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Silver-gadolinium polytetraphosphate $AgGd(PO_3)_4$ synthesis, structural study, IR spectroscopy and conductivity investigation

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Abstract

Crystals of a new silver-gadolinium, $AgGd(PO_3)_4$, have been synthesized for the first time by a flux method. The structure [monoclinic, $P2_1/n$, $a = 7.2378(2)$ Å, $b = 13.0913(5)$ Å, $c = 9.8136(4)$ Å, $\beta = 90.494(1)^\circ$, $V = 929.83(6)$ Å^3 and $Z = 4$] was solved by a three-dimensional Patterson function and refined to $R_1 = 0.0399$ ($wR_2 = 0.0885$) on the basis of 3270 unique observed reflexions using 164 parameters. $AgGd(PO_3)_4$ is isostructural to $NaLa(PO_3)_4$, $AgLa(PO_3)_4$ and $AgNd(PO_3)_4$. The structure is based upon long chain polyphosphate running along the shortest unit-cell direction and made up of PO_4 tetrahedra (with a period of four tetrahedra) sharing two corners, linked to the polyhedra of gadolinium and silver by common oxygen atoms to the chains. This type of organisation gives rise to a three-dimensional framework. Gadolinium atoms have an eight-fold coordination while silver atoms have approximately six oxygen neighbours. Infrared spectrum of $AgGd(PO_3)_4$ at room temperature, investigated in the frequency range 400–1500 cm^{-1}, confirms the atomic arrangement within the structure. The electrical conductivity of $AgGd(PO_3)_4$ has been measured on pellets of the polycrystalline powder and evaluated as a function of temperature. The conductivity of this phase was quite low and the values of 4.01×10^{-7} and 1.10×10^{-6} Ω^{-1} cm^{-1} were obtained at 803 and 873 K, respectively.

Keywords: Crystal structure; Silver-gadolinium polyphosphate; IR spectroscopy; Ionic conductivity

1. Introduction

The condensed phosphates of rare earths with general formula $M^IM^{III}(PO_3)_4$ (where M^I is a monovalent cation: Li, Na, K, Cs, ... and M^{III} is a rare earth: La, Sm, Ce, Nd, Dy, Pr, ...) which were the object of several researches have a considerable interest mainly for their optical properties, especially in laser technology [1–3]. The common chemical features of these polytetraphosphates indicate that they are stable under normal conditions of temperature and humidity [4–6]. The structures of the alkali–rare earth polytetraphosphates are generally characterized by long chains made by PO_4 tetrahedra each of which shares two corners with the others. In the course of our investigations on the existence and the crystal structures of ternary alkali lanthanide phosphates, we reported about the structure of the compounds $MGd(PO_3)_4$ (M = K, Cs) [7–9]. Previous studies dealing with double phosphates of alkali and rare earths [10–13] showed that these compounds crystallizes in several space groups such as $P2_1$, $C2/c$, $P2_1/c$ or $P2_1/n$, but no resolved structure with silver and gadolinium was mentioned in the literature. Up to now only few mixed Ag-rare earth tetraphosphates have been investigated: $AgSm(PO_3)_4$ [12], $AgPr(PO_3)_4$ [14] and $AgNd(PO_3)_4$ [15]. The two first compounds are obtained by study of the phase-equilibrium diagrams of the $AgPO_3$–$Ln(PO_3)_3$ (Ln = Sm and Pr) systems and they belong to the monoclinic system with $P2_1/c$ space group. Another new gadolinium phosphate crystal $AgGd(PO_3)_4$ was found in our laboratory. The present work is to report new results of crystal growth and refinement of the structure of $AgGd(PO_3)_4$ phosphate having the space group $P2_1/n$. This work, part of a systematic investigation of polyphosphates crystal chemistry, is the first example of a silver-gadolinium polyteraphosphate.

2. Experimental procedure

2.1. Synthesis

The preparation of single crystals of $AgGd(PO_3)_4$ is achieved through the use of the flux method by heating the mixture of 2.48 g of $AgNO_3$, 2.05 g of

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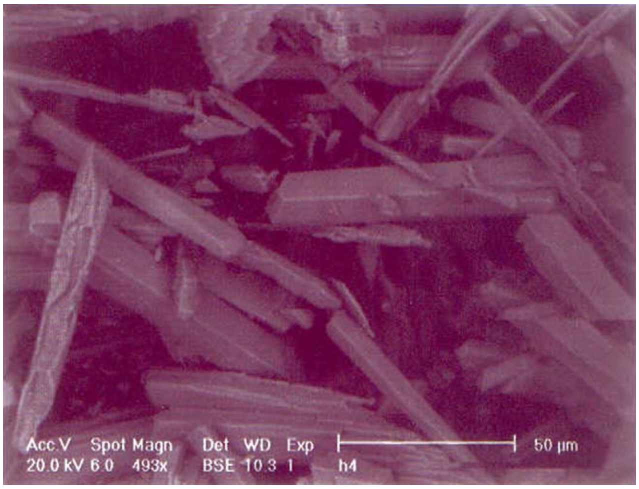

Fig. 1. Morphology of $AgGd(PO_3)_4$ crystals.

