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Characterization by X Ray Diffraction of Mechanically Alloyed Tripotassium Sodium Sulfate

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Nanocrystalline powder of tripotassium sodium sulfate ($K_3Na(SO_4)_2$ - KNS) was successfully obtained by mechanical alloying a mixture of potassium sulfate (K_2SO_4) and sodium sulfate (Na_2SO_4) with a proportion of 3:1 in a planetary mill. X ray powder diffraction (XRPD) was used to characterize this material. Powders produced with high milling times: 15, 30, 45 and 60 hours, have shown a single phase. For 60 hours of milling time, the powder was formed with very small grains (60 nm in average). We also prepared several samples with low milling times: 30, 60, 120, 150 and 180 minutes. The results for this series show that 120 minutes of milling is enough to produce a single crystalline phase of KNS. Therefore, we showed that a nanocrystalline powder of tripotassium sodium sulfate is easily obtained by mechanical alloying and that the grain size can be controlled by the amount of milling time.

Keywords: *sulfate, mechanical alloying, X ray, powder diffraction*

1. Introduction

The interest in the physical properties of nanoparticles has increased in the last decades because of the different properties encountered in these nanocrystalline materials when compared to their corresponding bulk. They present, in general, properties with innumerable technological applications, for example: there is a drastic variation of electric properties of materials in the nanosize regime attributed to the quantum confinement of charge carriers and associated modification of the band structure[1,2]. Furthermore, there are some nanoparticles with reduced value of conductivity in contrast to those of the single crystal or coarse-grained materials[3,4]. In some semiconductors, a decrease in the value of conductivity is expected due to the narrowing of valence and conduction bands resulting in an increase of forbidden energy gap. Reduced particle size is also needed for improved sintering abilities, that means decreased sintering temperatures, increased density of sintered powders[6] and shorter reaction times, as compared with the classical ceramic synthesis.

The crystal of tripotassium sodium sulfate (abbreviated as KNS) is the most investigated member of the glaserite family. This family also includes $K_3Na(CrO_4)_2$, $K_3Na(SeO_4)_2$ and $K_3Na(MoO_4)_2$. The members of this family are characterized by showing a sequence of phase transitions[1] and a predicted and not observed ferroelastic phase transition[1] around 75 K for KNS. The space group of the KNS is P $\bar{3}$ m1 and the lattice parameters[3] are a = 5.6801 Å and c = 7.309 Å. Single crystals of KNS can be obtained by various methods including slow evaporation of an aqueous solution[4]. In this work we are interested in structurally characterize the nanocrystalline powder of KNS produced by mechanical alloying using X ray powder diffraction. Special attention is given to the grain size as a function of milling time.

2. Experimental

In this work, mechanical alloying has been successfully used to produce nanocrystalline powder of tripotassium sodium sulfate (KNS). This procedure is analogous to the one used for other materials, hydroxylapatite[5] for example. Commercial powders of K_2SO_4 (Vetec 99%) and Na_2SO_4 (Vetec 99%) were used in the preparation of KNS. The reaction used was the following:

$$3K_2SO_4 + Na_2SO_4 \rightarrow (\text{IMPACTS}) \rightarrow 2K_3Na(SO_4)_2 \quad (1)$$

The reagents were ground on a Fritsch Pulverisette planetary mill with the stechiometric ratio 3:1 given in Equation 1. Mechanical alloying was carried out using sealed stainless steel vials and balls under air. Two sets of samples were produced; 30, 60, 120, 150 and 180 minutes, samples with low milling time; 15, 30, 45 and 60 hours, samples with high milling time.

The X ray diffraction (XRD) patterns were obtained at room temperature (300 K) in an X´Pert PRO Phillips powder diffractometer using the Bragg-Bretano geometry with Cu-Kα radiation. We used three seconds for each step of counting time, an angular step of 0.02° and with the tube at 40 KV and 40 mA.

