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Structural Alterations in Smithsonite during High-Energy Ball Milling

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Smithsonite, $ZnCO_3$, from Zamantı-Kayseri, Turkey, was subjected to high-energy milling. X-ray diffraction analysis was performed to study amorphisation in the structure and the alterations of bands in the structure were investigated by Fourier transform infrared spectroscopy. Characterization of milled smithsonite by X-ray diffraction analysis has shown that disappearance, decrease and/or shifting of the patterns occurred with mechanical activation, which means that amorphisation was taking place. Amorphisation was also demonstrated by Fourier transform infrared spectroscopy analysis, where shifting of band centers was observed.

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1. Introduction

Zinc sulfide ores, which can be easily separated from gangue and upgraded by flotation, are the most important conventional sources of zinc. As the secondary minerals, zinc oxide ores whose zinc bearing minerals are mainly various carbonate and silicates minerals, such as smithsonite ($ZnCO_3$), hydrozincite ($2ZnCO_3{\cdot}3Zn(OH)_2$), zincite (ZnO), willemite (Zn_2SiO_4) and hemimorphite ($Zn_4Si_2O_7(OH)_2{\cdot}H_2O$) are other sources for production of zinc. Because of the decline of zinc sulfides reserves, as well as the restriction on sulfur emission all over the world, zinc oxide ores with a huge reserve are paid attention [1, 2]. Smithsonite is naturally occurring zinc carbonate. This is one of the secondary minerals of zinc and its formation is controlled by the partial pressure of CO_2. Smithsonite is only stable at elevated CO_2 partial pressures [3, 4].

Mechanical activation by high intensity milling has been commonly used as an effective pretreatment method in various areas, such as mining, metallurgy and materials engineering. In mineral processing, the aim of coarse and fine grinding is to liberate the ore for downstream separation. Furthermore, fine grinding is also used after mineral separation in order to give concentrates the right particle size distribution or a sufficiently high surface area. Mechanical activation aims to enhance a reaction [5]. Mechanical activation of minerals makes it possible to reduce their decomposition temperature or causes a degree of disorder [6, 7].

In this study, smithsonite was subjected to high-energy ball milling and disorder in the crystalline structure of smithsonite were investigated using X-ray diffraction (XRD) and Fourier transform infrared analysis (FTIR). Process of obtaining of ZnO without calcination was also investigated for further hydrometallurgical processes.

2. Materials and methods

Smithsonite, $ZnCO_3$, obtained from Zamantı-Kayseri region in Turkey was crushed and sieved through 75 μm sieve for standardization of the particle size. Mechanical activation was performed in a Planetary Mono Mill Pulverisette 6, using tungsten carbide (WC) balls (10 mm in diameter) and tungsten carbide (WC) bowl (250 ml in volume). Ball-to-mass ratio and speed of main disk were kept constant at 20 and 600 $\text{rev}\,\text{min}^{-1}$ respectively. Activated and non-activated smithsonite samples were characterized by means of X-ray diffraction analysis (Rigaku SmartlabTM X-ray Diffractometer) and Fourier transform infrared spectroscopy (Shimadzu).

3. Results and discussion

X-ray diffraction analysis of non-activated smithsonite and smithsonite samples activated for 15, 30 and 60 min are given in Fig. 1. As seen from this figure, intensity of smithsonite peaks tended to decrease with milling time, such as peaks positioned at 25.14°, 32.64° and 38.74°. It was stated that after extended milling, line broadening and disappearance of diffraction peaks take place in X-ray patterns, which mean the formation of metastable, amorphous phase, because of the development of large number of dislocations. Their associated strain fields may lead to an overall decrease in long-range lattice periodicity [7, 8]. In addition, smithsonite peaks got lost after 60 min of mechanical activation and ZnO peaks were detected after 15 min of high-energy milling. It was detected from XRD analysis that smithsonite had decomposed and ZnO occurred during high-energy milling.

