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Qualitative Phase Analysis and Determination of Crystallographic Parameters of Fluorspar

***Ibrahim Muhammad Bagudo and Gidado Shehu**

Department of Physics, Umaru Musa Yar'adua University, Katsina, Nigeria.
*Corresponding Author's email: gidado.shehu@umyu.edu.ng Phone: +2348038366735

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ABSTRACT
The incorporation of fluorspar also known as Calcium fluorite (CaF2) as a passivation agent for improving photovoltaic performance has become one of the best ways for enhancing the efficiency of solar cells. During the fabrication of titanium dioxide/calcium fluoride (TiO2/CaF2) photoanodes, a dosage of CaF2 is used to optimize the crystal structure and consequently the photovoltaic performance for a better energy harvest. Owing to this remarkable application of CaF2, continuous exploration and intense studies of natural fluorite seem necessary for meeting the demand, ensuring reliability and quality assurance. In this research, the experimental studies on the phases and the crystal parameters of natural fluorite have been reported. Samples of CaF2 were considered for analyses using XRF and XRD techniques. XRF analysis determined the elemental composition of the sample. The obtained X-ray diffraction patterns were used for further analysis. The diffraction angle and intensity data of both samples were used to assess the peak parameters from the X'Pert Highscore plus which determine their phases and lattice parameters. Results confirmed its quality and reliability for use as a good passivation agent.

INTRODUCTION

The identification of phases for a given mineral sample is one of the main applications of classical X-ray powder diffraction. The phases found in samples of a crystalline solid with a regular 3-dimensional arrangement of the atoms may be major or minor, multiple or single. The measured diffraction peak positions and intensities are like a fingerprint of a particular crystalline phase. Identification can be accomplished by comparing the measured pattern with the entries in the reference databases using a search-match algorithm (Altay. M., 2020). This process is known as qualitative phase analysis. Qualitative phase analysis helps in achieving proper understanding of the formation mechanisms of a material mineral, which can provide reliable information regarding the presence of ores or fuels. The origin of crystallography as the general consideration of how crystals are built from small units can be traced to the study for the external appearance of natural minerals, such as fluorite, pyrite, quartz, and corundum, which clearly exhibit a good deal of symmetry.

A large amount of data for such minerals has been systematized by applying geometry and group theory. This corresponds to the infinite repetition of identical structural units (frequently referred to as a unit cell) in space. In other words, the structure of all crystals can be described by a lattice, with a group of atoms allocated to every lattice point.

Fluorite is a naturally occurring mineral which is commercially known as fluorspar. It occurs in the Middle Benue Valley and many other parts of the Northern Nigeria. The mineral is remarkable with a veritable bouquet of

brilliant colours ranging most commonly from light to dark blue. Apart from blue colour appearance in fluorite, the appearance of red, purple, yellow, green, and white also occur (Balogun et al 1997).

This optical property of fluorescence in fluorite may be due to the impurities present in the mineral. These impurities may also affect other properties such as electrical and thermal luminescence of mineral (Balogun et al., 1999; Mustafa T. et al., 2007).

Various ore deposits including fluorite deposits are formed by metamorphic rocks intruded by numerous alkaline granitoids (Seymen, 1984; Tu¨lu¨men, 1980). Fluorite deposits, in particular, are formed mostly as a result of hydrothermal processes. These processes occur in a range of different associations which include; REE bearing carbonatite, alkaline to peralkaline granitoids, highly differentiated S-type granites, sedimentary sequences, particularly passive margin carbonates and active continental margin settings (Dill et al., 2016 and Öztürket al., 2019). Some of major fluorite deposits in Africa are found in Nigeria, Kenya, Malawi and South Africa. However, fluorite is found in deposits of widely varying character around the world. In hot spring environment like Colorado and Vosges, it occurs as vein mineral associated with quartz, calcite and dolomite, in late crystallised hydrothermal products in granites, in sandstone like in Mississippi Valley in pegmatite veins like in Virginia. This atomic substitution helps the mineral to accommodate a large variety of impurities within its lattice structure, which greatly modify its various properties. Fluorspar of various origin have always been reported to have extremely variable colours as a result of physical disturbance in the crystalline structure and the compositional variation due to impurities such as inclusions and traces of other elements. The elemental composition of natural fluorites varies based on their geologicalplacements or origins of their deposits (Mangala and Patel, 1996; Balogun et al.,1997; G.S. Polymeris et al., 2006). This variation of the fluorite origin may be associated with some impurities which immensely affect its properties, including electrical, optical and thermal luminescence (Altay. M. 2020). Elemental trace of constituents of a given deposit as a function of its geological history determines the physical properties of the mineral and modifies the use to which it could be put. Available literature on fluorites for the past 2-3 decades shows that majority of the studies performed mainly in Nigeria and Turkey were on the TL properties of naturally occurring fluorite with only one reporting its elemental constitutions. However, a small number of works from Brazil and China reported the properties of fluorites (Altay. M. 2020). This paper gives a clear account for the quality of natural fluorite.