The analysis of the grain size (L_{hkl}) of the sulfate has been done to all samples using the Scherrer´s equation[6],

$$L_{hkl} = \frac{k\lambda}{\beta \cos\theta} \quad (2)$$

where k is the shape coefficient (values between 0.9 and 1.0), λ is the wavelength of the radiation, β is the full width at half maximum (FWHM) of the peaks of each phase and θ is the diffraction angle. For this purpose the β parameter has been corrected in order to represent only the effect of the grain size in the FWHM. Assuming a Gaussian function for the diffraction peaks and for the instrumental broadening, one can subtract the instrumental broadening using the following equation:

$$\beta_c = \sqrt{\varpi_{exp}^{\ 2} - \varpi_{inst}^{\ 2}} \quad (3)$$

where ϖ_{exp} corresponds to the experimental FWHM obtained for each sample. We have used the LaB6 (SRM 660-National Institute of Standard Technology) powder standard pattern to determine the instrumental line width (ϖ_{inst} = 0.08°) of the equipment close to the Bragg angle of 28°.

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In order to perform this calculation we have chosen two peaks, one at 24.1° and another at 31.3° and according to the space group P $\bar{3}$ m1 of KNS these peaks correspond respectively to hkl = 002 and hkl = 110, i.e. along and perpendicular to the c crystallographic axis of the diffracting grains. The shape coefficient k was assumed to be equal to 1, which means an approximately spherical shape of the grain.

3. Results and Discussion

In the Figure 1 it is shown the diffraction patterns of the $K_3Na(SO_4)_2$ (KNS) powder in log scale to enhance the low intensity peaks. In this figure, one has the reference pattern obtained from the literature (ICDD[7]) denoted by bars and the X ray powder diffraction of the (KNS) prepared for low milling time. It can seen that for times below 120 minutes there are traces of the original reagents used in the preparation (K_2SO_4 and Na_2SO_4). Peaks corresponding to the reagents are indicated by 'o' and 'x' in the figure.

Moreover, the X ray data in Figure 1 also shows that the formation of the KNS is very fast. Even for a very low milling time the peaks associated to KNS have already appeared. There is no formation of any other phases; the diffraction pattern is completely covered by the peaks associated with the KNS, K_2SO_4, marked as 'x', and the Na_2SO_4 phases, marked as 'o'. All patterns are obtained in ICDD[7]. The crystalline grain size of these samples are shown in Table 1.

