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Synthesis and characterization of calcium aluminum silicate hydroxide (CASH) mineral

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The synthesis of calcium aluminum silicate hydroxide (CASH) has been carried out under mild hydrothermal and solvothermal conditions. Different mineralizers such as HCOOH, HNO_3, CH_3COOH, HCl, mixed acids, NaOH and non-aqueous solvents like C_2H_5OH, *n*-butanol, glycol, methanol, etc., were employed in the synthesis of CASH. The crystals obtained were characterized by X-ray powder diffraction and FTIR spectroscopic techniques.

1. Introduction

Calcium aluminum silicate hydroxide (CASH) is a mineral of epidote group of sorosilicates, having the general formula $Ca_2Al_3Si_3O_{12}(OH)$. In nature it crystallizes in both orthorhombic and monoclinic systems at around 800 to 1000°C. CASH is a common mineral in basaltic rocks metamorphosed in the eclogite and amphibolite facies. It has a great commercial value because of its beauty, rarity and durability. This mineral is highly difficult to synthesize artificially because of its extremely complex structure and mineral chemistry.

In sorosilicates, two SiO_4 tetrahedra share a single apical oxygen atom and form isolated, double tetrahedral groups. Such Si_2O_7 groups and independent SiO_2 tetrahedra link chains of AlO_6 and AlO_4 $(OH)_2$ octahedra that share edges to form the monoclinic crystals characteristic of the epidote group. Formation at higher temperatures in regionally metamorphosed calcareous schists and shales and a twin-like doubling of the cell along the *a*-axis cause CASH to develop in the orthorhombic symmetry.

CASH and epidote show a close relationship between their atomic structures [1, 2].

The crystals of these silicates exhibit chatoyancy phenomena with vitreous luster and this optical property of the crystals has made them highly valuable. Several imitations of these CASH have appeared in the market. In the present work, the authors have synthesized for the first time small crystal of CASH using mild hydrothermal and solvothermal conditions.

2. Experimental

Hydrothermal crystallization of CASH was carried out at low temperature between 150–250°C. The starting materials (precursors) for the synthesis of CASH were prepared as gels in the laboratory, as they are more reactive and easily soluble in the mineralizer than commercially available reagent grade chemicals.

The selection and preparation of the precursor materials play an important role in the synthesis of CASH under hydrothermal conditions. The starting materials such as sillimanite (Al_2SiO_5), calcium carbonate ($CaCO_3$) and quartz (SiO_2) were used in the ratio 3: 4: 3 for the synthesis of CASH crystals under hydrothermal conditions. Sillimanite (Al_2SiO_5) gel was prepared using commercially available corundum (Al_2O_3) and quartz (SiO_2) gels. The greatest advantage of using

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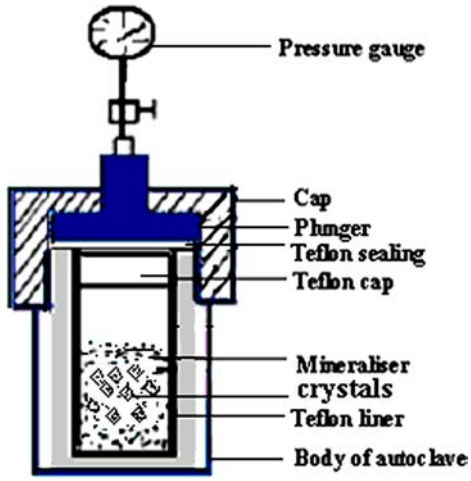

Figure 1 Schematic diagram of the autoclave used.

gels as starting material is that numerous and also complex phases can be intimately mixed. Gels are probably superior for studies of sub-solidus equilibrium melting temperature and at low levels of liquid present in the molten silicates [3]. The experiments on the hydrothermal synthesis of the title compounds were carried out using General Purpose autoclaves. The use of teflon liners helps in overcoming the entry of inclusions from the autoclave material into the resultant product [4]. The schematic diagram of hydrothermal autoclave used in the present work is shown in Fig. 1.

The starting gel materials were taken in appropriate molar proportions (sillimanite : calcite : quartz∼0.300 : 0.400 : 0.300) in a teflon liner. A suitable mineralizer of known concentration was added into the teflon liner and the entire mixture was stirred well until a homogeneous and relatively viscous solution was obtained. The autoclave assembly was then placed inside the furnace, whose temperature was slowly increased at the rate of 20°C per h. The experimental temperature was set between 150 and 250°C and the pressure between 60 and 80 bars depending upon the type of mineralizer used. Some experiments were carried out keeping precursor weight constant and varying the experimental temperature and vice versa. The pH of the growth medium was measured before and after each experimental run. After the experimental run, the autoclaves were quenched initially using an air jet and then water.

The products were washed thoroughly using double distilled water and ultrasonicated to remove all the excess or remaining acid content. The authors have tried a series of mineralizer solutions with varying concentrations : HCOOH, HNO_3, CH_3COOH, HCl, mixed acids, NaOH, C_2H_5OH, *n*-butanol, glycol, methanol, etc. Among these only HCOOH and *n*-butanol were found to be the most suitable mineralizers to crystallize these complex calcium aluminum silicate hydroxide complexes.

