Polyhedron 70 (2014) 188–193

Contents lists available at ScienceDirect

Polyhedron

journal homepage: www.elsevier.com/locate/poly

A composition-dependent “re-entrant” crystallographic phase transition in the substitutional metal acetylacetonate complex $(Cr_{1-x}Ga_x)(acac)_3$

M. Srinidhi Raghavan [a], Piyush Jaiswal [b], Nalini G. Sundaram [a], S.A. Shivashankar [c,a,*]

[a] Poornaprajna Institute of Scientific Research, Bangalore 560064, India
[b] Materials Research Centre, Indian Institute of Science, Bangalore 560012, India
[c] Centre for Nano Science and Engineering, Indian Institute of Science, Bangalore 560012, India

ARTICLE INFO

Article history:
Received 25 October 2013
Accepted 22 December 2013
Available online 8 January 2014

Keywords:
Metal organic complexes
Single-source precursors
$(Cr_{1-x}Ga_x)(acac)_3$
ICP-OES
Re-entrant behavior
Crystal structure

ABSTRACT

The formation of a complete solid solution between acetylacetonate (acac) complexes of chromium and gallium, $(Cr_{1-x}Ga_x)(acac)_3$ for $0.1 < x < 0.9$, has been investigated through the co-synthesis method. Well-crystallised, subliming solids are found to form for each nominal value of x, with thermal analysis confirming each composition to have a congruent melting point, making it a substitutional complex. Whereas the pure complexes (i.e. the end members of the solid solution, $x = 0$ and $x = 1$) are both centrosymmetric, a composition-dependent crystallographic phase transition to a non-centrosymmetric structure is found to occur for compositions with $0.4 < x < 0.9$. Such a “re-entrant” crystallographic transition is interpreted to be due to the drive to overcome the disorder present in certain centrosymmetric chromium-rich compositions, by going over to a non-centrosymmetric structure with a doubling of the unit cell. The substitutional complex is shown to lead to a substitutional oxide with the β-gallate structure.

1. Introduction

Metal acetylacetonates have been found to be suitable as precursors to metal oxides because of their molecular structure, stability, relative safety and ease of handling. They are often crystalline solids at room temperature and sublime at moderate temperatures, making them useful, in particular, as precursors to metal oxides and their thin films [1,2]. Furthermore, these compounds dissolve readily in common solvents, providing solutions which, when irradiated with microwaves or ultrasound, lead to nanostructured oxides [3,4]. It has also been shown that it is possible to synthesise solid solutions of metal acetylacetonates (abbreviated as acac’s), so that substitutional crystalline complexes with homogeneous compositions become available as precursors in materials synthesis [5]. The homogeneity of the substitutional complexes has been demonstrated through the determination of the crystal structures of such complexes by single-crystal X-ray diffraction. Substitutional acetylacetonates characterised in this manner have been employed in the CVD of substitutional metal oxides and silicates. A characteristic expected of such “single-source” CVD precursors is the homogeneity of the composition of the resulting film. This has indeed been demonstrated [5,6]. The use of substitutional complexes as “single-source precursors” can simplify the CVD apparatus and process by allowing the use of a single “precursor channel” where, ordinarily, two such channels would be needed.

Nevertheless, there are few reports in the open literature on investigations of complete solid solutions of two metal acetylacetonates or other metal β-diketonates [5–7]. Such complexes would be interesting as precursors to substitutional oxides, wherein the properties of the oxide may be modified systematically by substituting one metal for another. One may expect that oxide nanomaterials prepared (through an appropriate method) from such precursors would be homogeneous in composition, leading to the reliable tailoring of properties by appropriately adjusting the composition of the precursor.

It has recently been proposed by Kaneko et al. [8] that solid solutions in the Ga_2O_3–Cr_2O_3–Fe_2O_3 system, where each oxide is of the corundum structure, would form an interesting set of semiconductors because of the electronic and optical properties of the individual oxides. The authors have demonstrated the deposition of thin films of these oxides individually by CVD using the respective metal acetylacetonates as precursors. It would therefore be useful to investigate the formation of solid solutions between $Ga(acac)_3$ and $Cr(acac)_3$, so that they can be employed as “single-source” precursors for the CVD of the substitutional oxides $(Cr_{1-x}Ga_x)_2O_3$. An effort was therefore undertaken to synthesise the complexes $(Cr_{1-x}Ga_x)(acac)_3$, for variable x.

---

* Corresponding author at: Centre for Nano Science and Engineering, Indian Institute of Science, Bangalore 560012, India. Tel.: +91 8022933323; fax: +91 8023604656.

E-mail addresses: srinidhikm@gmail.com (M. Srinidhi Raghavan), piyush@mrc.iisc.ernet.in (P. Jaiswal), nalini@poornaprajna.org (N.G. Sundaram), shivu@mrc.iisc.ernet.in, shivu@cense.iisc.ernet.in (S.A. Shivashankar).

0277-5387/$ - see front matter © 2014 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.poly.2013.12.036

Metal acetylacetonates are also very interesting systems to study via single crystal X-ray diffraction methods because of their rich chemistry and the relative ease with which high-quality single crystals of the complexes can be grown. For example, co-crystallization of the acetylacetonate complexes of two transition metals results in a variety of crystal systems [9].

