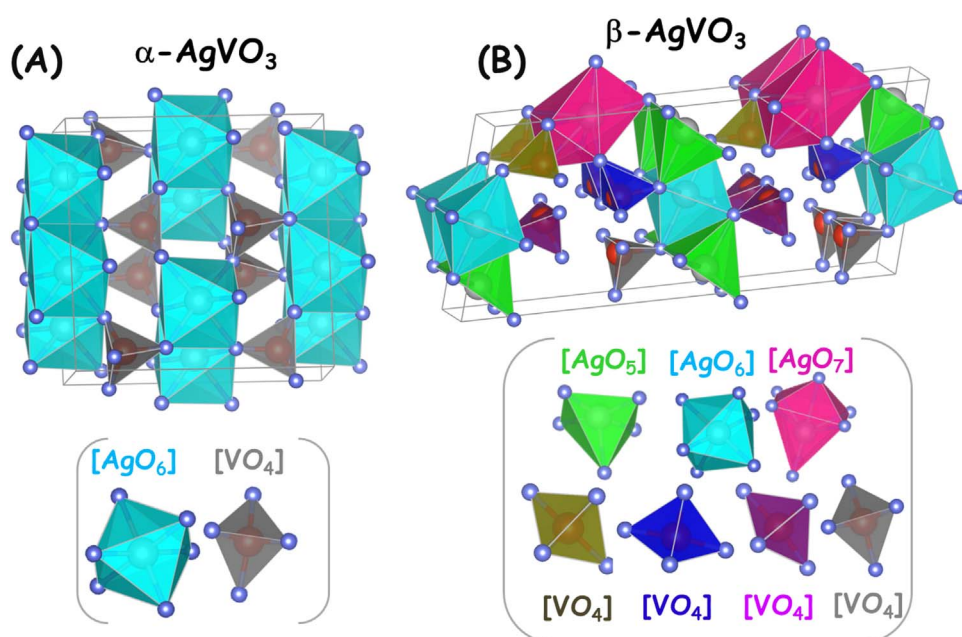


Fig. 3. Bulk structure of (A) $\alpha\text{-AgVO}_3$ and (B) $\beta\text{-AgVO}_3$, in terms of its constituent clusters.

being an essential feature and is capable of drastically influencing various properties.

Structural and electronic disorder include volume, planar, line, and point defects such as voids, twins, dislocations, and vacancies, which are inevitably generated during crystal nucleation and growth [23]. These disorders have attracted continuous attention owing to their significant influence on the formation and luminescent properties of the crystal, which are crucial to applications. A change in the degree of disorder in the crystal requires a change in crystal phase and can be controlled through the temperature involved in the crystal growth conditions. In other words, the degree of disorder of a fixed crystal phase remains constant regardless of crystal growth conditions.

An understanding of the transformation from α to β phase of AgVO_3 induced by temperature is directly related to the question of whether the basic nature of structural and electronic properties depends on short-range order (localized electronic states) and/or long-range order (extended electronic states and well-defined energy bands).

In the co-precipitation method, the crystallization process is controlled by the solvent, precursor, and temperature. These affect kinetic or/and thermodynamic factors, and in the present case the reaction temperature is the key factor determining the formation of β - AgVO_3 or α - AgVO_3 crystals. Temperature has a strong impact on local coordination, bond lengths, and bond angles of V and Ag cations in the clusters. The main structural difference between these AgVO_3 phases is given by displacements of the networks of former clusters, $[\text{VO}_4]$, and modifier clusters $[\text{AgO}_x]$ ($x = 5, 6, \text{ and } 7$). Therefore, consideration of the local atomic structure is essential to fully understand the phase transition.

