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Structural and spectroscopic study of arsenate and vanadate incorporation into apatite group: Implications for semi-quantitative estimation of As and V contents in apatite

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ABSTRACT

The solid solutions of mimetite-vanadinite series were synthesized at room temperature through aqueous precipitation method and were characterized with Scanning Electron Microscope-Energy Dispersive Spectrometer (SEM-EDS), X-ray diffraction (XRD), infrared and Raman spectroscopy. Based on the XRD analyses, it showed that all the samples crystallize with the same structure. A and c parameters vary smoothly with substitution of AsO_4^{3-} for VO_4^{3-}. In the FT-IR spectra of mimetite-vanadinite solid solutions series, the bands corresponding to stretching (ν_3) vibrations of AsO_4^{3-} and VO_4^{3-} ions were observed in the range 700–900 cm^{-1}, and the bending (ν_4) vibrations of O—As—O and O—V—O were observed in the range 310–400 cm^{-1}. In the Raman spectra, the bands attributed to vibrations in the VO_4^{3-} appeared at 830–700 cm^{-1}, 420–290 cm^{-1}. The bands attributed to vibrations in the AsO_4^{3-} appeared in the ranges 740–820 cm^{-1}, 410–310 cm^{-1}. In addition, the peak positions of the dominant antisymmetric stretching (ν_3) of V—O bond around 706 cm^{-1} of IR spectra for the prepared solids also varies with the different As/(As + V) ratio, and the relationship is linear, which can be an implication for semi-quantitative estimation of As and V contents in lead apatites.

1. Introduction

Mimetite $Pb_5(AsO_4)_3Cl$ and vanadinite $Pb_5(VO_4)_3Cl$ are secondary minerals, frequently occurring in the oxidation zones of lead deposits, and usually associated with pyromorphite $Pb_5(PO_4)_3Cl$ [1]. They are the minerals from lead-apatites family, often expressed by a general formula $Pb_5(XO_4)_3Y$, usually XO_4 representing coordinated tetrahedral oxyanions (e.g., PO_4^{3-}, AsO_4^{3-}, VO_4^{3-}), and Y representing monovalent electronegative anions (e.g., F^-, Cl^-, Br^-) [2]. In addition, the structure of most minerals from this group coincides with that of apatite $Ca_5(PO_4)_3F$, and is hexagonal, space group $P6_3/m$ [1,3]. Based on the similarity of chemical composition and structure, replacement of metal cations and anionic complexes commonly takes place in the mineral suit, thus forming a large amount of solid solutions between the end members. Phosphates, arsenates and vanadates are always substituted by each other in lead apatite naturally, while the pyromorphite, vanadinite and mimetite form a ternary system [1,4,5].

Recently, some efforts have been devoted to investigate the structural [6–9] and spectroscopic studies [3,5,10,11] of the pure lead apatites and the intermediate solid solutions, mostly due to their applications for in-situ immobilization of lead and arsenic from the contaminated soil and groundwater [12,13]. A previous XRD data of synthetic members of the pyromorphite-mimetite series was reported by Baker [14], who showed the relation between chemical composition and spacing d is linear. Adams and Gardner [11], in addition, reported the single-crystal vibrational spectra of pyromorphite, vanadinite and mimetite, obviously found the splitting effect of internal modes of tetrahedral oxyanions from aqueous solution to crystal site. Furthermore, a later investigation about the external modes of tetrahedral oxyanions in the crystal was conducted by Bartholomäi and Klee [11]. Previously, Bajda et al. [3] demonstrated that systematic changes of peak positions and intensities in the infrared and Raman spectra of samples with different content of phosphates and arsenates. However, the structural and spectroscopic knowledge of vanadinite was always focused on the pure members in nature [1], and only an abstract published the conclusion about the structural and spectroscopic study of the mimetite-vanadinite solid solution series [15], partly due to vanadinite is comparatively rare compared to pyromorphite and mimetite in the natural environment. Nevertheless, according to Muhammad [16], who has reviewed the

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Table 1
Summary of the synthesis and lattice parameters of $Pb_5(V_xAs_{1-x}O_4)_3Cl$ solid solutions.

Sample ID	Volumes of initial solutions(mL)				Lattice parameters			Solid composition by SEM-EDS analysis
	44 mM $Pb(NO_3)_2$	26 mM $Na_3AsO_4 \cdot 12H_2O$	26 mM $Na_3VO_4 \cdot 12H_2O$	9 mM NaCl	a (Å)	c(Å)	c/a	
0As4V	40	0	40	40	10.304	7.381	0.716	$Pb_5(VO_4)_3Cl$
1As3V	40	10	30	40	10.289	7.402	0.719	$Pb_5[(VO_4)_{0.732}(AsO_4)_{0.268}]_3Cl$
1.5As2.5V	40	15	25	40	10.287	7.425	0.721	$Pb_5[(VO_4)_{0.614}(AsO_4)_{0.386}]_3Cl$
2As2V	40	20	20	40	10.278	7.433	0.723	$Pb_5[(VO_4)_{0.48}(AsO_4)_{0.52}]_3Cl$
2.5As1.5V	40	25	15	40	10.272	7.441	0.724	$Pb_5[(VO_4)_{0.381}(AsO_4)_{0.619}]_3Cl$
3As1V	40	30	10	40	10.264	7.444	0.725	$Pb_5[(VO_4)_{0.231}(AsO_4)_{0.769}]_3Cl$
4As0V	40	40	0	40	10.252	7.451	0.726	$Pb_5(AsO_4)_3Cl$

