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Discussion

A discussion of the paper "Hydration reactions of nonstoichiometric barium orthoaluminates" by T.R.N. Kutty and M. Nayak

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1. Introduction

The paper by Kutty and Nayak [1], in which the hydration reactions of the nonstoichiometric barium orthoaluminates with the chemical formula $Ba_{1-x}Al_2O_{4-x}$ ($0 < x < 0.56$) are studied, is an interesting and useful development in regard to the study of cementitious materials.

According to Kutty and Nayak, the serial of $Ba_{1-x}Al_2O_{4-x}$ ($0 < x < 0.56$) compounds wherein Al is in 4-coordination, when in the presence of CO_2-free humid air is converted into hydrated product $Ba_{1-x}Al_2(OH)_{8-2x} \cdot YH_2O$, wherein Al is in 6-coordination. This is of particular interest. By heating the hydrated product to 600°C, it decomposes to $Ba_{1-x}Al_2O_{4-x}$. However, this hydrated product is highly sensitive on exposure to CO_2 and gives rise to barium aluminium carbonato-oxy-hydroxide.

This is a discussion about the application of absorption infrared (IR) spectroscopy in the study of barium orthoaluminate hydrates.

2. Discussion

In the use of IR absorption spectroscopy, Kutty and Nayak analyse and discuss the absorption bands in the IR spectra of hydrated sample $Ba_{0.76}Al_2(OH)_{7.52} \cdot H_2O$. They found an absorption band at 1440 cm^{-1} with a relative intensity that can be considered strong and probably has been erroneously assigned. Carbonates show strong infrared absorptions [2,3] in the region 1530–1320 cm^{-1} (asymmetric stretch ν_3), usually restricted to 1450–1400 cm^{-1}; medium strength bands between 890 and 800 cm^{-1} (out-of-the-plane bend ν_2); and at 760–670 cm^{-1} (asymmetric stretch ν_4). So the absorption band near 1440 cm^{-1}, assigned by Kutty and Nayak to the vibrations of Al-OH groups, is due to the asymmetric stretch ν_3 of CO_3^{2-} groups and the shoulder near to 840 cm^{-1} to the out-of-the-plane bend ν_2 of CO_3^{2-} groups, also.

The O-H stretching vibration gives rise to a strong, sharp band in the region 3700–3500 cm^{-1}. However, the stretching vibration in hydroxides is partnered by a bending vibration; this O-H bending frequency occurs in the 1200–600 cm^{-1} region. The absorption bands near to 1050 and 980 cm^{-1} in the IR spectra of the hydrated barium orthoaluminate presented in the Kutty and Nayak paper are bending vibrations of Al-OH groups.

By 27Al magic angle spinning, nuclear magnetic resonance (MAS, NMR), Kutty and Nayak found hydrated products that aluminium presents octahedral coordination in barium orthoaluminates. In that case it can be assigned the absorption bands near 760 and 550 cm^{-1}, the Al-O vibration in the AlO_6 group.

Table 1
Characteristic frequencies of AlO_n coordinated groups

	AlO_4 tetrahedra	AlO_6 octahedra	References
Al-O vibrational frequencies (cm^{-1})	900–800	Near 750	Kolesova [4–6]
	900–775 and 675–575	760 and 670	Schroeder and Lyons [7]
	Condensed: 900–700	Condensed: 680–500	Tarte [8–10]
	Isolated: 800–650	Isolated: 530–400	

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In Table 1 are collected the characteristic frequencies of AlO_n coordinated groups proposed by different authors [4–10].

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