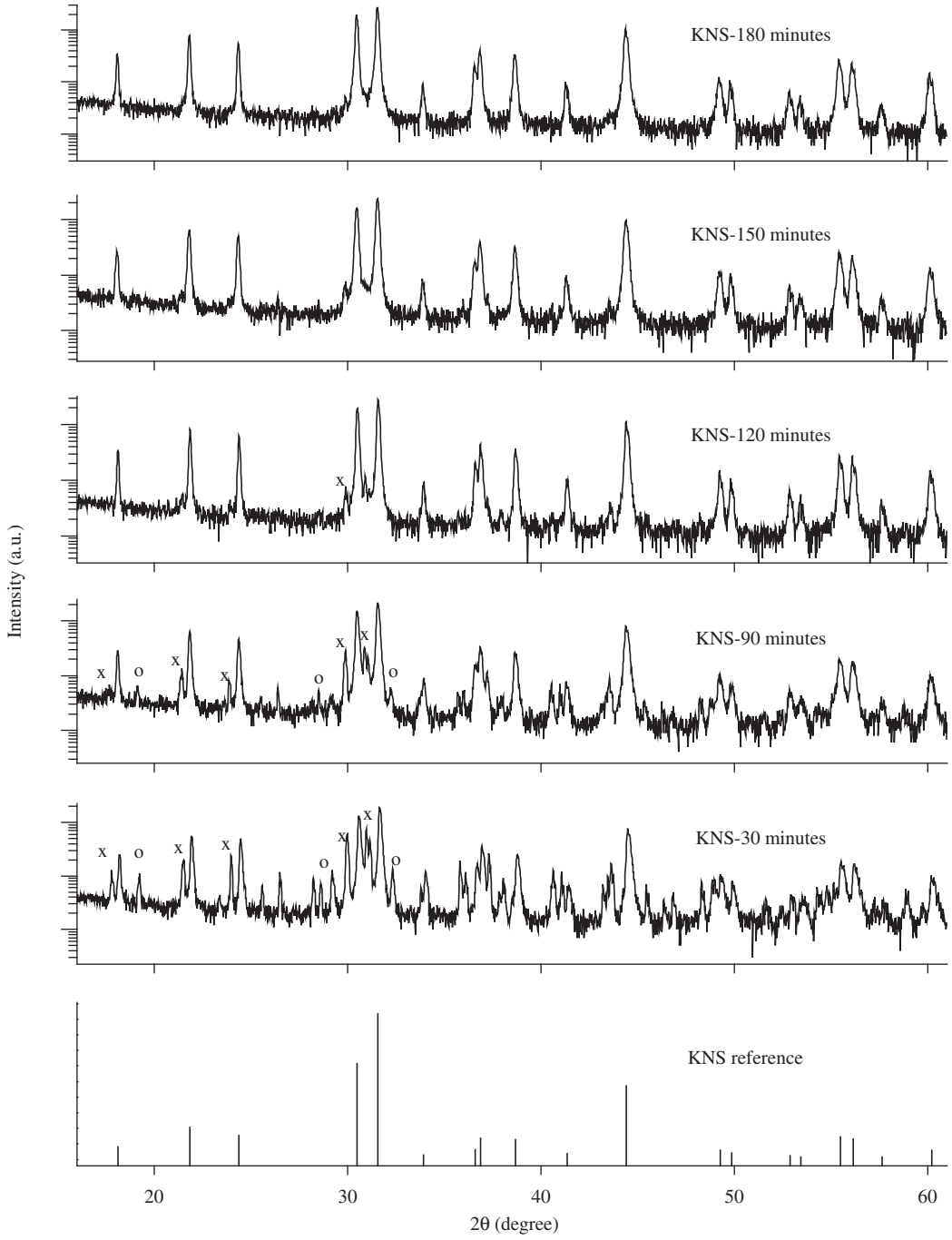

Figure 1. X ray powder diffraction pattern of the KNS powder prepared with low milling times, 30-180 minutes. The vertical bars are associated to the reference pattern of the KNS. The 'x' and 'o' symbols denote peaks from the K_2SO_4 and Na_2SO_4, respectively.

Figure 2 shows the diffraction patterns of the KNS for high milling time plus the reference pattern. No trace of another phase than the KNS has been found.

The results for the crystalline grain size determination for the samples in the high milling time set are shown in Table 2. It can be seen that there is a tendency to decrease the size of the grains as

Table 1. Average grain size of the samples with low milling time. Average error is 1 nm.

Milling time	30 minutes		90 minutes		120 minutes		150 minutes		180 minutes	
	Size	fwhm	Size	fwhm	Size	fwhm	Size	fwhm	Size	fwhm
110 – direction	117 nm	0.0784	95 nm	0.0961	153 nm	0.0600	178 nm	0.1173	121 nm	0.0755
002 – direction	133 nm	0.0680	111 nm	0.0812	170 nm	0.0531	80 nm	0.1125	164 nm	0.0617

