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Letter

Synthesis and characterization of β-$RbSc(CrO_4)_2$

P. Melnikov, L.C. Ferracin

Instituto de Química UNESP, CP 355, 14800-900 Araraquara, S.P., Brazil

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Abstract

Synthesis and crystallographic data are reported for the double rubidium–scandium chromate $RbSc(CrO_4)_2$. The parameters of the orthorhombic cell are $a=14.836(2)$ Å; $b=5.627(1)$ Å and $c=8.835(4)$ Å, $Z=4$. The compound is closely related to the lamellar double chromates with other alkali metal cations, iron, lanthanides and yttrium offering the advantage of obtaining inorganic materials for electronics.

Keywords: Double chromates; Rubidium; Scandium; Synthesis

1. Introduction

The double chromates of rubidium with scandium are completely different from the corresponding La–Lu counterparts [1] as is frequently the case with scandium. Low and high temperature forms of $RbSc(CrO_4)_2$ are glaserite-related compounds having both a monoclinic distorted (l.t.) and undistorted (h.t.) structure of $K_3Na(SO_4)_2$ [2].

The corresponding rare earth chromates $MeLn(CrO_4)_2$ where Me = K–Cs and Ln = La–Lu were shown to be good ionic conductors owing to the presence of rapidly migrating Me ions [3] but they are not easily obtained in the single crystal form and exhibit no polymorphism. According to the data available on the rubidium–iron double chromate $RbFe(CrO_4)_2$ [4] a third variety of $RbSc(CrO_4)_2$ may be expected to exist, thus bringing the number of structural types up to three. Here we report the preparation and structural characteristics of the orthorhombic $RbSc(CrO_4)_2$. This study has been undertaken because of the potential application of $RbSc(CrO_4)_2$ for the synthesis of inorganic materials. Scandium was recently mentioned as a dopant improving the quality of optic materials [5].

2. Experimental

A solution containing 1.67 g Rb_2CO_3, 0.1 g Sc_2O_3 and 1.45 g CrO_3 in 25 ml of water was used to grow $RbSc(CrO_4)_2$ in the form of single crystals. The initial mixture was slightly acidified and heated at 80 °C to remove all CO_2. The solution was heated in a sealed glass ampoule at 125 °C for two months, then needle-shaped purple crystals of typical thickness 0.1 mm were collected from the bottom, washed with water and selected for X-ray investigation. At the same time on the surface of the solution there appeared a fine film of orange crystals of $Rb_2Cr_2O_7$, exhibiting a typical powder diagram of this dichromate. Chemical analysis as performed by atomic absorption gave the following: 23.20 wt.% Rb; 12.44 wt.% Sc and 28.59 wt.% Cr (compare the calculated values 23.58 wt.% Rb; 12.40 wt.% Sc and 28.69 wt.% Cr). Cell parameters were refined by a diffractometric technique. Data collection was performed on a CAD-4 Enraf-Nonius Diffractometer, Mo Kα radiation using a graphite monochromator. The absorption spectrum was registered using a Spectrophotometer Guide Wave, model 260.

3. Results and discussion

X-ray studies showed an orthorhombic cell with the following parameters: $a=14.836(2)$; $b=5.627(1)$; $c=8.835(4)$ Å; $V=737.3(3)$ Å^3; $Z=4$. The space group is *Pnma*, and thus we have prepared the β-modification of $RbSc(CrO_4)_2$.

The absorption spectrum was registered to make sure that scandium sites were not partially occupied by Cr(III) ions. Such an autodoping during the process of preparation is difficult to avoid and then to detect by X-

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ray techniques. The spectrum reported in Fig. 1 showed bands (36.300, 25.600 and 18.200 cm^{-1}) consistent with the presence of the chromate ion CrO_4^{-2} [6]. A weak band near 12.800 cm^{-1} could not be attributed to Cr(III), since this forbidden vibration would not appear alone, without stronger bands allowed in the spectrum [6,7].