$NH_4H_2PO_4$ and 0.4 g of Gd_2O_3 in a Pt crucible at a temperature of 473 K for 4 h. Then the temperature was increased progressively at 2 K/min upto 823 K and it remains for 2 days. The obtained crystals are isolated after cooling with the rate of 40 K/day to reach 323 K. A double washing with warm water and nitric acid is necessary to eliminate the remaining Gd_2O_3 oxide. Colorless, transparent and parallelepiped-shaped crystals obtained by this procedure are suitable for X-ray analysis. The morphology of $AgGd(PO_3)_4$ crystals is shown in Fig. 1. It can be noted that this compound is stable in air and its formula was confirmed by refinement of the structure and IR spectroscopic absorption. Infrared absorption spectra of suspensions of crystalline powders in KBr were examined by a 733 Perkin-Elmer spectrophotometer in the 400–4000 cm^{-1} region.

2.2. Structure refinement

X-ray diffraction were made on a single crystal of $AgGd(PO_3)_4$ with a CCD area detector with graphite monochromated Mo Kα radiation (λ = 0.71073 Å). A suitable crystal was selected for X-ray study. Cell constants were determined from 3370 reflections with $I > 2\sigma(I)$, and corresponded to a monoclinic cell with $a = 7.2378(2)$ Å, $b = 13.0913(5)$ Å, $c = 9.8136(4)$ Å and $\beta = 90.494(1)°$. The space group $P2_1/n$ was assigned upon review of the systematic absences and an empirical absorption correction was applied. The crystal structure of $AgGd(PO_3)_4$ was solved by the heavy-atom method using SHELXS-97 program [16]. The gadolinium and silver atoms were first located and then all the phosphor and oxygen atoms were found in difference Fourier maps with SHELXL-97 program [17]. When all the atoms were refined anisotropically, the agreement factors R_1 and wR_2 converged, respectively, to 0.0399 and 0.0885. Crystal data details, the parameters used for the X-ray diffraction data collection and some results of the structure refinement are summarized in Table 1. Tables 2 and 3 present, respectively: the final fractional atomic coordinates, the anisotropic thermal parameters and the experimental valence sum calculations.

2.3. Complex impedance techniques

An analysis of the frequency response of the conductivity data is used to determine the electrical characteristics of ionic conductors. The polycrystalline $AgGd(PO_3)_4$ was crushed and pressed into pellets ($P = 62$ bar and $D = 2.58$). Silver electrodes were deposited. The electrical conductivity measurements were performed as a function of both temperature (751–873 K) and frequency (5 Hz–13 MHz) employing a Hewlett-Packard 4192 ALF automatic bridge monitored by a HP vectra microcomputer. The measurements were carried out in vacuum and at each interval; the sample was maintained few minutes at each temperature before collecting data, the temperature stability was ±1 K.

Table 1
Crystal data and structure refinement for $AgGd(PO_3)_4$

Crystal data	
Empirical formula	$AgGd(PO_3)_4$
Crystal system	Monoclinic
Space group	$P2_1/n$
Z	4
Temperature (K)	293(2)
Formula weight (g mol^{-1})	581.00
Unit-cell dimensions	
a (Å)	7.2378(2)
b (Å)	13.0913(5)
c (Å)	9.8136(4)
β (°)	90.494(1)
Volume (Å^3)	929.83(6)
Dx	3.113
$F(0\,0\,0)$	1020
Data collection	
Radiation	Mo Kα (λ = 0.71073 Å)
Monochromator	Graphite
Diffractometer: Enraf–Nonius	Kappa CCD
Absorption coefficient (mm^{-1})	9.91
θ range (°)	3.22–34.94
Index ranges	$-11 < h < 11$, $-18 < k < 21$, $-15 < l < 14$
Scan type	CCD scans
Reflections collected [$I > 2\sigma(I)$]	4060
Independent reflections [$I > 2\sigma(I)$]	3270
Refinement	
Refinement method	Full-matrix L.S. on F^2
Parameters refined	164
Weighting scheme	$\omega = 1/[\sigma^2 F_0^2 + \alpha P + \beta P]$, where $P = (F_0^2 + 2F_c^2)/3$
α	0.0453
β	0.5073
Absorption correction (analytical)	
T_{min}	0.5688
T_{max}	0.7932
Extinction coefficient	0.0012(2)
Goodness-of-fit	1.000
Final R indices [$I > 2\sigma(I)$]	
R_1	0.0399
wR_2	0.0885
Maximum shift/esd	0.001
Largest diffraction peak and hole (electron Å^{-3})	2.63, −1.85 (near Gd atom)

$R_1 = \sum[|F_0| - |F_c|]/\sum|F_0|$, $wR_2 = \left(\sum[W(F_0^2 - F_c^2)^2]/[W(F_0^2)^2]\right)^{1/2}$.

3. Results and discussion

3.1. Description of the structure

Views of the structure projected along b- and c-axis are shown in Figs. 2 and 3, respectively. As a result of our investigations, $AgGd(PO_3)_4$ was shown to be isostructural with $NaLa(PO_3)_4$, $AgLa(PO_3)_4$ [18] and $AgNd(PO_3)_4$ [15]. From a general point of view, this phosphate could be described as a long chain polyphosphate containing alternating $(PO_3)_n$ chains and (M^{3+}, M^+) cations along the [0 0 1] direction. One can assume that this atomic arrangement is characteristic of this family of polyphos-