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A novel method for synthesizing nano-crystalline $MgTiO_3$ geikielite

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Abstract. We report here for the first time a novel method of preparing nano-crystalline metatitanate, $MgTiO_3$ geikielite, with crystalline size varying from 20–40 nm. The preparation has been carried out by co-precipitation method involving titanium hydroxide and magnesium nitrate solution. The samples were characterized by using transmission electron microscopic, powder XRD and FT–IR spectroscopic studies. The sample annealed at 900 K for 2 h show ten X-ray diffraction peaks corresponding to the pure geikielite phase. FT–IR spectra of the nano-crystalline geikielite exhibit strong broad vibrational bands near 1000, 650 and 470 cm^{-1} arising from normal vibrations of the TiO_3 group.

Keywords. Nanomaterials; mineral; ceramics; geikielite; spectroscopic studies; Lunar minerals.

1. Introduction

Geikielite, $MgTiO_3$, is the magnesium analogue of ilmenite and typically occur in mantle derived rocks like kimberlites and carbonatites (Reto Giere and Lumpkin 2001). Geikielite also occurs as a common accessory mineral phase of the enstatite chondrite as inclusions (Guan *et al* 2000), and abundant in the Lunar rocks (Heiken *et al* 1991). The metatitanate, $MgTiO_3$ geikielite, has many industrial applications due to its dielectric properties in chip capacitors, high frequency capacitors, and temperature compensating capacitors in ceramic industries (Baek *et al* 1996; Mitchell *et al* 1998; Aryal *et al* 2006). Namgung *et al* (1993) suggested a possible superconductivity in Mg–Ti oxides in the temperature range of 50 K. In this paper, we report synthesis of nano-crystalline geikielite by co-precipitation method. The sample has been characterized by electron microscopic, powder X-ray diffraction and Fourier–transform infrared (FT–IR) spectroscopic methods.

2. Experimental

Geikielite sample has been prepared by co-precipitation method through the reaction: $Ti(OH)_4 + Mg(NO_3)_2 6H_2O \rightarrow MgTiO_3 + NH_4NO_3 + H_2O$, which was carried out at 1000 K for 8 h. The ammonium salts were dissolved in double distilled water. The formation of geikielite was confirmed by compositional studies by Hitachi S-520 scanning electron microscopy (SEM) operating in energy dispersive mode. The MgO content was determined as 33·58–33·56 wt% and TiO_2 content was found to be 66·43–66·36 wt% indicating the presence of pure geikielite phase (Parthasarathy and Manorama 2004, 2006).

The diffraction patterns were obtained by Siemens D-5000 powder diffractometer with HOPG graphite monochromator. Cu-Kα radiation with a wavelength of 0·154188 nm was used in all the diffraction experiments. Fourier transform–infrared spectroscopic (FT–IR) studies on the moganite-rich and quartz-rich samples have been carried out in ambient conditions, using BIORAD 175C FT–IR spectrometer adopting potassium bromide pellet method. Samples were scanned in the frequency range 4000–300 cm^{-1}. Each sample has been scanned for three times. Typical uncertainty in the wave numbers is about ± 2 cm^{-1}.

3. Results and discussion

Figure 1 shows the transmission electron microscopic image of the sample exhibiting nano-crystalline nature of the prepared sample. The crystallite size of the prepared sample is found to vary from 20–40 nm. The X-ray diffraction studies of the prepared sample showed only broad diffraction peaks indicating nano-crystalline nature of the geikielite samples. However, the samples annealed at 900 K for 2 h, show very sharp and well-resolved X-ray diffraction peaks (figure 2). All the observed XRD peaks were indexed to a rhombohedral unit cell with $a = 0{\cdot}5056(2)$ nm and $c = 1{\cdot}3900(4)$ nm, which are found to be in excellent agreement with the crystallographic data on synthetic geikielite (JCPDS Card No. 6-494). The observed Bragg peaks and the corresponding intensity are listed in table 1. It is clear from figure 2 and table 1 that the prepared sample contained only pure phase of geikielite. Differential

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*Author for correspondence (gpsarathy@ngri.res.in) thermal analyses and thermogravimetric studies on the sample revealed that the sample is stable up to 700 K and absence of any dehydration or decomposition reaction up to 700 K.