$\text{NH}_4\text{VO}_3(\text{aq})$ and $\text{AgNO}_3(\text{aq})$ are the starting materials for the synthesis of α and β single-crystalline AgVO_3 phases by the co-precipitation method. $\text{NH}_4^+(\text{aq})$ is released from the dissociation of $\text{NH}_4\text{VO}_3(\text{aq})$, and it can react with the Ag^+ cation to form the $[\text{Ag}(\text{NH}_3)_2(\text{H}_2\text{O})_4]^+$ complex. $[\text{Ag}(\text{NH}_3)_2(\text{H}_2\text{O})_4]^+$ and $\text{VO}_3^-(\text{aq})$ are the precursors of the $[\text{AgO}_x]$ ($x = 5, 6, 7$) and $[\text{VO}_4]$ clusters in the solid state, respectively.

The mechanism for the formation of crystals in liquid solution is complex but commonly driven by the intrinsic properties of the crystal and the environment. Fig. 4 illustrates the formation mechanism of α - or β - AgVO_3 crystals. Generally, a crystalline phase is generated as a result of ion aggregation processes in solution that lead to the formation of nuclei, associating to pre-nucleation clusters [24]. $[\text{Ag}(\text{NH}_3)_2(\text{H}_2\text{O})_4]^+(\text{aq})$ and $\text{VO}_3^-(\text{aq})$ rearrange to form amorphous crystal nuclei. In aqueous environments, water molecules donate oxygen atoms for oxide formation via hydrolysis and condensation processes. From here, $[\text{VO}_4]$ and $[\text{AgO}_x]$ ($x = 5, 6, \text{ and } 7$) are formed and they gain a certain size after a sufficient time to enable growth into macroscopic crystals. From these clusters, we can obtain mechanistic insights to explain the synthesis and experimental observations. To propose a formation mechanism, concerted and cooperative processes have to be separated in time and split into a sequence of individual reaction steps, and chemical reactions related to cluster aggregation,

α - and β - phase formation, and transformation. First, the reaction between the $[\text{AgO}_x]$ and $[\text{VO}_4]$ complex clusters occurs locally to form the initial crystal nucleus. Nucleation finishes immediately in oversaturated solutions and the crystal growth process begins. V cations only form $[\text{VO}_4]$ complex clusters, and Ag cations assume an octahedral coordination to form $[\text{AgO}_6]$ complex clusters when the metastable α - AgVO_3 is obtained; to form β - AgVO_3 , beside the $[\text{AgO}_6]$ complex clusters, two other coordination clusters are observed: $[\text{AgO}_5]$ and $[\text{AgO}_7]$.

On the basis of experimental results, it was found that tuning the temperature was a crucial step in the polymorphic control of AgVO_3 preparation. Increasing the temperature favors structural and electronic disorder, and induces the presence of under- and over-coordinated Ag ions ($[\text{AgO}_5]$ and $[\text{AgO}_7]$), hence the formation of β -phase is favored. In contrast, the more ordered α -phase is obtained at lower temperatures.

In the $[\text{Ag}(\text{NH}_3)_2(\text{H}_2\text{O})_4]^+(\text{aq})$ complex, Ag-N bonds are stronger than Ag-O bonds. At low temperature, the release of Ag cations is more difficult and formation of the α - AgVO_3 structure via linear organization is favored. At high temperature, the vibration increases and makes it easier to liberate Ag from $[\text{Ag}(\text{NH}_3)_2(\text{H}_2\text{O})_4]^+(\text{aq})$ and to enhance the formation of the β - AgVO_3 phase with more disorder over both short and medium distances.

Such variations in the atomic and electronic structure are expected to be responsible for kinetic and thermodynamic control of the synthesis of α - and β - AgVO_3 polymorphs. Higher temperatures generally favor thermodynamic kinetic control (β - AgVO_3), whereas lower temperatures favor kinetic reaction control (α - AgVO_3). Fine-tuning of the synthesis temperature controls the transformation from the metastable phase to the stable phase.

The formation of α - or β - AgVO_3 is dependent on the relative phase stability (thermodynamic factor) and the rate of product formation (kinetic factor). Order/disorder of the constituent clusters affects the selective synthesis of α - or β - AgVO_3 . α - AgVO_3 has a more ordered structure than β - AgVO_3 . The β phase is the most stable form of AgVO_3 , but a high reaction temperature is necessary to overcome the larger activation barrier, as pointed out in Fig. 5, and Fig. S1 in the Supporting Information. The formation of α - AgVO_3 takes place along a lower activation barrier than β - AgVO_3 , as illustrated in Fig. 5.