The entire Fourier transform infrared spectra of non-activated and activated smithsonite for different milling times are shown in Fig. 2a. Figure 2b and 2c represents the intervals of 2000–1000 cm^{-1} and 1000–400 cm^{-1}, respectively, which are given separately for understanding of the alteration occurring with mechanical activation.

For non-activated sample, positions of intense bands are at 1425.45 cm^{-1}, 869.93 cm^{-1} and 744.55 cm^{-1}.

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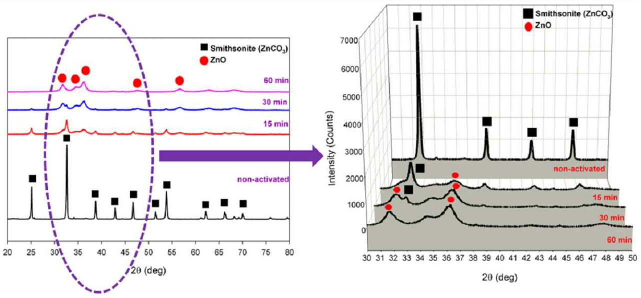

Fig. 1. XRD analysis of non-activated and activated smithsonite.

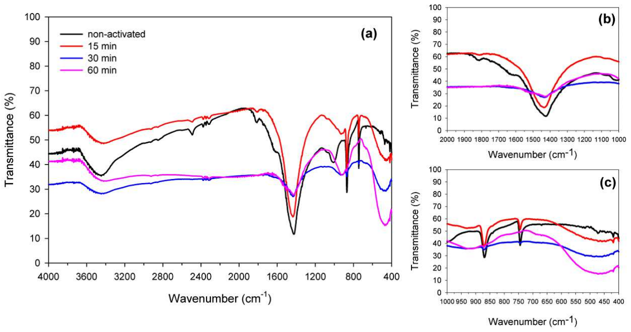

Fig. 2. (a) FTIR analysis of non-activated and activated smithsonite (b) 2000–1000 cm^{-1} region of FTIR and (c) 1000–400 cm^{-1} region of FTIR.

These bands correspond to v_3, asymmetric stretching of $(CO_3)^{2-}$, v_2, bending mode of carbonate and v_4, in phase bending mode of carbonate, respectively [9, 10]. In Fig. 2b transmittance change of 1437.03 cm^{-1} band is shown. This band is about to wither after the mechanical activation time of 30 and 60 min. Same phenomenon takes place for 869.93 cm^{-1} and 744.55 cm^{-1} bands. However 744.55 cm^{-1} band gets lost after 15 min of mechanical activation.

The other important alteration in spectrum has occurred at $\sim$ 472 cm^{-1}. As seen from Fig. 2a and 2c, this band, which is defined as the characteristic band of ZnO [11], becomes stronger with mechanical activation. Other weaker bands of non-activated sample are positioned at 2494.06 cm^{-1} and 2852.84 cm^{-1}. 2494.06 cm^{-1} band is assigned to a combination of the v_2 and v_3 vibrational modes. It is said that 2852.84 cm^{-1} band may arise from the first fundamental overtone of the v_3 band at around 1437 cm^{-1} [9]. Both these bands were getting weaker and had disappeared with increased mechanical activation duration, as shown in Fig. 2a. A broad band, centered at 3446.94 cm^{-1} for non-activated sample, corresponds to adsorbed water [10]. Transmittance of bands that correspond to carbonate anion has changed, decreased and disappeared with mechanical activation. But the $\sim$ 472 cm^{-1} centered band became stronger with mechanical activation, which means that the decomposition of smithsonite had occurred during milling.

4. Conclusions

Results of X-ray diffraction analysis show that the peaks of smithsonite decreased during high-energy ball milling and disappeared completely after 60 min of mechanical activation. Fourier transform infrared spectroscopy of non-activated and activated smithsonite also show that a decrease and/or shifting of the patterns occur during mechanical activation and that the transmittance of bands of carbonate anion was decreasing and disappeared. As a result, decomposition of smithsonite into ZnO occurs during high-energy ball milling.

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