MATERIALS AND METHODS

The minerals used in this study were natural fluorite collected from it's mining sites at Yantuwaru in Katsina State and other from Wukari local government, Taraba state. The two (2) natural fluorite samples having a bluish-green colour in appearance were considered for the experiments. The samples were grinded in the laboratory in to powder form.

EDXRF experiment was run with one of the fluorites to investigate the possibility that variations in trace and minor impurities compositions among fluorite samples might influence the crystal structure. XRD is also applied on two other fluorite samples. X'Pert High Score Plus was used to identify the phases of the XRD-analysed samples of the natural fluorite.

RESULTS AND DISCUSSION

X-ray Fluorescence (XRF) Results

Table 1: Detected Elements with their Percentage Concentrations

Detected Element	Concentration (%)		
	Fluorite A	Fluorite B	Mean
Si	1.1229	1.3559	1.2394
Al	0.3630	1.1400	0.7515
Mg	1.0400	0.5456	0.7928
Ca	61.5640	59.4350	60.4995
Ce	2.0000	0.9270	1.4635

A total of five (5) elements significantly showed up in XDXRF analysis with their mean percentage concentrations. The most pronounced compositional impurity appears to be Ce with concentration of 1.4635 % following Calcium with the significant concentration of about 60.4995 %. Silicon follows Ce with 1.2394 % concentration. Other concentration values of 0.7928 % and 0.7515 % go for Magnesium and Aluminium respectively (table 1). These elements have relatively insignificant percentages to cause any alteration in the structure of the fluorite samples.

X-ray Diffraction Results

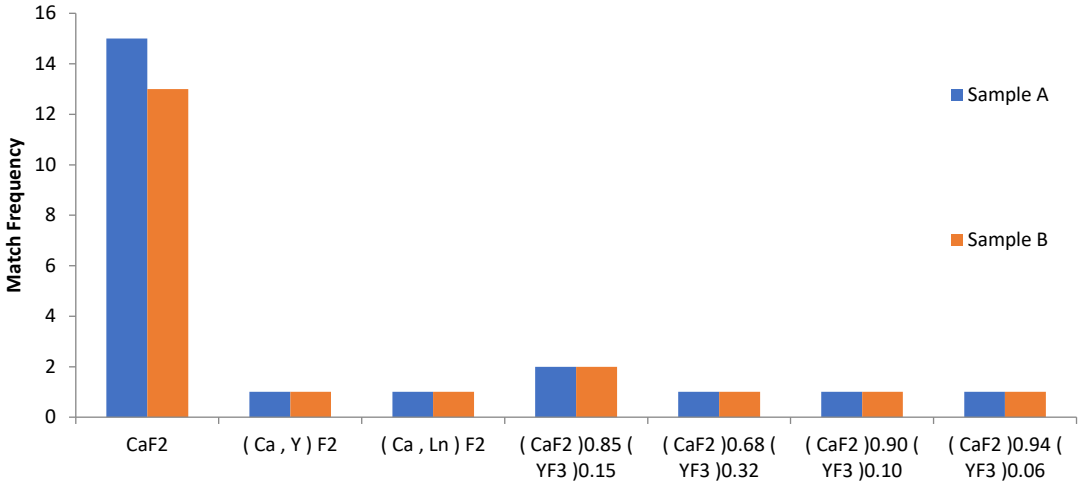

Figure 1: Match frequency for various fluorite phases

Search-match results show correspondence with CaF_2 indicating that the crystalline phase of both samples is predominantly CaF_2 with the absence of secondary or impurity peaks. However, other phases show insignificant correspondence. These include CalciumYttriumFluoride (Ca , Y) F_2, Fluorite,Yttrian (Ca,Ln)F_2, Calcium Yttrium Fluoride $(CaF_2)_{0.85}$ $(YF_3)_{0.15}$, Calcium Yttrium Fluoride $(CaF_2)_{0.68}$ $(YF_3)_{0.32}$, Calcium Yttrium Fluoride $(CaF_2)_{0.90}$ $(YF_3)_{0.10}$ and Calcium Yttrium Fluoride $(CaF_2)_{0.94}$ $(YF_3)_{0.06}$. The frequency of match gives this correspondence as presented in Figure 1.

Table 2: Observed and Calculated Values of Lattice Parameters

Lattice parameter	Observed value (for Fluorite A & B)	Calculated value (for Fluorite A & B)
a(Å)	5.4620	5.4502
b(Å)	5.4620	5.4502
c(Å)	5.4620	5.4502
Alpha α (°)	90.0000	90.0000
Beta β (°)	90.0000	90.0000
Gamma γ (°)	90.0000	90.0000

The density (g/cm^3) of unit cell as observed was 3.18 and 3.20 as calculated.

Both samples belong to cubic crystal system and space group of Fm-3m with Space group number 225 and having same values of their lattice parameters. However, the observed lattice parameters were slightly different from the calculated values (figure 3).