At low temperature, rearrangements between $[\text{VO}_4]$ and $[\text{AgO}_6]$ clusters take place along the reaction pathway via transition state TS1 to render the metastable α - AgVO_3 . In contrast, at higher temperatures, $[\text{AgO}_6]$ complex clusters tend to disorganize themselves, and new clusters are formed with different coordination values: $[\text{AgO}_5]$ and $[\text{AgO}_7]$; these three clusters rearrange with $[\text{VO}_4]$ to obtain the more disordered stable polymorph, β - AgVO_3 via transition state TS2. In addition, both α - AgVO_3 and β - AgVO_3 can be connected via transition state TS3 without the need for return to the initial state of nucleation; this path explains the temperature-induced phase transformation. We attribute the greater stability of β - AgVO_3 with respect to α - AgVO_3 to the high degree of structural and electronic disorder. Specifically,

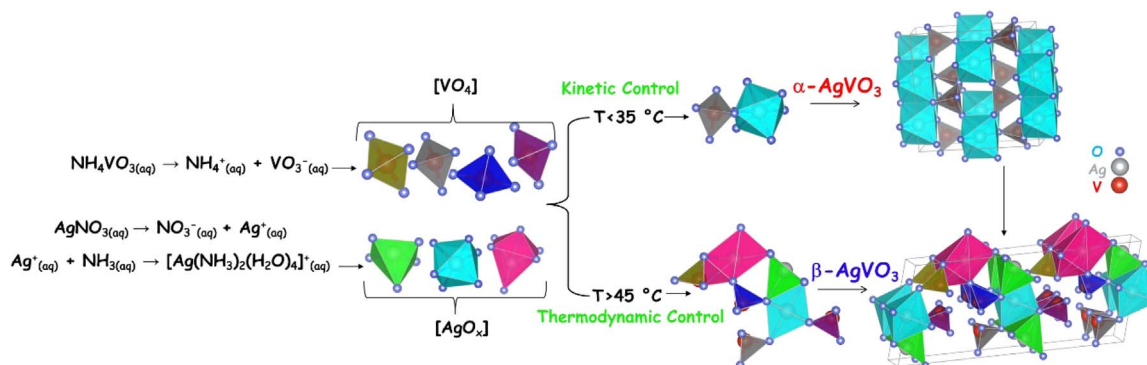


Fig. 4. Schematic representation for the formation mechanism proposed for the α - AgVO_3 and β - AgVO_3 crystals.

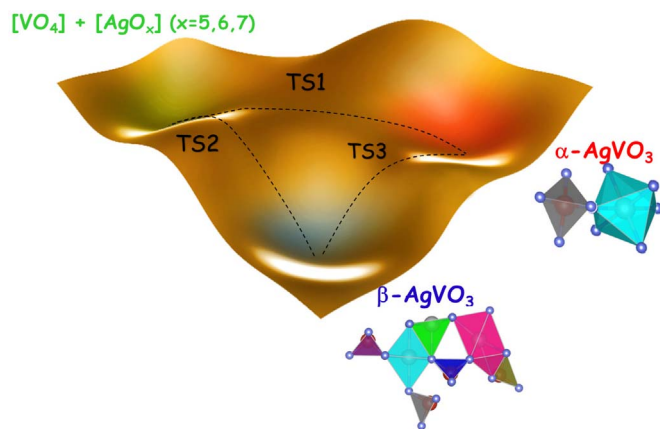


Fig. 5. Reaction coordinate diagram for the formation of α -AgVO₃ and β -AgVO₃ crystals.