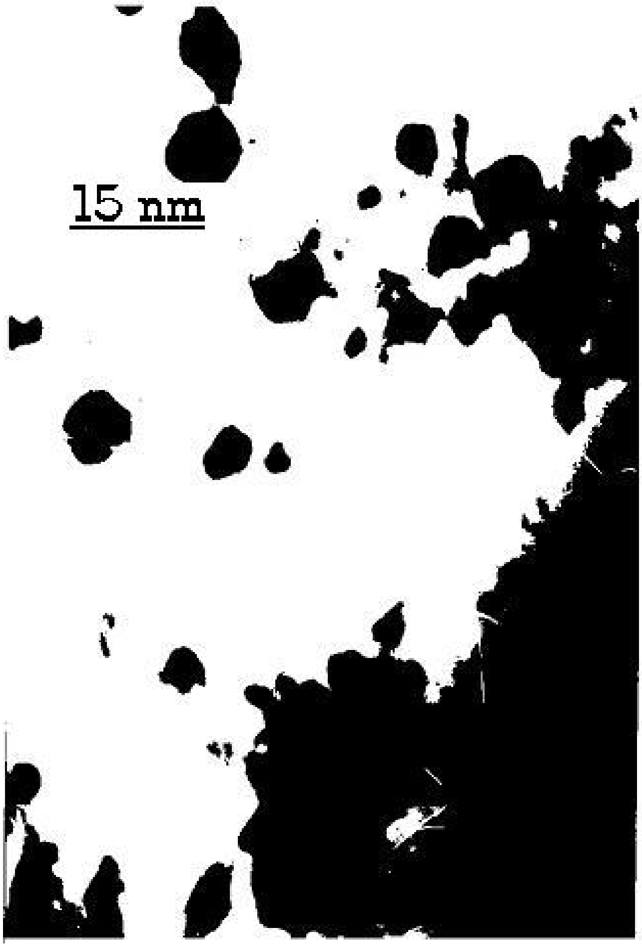

Figure 1. Transmission electron microscopic image of the nano-crystalline geikielite.

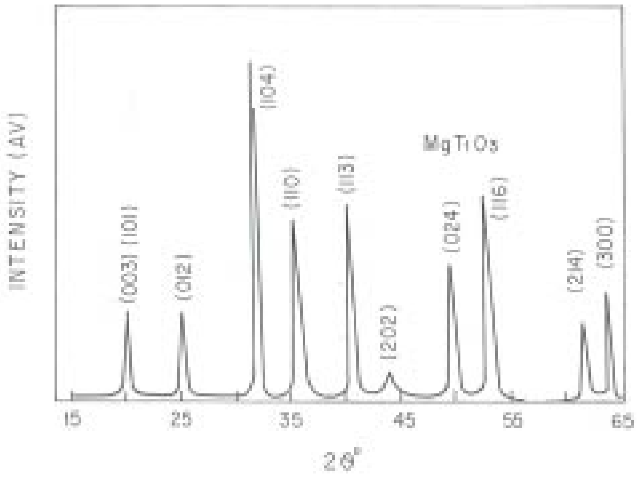

Figure 2. Powder X-ray diffraction pattern of annealed sample of geikielite.

Figure 3 shows the Fourier–transform infrared spectra of nano-crystalline geikielite sample (spectra A), exhibiting three broad absorption bands at 1000, 650 and 470 cm^{-1} arising from normal vibrations of the TiO_3 group. It is known that TiO_4 tetrahedron vibration bands in glassy materials occur at 760 and 770 cm^{-1} (Knight *et al* 1989). The observed wave numbers in the nano-crystalline geikielite are much too high to be assigned to the internal modes of the TiO_4 tetrahedron. Powdered infrared transmission spectra of natural geikielite showed infrared bands at 284, 350, 377, 420, 480, 550–620, 670 and 722 cm^{-1} (Reynard and Guyot 1994). The annealed samples of geikielite show seven well-resolved infrared bands at 350, 380, 625, 725, 820, 1000 cm^{-1}, which are assigned due to MgO_6 and TiO_6 octahedral vibrations. In the present investigation, we did not observe any infrared bands corresponding to hydroxyl or carbonic ions as reported earlier for karrooite (Baura Pena 1992), indicating the presence of pure phase of geikielite in the studied sample. Further work on high-pressure temperature phase stability of geikielite are under progress.

Table 1. Powder X-ray diffraction data of geikielite.

d-spacing (nm)	(*h k l*)	Intensity
0·4642	(003)	30
0·4184	(101)	30
0·3703	(012)	40
0·2723	(104)	100
0·2528	(110)	60
0·2219	(113)	70
0·2091	(202)	10
0·1852	(024)	40
0·1710	(116)	60
0·1494	(214)	30
0·1460	(300)	40

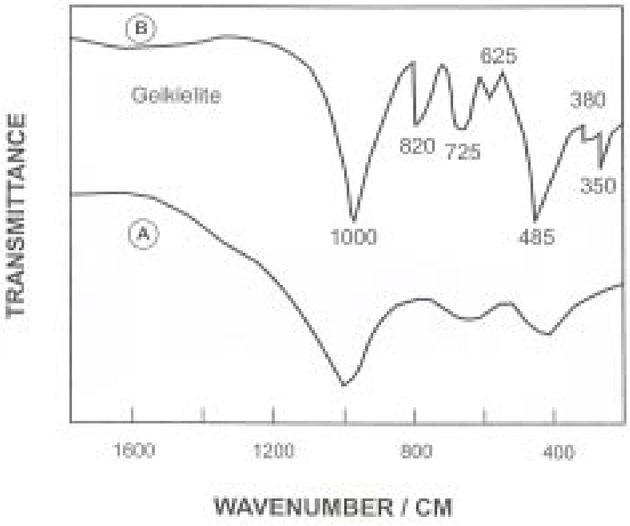

Figure 3. Powdered Fourier–transform infrared transmission spectra of the nano-crystalline geikielite (spectrum A) and annealed sample (spectrum B).

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