We did not proceed with structure determination, since it became quite clear that this compound is isostructural to $CsCr_3O_8$, which may also be written as $CsCr^{III}(Cr^{VI}O_4)_2$ [8]. The simulation of the structure using cell dimensions and known atomic coordinates gave for the Rb–Sc and Sc–Sc distances in $RbSc(CrO_4)_2$ the values 6.7 Å and 7.8 Å, respectively. They characterise the internal cavities between the infinite layers suitable for motion of the alkali metal ions, and in our case, are much bigger than the similar distances Rb–Eu and Eu–Eu specially computed for the isostructural compound, $RbEu(CrO_4)_2$. Earlier, the latter was shown to be a good ionic conductor [3]. These distances are 5.10 Å and 5.88 Å, respectively. Hence, in spite of the evident similarities and equal C.N. of Rb (10) the channels available for the migrating charge carriers are substantially larger ($\approx 1/3$) in the structure of $RbSc(CrO_4)_2$.

Table 1 provides a summary of the double chromates related to $RbSc(CrO_4)_2$ showing that the substitution (either partial or total) with a metal ion of an adequate size, keeping the structure intact, may facilitate the design of a particular inorganic material and/or change its properties in a desired direction. The role of Cr^{VI} may be played by P, As, V, S etc., that is the elements capable of forming tetrahedral anions, while Sc sites may be occupied by Fe^{III}, Cr^{III}, Y and Ln^{III}, where Ln = La–Lu. Finally, other alkali metal cations or NH_4^+-ion may be present instead of Rb^+. The number of Me ions (1 or 3) is given by the oxidation state of the anion-forming element.

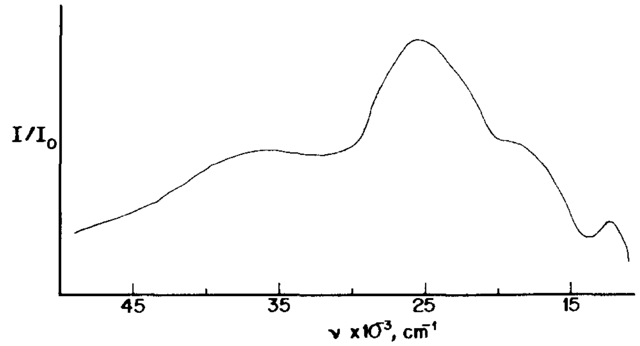

Fig. 1. Absorption spectrum of β-$RbSc(CrO_4)_2$.

Table 1
Double chromates structurally related to the orthorhombic $RbSc(CrO_4)_2$

$M^IM^{III}(CrO_4)_2$	Possible modes of substitution without altering the network	
$RbLn(CrO_4)_2$, Ln = Sm, Eu, Gd [1]	$La^{3+} \leftrightarrow Ln^{3+}$	
β-$RbFe(CrO_4)_2^-$ [4]	$Sc^{3+} \leftrightarrow Fe^{3+}$	
$CsCr_3O_8$ [8]	$Rb^+ \leftrightarrow Cs^+$;	$Sc^{3+} \leftrightarrow Cr^{3+}$
β-$NH_4Fe(CrO_4)_2^-$ [9]	$Rb^+ \leftrightarrow NH_4^+$;	$Sc^{3+} \leftrightarrow Fe^{3+}$
$KLn(CrO_4)_2$, Ln = Eu, Tb [10]	$Rb^+ \leftrightarrow K^+$; $Sc^{3+} \leftrightarrow Ln^{3+}$	

These possible substitutions suggest a range of compounds that may be envisaged as inorganic materials. Thus, by replacing lanthanum with europium, and scandium with terbium or manganese we obtain luminescent materials; by replacing scandium with Fe^{3+} we can obtain devices with a wide spectrum of magnetic properties, e.g. suitable for magnetic memory. Scandium in this case may be considered as a neutral diluter of Fe^{3+} in the network. Therefore we have undertaken further study to measure ionic conductivity, activation energy and other parameters of this chromate and its derivatives; the data will be published elsewhere.

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