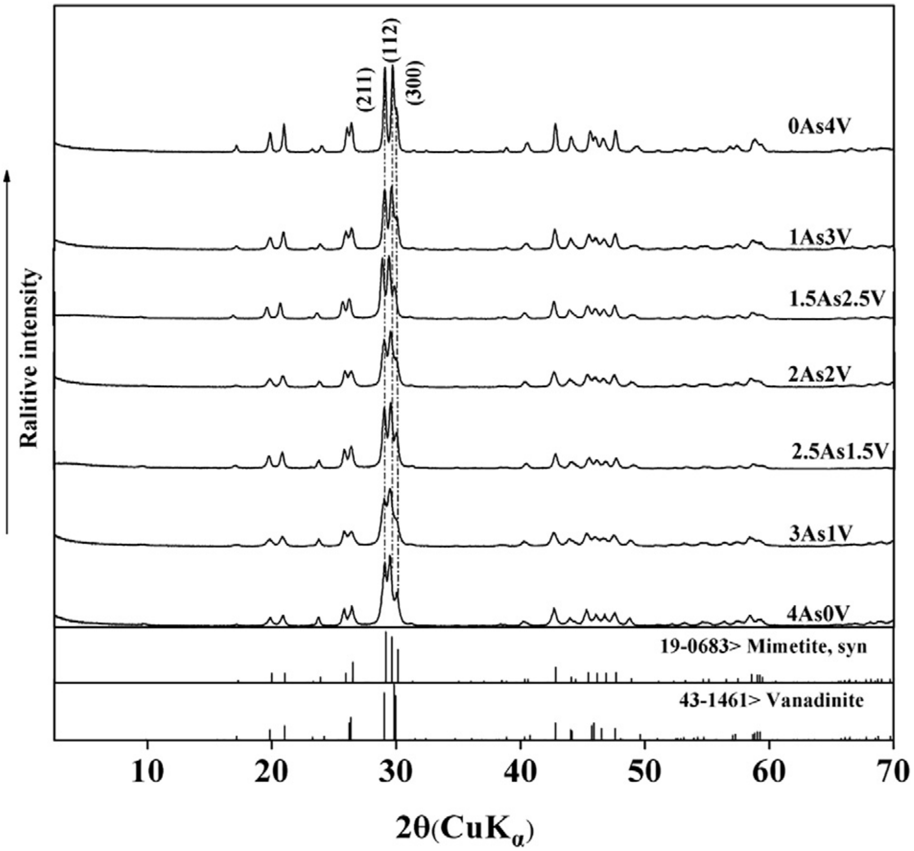

Fig. 1. XRD analysis for mimetite-vanadinite solid solution series.

advancement and research prospects of vanadium, this element is released to environment in large quantity from anthropogenic activities. The pentavalent vanadium may be the most toxic and mobile form which has a great influence of the human's health in the future. Based on the stable solubility for vanadinite in natural and the success application of pyromorphite and mimetite for in-situ immobilization of lead and arsenic, vanadinite has the potential to be a mineral trap for the in-situ immobilizing the vanadium from the contaminated soil and groundwater. In our work, X-ray diffraction, infrared spectroscopy (mid- and far-IR spectra), Raman spectroscopy and SEM-EDS are utilized to investigate the structural and spectroscopic characteristic of the synthetic mimetite-vanadinite solid solution series.

2. Materials and Methods

2.1. Mineral Synthesis

Analytical-grade chemicals and ultrapure water were used in the mineral synthesis and all experiments. The mimetite-vanadinite solid

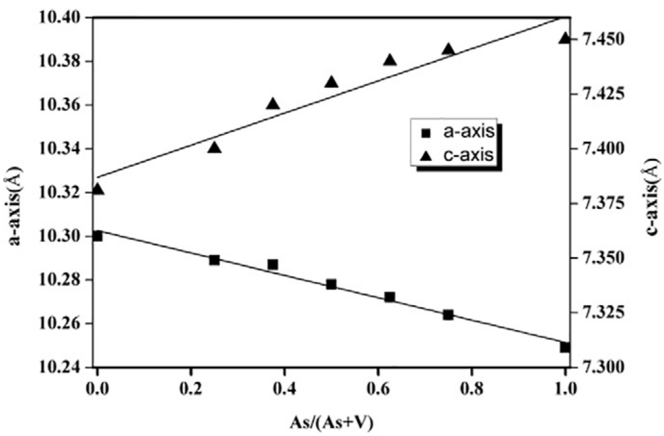

Fig. 2. Variation of a and c unit cell parameters with the different molar ratio of As/(As + V) in mineral cell.