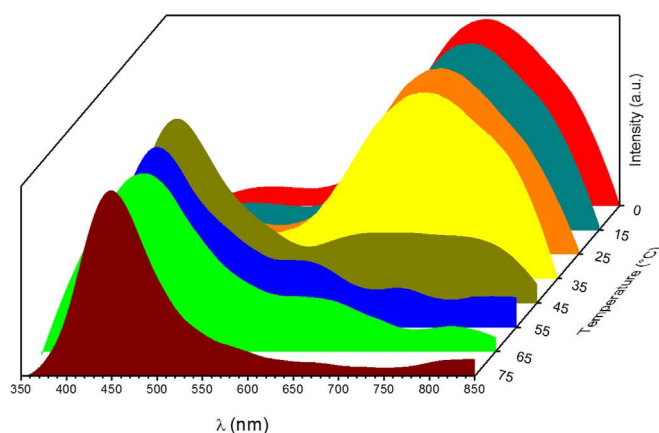
temperature acts on the internal energy of the system changing the kinetic energy. Finally, we recognize that other factors influence the selective synthesis of α - and β -AgVO₃ crystals such as solvent, pH, supersaturation, and solubility, but the above mechanism is in good agreement with our experiment.

The conduction band of AgVO₃ is controlled by the hybridization of V 3d orbitals with Ag 5s orbitals, while the valence band is associated with O 2p orbitals hybridized with Ag 3d orbitals, yielding a narrow band gap and highly dispersed conduction and valence bands. [16,21,25,26]. According to the broadband model, the PL emissions of a semiconductor are associated with distortions in the crystalline lattice. After the semiconductor is excited, the recombination process occurs due to these distortions. The electronic properties can thus be changed by structural distortions. In our case, PL emissions are very sensitive to changes in the first coordination sphere of Ag and V cations, i.e., Ag and V cations show distinct changes in the emission/excitation spectra and excited state dynamics with changes in their local symmetries.

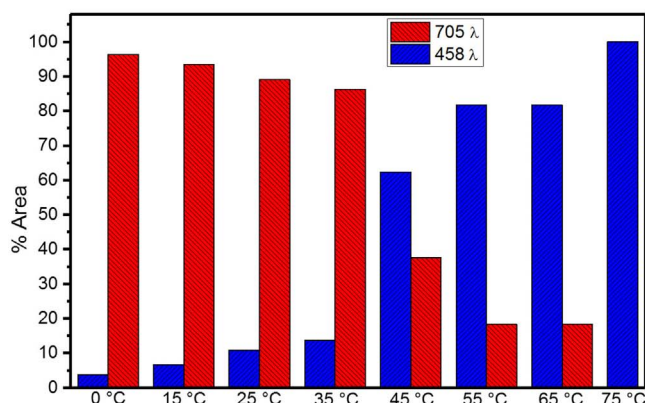
We reported the temperature and phase dependences of PL emissions from as-synthesized AgVO₃ samples. Fig. 6a shows the AgVO₃ phase dependence of the PL emission, which was observed at the maximum displacement as the AgVO₃ synthesis temperature increases, and thus with the change of phase from α - to β -AgVO₃. Hence, expansion of the band gap induced the increase of energy between the defect deep levels and the valence band, which caused the blue shift of the emission (Fig. 6a).

Each peak of the PL spectrum was deconvolved (see Fig. 6b). Initially, the emission maximum of α -AgVO₃ occurs predominantly at 705 nm, which is related to oxygen vacancies [AgO₆]. With increase in temperature, the band at 458 nm which is associated with β -AgVO₃ formation becomes more evident. The blue emission is a consequence of the presence of distorted [AgO_x] ($x = 5, 6, \text{ and } 7$) clusters and four types of distorted [VO₄] clusters in the β -AgVO₃ structure.

The color of the sample was evaluated using the Commission Internationale de l'Éclairage (CIE) chromaticity diagram; the results are presented in Fig. 7. The α -AgVO₃ samples obtained at 0, 15, 25, and 35 °C, exhibited red colors while the sample obtained at 45 °C (composed of a mixture of α -AgVO₃ and β -AgVO₃) displayed a purplish pink color. With further increase in the synthesis temperature, β -AgVO₃ was obtained and shift from green to blue was observed. These outcomes indicate that AgVO₃ is appropriate for applications in visible lamps, displays, and other optical devices. Moreover, the color of the light can be varied with the temperature of synthesis and therefore with the obtained phase (α , β , or the mixture of α and β).



a



b

Fig. 6. a: PL emission dependence of the AgVO₃ samples obtained at different synthesis temperatures. b: Percentage of area obtained with deconvolution of the PL spectra emission.