The probable chemical reaction in the synthesis of CASH when HCOOH is used as a mineralizer is as follows:

$$3Al_2SiO_5 + 4CaCO_3 + 3SiO_2 + HCOOH \rightarrow 2Ca_2Al_3Si_3O_{12}(OH) + 5CO_2.$$

The reactions will be different, when different mineralizers are used for synthesis of CASH crystals under hydrothermal and solvothermal conditions.

CASH crystals were obtained when the initial pH of the acid mineralizer was kept between 1.6–5.8 and that of the organic solvent (*n*-Butanol) was 8.5 (Table I). The crystals obtained using *n*-butanol at 150°C under solvothermal conditions were slightly bigger than the crystals obtained at different temperatures under hydrothermal conditions. It means organic solvents are more effective than the acids in the synthesis of CASH. The crystals obtained were well faceted crystals, semi-transparent to transparent.

TABLE I Representative experimental conditions for the synthesis of CASH

No.	Precursors,(gms)	Solvent	T°C	pH	Duration (Days)	Remarks
1	Al_2SiO_5, (0.300) $CaCO_3$, (0.400) SiO_2, (0.300)	Conc. HCOOH (6 ml)	250	1.7	4	colorless, transparent, tetragonal pyramid shaped crystals
2	Al_2SiO_5, (0.300) $CaCO_3$, (0.400) SiO_2, (0.300)	*n* -Butanol (8 ml)	150	8.5	3	light honey yellow coloured irregular semi-transparent crystals
3	Al_2SiO_5, (0.300) $CaCO_3$, (0.400) SiO_2, (0.300)	Conc. HNO_3 (6 ml)	240	1.2	6	no crystals
4	Al_2SiO_5, (0.300) $CaCO_3$, (0.400) SiO_2, (0.300)	*n* -Butanol (8 ml)	150	8.5	3	tetragonal pyramid shaped, transparent and colourless crystals
5	Al_2SiO_5, (0.300) $CaCO_3$, (0.400) SiO_2, (0.300)	HCOOH Conc. (6 ml)	250	1.6	4	irregular, colourless transparent crystals

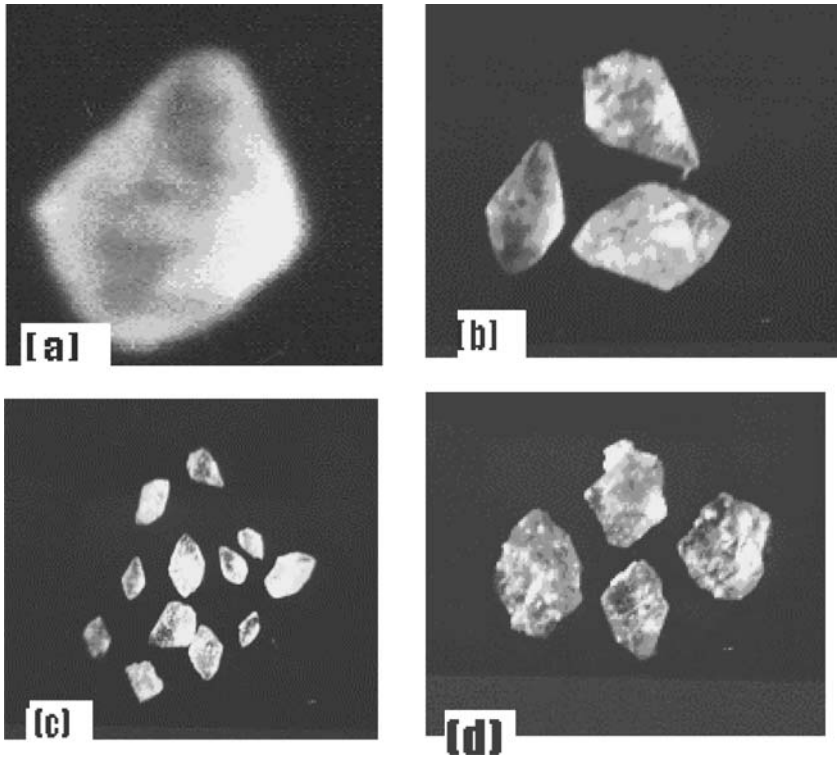

Figure 2 Representative photographs of CASH crystals (a) 45X (b) 45X (c) 15X (d) 25X.

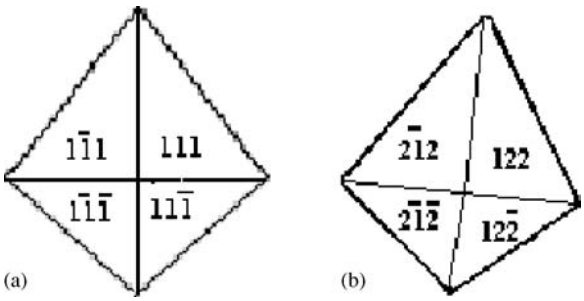

Figure 3 Schematic diagram of CASH crystals obtained under hydrothermal conditions: (a) tetragonal pyramid (b) hemimorphic tripyramid.