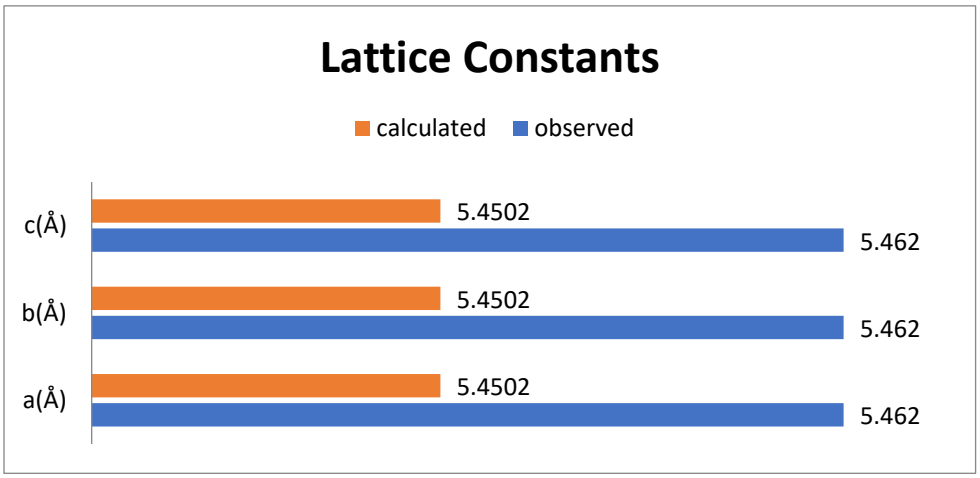

Figure 2: Difference between the calculated and observed lattice constants

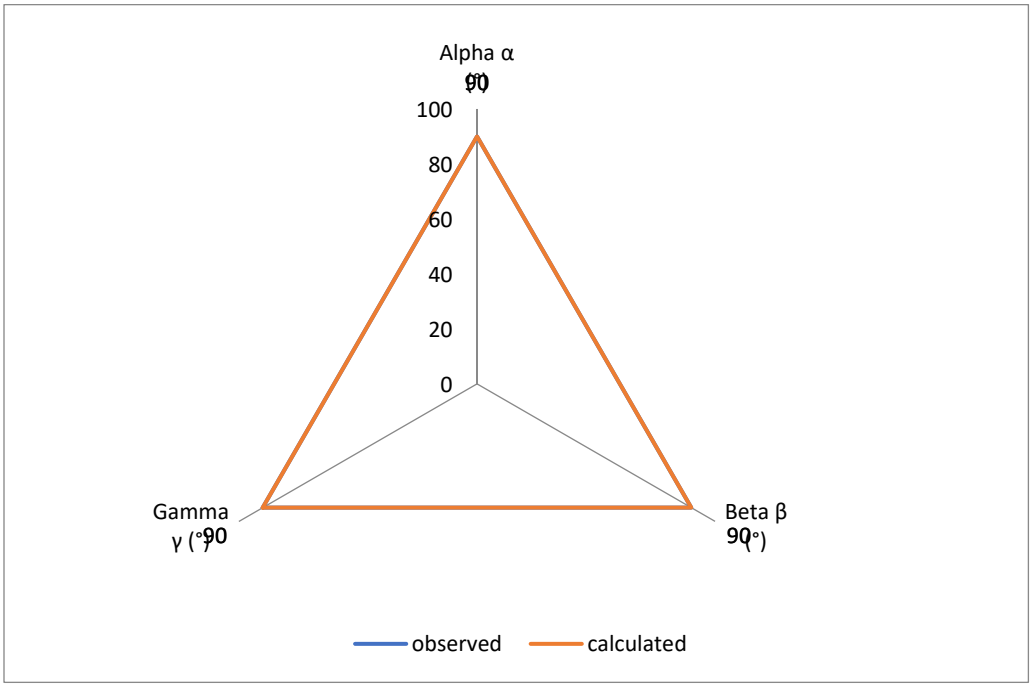

Figure 3: Interaxial angles for both observed and calculated lattices

In figure 2, the observed values (for fluorite A and B) of the lattice constants are slightly higher than the calculated values, indicating a larger unit cell size in them as a result of the increased distance between ions in the crystal lattice. The interatomic forces may possibly be weaker in fluorite A and B than the ones in calculated reference fluorite. This may result in some alterations in their electronic, optical or mechanical properties. However, the orthogonal nature of the interaxial angles shows high symmetry (figure 3), indicating a cubic structure with a highly ordered crystal lattice.

CONCLUSION

In this paper, combined analysis using XRF and XRD was performed to give the elemental composition and crystalline phase identification of natural fluorspar respectively. The X-ray diffraction patterns were also analyzed to determine other crystallographic parameters using X'Pert Highscore Plus. Results show conformity between the observed X-ray diffraction pattern and that found from the identified phase of both fluorite samples. The best agreement between the calculated and observed data was obtained for a cubic structure.

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