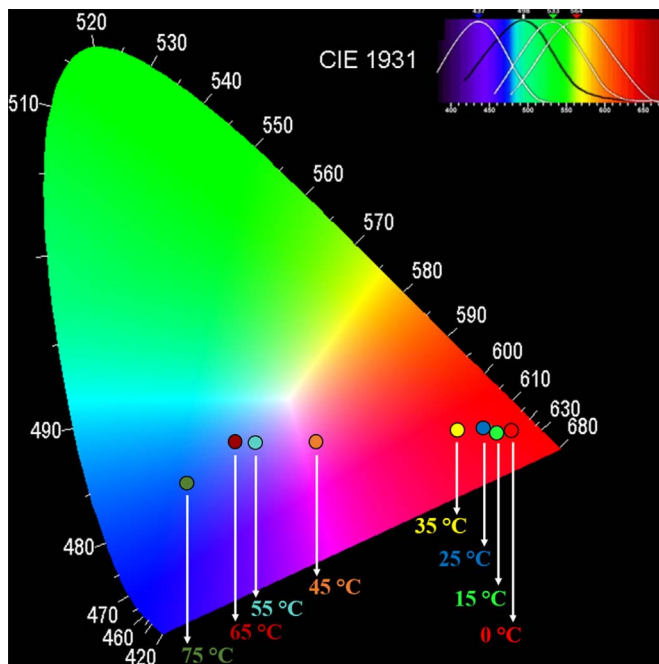


Fig. 7. CIE chromaticity diagram of AgVO₃ samples obtained at different synthesis temperatures.

4. Conclusions

Temperature is a versatile thermodynamic parameter that can be exploited in the pursuit of new materials. Polymorphism opens up the possibility of fine-tuning crystal packing without changing the chemical structure and offers a new avenue for optimizing device performance. Metastable polymorphs of complex oxides are interesting because of their ability to produce unique geometries and electronic structures with different bonding environments than the stable phase under normal conditions. To this end, the synthesis of metastable phases of a given material has recently experienced heightened interest. For many technological applications, it is mandatory to find more details from the different phases and their temperature-induced transformations. Specific temperature increase rates may trigger unexpected solid-state transformations producing otherwise inaccessible phases.

Phase transformations in solid-state materials are often rich, consisting of a hierarchy of rearrangements ranging from those occurring at the atomic level to those taking place at nano- and macroscopic length scales. Mechanistic understanding of these complex phase transformations and the control of their outcomes are central to materials science. The ability to measure and tune chemical thermodynamics and kinetics in the solid-state is at the heart of these aims. Here, we report a coprecipitation method for the polymorphic control of the α - and β -AgVO₃ polymorphs of AgVO₃ crystals with monoclinic structures by tuning the temperature. Phase transformation caused by the increase in synthesis temperature and can be ascribed to the higher thermodynamic stability of β -AgVO₃ than that of α -AgVO₃. Analysis of the PL emission as a function of temperature renders a wide range of color from red to blue. Temperature-induced transitions where the AgVO₃ system undergoes structural and electronic changes are evidenced from the PL measurements. Our understanding of this behavior relies on our ability to describe the structural and electronic characteristics such as the short-range order/disorder of the [VO₄] and [AgO_x] ($x = 5, 6, \text{ and } 7$) cluster building blocks of the monoclinic structures of both phases. These clusters are the species that truly react in this process and the mechanistic aspects of this phase transformation are understood in detail and dictate the product formation and kinetics of reactions. This mechanistic understanding has allowed the development of strategies to control the phase in the final product structure. The findings reported in this work highlight the capabilities and potential challenges of AgVO₃ polymorphs, and provide highly valuable optical properties, opening a wide space in generating photoluminescent materials.

Acknowledgements

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at <http://dx.doi.org/10.1016/j.ceramint.2017.12.161>.

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