3. Morphology

CASH crystals obtained at 250°C using formic acid as a mineralizer under hydrothermal conditions show tetragonal pyramidal shape and exhibit properties like vitreous luster, reddish yellow colour, transparent to subtransparent. The size of the crystals ranges from 0.85 mm to 1 mm (Fig. 2 a–c), whereas crystals obtained under solvothermal conditions using *n*-butanol as a mineralizer show irregular shape and size as shown in Fig. 2d. No crystals formed when HNO_3 was used as a mineralizer under hydrothermal conditions (Table I).

The schematic diagram showing the morphology of CASH crystals obtained is shown in Fig. 3a and b.

4. Characterization

CASH crystals obtained were subjected to powder X-ray diffraction and infrared spectroscopic studies. The X-ray diffraction patterns were recorded using Rigaku Miniflex X-ray diffractometer model IGC2, Rigaku Denki Co. Ltd, Japan. The cell values obtained for CASH crystals match well with the literature data. The powder X-ray diffraction pattern of a representative CASH crystal is shown in Fig. 4. The FTIR spectra were recorded for the representative CASH crystals using FTIR spectrophotometer, JASCO-460 PLUS, Japan. The representative FTIR

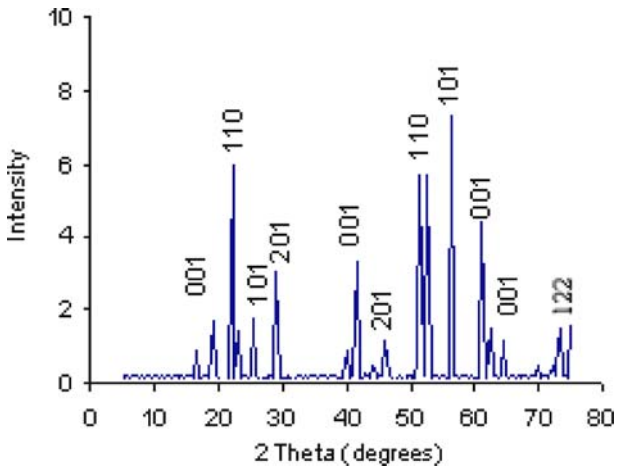

Figure 4 XRD pattern of hydrothermally synthesized CASH crystals.

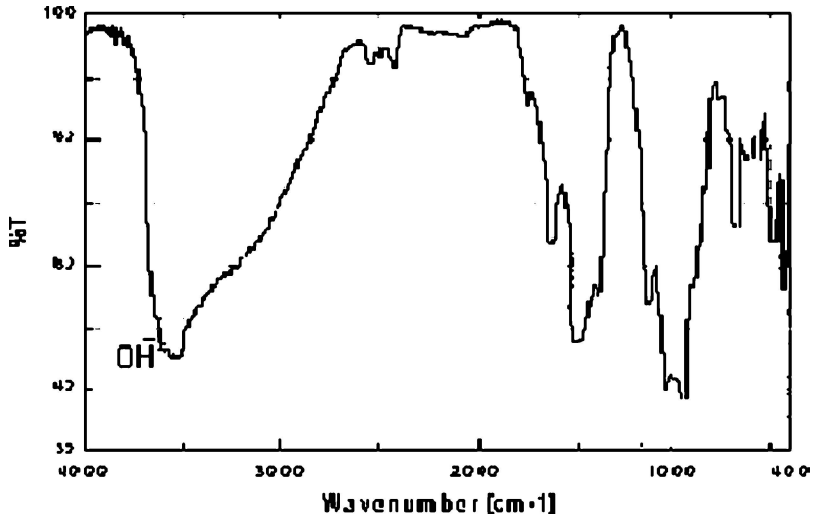

Figure 5 FTIR spectrum of the CASH crystals.

spectrum for the CASH crystals obtained under hydrothermal conditions shows the presence of OH^- radicals at 3700 to 3200 cm^{-1} range (Fig. 5) [5]. The presence of OH^- species in the CASH enhances its value and gives beauty. The splitting of absorption bands and the presence of multiple absorption bands in the range of 2600 to 400 cm^{-1} clearly indicate the complexity of the molecular structure of CASH.

5. Conclusions

The synthesis of CASH has been carried out under hydrothermal and solvothermal conditions in the temperature range of 150 to 250°C using both aqueous and non-aqueous mineralizers. The crystals obtained at 250°C using formic acid as a mineralizer under hydrothermal conditions show well developed crystal morphology with tetragonal pyramidal shape. Whereas crystals obtained using *n*-butanol as a mineralizer at 150°C show irregular shape and size. Thus the use of acid mineralizers is more effective than the organic solvent for the synthesis of CASH under hydrothermal conditions. The temperature and pH of the solution influence the crystallization and morphology of the crystals. The X-ray studies show that the phases obtained are quite pure and the X-ray data matches well with the literature data. The FTIR spectra show the presence of (OH^-) molecules and highly complex crystal structure for CASH.

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