It is well known that the formation of a solid solution of two metal complexes is possible only if the substituting ions are of similar size and that a difference of 15% ionic radii is the upper limit for any substitution to take place at the metal site [5,7]. Single crystal X-ray diffraction is a valuable tool to understand and characterize any changes in the crystal structure, occupancy and disorder occurring in such substitutional metal complexes. Most such substitutional transition metal "acac" complexes are found to be isostructural and the metal centre shows an occupancy disorder that has been studied by single crystal X-ray diffraction [7]. Pure acetylacetonates of chromium [7] and gallium [9] crystallize in the monoclinic crystal system with the centrosymmetric space group $P2_1/c$. However, pure $Cr(acac)_3$ is reported to show a disorder in one of the carbon atoms present in all three ligands, which has been treated with a split-atom model [5]. Interestingly, $Al(acac)_3$ which, like $Cr(acac)_3$, also crystallizes in an isomorphous space group [10], does not show any such disorder. A recent study [6] on aluminium-substituted $Cr(acac)_3$ indicates that as the aluminium substitution increases, the disorder on the carbon atoms of the ligands decreases. This result implies that when the percentage of chromium in the lattice is high, a large amount of disorder is found in the carbon atoms of the ligands.

In the present study, we have therefore undertaken to synthesise and study a series of Ga-substituted $Cr(acac)_3$ metal complexes at low temperature. A specific motivation for this effort was to examine whether the crystal structure changes as a function of metal substitution. Indeed, a crystallographic phase transition from a centrosymmetric to a non-centrosymmetric space group within the same crystal system as a function of metal composition is observed. Occupancy refinements have been carried out for all the compositions. The crystallographic disorder observed for some of the compositions has been handled with specific refinement strategies. A rational explanation has been attempted for the observed crystallographic phase transition and the loss of centrosymmetry.

2. Experimental

2.1. Synthesis

The substitutional complexes $Cr_{1-x}Ga_x(acac)_3$, $0.1 < x < 0.9$, were prepared by the co-synthesis method starting with the metal nitrates, following a procedure described earlier [6]. All reagents used were of analytical grade. In particular, calculated amounts of the metal nitrate solutions were mixed and stirred for 15 min to achieve homogeneity. Next, 2.4 ml of acetylacetone (20 mmol) was added to 2.5 ml of methanol and mixed well, following which this acetylacetonate solution was added into the metal nitrate solution and stirred until the solution became clear. The reaction mixture was neutralized by 30% ammonia solution added drop by drop until a pH of 7 was attained. The resulting purple-coloured solution was stirred for 1 h at room temperature. The solid precipitate thus obtained was separated through vacuum filtration, dried and recrystallized at 4 °C using a 10% methanol and acetone mixture as the solvent to obtain the purified powder material. The average yield of the reaction was ~92%.

Single crystals of selected compositions were obtained by dissolving the recrystallized powder material in a solvent made of 30% methanol and 70% acetone. The solution was stored for a few days at −4 °C to allow for slow evaporation of the solvent, resulting in the formation of single crystals.

2.2. Characterization

The recrystallized powder samples were characterised by various techniques. Fourier transform infrared (FTIR, Perkin Elmer Spectrum BX) spectroscopy was used to verify the presence of metal–oxygen bonds, viz. Cr–O and Ga–O bonds. Thermal analysis of the samples was carried out by simultaneous thermogravimetry and differential thermal analysis (TG/DTA, TA Instruments SDT Q600) to determine the volatility and the melting points of the different compositions. This was done with about 10 mg of each sample, taken in an alumina crucible and heated at a rate of 10 °C per minute in ambient flowing UHP nitrogen.

The metal composition of the samples was determined by ICP-OES analysis (Thermo-iCAP 6000 Series by Bruker). Solutions with five different known concentrations of Cr^{3+} and Ga^{3+} were prepared with the nitrates of the two metals and used to calibrate the system.

Powder XRD data on the substitutional acetylacetonates and the oxide samples derived from them were collected using Cu Kα radiation (Philips Model MPD.), at a scan rate of 2° per minute.

Single-crystal X-ray diffraction data were collected on carefully chosen crystals for the compositions $x = 0.1$, 0.3, 0.4, 0.5 and 0.9, using Mo Kα radiation in a Bruker AXS SMART APEX CCD diffractometer. The data were collected at 110 K using an Oxford Cryostream attachment cooled by liquid nitrogen. The X-ray generator was operated at 50 kV and 40 mA. For all the measurements, 606 frames per set were collected using SMART [11] with four different settings of φ (0, 90, 180 and 270°), with the ω-scan at −0.3° intervals, with a counting time of 15 s, keeping the sample-to-detector distance at 6.062 cm and with the 2θ value fixed at −28°. The data were reduced by SAINTPLUS [11], an empirical absorption correction was applied using the package SADABS [12] and XPREP [11] was used to determine the space group.

All the crystal structures were solved by direct methods using SIR92 [13] and refined by the full matrix least-squares method, using SHELXL97 [14], present in the program suite WINGX (version 1.63.04a). The conventional and weighted *R*-factors, and goodness of fit *S*, are based on *F* squared. All the hydrogen atoms were fixed on the methyl and the C–H groups stereochemically, according to geometry.

3. Results and discussion

Powder material for the different compositions could be obtained at high yields. Samples of all compositions were found by X-ray powder diffraction to be crystalline in the as-prepared form. The colour of the powders changed gradually from dark purple to white, as the nominal chromium content was reduced. The single crystals obtained by slow evaporation were transparent and displayed a similar range of colours. Single crystals as large as 10 × 10 × 1 mm could be grown for the Cr-rich compositions. Crystals of Ga-rich compositions were somewhat smaller. The crystals were examined by optical microscopy and found to be of high quality. The gradual change in the colour of the single crystals is indicative of homogeneous substitution at the metal site.

The FTIR spectra [SI] show the presence of both Ga–O and Cr–O bonds in the complexes, providing preliminary evidence that the intended substitution has taken place. The metal composition of the samples, as determined by ICP-OES analysis, is compared with the nominal composition in Table 1. It is seen that the nominal and actual compositions are in reasonably good agreement, with the deviation from the nominal composition becoming greater as the