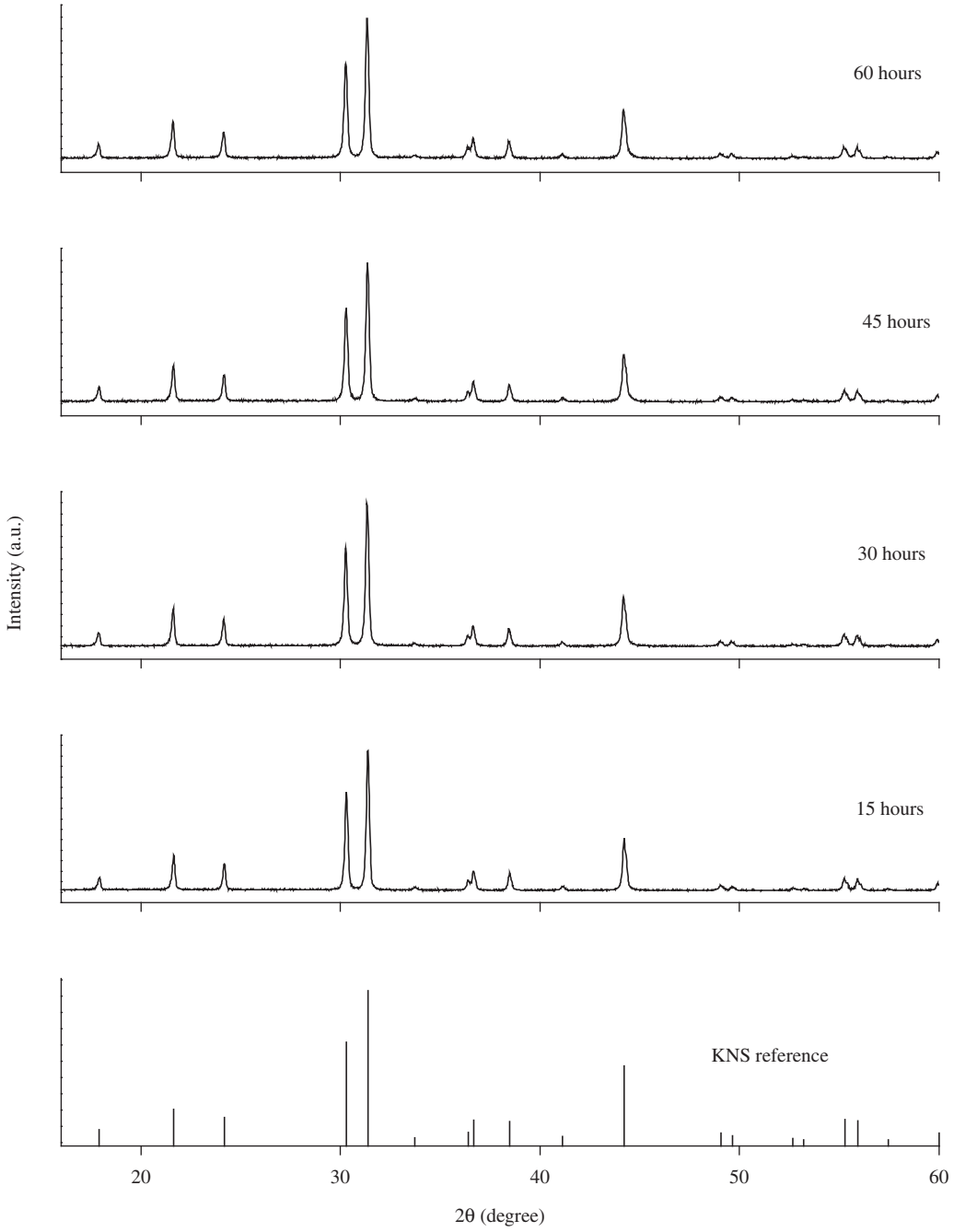

Figure 2. X ray powder diffraction pattern of KNS powder prepared with high milling time (15-60 hours) and the reference pattern of KNS.

Table 2. Average grain size of the samples with high milling time. Average error is 1 nm.

Milling time	15 hours		30 hours		45 hours		60 hours	
	Size	fwhm	Size	fwhm	Size	fwhm	Size	fwhm
110 – direction	72 nm	0.1269	67 nm	0.1374	64 nm	0.1432	63 nm	0.1443
002 – direction	66 nm	0.1374	63 nm	0.1443	61 nm	0.1489	59 nm	0.1534

the milling time is increased and it is also noted that the grains are smaller than the ones of the samples prepared with low milling time. So, this is an efficient method to obtain nanocrystalline powder of tripotassium sodium sulfate, and it can be also achieved with a low milling time.

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